HASHIMOTO, H. & TAKAI, Y. (1983). *Bull. Jpn Inst. Met.* **22**, 595-609.
HOWIE, A. (1963). *Proc. R. Soc. London Ser. A*, **271**, 268-287.
HOWIE, A. & WHELAN, M. J. (1961). *Proc. R. Soc. London Ser. A*, **263**, 217-237.
HUMPHREYS, C. J. & HIRSCH, P. B. (1968). *Philos. Mag.* **18**, 115-122.
ISHIZUKA, Z. (1980). *Ultramicroscopy*, **5**, 55-65.
KAMIYA, Y. & UYEDA, R. (1961). *J. Phys. Soc. Jpn*, **16**, 1361-1366.
O'KEEFE, M. A. (1979). *37th Ann. Proc. EMSA*, edited by G. W. BAILEY, pp. 556-557. Baton Rouge: Claitor.
OSIECKI, R. & THOMAS, G. (1971). *28th Ann. Proc. EMSA*, pp. 178-179. Baton Rouge: Claitor.
SMITH, G. H. & BURGE, R. E. (1962). *Acta Cryst.* **15**, 182-186.

Acta Cryst. (1985). A**41**, 347-353

Electron Density and the Chemical Bond. A Reappraisal of Berlin's Theorem

BY M. A. SPACKMAN AND E. N. MASLEN

Department of Physics, University of Western Australia, Nedlands, Western Australia 6009

(*Received* 4 *September* 1984; *accepted* 11 *January* 1985)

Abstract

An increase in the electron density in the binding region is often assumed to be essential to the stability of the nuclei in chemical bonds. This is not justified by the theorem on which the assumption is based, which demands only that there be electron density in the binding region. In its simplest form the theorem places few constraints on the deformation density, which differs markedly in character for different molecules. To understand the various ways of achieving stability of the nuclei it is necessary to study both the size and the location of features in the deformation density. The effect on binding is large only for features close to the nuclei.

Introduction

A number of careful experimental determinations of the electron distribution in crystals *via* X-ray diffraction have now been described. It is hoped that analysis of the electron density, $\rho(\mathbf{r})$, will clarify the nature of chemical bonding in each specific crystal or molecule, and perhaps provide new insight into chemical bonding in general. The most common method of analysis is in terms of a deformation density, $\Delta\rho(\mathbf{r})$, obtained by subtracting from $\rho(\mathbf{r})$ the electron density derived from a model of non-interacting spherical ground-state atoms. This reference model is termed the promolecule, or independent atom model (IAM).

There is a widespread misconception that $\Delta\rho(\mathbf{r})$ is necessarily positive (*i.e.* that there should be a significant peak) between the nuclei of bonded atoms, with the magnitude of this increase in density being directly related to the covalent/ionic character of the bond. Experimental and theoretical $\Delta\rho(\mathbf{r})$ maps that do not display the expected features have often been greeted with surprise.

This situation is the result of several factors, not the least of which is a preoccupation with positive features in $\Delta\rho$ maps and almost total neglect of the negative features. The chemical literature abounds with statements that lend support to the expectation that $\Delta\rho(\mathbf{r})$ should display substantial positive peaks between the nuclei. Some of these derive from the argument that H_2 and H_2^+ are paradigms of the covalent bond, while others arise from a misuse of a theorem by Berlin (1951) on chemical binding. When correctly applied, the theorem explains why $\Delta\rho$ does not necessarily increase between the nuclei.

In this work we seek to clarify the relationship between electron density functions (both ρ and $\Delta\rho$) and the electrostatic binding of atomic nuclei. We begin with examples of recent analyses of $\Delta\rho$ maps, giving a representative sample of views on the subject, from both experimental and theoretical work. We then discuss the consequences of Berlin's theorem and its misuse.

Basic concepts

The deformation density discussed in this work is obtained by subtracting from $\rho(\mathbf{r})$ a reference model of non-interacting spherically averaged ground-state atoms, This is almost exclusively used in experimental analyses of electron density distributions, and is also commonly applied in theoretical studies. An alternative reference model consisting of the atomic states that correctly describe the dissociated atoms with no interactions has been applied by Bader and coworkers (see Bader, 1981, and references therein) to diatomics and to polyatomics of high symmetry. The use of such a reference model for large polyatomic molecules with low symmetry is difficult. The IAM or promolecule based on spherical atoms can be applied to molecules and crystals quite generally. Other arguments in its favour are given by Ransil & Sinai (1972).

