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Density-Difference Maps in Quantum Chemistry*

E. Steiner

Department of Chemistry, University of Exeter, Exeter, England

Electron density-difference maps, used to study the changes that occur when a molecule changes its state or when the nuclei of a molecule change their relative positions, are generally useful only if the atomic densities cancel when one molecular density distribution is subtracted from the other. When, as in the case of the nonrigid internal rotation in ethane, such a cancellation of atomic densities is not possible the method of simple subtraction is no longer appropriate. It is shown that useful density-difference maps can nevertheless be obtained, when the changes in geometric parameters are small, by the calculation of two generalized density-difference functions: a point difference function which allows a comparison of the densities at corresponding points in the two systems, and a volume difference function to compare the amounts of charge in corresponding regions. The method is illustrated by consideration of a change in bond length of the nitrogen molecule and by the nonrigid internal rotation in ethane.

Key words: Density-difference maps.

1. Introduction

A straightforward and appealing way of representing the results of quantum mechanical calculations of the electronic structure of molecules is obtained from contour maps of orbitals and of electron-density distributions, and from density-difference maps to demonstrate the changes that occur when a system changes its state or when the nuclei of a molecule change their relative positions, as in bond formation and conformation changes. Well-known examples are the orbital maps of Wahl [1], the total density maps for diatomic molecules of Bader and co-workers [2], the corresponding density-difference maps showing the changes

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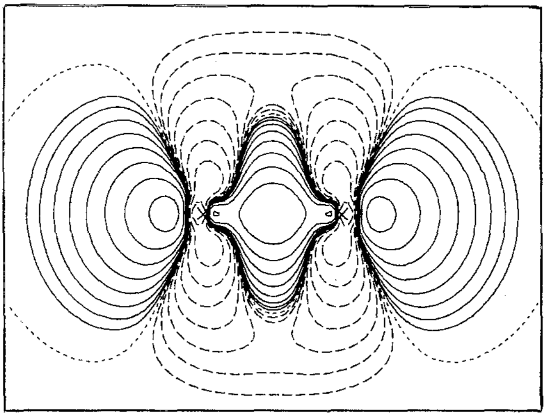


Fig. 1. Density-difference map for nitrogen molecule minus atoms. Zero contours are shown by dotted lines, positive contours by solid lines, negative contours by dashed lines. The contour values are 0, $\pm 0.001 \times 2^n a_0^{-3}$ $(n = 0, 1, 2, \ldots)$. The positions of nuclei in the plane are shown by crosses

in total density that occur when two atoms come together to form a molecule [2], and the difference maps of Jorgensen and Allen [3] showing the changes that accompany the internal rotation in ethane.

Typical electron density-difference maps for the nitrogen and ethane molecules are shown in Figs. 1 and 2. These, and all the maps discussed in this paper, have been obtained from SCF wave functions of "double-zeta" quality, calculated with the cusped-Gaussian basis $[c + 4s, 2p]$ for nitrogen [4] and $[c + 4s, 2p/2s]$ for ethane [5]. Fig. 1 shows the changes in total density that occur when two nitrogen atoms combine to form the stable molecule in its ground state. The density-difference map is obtained simply by subtracting the densities of the separate atoms from the molecular density, with the nuclei of the separate atoms coincident with the corresponding nuclei of the molecule. The small differences between Fig. 1 and the map calculated by Bader and co-workers [2] are mainly due to the absence of polarization functions from the basis used in the present work. Fig. 2 shows the changes in total electron density that accompany the rigid internal rotation of the ethane molecule from the eclipsed conformation to the staggered conformation. Fig. 2(a) is in a plane containing the C—C bond and two C—H bonds, the hydrogen on the left moving from the eclipsed position to the staggered position. Because the "atomic density" of this hydrogen does not cancel out, its presence tends to swamp the "molecular" effects on the left-hand side and, more important, in the C—C bond region. Fig. 2(b) is in the plane perpendicular to that in 2(a), and is perhaps the more informative since all the atomic densities have cancelled. It not only confirms the conclusions that can be drawn from 2(a) about the changes in the CH_3 group [6], but also shows the molecular effects in the C—C bond region.

