the inner ring angles and staggering the methylene groups. All four of the molecules studied in this work have similar angle strain, but the higher values for a_1, for II and IV (Table II), which have two oxygen atoms in their rings, do reflect the higher angle strain at oxygen atoms as compared to carbon. These molecules also have different numbers of eclipsing CH_2 groups. 3,4-Dihydropyran (I) has two pairs of adjacent CH_2 groups; 3,6-dihydropyran (III) and 1,4-dioxene (II) each have one pair; and 1,3-dioxene (IV) has no adjacent CH_2 groups. As a result, IV has a barrier to planarity that is 600 cm^{-1} lower in energy than the other three molecules. Somewhat surprisingly, the extra pair of adjacent CH_2 groups does not increase the barrier to planarity for I relative to II or III. In fact, all three molecules have similar barriers to planarity.

Although these potential energy surfaces fit the data well, small improvements could be realized by including other interacting vibrations. In particular, the out-of-plane double-bond twist (DB twist), which was neglected, no doubt couples somewhat with the single-bond ring-twisting mode. Weaker series of bending and twisting bands originating in the excited states of the DB twist have been assigned for 3,6-dihydropyran and 1,3-dioxene by DKSW, and these demonstrate a small amount of interaction with this mode. Inclusion of the DB twist in the calculations could improve the potential energy surface and slightly lower the calculated barriers to interconversion between the two twisted conformations. However, a three-dimensional potential surface calculation would be required if the DB twist were included, and the magnitude of the problem would become unmanageable. Only in one highly symmetric case[7] (1,3-disilacyclobutane) has a three-dimensional potential surface been successfully determined.

Conclusions

Although LRU's published potential energy surfaces give reasonable values for barriers to interconversion for I and II, their central barriers are too high and they predict the presence of stable bent conformations which have not been observed in the infrared and microwave spectra. In this work we have determined improved potential energy surfaces for the oxygen analogues of cyclohexene. Each of these has energy minima corresponding to the twisted conformations. The bent conformations are at saddle points on the surfaces and are not energetically stable. The barriers to planarity and the twist angles of the lowest energy structures determined here are somewhat higher than those determined from MM2 and microwave studies but are in much better agreement than the previous vibrational investigations. The potential energy surfaces are well defined by vibrational data at lower energies but are more poorly determined in the region of the central barrier. Thus, while we are confident that the barriers reported here are considerably better than those of LRU or DKSW, they are not determined with the same confidence as barriers for four- and five-membered ring molecules.[1-4] Nonetheless, the results of this work, when viewed together with the NMR and microwave results, help provide a coherent picture of the conformational energy differences for these four molecules.

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Chemical Deformation Densities.[†] 1. Principles and Formulation of Quantitative Determination

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Abstract: Molecular electron densities are often examined in the form of difference densities (DDs). Conventionally they are defined with respect to the superimposed densities of the *spherically averaged* atoms. These DDs are denoted here as *total difference densities* (TDDs). They are particularly useful for the discussion of the electrostatic fields created by molecules in the space around them. However, only atoms with spatially nondegenerate ground states are of necessity spherically symmetric. Most atoms with open p and d shells are not, and consequently their TDDs are often dominated by *quadrupolar* density distributions which are the result of the *orientation of the undeformed atomic ground states*. These orientational effects can be quite large and hide the genuine *atomic deformations* that are associated with molecule formation. Because of the superposition of the atomic orientation and chemical deformation effects, it is intrinsically difficult to compare TDDs of different systems, and the term "deformation densities" for them seems unfortunate. As a more appropriate quantity for the elucidation of the nature of chemical binding, *chemical deformation densities* (CDDs) are defined here with respect to the reference density of a promolecule whose *unperturbed* atoms, in addition to being *positioned* at their correct places in the molecule, have their ground-state multipoles uniquely *oriented*. This procedure is also a natural one from an information theoretical point of view. An unambiguous algorithm is formulated for the determination of the atomic orientation parameters and for the construction of CDDs from given molecular electron densities. An algorithm for the evaluation of orientation parameters from X-ray scattering data is presented elsewhere.

1. Introduction and Concepts

It has become customary to discuss electron density distributions in molecules and crystals in terms of difference densities defined with respect to reference densities of "promolecules". Conventionally these are chosen as superpositions of *spherically averaged* (and thermally smeared) densities of free atoms placed at optimal positions. We shall call such difference densities *total difference densities* (TDDs). By contrast, we propose here that not only the positions but also the *orientations of the nonspherical multipolar electron densities of the atoms in their ground states* be optimized when forming reference densities. The resulting difference densities are denoted as *chemical deformation densities* (CDDs).

In this first section the fundamental considerations are outlined. In the second section the mathematical definition of CDDs and an algorithm for their numerical determination are presented. In

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the subsequent paper[1] the new approach will be applied to the theoretically calculated densities of some two to five atomic molecules, and the resulting CDD maps will be analyzed.

1. Total Difference Density and Chemical Difference Density. Since the early 19th century chemists believed that chemical bonds are caused by interatomic forces that arise from electric charges.[2-8] During the past two decades considerable efforts have been made to determine accurately electronic charge distributions in molecules and solids, both experimentally and theoretically,[9-13] to gain a deeper understanding of chemical bonding and chemical reactivity.

A significant fraction of the *intermolecular* interactions is due to *electrostatic* forces between essentially unperturbed molecules. These contributions are important, e.g., for the packing order of molecular crystals and adsorbates, for the structure of polar liquids, and for hard acid–hard base reactivities. The effective electrostatic field *outside* a molecule (i.e., where its density is practically vanishing due to exponential decay) is determined by the *total* electron density inside the molecules, or equivalently by the *total* difference density TDD (since the subtracted superposition of spherical, neutral atoms does not create any electrostatic multipole field in the region outside the molecular density distribution).

In principle, the total electron density also uniquely determines the *intramolecular* total energy (Hohenberg–Kohn–Sham theorem[14,15]). Unfortunately, no simple and robust energy functional of the diagonal one-electron density is as yet known with chemical accuracy, although significant progress has been made during the past decades.[15-20] Therefore, rather than following this approach literally, attempts have been made to relate bonding energies and/or forces between the atoms in a molecule to the density *difference* between the actual molecule and a constructed spherical "promolecule"[21] (the so-called "independent spherical atom model"[11,22]). An alternative approach uses the *second derivatives* of the molecular density.[23-25]

In this context it has often been stated that the presence of density accumulations at bond centers (i.e., maxima in the difference density map, or minima in the Laplacian of the density) are indicative of covalent bonding.[6,22-28] Indeed, many compounds consisting of first- and second-row atoms with nondegenerate ground states (H, Li, Be, N) or with highly symmetric valence states (C(sp^3)) show difference densities, which conform to these traditional ideas.[9-11] They show large positive difference density values, i.e., electron density accumulations, at the centers of strong covalent bonds. Longitudinal and transversal shifts of such "bond charges" imply polar and bent bonds, respectively. Charge accumulations "behind" the atoms may be taken as indications of lone pairs. Typical values for the maxima of bond and lone-pair difference densities in such molecules are of the order of $+^1/_2$ e/Å^3.

