Atomic Charges and Electron Density Partitioning*

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Abstract

Atomic charges are derived from two dissimilar methods of partitioning the electron density of diatomic molecules. The results given by both methods are similar, with the exception of those for molecules containing lithium; factors responsible for this discrepancy are explored. The charges derived are correlated closely with electronegativity differences and with dipole moments. They follow chemically sensible trends and have reasonable magnitudes. The partitioning methods used in the derivation can also be applied to the analysis of diffraction data for crystalline solids.

1. Introduction

X-ray diffraction provides information on the electron distribution in the scattering material. The Bragg experiment enables us to construct a three-dimensional image of the electron distribution in a crystal. The reliability of properties inferred from these distributions depends on the accuracy of structure factor moduli determined from reflection intensities. This requires a clear understanding of the roles of the various factors affecting the measured intensity. Recent work by Mathieson (1983, 1984 and references therein) on the nature of the Bragg reflection shows avenues for improving the reliability of measured structure factors, hopefully to an accuracy of 1% or better. This would bring routine measurements closer to the near ideal case of silicon, for which structure factors, derived from two different experiments, agree within their respective error bars (Aldred and Hart 1973; Teworte and Bonse 1984); in this case accuracies of better than 0.1% were achieved for two different wavelengths.

Considerable effort has also been devoted to the mapping of electron density distributions from accurate diffraction data (see e.g. Becker 1980; Coppens and Hall 1983) and to deriving physical properties from electron and nuclear charge distributions (see e.g. Spackman and Stewart 1984). We focus attention here on the derivation of atomic charges from the electron distributions. The subject of atomic charges has gained notoriety as a consequence of a wide range of values obtained by different techniques. It is not our aim to review those efforts in detail, but to demonstrate that similar and sensible atomic charges can be derived from the electron distribution by well defined but different methods.

* Dedicated to Dr A. McL. Mathieson on the occasion of his 65th birthday.

A molecule or crystal may be divided into atom-like fragments or pseudo-atoms. We then explore the differences between these and free atoms, and the extent to which the fragments are transferable from one system to another. This approach is consistent with the traditional chemical concepts of transferable functional groups (e.g. acidic, basic, carboxyl, ketone etc.). The label for each group denotes its particular type of reactivity, which is the essence of chemistry.

The properties of functional groups are, in many cases, related to the distribution of charge. It is particularly convenient to characterize the broad aspects of this distribution by a set of net atomic charges. These describe the difference between the atom-like fragments and free atoms. The non-uniqueness of such values is rightly emphasized (see e.g. Mulliken 1978; Harrison 1980; Stewart and Spackman 1981; Catlow and Stoneham 1983) but, even so, these charges are valuable indicators of chemical behaviour. As Harrison (1980) has pointed out, emphasis on the nonuniqueness of the atomic charge would be quibbling if the more sensible calculations gave essentially the same results.

The simplest chemical systems which may be used to assess the value of any charge partitioning scheme are diatomic molecules. Their electron density distributions may be obtained in a consistent manner from theoretical calculations of molecular wavefunctions. Although the results apply directly only to these simple molecules, most of the conclusions can be extended to crystalline solids. Similar procedures can be applied to solids, and the results should not be less valid than those for molecules.

2. Desiderata for Charge Partitioning

In comparing different schemes we examine the criteria necessary for a successful partitioning. The promolecule, which is fundamental to this examination, is a reference model consisting of overlapping spherically averaged ground-state atoms situated at the appropriate nuclear positions. It is a well-defined quantum mechanical entity, derived from a trial wavefunction consisting of non-interacting atomic wavefunctions. We note that electrons on different atoms are treated as distinguishable. The electron density of the promolecule is

$$\rho^{\rm pro}(r) = \sum_a \rho^{\rm at}_a(r).$$

A successful scheme must

- (i) be independent of the theoretical formalism or experimental method used to determine the distribution;
- (ii) be no more difficult to apply to polyatomic systems or solids than it is to diatomic molecules;
- (iii) yield zero charge transfer for the promolecule;
- (iv) partition the electron density into fragment volumes associated with each of the nuclei, and such fragments may overlap with each other, or be mutually exclusive;
- (v) be robust to small changes in $\rho(r)$ (i.e. be minimally dependent on small differences in the curvature of the electron density);
- (vi) be defined in simple terms which are computationally tractable.