The density-difference maps in Figs. 1 and 2 are useful because of the complete or almost complete cancellation of atomic densities. In the case of the internal rotation in ethane this has been made possible by considering a *rigid* rotation only, in which the bond lengths R_{CC} and R_{CH} and the bond angle ∠HCH are the same in both conformations. Difficulties in the production of useful difference

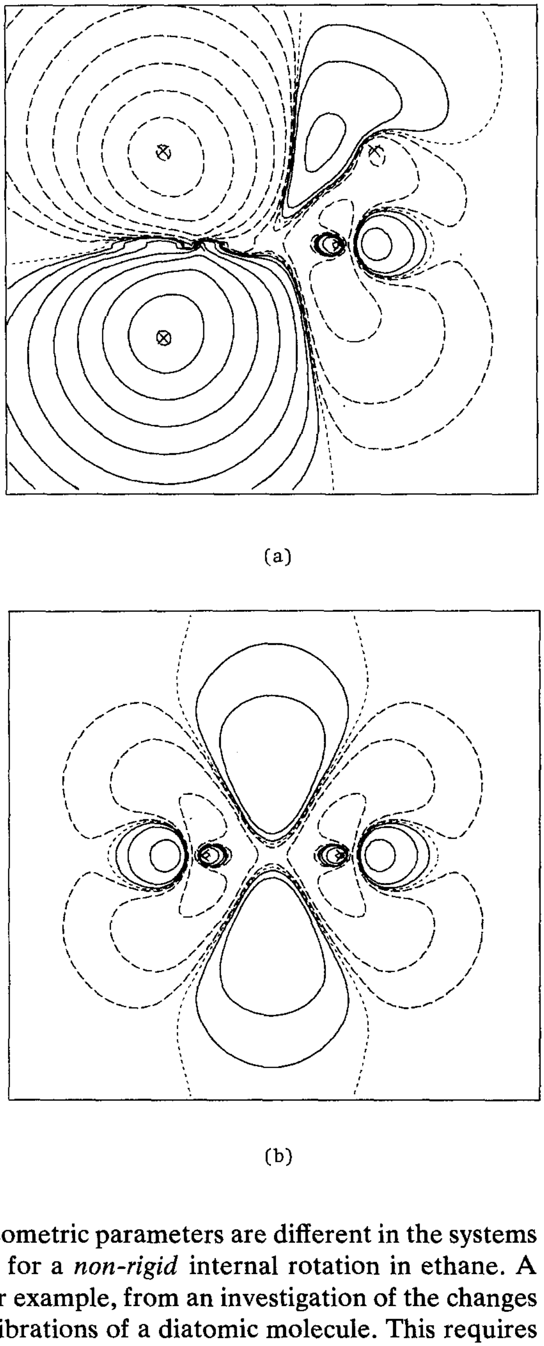
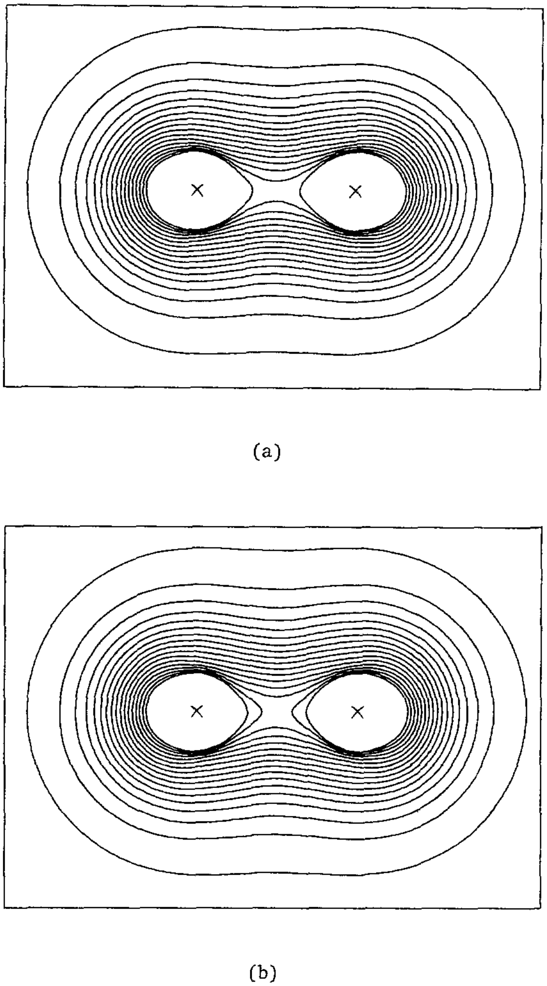