0108-7673/85/040347-07$01.50

Given the one-electron density function, its electrostatic properties may be calculated by treating it as a classical charge cloud (McWeeny & Sutcliffe, 1969). This interpretation of $\Delta\rho$ follows from the Hellmann–Feynman electrostatic theorem (Hellmann, 1937; Feynman, 1939). We do not consider the role of the kinetic energy, which on bonding undergoes changes of the same order of magnitude as the potential energy (Ruedenberg, 1962; Feinberg & Ruedenberg, 1971). We avoid a debate on the merits of ignoring the role of the kinetic energy in bonding, since our concern here is with the electrostatic properties derived from the analysis of $\Delta\rho$ maps.

It is important to clarify our use of the words *binding* and *bonding.* There is understandable confusion between the terms, which are frequently used interchangeably, with results for one being used to imply something about the other. These terms were applied by Berlin (1951) to two distinct aspects of molecule formation. *Binding* relates to the forces acting on the nuclei in molecule formation, whereas *bonding* is concerned with the corresponding changes in energy. This is a commonly accepted convention (see Mulliken, 1978; Bader, 1981).

Experimental results

Early experimental determinations of $\Delta\rho$ concentrated on organic molecular crystals and covalent semiconductors, where the accumulation of electron density between bonded nuclei (*e.g.* C–C, C–H, C–N, Si–Si) is well known. When the technique became more firmly established different types of bonds were explored. Recently $\Delta\rho$ maps have been published for such exotic materials as SiP_2 and $LiAlB_{14}$. When more types of bonds were examined, apparently unsettling features were observed in $\Delta\rho$ maps.

In a study of *p*-nitropyridine *N*-oxide by Coppens & Lehmann (1976) none of the N–O bonds showed deformation density near the bond midpoint. The authors concluded that 'the complete absence of experimental density in the N–O bonds, which are electrostatic binding regions (Berlin, 1951), is difficult to understand'. In a review by Coppens & Stevens (1977) it was noted that, with few exceptions, maps for most bonds studied to that time show extra density near the midpoints of covalent bonds. Notable exceptions were provided by experimental maps for Cl_2 (Stevens, 1979), and theoretical maps for H_2O_2 (Coppens & Stevens, 1977) from the wavefunctions of Dunning & Winter (1971).

The experimental $\Delta\rho$ distributions for Cl_2 suffered from considerable difficulties associated with the collection of single-crystal X-ray data from a sample, grown *in situ*, of a weakly bound solid at 90 K. The theoretical maps for H_2O_2 do not suffer from such problems, and led Savariault & Lehmann (1980) to undertake an experimental electron density study. The resulting experimental $\Delta\rho$ maps (from a noncentrosymmetric structure) supported the theoretical calculations in all respects: 'The common feature is the absence of positive electron density between oxygen atoms. This is in contrast to what is generally observed, but it seems as well in disagreement with the requirement of balance of the electrostatic forces on the nuclei'. Savariault & Lehmann present qualitative arguments in support of their results, and on the nature of binding between atoms with electron-rich valence shells. However, they miss a most important point, as we demonstrate below. Since that time many more examples have been encountered, including tetrafluoroterephthalodinitrile ($C_8F_4N_2$) (Dunitz, Schweizer & Seiler, 1983) and 4,5,10,11-tetraoxa-1,2,7,8-tetraazatricyclo[6.4.1.1^{2,7}]tetradecane ($C_6H_{12}N_4O_4$)(Dunitz & Seiler, 1983), in which little or no electron density accumulation is observed in C–F, O–O, C–O and N–N bonds. As Dunitz & Seiler (1983) note, these results seem 'to contradict the conventional view that a build up of charge between the nuclei is necessary for covalent chemical bonding'.

A widely believed corollary to the expectation that $\Delta\rho(\mathbf{r})$ should display substantial positive peaks between the nuclei is that the less the accumulation in the bond, the more ionic is its character. This is evident from the work on Li_2BeF_4 (Collins, Mahar & Whitehurst, 1983), as well as in $LiAlB_{14}$ (Ito & Higashi, 1983) and SiP_2 (Chattopadhyay & von Schnering, 1984).

These premises have become the basic assumptions on which analyses of experimental $\Delta\rho$ maps are based. An example is the study of bonding in lithium tetrafluoroberyllate (Collins, Mahar & Whitehurst, 1983) in which the authors state that 'deformation density maps should show an accumulation of charge in the bonding region between atoms engaged in covalent bonding'. The experimental results display the (anticipated) charge accumulation between Be and F, but an absence of such an accumulation between Li and F is cited as failure to support the proposed covalent character of the Li–F bond. This latter point is made despite the absence of peaks in $\Delta\rho$ maps for O–O or N–O bonds discussed above, which can hardly be used to demonstrate that those bonds are not covalent.