Recently however, critical observations have been published regarding this view.[25,29-33] For example, in compounds with asymmetrically coordinated second-row atoms, which have open p shells and degenerate P ground states (in particular B, O, or F), difference densities often have completely different appearances. They exhibit density *depressions* as large as -3 e/Å^3 in the bond regions and at the anticipated lone-pair positions.[9-13,34-37] These unexpected findings have led to the consideration of a special type of covalent bond typical for electron-rich molecules (as, e.g., F_2 or H_2O_2), where the bonding interactions share certain characteristics of typical closed-shell repulsions such as between two argon atoms.[23,28] Although such repulsions certainly exist for the nonbonded lone pairs of O and F, it would seem that the existence of a conventional covalent bond in addition to the nonbonded repulsions is nonetheless a useful concept for the intuitive understanding of the chemistry of such molecules. We would prefer to sharpen rather than to eliminate qualitative concepts which have proven useful up to now.

The just-mentioned unexpected density features can in fact be readily understood[30-34] by taking into account that these difference densities are defined with respect to *spherically averaged* atomic densities. The large negative difference density values simply reflect the fact that, even when free, atoms in degenerate ground states may have nonspherical quadrupolar or higher multipolar electron density distributions. Already at "zeroth order of perturbation", i.e., at *very* large distances where chemical energetic interactions are practically nonexistent, the very weak long-range influence of other atoms have an *orienting* effect on an essentially free atom with a degenerate ground state. Completely free atoms may be prepared either as oriented pure states or as spherically averaged mixed states. Therefore it is equally reasonable to choose the reference density for such atoms as *nonspherical* (see, e.g., ref 26, 29, 38) with appropriately oriented quadrupolar ground-state densities.[33] This *orientation* of the ground-state atoms can have a much larger impact on the density than those density *deformations* that result from the bonding interactions. We also note that the electrostatic interaction of superimposed oriented undeformed atoms usually contributes a substantial fraction of the bond energy.[32]

We denote the difference densities obtained with the oriented nonspherical atomic reference densities as *chemical deformation densities* (CDDs). It is found[1] that they do not exhibit the ap-

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parent "anomalies" for the TDDs in the cases of electron-rich atoms of the second row with open p shells (N, O, or F). The orientation of open d shells in transition-metal compounds has already attracted attention (see, e.g., Coppens[39]). The orientation of open p shells of second- and higher-row main-group elements is even more important.

In light of these observations, the arbitrary choice of spherically symmetric atomic ground-state ensembles as reference densities, while useful for the analysis of intermolecular interactions and for the standardization of difference maps, seems inappropriate for the analysis of chemical interactions inside a molecule. Only if the atoms have nondegenerate spherical ground-states, i.e., when the TDD coincides with the CDD, does it represent the chemical deformation effects of the free atoms. In other cases, the total difference density (TDD) is dominated by the zeroth-order orientation of the atomic quadrupolar ground states. The conventional ("standard"[30]) total difference densities thus embody two different effects, namely, (i) *large orientation effects* found in nonspherical atoms with degenerate or quasidegenerate ground states. These orientation effects already come about by arbitrarily small interactions without any intraatomic energy changes. While often a considerable contribution to the bond energy is ascribable to the electrostatic interaction of these superimposed oriented ground-state atoms,[32] the magnitude of the orientation is not a measure of the magnitude of these interactions. (ii) *Smaller chemical deformation effects* which accompany the chemical interactions. Although these deformations are associated with "energetic promotions" of the individual atoms, the concomitant interatomic bonding effects stabilize the molecule slightly. It seems therefore inappropriate to call the total difference density a "deformation" density".[10-12]

It is apparent that we disagree with the view that the total difference density, based on spherical reference atoms, adequately describes the low symmetry of atoms when they become part of a molecule.[35] It is certainly true that the TDD clearly exhibits the deviation of the molecular density around each atom from spherical symmetry and thereby provides a basis for understanding the multipolar interatomic Coulombic interactions. However, the cornerstone of our position is the observation that, nearly always, the dominant contributions to these nonsphericities result from *intraatomically isoenergetic orientations of atoms with degenerate ground-state wave functions*. Only a small fraction of the nonsphericity is due to the *additional deformations* that are associated with energy-stabilizing bonding interactions. These deformations are exhibited by our chemical deformation density. It seems to us that the TDD alone is a rather unwieldly tool for examining the details of and distinguishing the various contributions to the bond-forming energy changes.

There exist many different possibilities to define useful DDs. As Lipscomb[52] stated, no single choice can be expected to appeal to all theorists and experimentalists. Some choices are most appropriate for specific interpretational purposes, others (e.g., the TDD) are more convenient from the technical point of view of easy determination (structure analysis using the standard spherical atomic form factors) and data communication.

2. Information Processing and Data Compactation. The standard procedure of extracting the information contained in the total electron density distribution consists of two parts. First, the molecular structure and the thermal motions are presented in terms of positional and thermal *parameter values*. Second, the remaining total difference density which, as we have seen, embodies isoenergetic orientations as well as promotional deformations of the atoms, is displayed by a *distribution function* in space. Since the positions, the vibrational amplitudes, the orientations, and the deformations of the atoms are all consequences of the chemical interactions, this particular division into parametric and nonparametric information is arbitrary.

The original X-ray scattering data sets are voluminous. Fourier transformation yields total electron density distributions that are represented by similarly voluminous data sets. Measured by the number of bits needed for storage, the amount of information appears to be very large. However, the total scattering or density data are in fact highly redundant, and the physically interesting amount of information is much smaller. This is so because the possible data sets stem from a rather limited family of data sets: Any observed set corresponds to a density distribution, which must be similar to the superposition of known *atomic* quadrupolar densities (see i below), *placed* at typical distances (see ii below), smeared *vibrationally* (see iii below), *oriented* toward the nearest neighbors (see iv below), and *deformed* slightly by intramolecular, and eventually by intermolecular interactions (see v below).

Indeed, it is just the restriction to such density distributions that forms the basis for the "direct methods" of structure determination and for the extraction of phase information from intensity data.[40,41] It is the atomic composition of matter and the ensuing redundancy of the measured data that make the phase problem solvable.

To make the considerations quantitative, let us assume that we have measured about 10^4 reflections. Each reflection is specified by three independent angles and an intensity. An accuracy of the angles of $10^3 = 2^{10}$ corresponds to 10 bits per value. A relative accuracy of the intensities of the order of a percent corresponds to 6–7 bits for the mantissa. Since the intensity range extends over, say, 6 orders of magnitude, we need 4–5 bits to represent the binary exponent $\in [0,20]$. It follows that the *total* information amounts to a about 5×10^5 bits.