Fig. 2. Rigid internal rotation in ethane. (a) Density-difference map for staggered ethane minus eclipsed ethane in a plane containing the C—C bond and two C—H bonds. (b) Map in the plane containing the C—C bond and perpendicular to (a). The contour values are 0, $\pm 0.00002 \times 4^n a_0^{-3}$ $(n = 0, 1, 2, \ldots)$

maps arise however when such geometric parameters are different in the systems to be compared. This is the case for a *non-rigid* internal rotation in ethane. A much simpler case is obtained, for example, from an investigation of the changes in bonding that accompany the vibrations of a diatomic molecule. This requires taking the difference of the electron densities at two values of the bond length. Fig. 3 shows the total density of the nitrogen molecule at two values of the bond length, $2.068a_0$ and $2.1a_0$. Fig. 4 shows the density-difference maps for the process $R = 2.1a_0 \rightarrow 2.068a_0$ obtained by (a) superimposing the two centres and

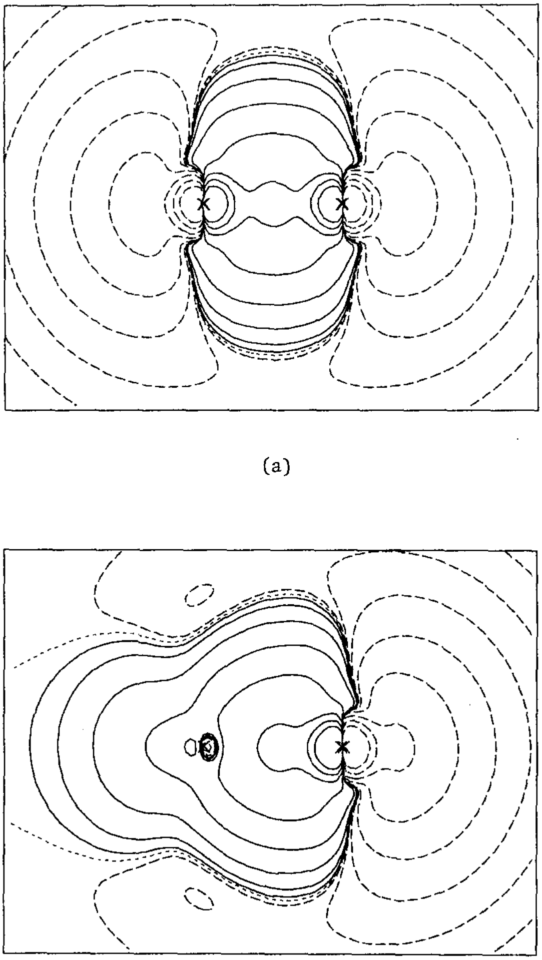


(a)

(b)

Fig. 3. Total density for the nitrogen molecule in a plane containing the nuclei at internuclear distance (a) $2.068a_0$, (b) $2.1a_0$. The contour values are $0.02+0.04na_0^{-3}$ ($n=0, 1, 2, \ldots$).

(b) superimposing the left-hand nuclei. In 4(a) the displacements of the nuclei result in an incomplete cancellation of the atomic densities, and a misleading representation of the density-difference distribution everywhere outside the region around the centre of the bond. In 4(b) the coincidence of the left-hand nuclei results in a correct representation of the difference distribution on that side of the molecule. The two maps together do not however provide a very informative picture of the changes. There is a not too unexpected overall increase in electron density in the bond region as the bond length is decreased, and 4(b) shows that this increase is smaller near the nuclei than at the centre of the bond, with even a hint of a slight decrease very close to the nuclei. However, more information about how the charge is redistributed requires either some form of integration over suitable volumes or, as is shown in the following sections, the calculation of a new type of density-difference distribution that takes into account (small) changes in bond lengths and bond angles.