There are two schemes satisfying most of these conditions in common use at present.

3. Bader Partitioning

The virial partitioning method of Bader and coworkers divides the space of a molecular system into non-overlapping fragment volumes in a manner dictated by the topography of $\rho(r)$. The partitioning surface is described by the collection of all paths of steepest descent originating from each internuclear saddle point and terminating at infinity. The surfaces are uniquely defined for any system. The beauty of such partitioning is that many properties of a system, including the total energy, may be partitioned into fragment contributions. We focus on the electron density, and on the net charge for each fragment in particular.

Previous applications of Bader's partitioning scheme yielded electron populations reflecting some aspects of chemical behaviour (e.g. ionicity and acidity), as is evident from the analyses of diatomic molecules by Bader and Beddall (1973), Bader et al. (1973), Bader and Messer (1974), and of aliphatic alcohols and amines by Stutchbury and Cooper (1983). The fact that typical electron populations for the fragments are usually quite different from those of neutral atoms has received limited attention so far. Oxygen populations, for example, are typically between 9.0 and 9.5 electrons, suggesting a charge transfer of ~ 1.5 electrons. This is a surprising result for molecules such as CO and CH₂OH. It has been noted by several authors (Jolly and Perry 1973; Politzer et al. 1975) that charges obtained from a similar but earlier scheme due to Bader et al. (1971) were frequently inconsistent with those derived from most other methods, but no explanation for this behaviour has been offered. However, the explanation is simple: Bader's partitioning schemes as previously applied do not yield zero charges for the promolecule, and hence do not satisfy condition (iii) above. In other words, an electron distribution with no inherent charge transfer (that for the promolecule) yields quite substantial charges with Bader's scheme (Spackman and Maslen 1985).

To correct this deficiency, we partition the promolecule electron density into fragments defined by the molecular electron density $\rho^{\text{mol}}(r)$, and subtract these from the corresponding fragments for the molecule. This is equivalent to partitioning $\Delta \rho(r)$, the deformation electron distribution, which provides values reflecting real movements of charge from that for the promolecule. All charges reported below as Δq^{B} are derived from this modified Bader partitioning of $\Delta \rho(r)$. Charges on oxygen obtained in this manner are smaller, and are always less than 0.8 electrons. We demonstrate later that these values are more consistent with chemical behaviour.

4. Hirshfeld Partitioning

Unlike the previous scheme, Hirshfeld's method of partitioning $\rho(r)$ apportions the molecular electron density among all of the atoms, according to a simple formula. Hirshfeld (1977) defined a weighting function

$$w_a(\mathbf{r}) = \rho_a^{\rm at}(\mathbf{r}) / \rho^{\rm pro}(\mathbf{r})$$

such that the atomic fragment electron density is given by

$$\rho_a^{\text{frag}}(r) = w_a(r) \rho^{\text{mol}}(r).$$

These fragment electron distributions are overlapping and continuous, unlike the Bader fragment volumes which end abruptly at boundary surfaces. The total electron count and various moments of the atom-like fragment density are obtained by integration over $\rho_a^{\rm frag}(r)$. The net atomic charge, which is the quantity of interest, is obtained by integration over the deformation density.

Both the Bader and Hirshfeld partitioning schemes thus partition $\Delta\rho(r)$, but in quite different ways. The first is a division into discrete non-overlapping volumes associated with each nucleus, and the second yields overlapping fragments which are continuous everywhere. The results are nevertheless consistent, and suggest that any sensible partitioning of $\Delta\rho(r)$ should produce meaningful atomic charges. The $\Delta\rho(r)$, which describes the transfer of electron density directly, is much smaller than $\rho(r)$. Charges based on $\Delta\rho(r)$ are far less sensitive to changes in the partitioning formula than those based on $\rho(r)$, which includes the large invariant promolecule contribution.