Fourier transformation yields the electron density distribution in the unit cell. With a spatial resolution of $^1/_4$ Å there are about 6×10^4 grid points in a unit cell of 10 Å. Typically, densities are obtained with an accuracy of a few percent, corresponding to about 5 bits per mantissa. The measurable density values spread over a range of, say, 5 decades, corresponding to 4–5 bits for the exponents. Hence the total information contents in the density distribution function amounts to about 5×10^5 bits. Thus, the Fourier transformation of the scattering data has not changed the amount of *formal* information—as it should be. Of course, this does not contradict the fact that by interpolation on a finer grid, details like density maxima, which are only implicitly given by the data on the coarse grid, can be represented explicitly. Namely, by increasing the number of grid points, it is easily possible to arbitrarily increase the number of bits, which are needed to store the density file, above the minimal number.

What *physical* knowledge can we gain from this formal information?

(i) For each atom in the unit cell (say, about 50 atoms) we obtain the *nuclear charge*, each $Z \in [1,100]$ corresponding to about 7 bits.

(ii) The Cartesian *coordinates* are obtained with a typical accuracy of a few 10^{-3} Å, corresponding to 12 bits for each dimension of about 10-Å extension. (i) and (ii) amount to about $(3 \times 12 + 7) \times 50 = 2 \times 10^3$ bits.

(iii) The atoms undergo *vibrations*. The harmonic vibrational tensors with a few percent accuracy for each of the 6 components (and eventually anharmonic corrections) comprise about 40 bits for each atom, which amounts to another total of about 2×10^3 bits.

(iv) Some of the atoms have open p or d shells, which should be appropriately *populated and oriented*. For orbital angular momentum l, we need $l(2l + 3)$ parameters (see below) which, if determined with several percent accuracy, add up to a few 10^3 bits.

(v) Finally we can extract additional parameters that describe the *chemical deformation*, namely, spatial expansions or contractions of atomic valence shells or subshells (so-called κ parameters), charges on atoms, and possibly additional multipole contributions of different strengths, directions, and spatial extensions. This type of density modeling is actually performed in

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the multipole expansion approach (see, e.g., refs 9–11, 38, 43). The respective information corresponds to up to several 10^3 bits for the whole unit cell.

Consequently, the *formal* information contents of a density distribution (more than 10^5 bits) is by more than 1 order of magnitude larger than the *physical* information contents (less than 10^4 bits). Thus, as is not uncommon for original data sets, there is a large information defect or so-called "missing surprisal" in the scattering or density data. As already mentioned, this is due to the fact that only very special density distribution functions appear in nature.

By stepwise extraction of the various mentioned types of physical information, each of the order of a few 10^3 bits, both the range of magnitudes and the relative accuracies of the remaining difference densities or difference scattering amplitudes are reduced. For instance, upon subtracting the vibrating spherical atom promolecule density from the total molecular density, the resulting TDD values become so small that 5 bits for each value are sufficient instead of the 10 bits for the total density values.

Each of the four steps of data compaction, i.e., the determination of the structural parameters (i and ii), the thermal smearing (iii), the atomic orientations (iv), and the genuine chemical deformations of the atoms (v), reduces the formal amount of information of 5×10^5 bits by about one-quarter. *In each step, about 10^5 bits of formal information are converted into a few 10^3 bits of physically relevant information.*

If the accuracy and the number of the original data are less than assumed above, then the amount of formal information may already be exhausted after two or three steps of the data compactation process. The four kinds of physical information about the system, which can be extracted from X-ray scattering or electron density data, are hierarchically ordered in the sense that they correspond to different levels of accuracy of the original data. It therefore seems logical to perform as many of these steps as possible to eliminate the redundancy of the density distribution function and to represent the measured information as compactly as possible in the form of parameter sets that embody meaningful and clear physical interpretations.

Traditionally, only the first two data compactation steps are performed. That is, one obtains the structural and thermal *parameters*, which can be discussed *quantitatively*. The remaining types of physical information, i.e., the atomic orientations and the chemical deformations, are usually not distinguished from each other, neither in the analysis nor in the discussion of the densities. Atomic orientations and chemical deformations are being represented combined together, in the form of multipole deformation parameters, or even in the redundant qualitative form of TDD maps. In those cases where orientation effects dominate, the chemical deformation features become buried and masked. Total difference density maps of different molecules, in which the atoms undergo different orientations, can therefore not be compared with regard to the chemical deformation effects.

3. Present Approach. The concept that molecules consist of atoms is "only" a model. However, it has proven eminently useful in the field of chemistry, both theoretically and practically. If we accept this model, then we have also to accept (i) that a major contribution to the binding energy can already be recovered by the superposition of undeformed atomic charge distributions, (ii) that atomic ground states may be spherical as well as nonspherical, and (iii) that the total molecular density deviates only slightly from the superposition of undeformed, nonspherical oriented atomic ground states. The goal of representing the molecular density information in terms of structural, thermal, orientational, and deformational *parameters* is therefore not arbitrary but is in fact appropriate to the chemical concept of atoms in molecules. These considerations confirm our opinion that it should be fruitful to split the total difference density (TDD) into two parts,[33] namely, (i) the *orientation effects* which do not involve *intra*atomic energy changes but arrange the atomic electrons for optimal interaction and (ii) the smaller *"chemical" deformation effects* which reflect the results of the chemical interactions on the atomic densities. Both types of information can then be separately quantified.

The idea of oriented atomic ground states is not new (compare ref 12, 26, 29, 30, 31). Specific orientations have been proposed by using intuitive reasoning based on the VB approximation or other models (we will call those DDs the "naive" ones). For very simple cases the chemical deformation densities have been examined in different contexts by Hall, Parr, Ruedenberg, Schwarz, and co-workers.[29–33,42] However, what is missing so far is an *unambiguous*, *general operational definition* of orientational parameters, which play a role similar to that of the positional and thermal parameters used in conventional X-ray structure refinements. Such a definition of orientational parameters and of genuine chemical deformations is formulated below. The approach will be carried through for molecules where the atomic orientations cannot be guessed at by symmetry, and numerical values will be obtained for the parameters describing the orientations. The chemical deformation effects will still be left in the form of a graphical CDD distribution. In cases of limited experimental accuracy that is insufficient to determine the small chemical deformations, the determination of the orientation parameters of the degenerate atomic ground states in the molecule may still be possible. As has been stressed by Hirshfeld,[43] accurate structural parameters can be obtained only if electron density parameters are adjusted simultaneously. The present approach assumes that the total molecular *density* is given. Theoretical, quantum chemical ab initio densities are analyzed here, but by the same formalism, one could also analyze densities derived experimentally. An alternative approach, which is based on the direct evaluation of original X-ray *scattering data*, will be described elsewhere.[51]