(a)

(b)

Fig. 4. Density-difference maps for nitrogen at $R = 2.068a_0$ minus nitrogen at $R = 2.1a_0$ with (a) molecular centres coincident, (b) left-hand nuclei coincident. The contour values are as in Fig. 2

2. Generalized Density-Difference Functions

Consider a system whose geometry (or that part of interest) can be specified by a finite number of reference points $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$, which may be the positions of some or all of the nuclei of a molecule and possibly some other convenient points. Let $P_1(\boldsymbol{r})$ be a density function for this sytem. Consider also a second system with corresponding reference points $\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N$ and density function $P_2(\boldsymbol{s})$. A conventional density-difference function is then obtained if a common origin and common metric (a common coordinate system) can be chosen such that $\boldsymbol{s}_i = \boldsymbol{r}_i$, $i = 1 \rightarrow N$:

$$\Delta P(\boldsymbol{r}) = P_1(\boldsymbol{r}) - P_2(\boldsymbol{r}). \tag{1}$$

Two reference points, the positions of the nuclei, are used in Fig. 1, and four reference points, the positions of the nuclei in the plane for either conformation, are used in Fig. 2(a).

The problems illustrated in Fig. 4 arise because the obvious sets of reference points, the positions of the nuclei in the two systems, cannot be brought into coincidence by any choice of common coordinate system. It is always possible however to find a coordinate transformation

$$\boldsymbol{r}=f(\boldsymbol{s}) \tag{2}$$

which maps the points $\boldsymbol{s}_i$, say, onto the points $\boldsymbol{r}_i$. Such a transformation is not unique of course, and not necessarily linear, the only requirement being that $\boldsymbol{r}_i=f(\boldsymbol{s}_i)$, $i=1\rightarrow N$. Two types of transformation of the corresponding density function can usefully be considered. The first may be called a "point transformation",

$$P_2'(\boldsymbol{r})=P_2(\boldsymbol{s}) \tag{3}$$

the value of the transformed function P_2' at point $\boldsymbol{r}$ being the value of the original density function P_2 at point $\boldsymbol{s}$. A "point density-difference" function is then defined as

$$\Delta P'(\boldsymbol{r})=P_1(\boldsymbol{r})-P_2'(\boldsymbol{r})=P_1(\boldsymbol{r})-P_2(\boldsymbol{s}). \tag{4}$$

The second type of transformation of the density function arises from a consideration of the integral of the density function over the whole space; for example, the total charge in the case of a charge distribution. The total value should be invariant under the transformation. Thus, if $P_2''(\boldsymbol{r})$ is a transformed density satisfying this requirement, then, formally,

$$\int P_2(\boldsymbol{s})\,dv_s=\int P_2''(\boldsymbol{r})\,dv_r=\int P_2''(\boldsymbol{r})\frac{dv_r}{dv_s}\,dv_s. \tag{5}$$

This is not generally true for $P_2''(\boldsymbol{r})=P_2(\boldsymbol{s})$ unless $dv_r/dv_s=1$, in which case we return to the case of a common coordinate system. The invariance of the total value is clearly satisfied if

$$P_2''(\boldsymbol{r})=P_2(\boldsymbol{s})\frac{dv_s}{dv_r}. \tag{6}$$

This may be called a "(relative) volume transformation", and gives the second generalized density-difference function

$$\Delta P''(\boldsymbol{r})=P_1(\boldsymbol{r})-P_2''(\boldsymbol{r})=P_1(\boldsymbol{r})-P_2(\boldsymbol{s})\frac{dv_s}{dv_r}. \tag{7}$$

Both the density distributions (4) and (7) involve a mapping of the reference points of the second system onto those of the first. A more general procedure involves a mapping of both systems onto a third. Given a "standard" set of reference points $\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_N$ and the coordinate transformations

$$\boldsymbol{R}=f_1(\boldsymbol{r})=f_2(\boldsymbol{s}) \tag{8}$$

such that

$$\boldsymbol{R}_i = f_1(\boldsymbol{r}_i) = f_2(\boldsymbol{s}_i), \qquad i = 1 \to N \tag{9}$$

the point density-difference function in "$\boldsymbol{R}$-space" is

$$\Delta P'(\boldsymbol{R}) = f_1(\boldsymbol{r}) - f_2(\boldsymbol{s}) \tag{10}$$

and the corresponding volume density-difference function is

$$\Delta P''(\boldsymbol{R}) = f_1(\boldsymbol{r}) \frac{dv_r}{dv_R} - f_2(\boldsymbol{s}) \frac{dv_s}{dv_R}. \tag{11}$$

This more general formulation can be used to avoid any bias towards either system.

It is necessary now to specify the coordinate transformations (8), and for simplicity the one-dimensional case is considered first.