5. Comparison between Derived Atomic Charges

We have applied the Hirshfeld and modified Bader partitioning schemes to derive net atomic charges for a range of heteronuclear diatomic molecules. The molecular electron distributions $\rho^{mol}(r)$ were obtained from the near Hartree–Fock limit wavefunctions reported by Cade and Huo (1973, 1975) and McLean and Yoshimine (1967). The atomic electron densities used to construct $\rho^{pro}(r)$ were obtained from the analytic Hartree–Fock limit wavefunctions of Clementi and Roetti (1974). The molecules represent all first row atoms in various bonding environments and include heavier atoms up to chlorine.

All atomic charge values were obtained by numerical integration (gaussian quadrature up to 250 points) over the electron density functions in two dimensions, since the electron distributions have cylindrical symmetry. In general, the values reported are accurate to within 0.005 electrons, and frequently better than 0.001 electrons. The lighter the atoms in the molecule the more accurate is the charge transfer value. Residual errors are small enough to ensure that they do not affect the validity of any of the conclusions drawn.

Since we are dealing only with diatomic molecules, we minimize repetition of numbers by adhering to a simple convention. For the diatomic molecule AB we report *electron transfer* values Δq , which represent the number of electrons transferred from A to B. The net charges on each atom are readily derived from these values. The conventional nomenclature for the molecule AB is used where possible, i.e. the electropositive atom is usually placed first (e.g. LiF or BeO). For graphical representation of the results a more consistent convention is required, and so the Δq value represents the electron transfer from the heavy to the light atom. The use of this convention is indicated specifically when it is employed.

The charge transfer values obtained from the two partitioning schemes are reported in Table 1. For Bader's partitioning we list three values for each molecue: Δq^{pro} ,

Mole-	Bader			Hirshfeld	Ref.
cule	$\Delta q^{ m pro}$	Δq^{mol}	$\Delta q^{ m B}$	Δq^{H}	
LiH	0.644	0.911	0.267	0.414	Α
BeH	0.750	0.868	0.118	0.193	Α
BH	0.720	0.753	0.033	0.075	Α
СН	0.019	0.032	0.013	-0.016	Α
NH	-0.236	-0.322	-0.086	-0.091	Α
ОН	-0.428	-0.584	-0.156	-0.164	Α
HF	0.585	0.759	0.174	0.228	Α
NaH	0.356	0.810	0.454	0.413	Α
MgH	0.508	0·796	0.288	0.282	Α
AlH	0.613	0.825	0.212	0.228	Α
SiH	0.627	0.795	0.168	0.125	Α
РН	0.488	0.580	0.092	0.034	Α
SH	0.123	0.094	-0.029	-0.050	Α
HC1	0.108	0.240	0.132	0.124	Α
LiF	0.650	0.937	0.287	0.624	В
LiF	0.607	0.940	0.333	0.619	C
BeF	0.777	0.945	0.168	0.328	В
BF	0.962	0.940	-0.022	0.118	В
CF	0.748	0.781	0.033	0.080	В
NF	0.324	0.439	0.115	0.112	В
NaF	0.425	0.941	0.516	0.677	С
AlF	0.711	0.974	0.263	0.357	С
LiO	0.651	0.932	0.281	0.580	В
BeO	1.151	1.692	0.541	0.647	В
BO	1.216	1.552	0.336	0.376	В
CO	1.220	1.346	0.126	0.139	В
СО	1.241	1.363	0.122	0.138	С
NO	0.380	0.495	0.115	0.086	В
MgO	0.680	1.413	0.733	0.678	С
SiO	1.184	1.633	0.449	0.461	С
LiN	0.666	0.916	0.250	0.542	В
BeN	0.731	1.236	0.505	0.415	В
BN	0.979	0.836	-0.143	-0.001	В
CN	0.810	1.123	0.313	0.198	В
PN	1.310	1.741	0.431	0.289	С
LiC	0.599	0.883	0.284	0.444	В
BeC	0.574	0.853	0.279	0.233	В
LiB	0.515	0.761	0.246	0.257	В
BeB	0.334	0.438	0.104	0.086	В
LiCl	0.624	0.926	0.302	0.553	C
NaCl	0.428	0.915	0.487	0.620	С

 Table 1. Atomic charges obtained from the partitioning schemes of Bader and Hirshfeld

A Cade and Huo (1973).