In the conventional data compactation process of X-ray scattering measurements two types of physical information, namely, the *atomic coordinates* and the *vibrational amplitudes*, are obtained by successively reducing the scattering difference amplitude values through least-squares techniques. We proceed in the same manner in the case of the *orientation parameters*. If ρ^M is the electron density distribution of the molecule or crystal and $\sum_A \rho^A(s^A)$ is the superposition of the (thermally smeared and) oriented atomic ground-state densities with parameters s^A, then we define the *chemical deformation density* by

$$\Delta\rho^M(s^A) = \rho^M - \sum_{A}^{M} \rho^A(s^A) \qquad (1)$$

where the sum runs over all atoms A in the molecule M. $\Delta\rho^M$ depends on the positional, thermal, *and orientational* parameters s^A of the atoms. To transfer as much information as possible from the three-dimensional distribution function ρ^M into the parameters s^A, we determine the optimal parameters s_0^A of the atom A in the molecule M by minimizing the integrated square of the residual chemical difference density:

$$\frac{d}{ds^A}\int dr^3\, |\Delta\rho^M(s^A)|^2 = 0 \quad \text{for } s^A = s_0^A \qquad (2)$$

The minimized chemical difference density $\Delta\rho^M(s_0^A)$ then describes the "truly" chemical polarizations and deformations of the atoms A in the molecule M.

An approach that is in some respects similar to ours has been proposed and applied many years ago by Dawson,[44] Coppens,[45] and others. There is however an essential difference: These authors model the *total electron density* by a superposition of products of atomic orbitals. Their aim was to *represent ρ^M optimally*, thereby accounting simultaneously for *both* the orientations *and* the chemical deformations of the atomic ground states in a molecule or crystal. To this end, variable s^2, p^2, and s–p hybrid

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densities, two-center densities, etc., were used, and a *large number of parameters* was introduced, which turned out to be highly correlated.

Our aim is different. We want to *define and determine the orientations and the deformations separately*. Since there are only a few orientational parameters and since they are expected to be only weakly dependent on each other or on the thermal parameters, intensity, or density, data of medium accuracy should already be sufficient for their determination. The mathematical and conceptual implementation of this objective is the subject of the next section.

2. Orientation of an Atom in a Molecule

1. Atomic Densities. To a first approximation, a polyatomic system is composed of atoms in their ground states. The corresponding atomic electron density $\rho^A(r)$ is uniquely defined, if the wave function Ψ^A is (spatially) nondegenerate like that of H(^{2}S), Li(^{2}S), Be(^{1}S), or N(^{4}S). However, many atoms have N-fold spatially degenerate ground states, for instance, B(^{2}P), C(^{3}P), O(^{3}P), or F(^{2}P) with $N = 3$. In these cases the most general description of the atomic ground-state contribution in a molecule is given by a mixed ensemble density operator P^A. The quantitative values of the matrix elements representing this operator embody what we have loosely called the atomic "orientation".

To quantify our approach, it is necessary to define exactly what is meant by the "ground state" in the present context. Strictly speaking, the atomic states are only *nearly* degenerate because of the splitting into *spin–orbit components*. However, the $^2P_{1/2}$–$^2P_{3/2}$ splittings of B or F are negligible in comparison to chemical interaction energies. This is of course no longer the case for the heaviest homologues (Tl and I, respectively) with spin–orbit splittings of the order of 1 eV. In such cases the question of which states should be included in the nearly degenerate ground-state ensemble has to be carefully examined.

If we include different spin–orbit components, then it may also be reasonable to include different *L–S components* of a given configuration in the ground-state ensemble (sometimes called the average level ensemble). For instance, if one wants the density operator P^A to be flexible enough to describe p_x, p_y, p_z orbital occupancies between zero and two in carbon (or oxygen) atoms, ^{1}D and/or ^{1}S states of the ground configuration s^{2}p^2 (or s^{2}p^4, respectively) must be included in the ensemble, in addition to the ^{3}P ground state. Nitrogen has a spherical s^{2}p^3 ^{4}S ground state but is strongly quadrupolar in several compounds corresponding to the population of ^{2}P or ^{2}D states. However, the (diagonal) one-electron density does not uniquely determine the many-electron states to be included in the ensemble. For instance, a density that can be obtained from a p^2 ^{3}P state alone can also be reproduced by a mixture of other p^2 states.

In the case of a transition metal, lanthanoid, or actinoid atom, *nd–(n + l)s or nf–(n + l)d promotion*, respectively, does not cost more energy than the spin–orbit splitting or the L–S separation. It causes, however, large charge redistributions, which should be easily measurable. In these cases, it would seem appropriate to include even different configurations (orbital occupation schemes) in the ground ensemble.

By contrast, *n*s–*n*p promotion within a shell is usually energetically more expensive, but it results in smaller density changes. The density changes are especially small in the second row (B to F), where the positions of the density maxima of the 2s and 2p shells differ by only a few percent (see, e.g., ref 45, 46). Consequently s–p hybridization in second-row molecules is very difficult to determine by density measurements. To avoid spurious results, one should probably not try to account for 2s–2p promotion with the presently available accuracy of experimental density data.

In the case of strongly polar or ionic compounds it may be more sensible to consider *ionic configurations* in the reference ensemble. There may exist even other cases. There exists no universally valid collection of states for inclusion in the atomic "quasi-ground-state" reference ensembles. One should include those atomic states that, on one hand, are low in energy in comparison to the bond energy and, on the other hand, turn out to contribute significantly to the "orientational fine structure" of the density of a given molecule, say $\Delta\rho$ contributions of the order of several e/Å^3. By contrast, "chemical hyperfine structures" of the density of no more than a few 0.1 e/Å^3, in particular when requiring highly promoted atomic states for their representation, should be accounted for by the residual chemical deformation density.

In a certain sense chemistry is a classification science,[47] and there exist many situations where the most useful classification scheme is not clearcut and, certainly, is not known in advance. In such cases it must be deduced by a detailed analysis of the given data. Which states ought to be included in the atomic reference ensemble will then be an additional *result* of the density analysis. In this manner one can extract from the experimentally or theoretically determined total electron density both *qualitative* information regarding the low-lying atomic states which are dominantly important for the molecular density and *quantitative* information regarding the populations and orientations of these degenerate or near-degenerate states. We stress again that the aim of interpreting densities is not the optimal reproduction of given molecular densities, but its splitting up into physically meaningful contributions. It is our premise that the biggest contribution is given by the superposition of the oriented atomic ground ensemble densities. A smaller density contribution, CDD, is then due to energetically expensive perturbations of the atoms occurring during bond formation, which do not necessarily result in significant changes of the one-electron density.