3. The One-Dimensional Case

Consider a linear density function $P(x)$ and the transformation $X = f(x)$ subject to the conditions $X_i = f(x_i)$, $i = 1 \to N$, as illustrated in Fig. 5. The simplest coordinate transformation corresponds to a linear scaling in each interval i:

$$X - X_i = (x - x_i) \frac{(X_{i+1} - X_i)}{(x_{i+1} - x_i)}$$

for $x_i < x < x_{i+1}$, $i = 1 \to N - 1$. In the "end intervals" $x < x_1$ and $x > x_N$ it can be assumed that $X - X_i = x - x_i$.

The change in the bond length of the nitrogen molecule discussed in Section 1 can be used as an example of the linear case. Fig. 6 shows the difference maps obtained by mapping both systems onto a reference structure with the mean bond length of $2.048a_0$. The point difference map in Fig. 6(a) exhibits all the important features of the simple difference maps 4(a) and 4(b), the only noticeable discrepancies being very near to the nuclei within the bond region. The volume difference map in Fig. 6(b) on the other hand shows quite dramatically how the charge is redistributed as the bond is shortened, with a movement of charge

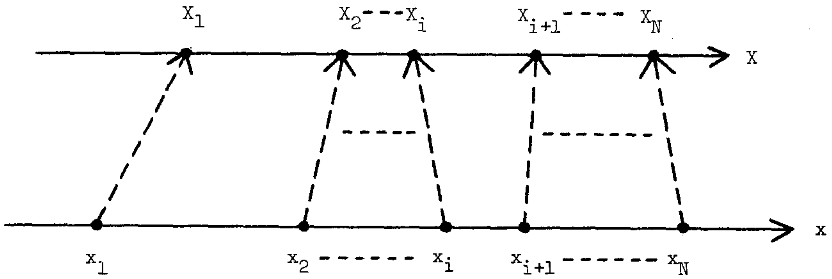
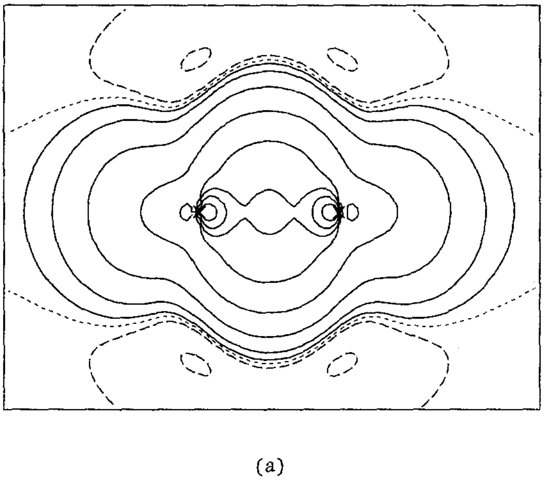


Fig. 5



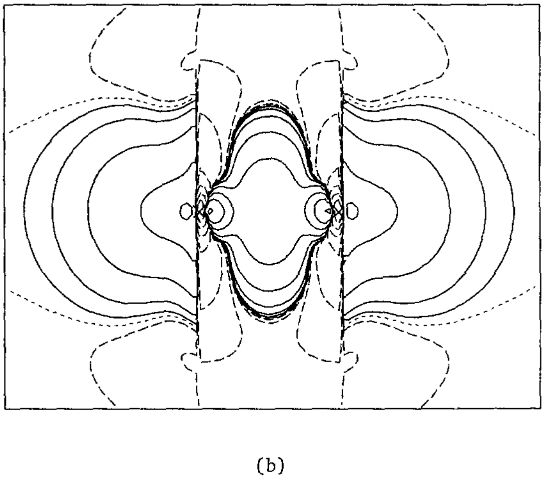


Fig. 6. Generalized density-difference maps for nitrogen at $R = 2.068a_0$ minus nitrogen at $R = 2.1a_0$. (a) Point density-difference. (b) Volume density-difference. The contours values are as in Figure 2

away from the nuclei towards the centre of the molecule and into the regions behind the nuclei. There are some striking similarities between 6(b) and the bond-formation map in Fig. 1. Both show the characteristic two-way transfer of charge, which can be interpreted in terms of an increased participation of p_σ atomic orbitals in the bonding, and a charge deficit on each nucleus reminiscent of a p_π atomic density. These similarities suggest that the volume density-difference distribution provides a valid tool for the interpretation of changes in charge distributions when the conventional methods are inappropriate.