^B Cade and Huo (1975).

^C McLean and Yoshimine (1967).

the charge transfer obtained from integration of $\rho^{\text{pro}}(r)$ with surfaces defined by $\rho^{\text{mol}}(r)$; Δq^{mol} , the charge transfer from integration of $\rho^{\text{mol}}(r)$ inside surfaces defined by $\rho^{\text{mol}}(r)$; and Δq^{B} , the difference between Δq^{mol} and Δq^{pro} [or the charge transfer obtained via integration of $\Delta \rho(r)$ inside the surfaces defined by $\rho^{\text{mol}}(r)$]. For

Hirshfeld's scheme we tabulate only $\Delta q^{\rm H}$, that is Δq obtained from $\Delta \rho(r)$, since Δq for the promolecule is zero by virtue of its definition. Table 1 contains results for 39 heteronuclear diatomic molecules, with duplicate results for different wavefunctions for CO and LiF, which are discussed below.

The decomposition of Δq^B in Table 1 into promolecule and molecule contributions shows that Bader's partitioning yields substantial charge transfer even when applied to the promolecule. The magnitude of Δq^{pro} is close to Δq^{mol} in all cases; Δq^B , the difference between them, never exceeds 0.8 electrons. For PN, for instance, both the promolecule and molecule indicate charge transfers of 1.310 and 1.741 electrons respectively, whereas the actual charge transferred from P to N is only 0.431 electrons. The smaller value is in far better accord with chemical behaviour, since both elements belong to the same column in the periodic table, and with the expectation that PN should be only slightly more ionic than N₂.

There is general agreement between Δq^B and Δq^H , with little evidence of broad systematic trends among the discrepancies. Closer inspection indicates that Δq^B is uniformly lower than Δq^H for Li containing compounds, the only exception being LiB, for which the internuclear distance is exceptionally long (4.5 a.u.; where 1 a.u. = 52.9177 pm). We can test the correlation between Δq^B and Δq^H quantitatively. Each charge transfer value implies two net atomic charges, providing 82 values for comparison of the two schemes. This includes duplicate results for the CO and LiF molecules. A least squares fitted line with Δq^B as abscissa and Δq^H as ordinate yields a slope of 1.157. The intercept is zero by symmetry, and the correlation coefficient is 0.943. Omission of the Li containing molecules gives a line of best fit (66 points) with a slope of 1.016 and correlation coefficient of 0.968. Clearly the two estimates of charge transfer are closely related to each other, especially if we exclude molecules containing lithium.

The factors responsible for the disparity between values obtained for molecules containing Li are revealed by an examination of the partitioning surfaces defined by $\rho^{mol}(r)$ in Bader's scheme. Maps of virial surfaces for first row hydrides (see Fig. 2 of Bader and Beddell 1973) and second row hydrides (see Fig. 2 of Bader and Messer 1974) have been published. The surface defined for the Li fragment in LiH is unlike the others, in that it tends to close tightly around the Li nucleus. All other surfaces in these studies traverse the internuclear region along a curve roughly perpendicular to the bond axis. However, a surface similar to that for LiH is defined about the Li nucleus in LiF (see Fig. 2-23 of Bader 1981). The wavefunctions used for both diagrams were studied here. Since the Li surfaces curve around the Li nucleus, integration of $\Delta \rho$ inside the boundary excludes a substantial volume of negative density away from the bond axis, which is nevertheless closer to the Li nucleus than the H or F nucleus. In Fig. 1 we give maps of $\Delta \rho$ for LiH and LiF with these virial surfaces superimposed. It is obvious that if the surfaces were more nearly perpendicular to the bond, as they are for the other hydrides, the charge transfer for Li would be greater. Hence $\Delta q^{\rm B}$ would be closer to $\Delta q^{\rm H}$. Although the magnitude of $\Delta \rho$ in this region is not large, the density about Li in these molecules is diffuse. Contributions from regions well outside the map borders in Fig. 1 are still significant.