Theoretical descriptions of bonding and binding

These expectations of analyses of experimental $\Delta\rho$ maps seem to arise from theoretical descriptions of the chemical bond, which lend support to the view that electron density should accumulate between the nuclei. An early example is the statement by Feynman (1939) that 'the strongest and most attractive forces arise when there is a concentration of charge between two nuclei. The nuclei on each side of the concentrated charge are each strongly attracted to it. Thus they are, in effect, attracted to each other. In an H_2 molecule, for example, the antisymmetrical wave function, because it must be zero exactly between the two H atoms, cannot concentrate charge between them. The symmetrical solution, however, can easily permit charge concentration between the nuclei, and hence it is only the solution which is symmetrical that leads to strong attraction, and the formation of a molecule, as is well known. It is clearly seen that concentrations of charge between atoms lead to strong attractive forces and, hence, are properly called valence bonds'. Feynman is quite clearly referring to *accumulation* of charge between the nuclei and near the bond midpoint, and not just to the overlap of their atomic charge clouds. Although he uses H_2 as an example, he is extrapolating to bonding generally.

In a description of the changes in $\rho(\mathbf{r})$ as atoms are brought together, Slater (1972) claims that the Hellmann–Feynman theorem can tell us where $\rho(\mathbf{r})$ must change. 'It must correspond to a nonspherical charge distribution, with excess electronic density in the region which Berlin calls the binding region. For then each nucleus will be attracted to this electronic charge in the binding region'. Slater adds that such a charge concentration has been shown for the hydrogen molecule.

As observed by Dunitz & Seiler (1983), and as is evident from the quoted sections, these descriptions of bonding are influenced by the belief that H_2 and H_2^+ are paradigms of the covalent or electron-pair bond. Mulliken (1978) writes that 'in [some] respects then, the bonding in H_2^+ is a prototype for chemical bonding in general', and McWeeny (1979) describes how the attraction of the nuclei towards the accumulation in $\Delta\rho$ for H_2 leads to 'a typical electron-pair bond'.

The deformation density for the hydrogen molecule has the unusual property of displaying an increase throughout the whole of the binding region in the vicinity of the bond axis, and a corresponding decrease beyond the nuclei. It is therefore easy to understand the expectation that $\Delta\rho$ be positive between the nuclei of bonded atoms if it is believed that H_2^+ and H_2 are typical of bonding in general. This belief is refuted by Hirshfeld & Rzotkiewicz (1974), Maclagan (1971) and Bader & Beddall (1972) where the point is strongly made that the distribution of charge and the binding in H_2 and H_2^+ is atypical and these systems are unsatisfactory for a general discussion of the chemical bond. However, such comments appear not to have been widely heeded. For H_2 the total binding force exerted by the electrons on the nuclei is in the same direction as the small component of that force due to the electrons near the bond centre, but this situation is not necessarily true for diatomic molecules in general.

The conventional viewpoint is also allegedly supported by Berlin's theorem (Berlin, 1951). As discussed by Hirshfeld & Rzotkiewicz (1974), the promolecule leads to a net repulsive force between the nuclei arising from their incomplete screening by the electron distributions. Thus Bamzai & Deb (1981) conclude that '$\Delta\rho(\mathbf{r}) > 0$ in the binding region is a necessary (though not sufficient) condition for binding'. Bader (1981) argues that the promolecule density 'happens to be one which places insufficient density in the binding region ... to ever exceed or balance the forces of repulsion. Thus one has an immediate test of a *necessary* (but not sufficient) requirement for binding: The $\Delta\rho(\mathbf{r})$ function must exceed zero within the binding region'. Other statements in the same publication show that Bader refers not to the binding region generally, but to the central region between the nuclei specifically. Thus, $\Delta\rho(\mathbf{r})$ maps for H_2 and N_2 illustrate 'a necessary common characteristic, namely, an accumulation of charge in the binding region. Similarly the $\Delta\rho(\mathbf{r})$ maps for the unstable systems He_2 and Ne_2 both exhibit a depletion of the charge density in the binding region'. It is evident from the $\Delta\rho(\mathbf{r})$ maps for Ne_2 [Fig. 2.9(*a*) of Bader, 1981] that he refers to an electron-deficient region with density less than $-0{\cdot}2\,e\,\text{Å}^{-3}$ midway between the nuclei. Although there are maxima approximately $0{\cdot}8\,e\,\text{Å}^{-3}$ in height inside the binding region, but nearer to the nuclei, Ne_2 is repulsive. F_2, for which there are deficiencies in the binding region exceeding $-1{\cdot}0\,e\,\text{Å}^{-3}$ near the nuclei (exerting a large but repulsive force on the nuclei as discussed below) is a stable molecule, using binding as our criterion for stability. These apparent contradictions are addressed neither by Bader (1981), nor in the original work by Bader, Henneker & Cade (1967), where the emphasis is on orbital contributions to the forces on the nuclei. This orbital decomposition obscures what is really a simple picture, as is illustrated in the following sections.