4. The Three-Dimensional Case

If a volume density is expressed in terms of a set of orthogonal coordinates (x_1, x_2, x_3) then the simplest general procedure is to transform each coordinate separately,

$$X_i = f_i(x_i)$$

and the discussion of the one-dimensional case then applies to each coordinate. Except in special cases of very high symmetry it is most convenient to work in cartesian coordinates, with one of the coordinate axes perpendicular to the plane of interest.

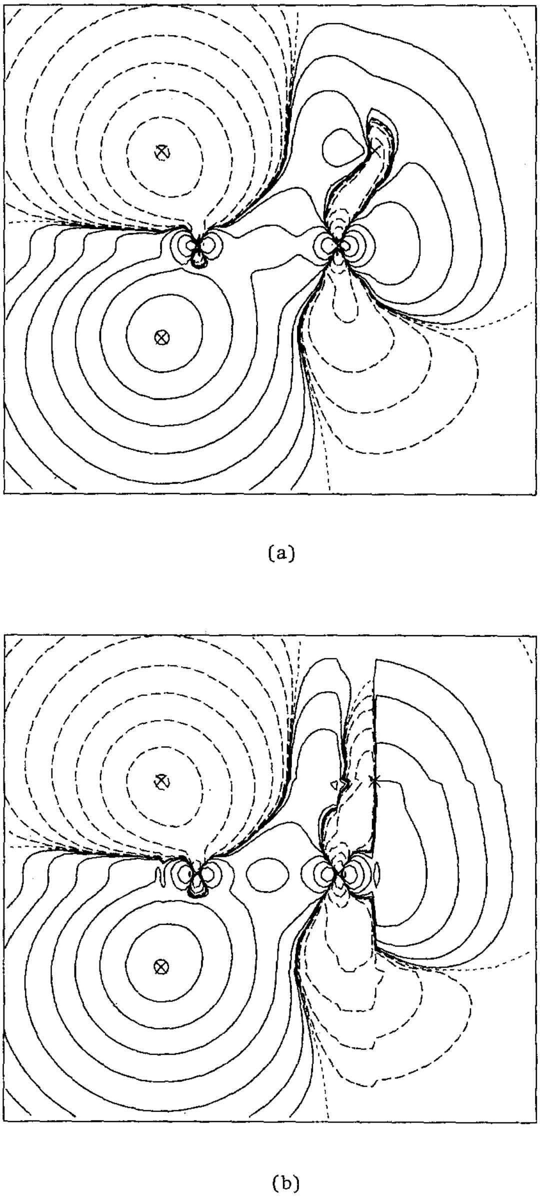
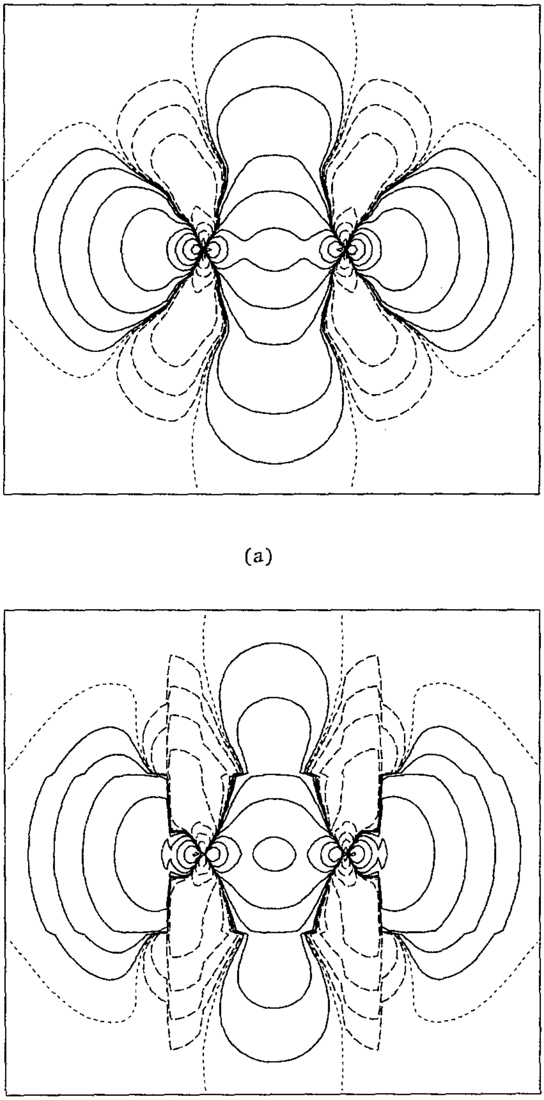