2. Density Matrix for Open-p-Shell Atoms. Let the N states of atom A included in its ground ensemble be described by many-electron wave functions Ψ_i^A. The *many-electron-state density* operator of this atomic ensemble is given by

$$P^A = \sum_{ij}^{N} |\Psi_i^A\rangle \mathbf{P}_{ij}^A \langle \Psi_j^A| \tag{3}$$

The density matrix $\mathbf{P}_{ij}^A$ fulfills the following three conditions:

hermiticity $\quad \mathbf{P}_{ij}^A = \mathbf{P}_{ji}^{A+} \quad$ (4a)

normalization $\quad \mathrm{tr}\,(\mathbf{P}_{ij}^A) = 1 \quad$ (4b)

representability $\quad 0 \leqslant \Omega_i^A \leqslant 1 \quad$ (4c)

where Ω_i^A are the eigenvalues of $\mathbf{P}_{ij}^A$. At the orbital level eq 4c reduces to the original simple form of the Pauli principle. We note that the constraint (4c) is much less restrictive than that proposed by Massa et al.[48]

A simple way[49] to account for eq 4b and 4c is the following representation of the eigenvalues in terms of $N - 1$ hyperspherical angles α_i:

$$\Omega_1^A = \cos^2 \alpha_1$$

$$\Omega_2^A = \sin^2 \alpha_1 \cos^2 \alpha_2$$

$$\Omega_3^A = \sin^2 \alpha_1 \sin^2 \alpha_2 \cos^2 \alpha_3 \text{ etc.}$$

$$\Omega_N^A = \sin^2 \alpha_1 \sin^2 \alpha_2 \ldots \sin^2 \alpha_{N-1} \tag{4d}$$

In general the atomic density matrix $\mathbf{P}^A$ is neither necessarily diagonal nor idempotent ($\mathbf{P}^A \cdot \mathbf{P}^A \neq \mathbf{P}^A$), except in the case of a single pure state. The $\mathbf{P}^A$ matrix can be expressed as

$$\mathbf{P}^A = \mathbf{V}^A \cdot \mathbf{\Omega}^A \cdot \mathbf{V}^{A\dagger} \tag{5}$$

where $\mathbf{\Omega}^A$ is the diagonal matrix of the eigenvalues Ω_i^A, and $\mathbf{V}^A$ is a unitary matrix which may be expressed in terms of an antihermitean matrix $\mathbf{Y}^A$:

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(46) Smith, C. M.; Hall, G. G. *Int. J. Quantum Chem.* **1987**, *31*, 685.

(47) Primas, H. *Chemistry, Quantum Mechanics and Euctionism*; Springer: Berlin, 1981.

(48) Massa, L.; Goldberg, M.; Frishberg, C.; Boehme, R.; LaPlaca, S. *Phys. Rev. Lett.* **1985**, *55*, 6, 622, and references given therein. Frishberg, C. *Int. J. Quantum Chem.* **1986**, *30*, 1.

(49) Hoffman, D. K.; Raffenetti, R. C.; Ruedenberg, K. *J. Math. Phys.* **1972**, *13*, 528.

$$\mathbf{V}^{\mathrm{A}} = \exp(\mathbf{Y}^{\mathrm{A}}) \tag{6}$$

The state-density operator P^{A} determines the *one-electron-density* operator ρ^{A} uniquely, whereas the inverse is in general not true. In an orbital basis φ_μ^{A} the general expression for ρ^{A} reads

$$\rho^{\mathrm{A}} = \sum_{\mu,\nu} |\varphi_\mu^{\mathrm{A}}\rangle \rho_{\mu\nu}^{\mathrm{A}} \langle \varphi^{\mathrm{A}}| \tag{7}$$

The atomic electron density is then given by the trace

$$\rho^{\mathrm{A}}(r) = \mathrm{tr}\,(\rho^{\mathrm{A}}) = \sum_{\mu\nu} \varphi_\mu^{\mathrm{A}}(r)\cdot\rho_{\mu\nu}^{\mathrm{A}}\cdot\varphi_\nu^{\mathrm{A}*}(r) \tag{8}$$

For the sake of simplicity, we may assume without loss of generality that the basis orbitals are real.

Let us now introduce the symmetry adapted SCF[53] or FORS-MCSCF[54] approximation to the ground state of main-group atoms, which restricts the form of the Ψs in eq 3 without modifying eq 4. The finite orbital basis of atom A consists of the core orbitals $c^{\mathrm{A}} = c^{\mathrm{A}}(r)$ and of the s and p valence orbitals $s^{\mathrm{A}} = s^{\mathrm{A}}(r)$, $p_i^{\mathrm{A}} = p_i^{\mathrm{A}}(r)$ $(i = x, y, z)$. $\rho^{\mathrm{A}}(r)$ is then simply given by

$$\rho^{\mathrm{A}}(r) = \sum_c^{\mathrm{A}} W_c^{\mathrm{A}}\cdot(c^{\mathrm{A}})^2 + W_s^{\mathrm{A}}\cdot(s^{\mathrm{A}})^2 + \sum_{i,j}^{n} \rho_{ij}^{\mathrm{A}}\cdot p_i^{\mathrm{A}}\cdot p_j^{\mathrm{A}} \tag{9}$$

$W_c^{\mathrm{A}} = 2$ and W_s^{A} are the occupation numbers of the core and *s*-valence orbitals. Since the degenerate ground states with an open p shell are of P type and since, therefore, N in eq 3 is equal to n in eq 9 ($n = N = 3$), there exist unique and simple relations between the P_{ij}^{A} for these states and the ρ_{ij}^{A} for the orbitals at the symmetry-restricted Hartree–Fock level. They are for boron, aluminum, ... ($\mathrm{p}^1\ {}^2\mathrm{P}$)

$$\rho_{ij}^{\mathrm{B}} = P_{ij}^{\mathrm{B}} = \delta_{ij}/3 + dP_{ij}^{\mathrm{B}} \tag{10a}$$

for carbon, silicon, ... ($\mathrm{p}^2\ {}^3\mathrm{P}$)

$$\rho_{ij}^{\mathrm{C}} = \delta_{ij} - P_{ij}^{\mathrm{C}} = 2\delta_{ij}/3 - dP_{ij}^{\mathrm{C}} \tag{10b}$$

for nitrogen, phosphorus, ... ($\mathrm{p}^3\ {}^4\mathrm{S}$)

$$\rho_{ij}^{\mathrm{N}} = \delta_{ij} \tag{10c}$$

for oxygen, sulfur, ... ($\mathrm{p}^4\ {}^3\mathrm{P}$)

$$\rho_{ij}^{\mathrm{O}} = \delta_{ij} + P_{ij}^{\mathrm{O}} = 4\delta_{ij}/3 + dP_{ij}^{\mathrm{O}} \tag{10d}$$

for fluorine, chlorine, ... ($\mathrm{p}^5\ {}^2\mathrm{P}$)

$$\rho_{ij}^{\mathrm{F}} = 2\delta_{ij} - P_{ij}^{\mathrm{F}} = 5\delta_{ij}/3 - dP_{ij}^{\mathrm{F}} \tag{10e}$$