On the matter of the ionic nature of a bond, it is widely believed that 'ionicity' can be obtained from a knowledge of the electron density. According to Catlow & Stoneham (1983) in a review article on ionicity in solids, it is equally well known that this belief is false. However, this ignores the work of Bader & Henneker (1965) where characteristics of ionic bonding were discussed for LiF, and similar analyses of a series of alkali halide diatomics by Curtiss, Kern & Matcha (1975). Although Curtiss *et al.* define $\Delta\rho$ relative to a reference model of non-spherical atoms their conclusions are relevant here. The $\Delta\rho$ maps clearly show the transfer of charge from the alkali to the halide atom, and the amount of charge transfer correlates with the electronegativity difference of the atoms. There is no evidence for the common belief that a decreasing $\Delta\rho$ indicates a more ionic bond.

Berlin's theorem

Berlin (1951) considered an electrostatic model of a diatomic molecule, relating the external force F required to hold two nuclei at a fixed separation R to the integrated electron density in specific regions of space *via* a Hellmann-Feynman-type argument. In atomic units the force F is given by

$$F = Z_1 Z_2 / R^2 - \tfrac{1}{2}\int f\rho \, \mathrm{d}\tau, \qquad (1)$$

where Z_1 and Z_2 are the nuclear charges. f, the component of the total force per unit charge exerted on the nucleus along the internuclear axis, is given by

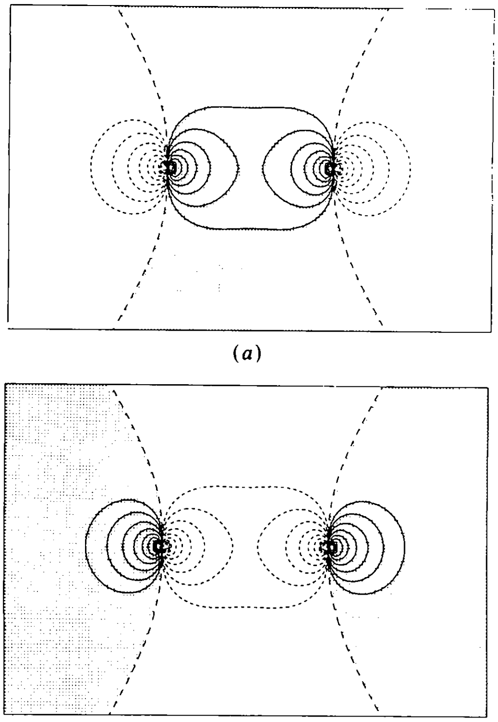
$$f = (Z_1/r_1^2)\cos\theta_1 + (Z_2/r_2^2)\cos\theta_2. \qquad (2)$$

The other variables have their usual meanings (Berlin, 1951). When F is zero, equilibrium is obtained.

One step is crucial to Berlin's definition of binding and antibinding regions. Berlin states that 'the quantity ρ is positive and never changes sign' and hence we can separate F into regions where $f > 0$ and $f < 0$,

$$F = Z_1 Z_2 / R^2 - \tfrac{1}{2}\int_{f>0} f\rho \, \mathrm{d}\tau - \tfrac{1}{2}\int_{f<0} f\rho \, \mathrm{d}\tau. \qquad (3)$$

Negative charge in regions where $f > 0$ binds the nuclei (*i.e.* reduces F) and negative charge in regions where $f < 0$ increases F. Therefore, the binding and antibinding regions in a diatomic molecule are naturally defined, and are separated by the surface defined by $f = 0$.


(*a*)

(*b*)

Fig. 1. The effective force, f, for (*a*) positive and (*b*) negative electron density functions for N_2. The shaded regions coincide with positive effective f, and are the classical binding regions (*cf.* Fig. 4 by Berlin, 1951). Antibinding regions are not shaded. The map borders are 3·175 by 2·117 Å, with an internuclear distance of 1·094 Å. Successive contours differ by factors of two, beginning at ±25·0 e Å^{-2}. Positive contours are solid, zero contour long dashes and negative contours short dashes.

Berlin is quite emphatic about the need for ρ to be positive everywhere, which enables the integral in (1) to be separated into two parts as in (3). His binding regions therefore apply to the total electron density of the molecule, but not to the deformation density, $\Delta\rho$. Applying arguments derived by assuming a positive density function for $\Delta\rho$ is a misuse of Berlin's theorem.

Nevertheless, it is possible to deduce information about $\Delta\rho$ since it consists of regions of positive and negative electron density, which behave electrostatically like negative and positive charges, respectively. If we postulate that ρ is negative we again deduce (3) from (1) directly but now the binding and antibinding regions are interchanged. Note that the nuclei are still positively charged.