Fig. 7. Nonrigid internal rotation in ethane. Generalized density-difference maps for staggered minus eclipsed in a plane containing the C—C bond and two C—H bonds, as in Fig. 2(a). (a) Point density-difference. (b) Volume density-difference. The contour values are as in Fig. 2

The non-rigid internal rotation in ethane can be used as an example of the general case. The geometric parameters used are $R_{\mathrm{CC}} = 2.901a_0$, $R_{\mathrm{CH}} = 2.051a_0$, $\angle\mathrm{HCH} = 107.8°$ for the staggered conformation, and $R_{\mathrm{CC}} = 2.929a_0$, $R_{\mathrm{CH}} = 2.049a_0$, $\angle\mathrm{HCH} = 107.4°$ for the eclipsed. These values have been obtained by minimizing the total energy of each conformation, the optimum energies being $-79.21646E_H$ and $-79.21207E_H$, giving a barrier of 11.5 kJ mol^{-1}. Figs. 7 and 8 show the density-difference maps, staggered minus eclipsed, obtained from a



(a)

(b)

Fig. 8. As in Fig. 7, but in the plane containing the C—C bond and perpendicular to that in Fig. 7, as in Fig. 2(b)

linear mapping onto the reference structure with mean parameter values $R_{CC} = 2.915a_0$, $R_{CH} = 2.050a_0$, $\angle HCH = 107.6°$. Fig. 7 shows the point and volume density-difference maps in a plane containing the C—C bond and two C—H bonds, as in Fig. 2(a), whilst Fig. 8 shows the maps in the plane perpendicular to this, as in Fig. 2(b).

The differences between the point and volume distributions are much less striking than those observed for a simple change in bond length, with the volume distributions merely reinforcing the trends shown by the point distributions. The maps show that the relaxation of the nuclear structure results in a much greater reorganization of the electron distribution than in a rigid rotation (Fig. 2). Fig. 8 in particular shows that the rotation from the eclipsed conformation to the more stable staggered conformation is accompanied by a two-way transfer of charge from each CH_3 group, parallel to the principal axis of the molecule, which is qualitatively similar to that shown in Fig. 1 for bond formation. This is not observed for the rigid rotation, and suggests that a reinterpretation of the internal rotation in ethane may be necessary. This will be the subject of a subsequent paper.

5. Discussion

The work described in this paper represents an attempt to solve the problem of producing physically significant electron density-difference maps when the conventional method of simple subtraction is inappropriate. The use of the generalized difference functions, introduced in Sect. 2, appears to be one way of achieving this, but the procedure is clearly open to criticism on a number of grounds. Most serious is the lack of uniqueness of the coordinate transformation required to map one (small) finite set of reference points onto another. It is suggested that the piecewise linear scaling method discussed in Sect. 3 is probably the least subjective transformation, and produces physically meaningful results, at least when the changes in geometric parameters are small. A very noticeable feature of this method however are the discontinuities in the volume difference distribution resulting from the use of different scaling factors in the different intervals defined by the reference points. Although this is aesthetically displeasing, any method devised to avoid the discontinuities necessarily introduces a subjective element and greater arbitrariness into the method, and the author has not been able to find a satisfactory alternative. Finally, the use of cartesian coordinates in Sect. 3 results in a division of space into "intervals" that are rectangular parallelepipeds, and this may not always be the most appropriate choice. The method does not however rely on this choice of coordinates.

Molecular density-difference maps are useful in general only if the atomic densities can be persuaded to cancel, in order that they do not swamp the small changes of interest. When this is not possible by the conventional method of simple subtraction then, despite the possible objections, the generalized difference functions appear to provide the only suitable alternative. The point difference function coupled with the linear scaling method allows a systematic comparison of the densities at corresponding points in the two systems, whilst the volume difference function can be used to compare the amounts of charge in corresponding regions.

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