where dP_{ij}^{A} is the deviation of P_{ij}^{A} from the statistical average, i.e., $\mathrm{tr}\,(dP^{\mathrm{A}}) = 0$. Consequently, in the Hartree–Fock approximation, ρ_{ij}^{A} (given in a space-orbital basis) is a hermitean matrix with its eigenvalues W_i^{A} restricted as follows:

$$\begin{array}{lll}
\text{group III:} & \sum_i W_i^{\mathrm{A}} = 1;\quad 0 \leqslant W_i^{\mathrm{A}} \leqslant 1 & (\text{for } {}^2\mathrm{P}) \\
\text{group IV:} & \sum_i W_i^{\mathrm{A}} = 2;\quad 0 \leqslant W_i^{\mathrm{A}} \leqslant 1 & (\text{for } {}^3\mathrm{P}) \\
\text{group V:} & \sum_i W_i^{\mathrm{A}} = 3;\quad W_i^{\mathrm{A}} = 1 & (\text{for } {}^4\mathrm{S}) \\
\text{group VI:} & \sum_i W_i^{\mathrm{A}} = 4;\quad 1 \leqslant W_i^{\mathrm{A}} \leqslant 2 & (\text{for } {}^3\mathrm{P}) \\
\text{group VII:} & \sum_i W_i^{\mathrm{A}} = 5;\quad 1 \leqslant W_i^{\mathrm{A}} \leqslant 2 & (\text{for } {}^2\mathrm{P})
\end{array} \tag{11}$$

If all states of the same configuration or if states of some other configurations, e.g., of ionic configurations, are included in the ensemble of eq 3, then the restraints on the orbital occupations become less stringent. This also holds in those cases of open d shells where the L value of the ground state is larger than l (i.e., $L > 2$). The most general restriction is of course

$$0 \leqslant W_i^{\mathrm{A}} \leqslant 2 \tag{12}$$

In this context it should be mentioned that the idempotency constraint[48] is not a reasonable assumption for the atomic reference densities ρ_{A} since it presumes that each of them can be derived from a single-determinant wave function whereas, in fact, ρ_{A} necessarily represents the density of an *ensemble* of atomic pure-state wave functions. Within the context of a molecular wave function, an atom can almost never be modeled by one pure-state atomic wave function, be it single or many determinantal, but only by an ensemble. (It may also be noted that idempotency would apply only in the spin–orbital basis and that there are infinitely many single determinants that yield the same electron density,[55] i.e., density matrix trace.)

Writing in analogy to eq 5 for ρ_{ij}^{A}

$$\rho^{\mathrm{A}} = \mathbf{U}^{\mathrm{A}}\cdot\mathbf{W}^{\mathrm{A}}\cdot\mathbf{U}^{\mathrm{A}\dagger} \tag{5a}$$

we can express the atomic one-electron density of an open p shell in the form

$$\rho^{\mathrm{A}}(r) = \sum_c^{\mathrm{A}} 2(c^{\mathrm{A}})^2 + 2(s^{\mathrm{A}})^2 + \sum_{ijk} W_k^{\mathrm{A}} U_{ik}^{\mathrm{A}} U_{jk}^{\mathrm{A}*} p_i^{\mathrm{A}} p_j^{\mathrm{A}} \tag{13}$$

The W_k^{A} are restricted by eq 11, by eq 12, or by alternative equations, corresponding to eq 4c.[51] The unitary orbital transformation matrices U_{ik}^{A} can be represented by an equation analogous to eq 6:

$$\mathbf{U}^{\mathrm{A}} = \exp(\mathbf{X}^{\mathrm{A}}) \tag{6a}$$

The columns of $\mathbf{U}$ represent the coefficients of the "natural local atomic p orbitals" p_k^{A} of atom A in the molecule and determine their *directions*. The W_k^{A} are the corresponding *occupation numbers*:

$$\rho^{\mathrm{A}}(r) = \sum_c^{\mathrm{A}} 2(c^{\mathrm{A}})^2 + 2(s^{\mathrm{A}})^2 + \sum_k^{n} W_k^{\mathrm{A}} (p_k^{\mathrm{A}})^2 \tag{14}$$

Since we attempt only to generate the real trace $\rho(r)$ of the density operator ρ with kernel $\rho(r,r')$ and density matrix ρ_{ij}, the imaginary part of ρ_{ij} remains undetermined. The most natural choice is to set the $l(2l + 1)$ parameters of $\mathrm{Im}\,(\rho)$ equal to zero so that ρ and $\mathbf{U}$ become real. (Another choice of $\mathrm{Im}\,(\rho)$, favored by Massa et al.,[48] yields the idempotency.) In the case of p orbitals, the real orthogonal matrix $\mathbf{U}$ contains three real independent parameters which specify the rotation of the set of the three natural p AOs in real space, all of which have the same shape. This is no longer so for $l > 1$. In the general case of an open l shell, the real matrix $\mathbf{U}$ contains $l(2l + 1)$ degrees of freedom. For instance, for a d shell with $l = 2$, $\mathbf{U}$ has 10 independent parameters, three of which can be used to determine the directions of the main axes and seven to determine the *shapes* of the five natural d orbitals.

3. Equations for the Atomic Density Contributions. We introduce the notation

$$\delta_s^{\mathrm{M}}(r) = \rho^{\mathrm{M}} - \sum_{\mathrm{A},c}^{\mathrm{M}} 2(c^{\mathrm{A}})^2 - \sum_{\mathrm{A}}^{\mathrm{M}} W_s^{\mathrm{A}}(s^{\mathrm{A}})^2 \tag{15}$$

$$V_0 = \int \mathrm{d}r^3\, (\delta_s^{\mathrm{M}})^2 \tag{16}$$

$$h_{ij}^{\mathrm{A}} = \int \mathrm{d}r^3\, p_i^{\mathrm{A}} \delta_s^{\mathrm{M}} p_j^{\mathrm{A}} \tag{17}$$

$$g_{ijmn}^{\mathrm{A}\,\mathrm{B}} = \int \mathrm{d}r^3\, p_i^{\mathrm{A}} p_j^{\mathrm{A}} p_m^{\mathrm{B}} p_n^{\mathrm{B}} \tag{18}$$

$\delta_s^{\mathrm{M}}(r)$ is that part of the molecular density that is *not* due to spherically symmetric contributions of occupied (frozen) atomic shells. The h_{ij}^{A} are one-electron two-index integrals over atomic open-shell orbitals, in our case p AOs. If M_0 is the number of

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(50) Rollett, J. S. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon: Oxford, 1982; p 338. Rollett, J. S. In *Methods and Applications in Crystallographic Computing*; Hall, S. R., Ashida, T., Eds.; Clarendon: Oxford, 1984; p 161. Diamond, R. *Ibid.*, p 174.

(51) Ruedenberg, K.; Schwarz, W. H. E. *Acta Crystallogr., Sect. A*, to be submitted.