From Fig. 1, which summarizes the results for the cases $\rho > 0$ and $\rho < 0$ for a homonuclear diatomic (N_2), it is clear that there is more than one way for electrostatic binding to occur. The more obvious is for ρ to increase between the nuclei. The other possibility, in the absence of additional constraints on the density, is for ρ to decrease outside the nuclei, along the internuclear axis. The latter case is generally ignored but is clearly just as valid as the former. Hence, contrary to the views expressed by Bader (1981) and Bamzai & Deb (1981), the condition $\Delta\rho > 0$ between the nuclei is *neither necessary nor sufficient* for binding.

The matter may be resolved on the basis of a qualitative argument and it is not necessary to distinguish between $\Delta\rho$ maps calculated with spherical or aspherical reference atom models. There is a difference in the way in which the two reference models shield the nuclei, and the forces due to the reference model differ in the two cases. However, this difference is one of degree and not of kind, since both reference models fail to bind the nuclei, and the corresponding deformation densities must still lead to zero net forces on the nuclei in each case.

It is important to consider the spatial nature of f, (2), the function weighting the electron density in the integral in (3). The numerical value of f is maximal along the internuclear axis where θ_1 and θ_2 are 0 or π, and close to each nucleus where r_1 or r_2 is small. Thus, compact regions of large $\Delta\rho$ close to the nuclei along the bond axis are far more important than diffuse regions of low electron density further from the nuclei. These conclusions are obvious in the contoured maps of f shown in Fig. 1. Notice that the contours of each sign on the map differ by successive factors of two, increasing from ±25·0 e Å^{-2} to more than ±10^5 e Å^{-2} close to the nuclei. These observations are by no means new (*e.g.* see Bader, Henneker & Cade, 1967) but the mapping of $f\Delta\rho$ as well as $\Delta\rho$ distributions for diatomics enables a clear distinction between the regions of $\Delta\rho(\mathbf{r})$ that are binding and antibinding. It also indicates which contribution is more important, as illustrated in the following section.

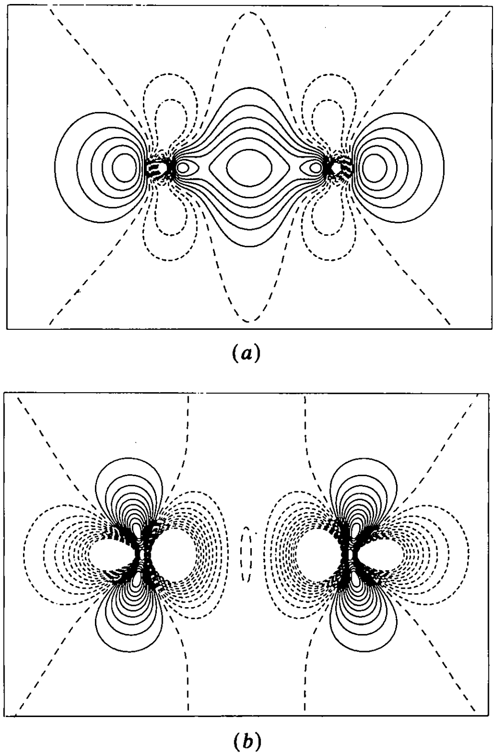
Binding in N_2 and F_2

We now examine the covalently bonded molecules N_2 and F_2; there can be no argument that either displays ionic character. Fig. 2 shows the deformation density maps resulting from subtraction of the promolecule based on the spherical atomic functions from Clementi & Roetti (1974). The molecular electron density functions are derived from the wavefunctions of Cade & Wahl (1974); that for N_2 is regarded as achieving true Hartree–Fock accuracy, while that for F_2 is only slightly inferior. It is important to remember that $\Delta\rho$ is relative to the promolecule, for which the forces on the nuclei are repulsive.

These wavefunctions are sufficiently accurate for us to treat the resulting $\Delta\rho$ features as realistic. The wavefunctions underestimate the experimental binding energies by 4·7 and 3·0 eV for N_2 and F_2 respectively, and hence are of similar quality. The difference in the electron density between these Hartree–Fock calculations and configuration interaction or multiconfiguration wavefunctions is small enough to be neglected (Zuvia & Ludena, 1978; Stephens & Becker, 1983).

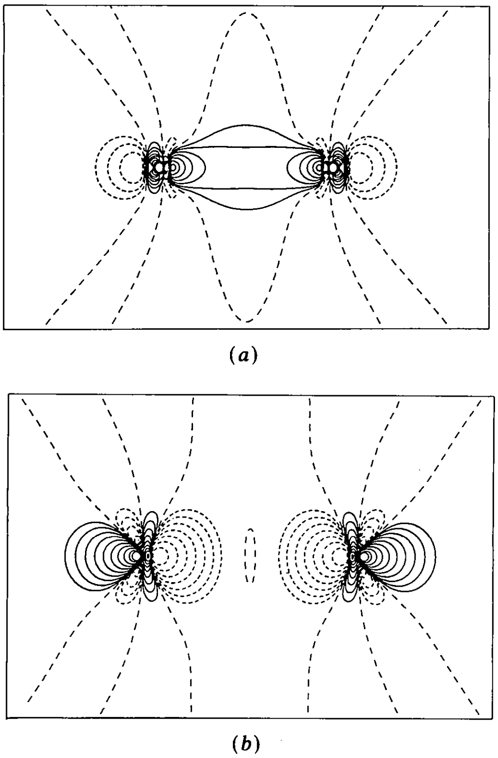
$\Delta\rho$ for N_2 is characterized by a large accumulation at the bond midpoint ($>1{\cdot}3$ e Å^{-3}) with smaller peaks beyond the nuclei along the bond axis. However, $\Delta\rho$ for F_2 displays almost no accumulation of density between the nuclei, except for a sharp peak adjacent to each nucleus. The major features in the map are large deficits of density ($<-3{\cdot}0$ e Å^{-3}) on either side of the nuclei along the bond axis. Both wavefunctions yield essentially zero net force on the nuclei, but each describes quite different means of achieving equilibrium.

To study this in more detail we examine the form of the integrand of (1) for the deformation density, $f\Delta\rho$. Pictorially we envisage this as the multiplication of Fig. 1(*a*) with Fig. 2(*a*) for N_2. Fig. 3 displays the corresponding contour maps of $f\Delta\rho$, for both N_2 and F_2, contoured at intervals differing by successive factors of two, and starting at ±25·0 e^2 Å^{-5}. The map of $f\Delta\rho$ has nodes at the same locations as those of f and $\Delta\rho$; positive regions of $f\Delta\rho$ bind the nuclei, whereas negative regions are antibinding.


(*a*)

(*b*)

Fig. 2. Deformation density maps, $\Delta\rho$, for (*a*) N_2 and (*b*) F_2. The map borders are both 3·175 by 2·117 Å, with internuclear distances of 1·094 Å for N_2 and 1·418 Å for F_2. Contours are equally spaced at intervals of 0·2 e Å^{-3} between 2·0 and $-2{\cdot}0$ e Å^{-3}. Positive, zero and negative contours as in Fig. 1.


(*a*)

(*b*)

Fig. 3. Contour maps of the force per unit charge multiplied by the deformation density, $f\Delta\rho$, for (*a*) N_2 and (*b*) F_2. Map borders and internuclear distances as in Fig. 2. Contours differ by successive factors of two, starting from ±25·0 e^2 Å^{-5}. Positive, zero and negative contours as in Fig. 1.

Evidently the major source of binding in N_2 is the sharp dipole deformation about the nuclei, readily seen in Fig. 2(*a*). That is, the accumulation within ~0·20 Å of the nuclei inside the binding region and the deficiency within the same distance of the nuclei, but inside the antibinding region, are both binding in N_2. Moreover, despite the fact that the region between the nuclei, near the midpoint of the bond, is clearly binding, it contributes little to the force on the nuclei, bearing in mind that successive contours in Fig. 3 differ for a factor of two. The diffuse accumulations beyond the N nuclei in Fig. 2(*a*) are seen to be only weakly antibinding and have little influence on the binding in N_2.

In F_2, as in N_2, large binding contributions arise from the sharp dipole about the nucleus, but there the similarity ends. The large deficiency of electron density between the nuclei evident in Fig. 2(*b*) is shown in Fig. 3(*b*) to be strongly antibinding as expected. Lobes of accumulation of density perpendicular to the bond axis, disposed along the boundary between binding and antibinding regions, make a negligible net contribution to binding in F_2. It is the deep deficit of electron density beyond the nuclei and extending along the bond axis that contributes most to the binding in F_2.

It is important to emphasize that, in both cases, the only substantial contributions to the overall binding come from regions along the internuclear axis and within ~0·4 Å of the nuclei. The build up of density near the midpoint of the bond, commonly observed in experimental $\Delta\rho(\mathbf{r})$ distributions for C–C bonds, plays almost no role in binding the nuclei. It is not a necessary condition for binding.