(52) Lipscomb, W. N. *Trans. Am. Cryst. Assoc.* **1972**, *8*, 79.

(53) Roothaan, C. C. C. *Rev. Mod. Phys.* **1960**, *32*, 179.

(54) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41.

(55) Harriman, J. E. *Phys. Rev. A* **1981**, *24*, 680.

atoms with an open shell of angular momentum l ($n = 2l + 1$), there are $M_0 n(n + 1)/2$ different integrals (taking no account of any molecular symmetry). The g^{AB}_{ijmn} are one-electron four-index integrals of the density–density overlap type. In the most general case and without accounting for the O_3 symmetry of the AOs, the number of different integrals is of the order of $M_0^2 n^4/24$. Consequently, there are at most a few hundred two-index integrals and a few 10^4 four-index integrals, which can all be stored in the fast memory.

After insertion of eq 14–18 into eq 2, the integrated squared "chemical difference density" I becomes

$$I = \int \Delta\rho^2 \,\mathrm{d}r^3 = V_o - 2 \sum_{\mathrm{A}ijk} h^{\mathrm{A}}_{ij} U^{\mathrm{A}}_{ik} U^{\mathrm{A}}_{jk} W^{\mathrm{A}}_{k} + \sum_{\mathrm{A}ij\mathrm{B}mnkl} g^{\mathrm{A}\,\mathrm{B}}_{ijmn} U^{\mathrm{A}}_{ik} U^{\mathrm{A}}_{jk} U^{\mathrm{B}}_{ml} U^{\mathrm{B}}_{nl} W^{\mathrm{A}}_{k} W^{\mathrm{B}}_{l} \tag{19}$$

This expression is similar to the quantum chemical multiconfiguration energy expression, where the **U** matrix corresponds to the LCAO-MO vectors and the **W** vector corresponds to the CI coefficients. We now introduce the transformed two- and four-index integrals

$$H^{\mathrm{A}}_{IJ} = \sum_{ij} h^{\mathrm{A}}_{ij} U^{\mathrm{A}}_{iI} U^{\mathrm{A}}_{jJ} \tag{20}$$

$$G^{\mathrm{A}\,\mathrm{B}}_{IJMN} = \sum_{ijmn} g^{\mathrm{A}\,\mathrm{B}}_{ijmn} U^{\mathrm{A}}_{iI} U^{\mathrm{A}}_{jJ} U^{\mathrm{B}}_{mM} U^{\mathrm{B}}_{nN} \tag{21}$$

In the following we use the abbreviations

$$H^{\mathrm{A}}_{KK} = H^{\mathrm{A}}_{K} \tag{20a}$$

$$G^{\mathrm{A}\,\mathrm{B}}_{KKLL} = J^{\mathrm{AB}}_{KL} \tag{21a}$$

This yields

$$I = V_o - 2\sum_{\mathrm{A}k} H^{\mathrm{A}}_{k} W^{\mathrm{A}}_{k} + \sum_{\mathrm{A}k\mathrm{B}l} W^{\mathrm{A}}_{k} J^{\mathrm{AB}}_{kl} W^{\mathrm{B}}_{l} \tag{22}$$

This expression has to be minimized with respect to variations of the orthogonal matrices U^{A}_{ij} and the natural occupation numbers $W^{\mathrm{A}}_{\mathrm{K}}$. The W^{A}_{k} are subject to the aforementioned constraints of charge conservation (Q_ν) for individual atomic shells, for individual atoms, or for collections of atoms (e.g., for the whole unit cell). All these constraints are of the general form

$$\sum_{\mathrm{A}k} W^{\mathrm{A}}_{k} \lambda^{\mathrm{A}}_{k\nu} = Q_\nu, \quad \nu = 1, 2, \ldots \tag{23}$$

where the $\lambda^{\mathrm{A}}_{K\nu}$ are certain constants (compare eq 10–12). If the Lagrangean multipliers corresponding to these side conditions are denoted by ϵ_ν, then the constrained variation with respect to the W^{B}_{l} leads to the following system of linear equations for the W^{B}_{l} and ϵ_ν:

$$\begin{pmatrix} J^{\mathrm{AB}}_{kl} & \lambda^{\mathrm{A}}_{k\nu} \\ \lambda^{\mathrm{B}\dagger}_{l\mu} & 0 \end{pmatrix} \begin{pmatrix} w^{\mathrm{B}}_{l} \\ \epsilon_\nu \end{pmatrix} = \begin{pmatrix} H^{\mathrm{A}}_{k} \\ Q_\mu \end{pmatrix} \tag{24}$$

The second line of eq 24 is identical with eq 23.

The variation of the U^{A}_{ik} has to be performed under the constraint of unitarity. This is most easily achieved if we express the $\mathbf{U}^{\mathrm{A}}$ by eq 6a. With the abbreviation

$$F^{\mathrm{A}}_{IJ} = H^{\mathrm{A}}_{IJ} - \sum_{\mathrm{B}l} G^{\mathrm{A}\,\mathrm{B}}_{IJll} W^{\mathrm{B}}_{l} \tag{25}$$

the variation with respect to the X^{A}_{ij} in eq 6a leads to

$$F^{\mathrm{A}}_{IJ} = 0 \tag{26}$$

The upper set of the equation system (24) may also be expressed as

$$F^{\mathrm{A}}_{II} = \sum_{\nu} \lambda^{\mathrm{A}}_{i\nu} \epsilon_\nu \tag{27}$$

We note the similarity with the quantum mechanical Hartree–Fock equations. Here too, one has to be aware of the so-called Hartree–Fock instability. This means that the smallest value of the integral I of a symmetrical molecule may correspond to inequivalent orientations and occupations of the p AOs on equivalent atoms so that the promolecule of the oriented atoms would not reproduce the full symmetry of the molecule. Instead of determining such a "symmetry-unrestricted Hartree–Fock" solution, one can also determine a fully symmetric promolecule by a "restricted Hartree–Fock" type procedure.