An accurate integration of the maps in Fig. 3 is difficult because of the rapid changes in $f\Delta\rho$ close to the nuclei, resulting from the r^{-2} dependence of f. An estimate of the reliability of the $f\Delta\rho$ maps in Fig. 3 can be obtained by visual inspection, bearing in mind that the regions away from the bond axis must be weighted by their distance from the axis. We see that $\int f\Delta\rho\, d\tau$ for F_2 is small whereas the integral for N_2 must be larger because of the predominance of positive regions along the internuclear axis. The exact value of the integral can be obtained from the promolecule, since

$$F = Z_1Z_2/R^2 - \tfrac{1}{2}\int f(\rho_{\text{promol}} + \Delta\rho)\, d\tau = 0,$$

assuming zero net forces on the nuclei in both molecular wavefunctions. Thus we find that $\int f\Delta\rho\, d\tau$ is the nuclear charge multiplied by the penetration field, $E_{p,A}$, defined by Hirshfeld & Rzotkiewicz (1974) and tabulated by them for F_2 and N_2. We obtain $\int f\Delta\rho\, d\tau$ equal to 4·30 and 0·51 e^2 Å^{-2} for N_2 and F_2 respectively, in accordance with our visual estimates. The lower value reflects both the longer nuclear separation (1·418 Å compared with 1·094 Å) and the more compact atomic electron distribution for F compared with N.

In the light of these findings, we comment on earlier attempts to account for deformation densities in bonds between atoms with electron-rich valence shells (*e.g.* N–O, O–O and C–F). Experimental $\Delta\rho(\mathbf{r})$ maps obtained for such bonds are qualitatively similar to Fig. 2(*b*) for F_2 [see especially the O–O bonds in Savariault & Lehmann (1980) and Dunitz & Seiler (1983)]. Several authors have ascribed the loss of electron density in the internuclear region to the operation of the Pauli exclusion principle, which leads to a necessary decrease in electron density in this region, and we do not dispute this description. However, this is undoubtedly antibinding in nature. The binding mechanisms are therefore expected to be a combination of polarization of the core into the binding region (Coppens & Lehmann, 1976; Savariault & Lehmann, 1980) and polarization of the π-bonding orbitals toward the binding region (Savariault & Lehmann, 1980). The first effect may be interpreted as the sharp dipolar deformation close to the nuclei in Figs. 2(*a*) and (*b*), and as discussed above is strongly binding. This effect cannot however be observed in current experimental $\Delta\rho$ maps because of thermal motion and the lack of resolution of the X-ray diffraction experiment. Savariault & Lehmann (1980) identify the polarization of π-bonding orbitals discussed by Hirshfeld & Rzotkiewicz (1974) with polarized 'lone pairs' (*i.e.* the lobes of $\Delta\rho$ accumulation in F_2 and H_2O_2). As shown above these lobes are disposed along nodes in f, (2), and contribute little to the overall binding in such systems. The most important binding mechanism is the deep extensive deficit of electron density beyond each of the nuclei in the antibinding region. This appears to have escaped notice previously.

It may appear that this description of the role of the π-bonding orbitals is at variance with that of Hirshfeld & Rzotkiewicz. We point out that the two analyses are based on arbitrary partitionings of the electron distribution: ours is a spatial subdivision of $\Delta\rho$, whereas that of Hirshfeld & Rzotkiewicz (1974) depends on an energetic partitioning (*i.e.* orbitals).

Discussion

We have presented a reappraisal of Berlin's binding and antibinding regions based on positive and negative charge densities, which is appropriate to a discussion of binding *via* $\Delta\rho$ maps. Analysis of binding in terms of the weighted function $f\Delta\rho$ is more informative than crude considerations depending only on the sign of $\Delta\rho$ in broad binding and antibinding regions. It provides a clearer understanding of the role of $\Delta\rho$ distributions in chemical binding, and explains how deformation density maps with an increase and a deficit of electron density between the nuclei can both lead to binding relative to the promolecule.

Nevertheless the value of analyses of $\Delta\rho$ in terms of binding alone must be questioned. It is clear from our analyses on N_2 and F_2 that major sources of binding are large sharp changes in density close to the nuclei. The deformation density in the centre of the bond, or far beyond the nuclei, plays little or no role in binding the nuclei. This does not imply, however, that broad topographical features are unimportant in chemical bonding. The broad topographical characteristics of the density are determined by the requirements of antisymmetry in the wavefunction, modulated by polarization terms that minimize the energy. These broad features make significant contributions to the binding energy, which is fundamental to chemical bonding.

This work was supported by the Australian Research Grants Scheme.

References

BADER, R. F. W. (1981). *The Force Concept in Chemistry*, edited by B. M. DEB, pp. 39-136. New York: Van Nostrand Reinhold.

BADER, R. F. W. & BEDDALL, P. M. (1972). *J. Chem. Phys.* **56**, 3320-3329.

BADER, R. F. W. & HENNEKER, W. H. (1965). *J. Am. Chem. Soc.* **87**, 3063-3068.