4. Iterative Method for the Determination of U^{A}_{ij} and W^{A}_{k}. The simplest way of minimizing I (eq 19 or 22) is by the Gauss–Newton or Newton–Raphson techniques.[50] We expand $\Delta\rho$ in I (eq 19) in a Taylor series up to first or second order, respectively, in the X^{A}_{ij} and W^{A}_{k} around the approximate optimal values ${}_0X^{\mathrm{A}}_{ij}$ and ${}_0W^{\mathrm{A}}_{k}$, for which I takes the value ${}_0I$;

$$\mathbf{U}^{\mathrm{A}} = \exp(\mathbf{X}^{\mathrm{A}}) = {}_0U^{\mathrm{A}}(1 + \Delta X^{\mathrm{A}} + (\Delta X^{\mathrm{A}})^2/2) \tag{28}$$

$$I = {}_0I + \sum_{\mathrm{A}k} \frac{\partial_0 I}{\partial W^{\mathrm{A}}_{k}} \Delta W^{\mathrm{A}}_{k} + \sum_{\mathrm{A}ij} \frac{\partial_0 I}{\partial X^{\mathrm{A}}_{ij}} \Delta X^{\mathrm{A}}_{ij} + \sum_{\mathrm{A}ij\mathrm{B}l} \frac{\partial^2{}_0 I}{\partial X^{\mathrm{A}}_{ij} \partial W^{\mathrm{B}}_{l}} \Delta X^{\mathrm{A}}_{ij} \Delta W^{\mathrm{B}}_{l} + \frac{1}{2} \sum_{\mathrm{A}k\mathrm{B}l} \frac{\partial^2{}_0 I}{\partial W^{\mathrm{A}}_{k} \partial W^{\mathrm{B}}_{l}} \Delta W^{\mathrm{A}}_{k} \Delta W^{\mathrm{B}}_{l} + \frac{1}{2} \sum_{\mathrm{A}ij\mathrm{B}mn} \frac{\partial^2{}_0 I}{\partial X^{\mathrm{A}}_{ij} \partial X^{\mathrm{B}}_{mn}} \Delta X^{\mathrm{A}}_{ij} \Delta X^{\mathrm{B}}_{mn} \tag{29}$$

Minimizing I yields improved values:

$$\begin{aligned} {}_1W^{\mathrm{B}}_{l} &= {}_0W^{\mathrm{B}}_{l} + \Delta W^{\mathrm{B}}_{l} \\ {}_1X^{\mathrm{B}}_{mn} &= {}_0X^{\mathrm{B}}_{mn} + \Delta X^{\mathrm{B}}_{mn} \end{aligned} \tag{30}$$

where the improvements are obtained from the equation

$$\begin{pmatrix} I_W \\ I_X \\ 0 \end{pmatrix} + \begin{pmatrix} I_{WW} & I_{xw} & \lambda \\ I_{XW} & I_{xx} & 0 \\ \lambda & 0 & 0 \end{pmatrix} \begin{pmatrix} \Delta W \\ \Delta X \\ \epsilon \end{pmatrix} = 0 \tag{31}$$

The constraints (4b), (4c), and (23) have been incorporated explicitly. The expressions for the first and second derivatives are given by

$$I_W\colon\ \partial_0 I/\partial W^{\mathrm{A}}_{k} = -2{}_0F^{\mathrm{A}}_{kk} \tag{32a}$$

$$I_X\colon\ \partial_0 I/\partial X^{\mathrm{A}}_{ij} = -4{}_0F^{\mathrm{A}}_{ij}(W^{\mathrm{A}}_{j} - W^{\mathrm{A}}_{i}) \tag{32b}$$

$$I_{WW}\colon\ \partial^2{}_0 I/\partial W^{\mathrm{A}}_{k} \partial W^{\mathrm{B}}_{l} = 2{}_0J^{\mathrm{AB}}_{kl} \tag{32c}$$

$$I_{XW}\colon\ \partial^2{}_0 I/\partial X^{\mathrm{A}}_{ij} \partial W^{\mathrm{B}}_{l} = 4{}_0G^{\mathrm{A}\,\mathrm{B}}_{ijll}(W^{\mathrm{A}}_{j} - W^{\mathrm{A}}_{i}) - 4{}_0F^{\mathrm{A}}_{ij}(\delta^{\mathrm{AB}}_{jl} - \delta^{\mathrm{AB}}_{il}) \tag{32d}$$

$$\begin{aligned} I_{XX}\colon\ \partial^2{}_0 I/\partial X^{\mathrm{A}}_{ij} \partial X^{\mathrm{B}}_{mn} = {}& 8{}_0G^{\mathrm{A}\,\mathrm{B}}_{ijmn}(W^{\mathrm{A}}_{j} - W^{\mathrm{A}}_{i})(W^{\mathrm{B}}_{n} - W^{\mathrm{B}}_{m}) - \\ & 2\{\delta^{\mathrm{AB}}_{im}[F^{\mathrm{A}}_{jn}(W^{\mathrm{A}}_{i} + W^{\mathrm{B}}_{m}) - L^{\mathrm{A}}_{jn}] - \delta^{\mathrm{AB}}_{jm}[F^{\mathrm{A}}_{in}(W^{\mathrm{A}}_{j} + W^{\mathrm{B}}_{m}) - L^{\mathrm{A}}_{in}] + \\ & \delta^{\mathrm{AB}}_{jn}[F^{\mathrm{A}}_{im}(W^{\mathrm{A}}_{j} + W^{\mathrm{B}}_{n}) - L^{\mathrm{A}}_{im}] - \delta^{\mathrm{AB}}_{in}[F^{\mathrm{A}}_{jm}(W^{\mathrm{A}}_{i} + W^{\mathrm{B}}_{n}) - L^{\mathrm{A}}_{jm}]\} \end{aligned} \tag{32e}$$

where we have used the symbols F (eq 25), J and G (eq 21, 21a), and

$$L^{\mathrm{A}}_{ij} = (W^{\mathrm{A}}_{i} + W^{\mathrm{A}}_{j})H^{\mathrm{A}}_{ij} - \sum_{k}^{\mathrm{A}} (W^{\mathrm{A}}_{i} G^{\mathrm{A}\,\mathrm{A}}_{iijk} + W^{\mathrm{A}}_{j} G^{\mathrm{A}\,\mathrm{A}}_{jjik}) W^{\mathrm{A}}_{k} \tag{33}$$

The total expressions listed correspond to a Newton–Raphson procedure. Deletion of the terms in the braces ({}) yields the Newton–Gauss procedure. The former converges faster close to the minimum. But the latter *always* yields a direction along which *I decreases* initially. By contrast the former can converge on a saddle point or a maximum. This happens when the Hessian (D^2I) has negative eigenvalues e_i.

For special symmetries the Hessian may have zero eigenvalues corresponding to redundant parameters. To treat these cases correctly, we diagonalize the Hessian:

$$D^2I|c_i\rangle = e_i|c_i\rangle \tag{34}$$

and represent eq 31 in the basis of the eigenvectors $|c_i\rangle$:

$$\langle c_i|DI\rangle + e_i\langle c_i|\Delta\rangle = 0 \tag{35}$$

The desired correction vector $|\Delta\rangle$ for the parameters $W_l^{\mathbf{B}}$ and $X_{mn}^{\mathbf{B}}$ 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 δ. 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 $W_l^{\mathbf{B}}$ and $U_{mn}^{\mathbf{B}}$. 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 $W_l^{\mathbf{B}}$ and $U_{mn}^{\mathbf{B}}$ (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.

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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 ρ_{mol} and the superposition of uniquely defined atomic reference densities ρ_{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 ρ_{at} and, hence, of the CDD, $\Delta\rho = \rho_{\text{mol}} - \rho_{\text{at}}$. 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

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

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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