BADER, R. F. W., HENNEKER, W. H. & CADE, P. E. (1967). *J. Chem. Phys.* **46**, 3341-3363.

BAMZAI, A. S. & DEB, B. M. (1981). *Rev. Mod. Phys.* **53**, 95-126.

BERLIN, T. (1951). *J. Chem. Phys.* **19**, 208-213.

CADE, P. E. & WAHL, A. C. (1974). *At. Data Nucl. Data Tables*, **13**, 339-389.

CATLOW, C. R. A. & STONEHAM, A. M. (1983). *J. Phys. C*, **16**, 4321-4338.

CHATTOPADHYAY, T. & VON SCHNERING, H. G. (1984). *Z. Kristallogr.* **167**, 1-12.

CLEMENTI, E. & ROETTI, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177-478.

COLLINS, D. M., MAHAR, M. C. & WHITEHURST, F. W. (1983). *Acta Cryst.* **B39**, 303-306.

COPPENS, P. & LEHMANN, M. S. (1976). *Acta Cryst.* **B32**, 1777-1784.

COPPENS, P. & STEVENS, E. D. (1977). *Adv. Quantum Chem.* **10**, 1-35.

CURTISS, L. A., KERN, C. W. & MATCHA, R. L. (1975). *J. Chem. Phys.* **63**, 1621-1633.

DUNITZ, J. D., SCHWEIZER, W. B. & SEILER, P. (1983). *Helv. Chim. Acta*, **66**, 123-133.

DUNITZ, J. D. & SEILER, P. (1983). *J. Am. Chem. Soc.* **105**, 7056-7058.

DUNNING, T. H. & WINTER, N. W. (1971). *Chem. Phys. Lett.* **11**, 194-195.

FEINBERG, M. J. & RUEDENBERG, K. (1971). *J. Chem. Phys.* **54**, 1495-1511.

FEYNMAN, R. P. (1939). *Phys. Rev.* **56**, 340-343.

HELLMANN, H. (1937). *Einfuhrung in den Quantenchemie.* Leipzig: Franz Deuticke.

HIRSHFELD, F. L. & RZOTKIEWICZ, S. (1974). *Mol. Phys.* **27**, 1319-1343.

ITO, T. & HIGASHI, I. (1983). *Acta Cryst.* **B39**, 239-243.

MACLAGAN, R. G. A. R. (1971). *Mol. Phys.* **22**, 821-830.

MCWEENY, R. (1979). *Coulson's Valence.* Oxford Univ. Press.

MCWEENY, R. & SUTCLIFFE, B. T. (1969). *Methods of Molecular Quantum Mechanics.* London: Academic Press.

MULLIKEN, R. S. (1978). *Annu. Rev. Phys. Chem.* **29**, 1-30.

RANSIL, B. J. & SINAI, J. J. (1972). *J. Am. Chem. Soc.* **94**, 7268-7276.

RUEDENBERG, K. (1962). *Rev. Mod. Phys.* **34**, 326-376.

SAVARIAULT, J.-M. & LEHMANN, M. S. (1980). *J. Am. Chem. Soc.* **102**, 1298-1303.

SLATER, J. C. (1972). *J. Chem. Phys.* **57**, 2389-2396.

STEPHENS, M. E. & BECKER, P. J. (1983). *Mol. Phys.* **49**, 65-89.

STEVENS, E. D. (1979). *Mol. Phys.* **37**, 27-45.

ZUVIA, M. & LUDENA, E. V. (1978). *Int. J. Quantum Chem.* **14**, 1-11.

Acta Cryst. (1985). **A41**, 353-355

Geometrical Representation of the Algebraic Properties of Crystallographic Slip Systems

BY CLAUDE TAVARD, FRANÇOIS ROYER AND PATRICE TWARDOWSKI

Centre de Recherches 'Matière, Rayonnements et Structures', Faculté des Sciences, Ile du Saulcy, 57045 Metz CEDEX, France

(*Received* 5 *June* 1984; *accepted* 1 *January* 1985)

Abstract

Highly symmetrical crystalline materials usually possess a sufficient number of equivalent slip systems to accommodate a given plastic strain, *i.e.* to identify five components in a second-rank tensor. A direct geometrical representation would thus require a five-dimensional space when applied to any superabundant set of slip systems. However, such a difficulty can be avoided: a three-dimensional polyhedron of appropriate crystallographic symmetry is found to provide a correct description of all interdependence relationships between the glide systems. As an example, this isomorphism is used here in the effective selection of active slips.

The accommodation of a given plastic strain in polycrystalline materials may involve a number of different mechanisms (depending on dislocation motions) and their possible combinations such as slip or twin-

0108-7673/85/040353-03$01.50