The shapes of the virial surfaces near the edge of the maps in Fig. 1 are curious; that for LiH becomes almost linear in the projection on the plane of the mapping, whereas that for LiF appears to be closing in on the Li nucleus, back towards the



Fig. 1. Deformation density maps $\Delta\rho(r)$ for (a) LiH and (b) LiF. The contour interval is $0.1 \ e \text{\AA}^{-3}$; map borders are 9 by 8 a.u., with the nuclear positions indicated on the horizontal borders. Molecular wavefunctions are from Cade and Huo (1973, 1975).

bond axis. This conflicts with the monotonic decrease in $\rho^{mol}(r)$ expected as r tends to infinity, and with the elliptical asymptotic shape of contours of $\rho^{mol}(r)$ expected for diatomic molecules. The surface defined by $\rho^{mol}(r)$ for LiF does indeed close



Fig. 2. Total electron density maps $\rho(r)$ for LiF from the wavefunctions of (a) Cade and Huo (1975) and (b) McLean and Yoshimine (1967). Successive contours differ by a factor of 10; the smallest contour enclosing the Li nucleus is $1 \cdot 0 \ ea.u.^{-3}$, and the smallest around the F nucleus is $10 \cdot 0 \ ea.u.^{-3}$. The virial surfaces are indicated by dashed curves. Map borders are 30 by 20 a.u., with nuclear positions indicated on the horizontal borders.

back onto the molecular axis, as is shown in Fig. 2*a*, where $\rho^{\text{mol}}(r)$ is contoured at logarithmic intervals, and the dimensions of the map are expanded. The asymptotic nature of the molecular electron density is far from elliptical, and shows the influence of a large contribution from the 1π orbital, which has a node along the internuclear axis.

To explore the wavefunction dependence of these surfaces, we plotted (see Fig. 2b) $\rho^{\text{mol}}(r)$ and the corresponding virial surface for the wavefunction for LiF by McLean and Yoshimine (1967). Whereas the two electron densities in Fig. 2 essentially superimpose at distances from the nuclei of the order of the bond length, they differ

radically at larger distances. As a consequence, the boundary surfaces defined by $\rho^{mol}(r)$ also change dramatically at large distances from the nuclei. Although the two wavefunctions are computed at slightly different bond lengths (2.955 and 2.9877 a.u. for Figs 2*a* and 2*b* respectively), the difference is too small to account for the changes in the electron densities. It is claimed that both wavefunctions are near the Hartree-Fock limit. Although they are constructed from slightly different basis sets, the corresponding energies differ by only 0.033 eV, with the McLean and Yoshimine value being lower.

Although boundary surfaces for the two LiF electron densities differ radically, the Δq^{mol} values from Table 1 are nearly identical. However, Δq^{pro} is greater for the wavefunction of Cade and Huo (Fig. 2*a*) than for that of McLean and Yoshimine (Fig. 2*b*). This is expected since the volume of integration of $\rho^{\text{pro}}(r)$ is substantially smaller for the former. Thus, the Δq^{B} values differ by almost 0.05 electrons for the two wavefunctions; Δq^{H} is much more robust, differing by only 0.005 electrons.

This sensitivity of Δq^B to subtle details of the electron density is worrying, since the basis sets for both wavefunctions are large and the energies are similar. For CO, two particularly high quality wavefunctions were obtained from the same sources. Both were calculated at the same internuclear distance, and show an energy difference of ~ 0.085 eV, with the McLean and Yoshimine value again being lower. The total densities and virial surfaces were examined closely to assess the degree of correspondence between these high quality Hartree–Fock wavefunctions. The virial surfaces can be superimposed out to ~ 7 a.u. from the bond axis. However, the long range behaviour of the densities differs radically, by an order of magnitude at ~ 9 a.u. from the oxygen nucleus along the bond axis. Although Δq^B values differ only by a small amount (0.004 electrons), as expected from the similarity of the virial surfaces, the difference is greater than that between Δq^H values (0.001).

The wavefunction dependence of the electron density at large distances from the nuclei is clearly due to the lack of completeness of the basis sets used for the expansion of the molecular orbitals. The similarity of the energies shows their insensitivity to the nature of the wavefunction at such distances. This behaviour is consistent with the basis set dependence reported for quadrupole moments by McCullough (1981), for polarizabilities by Christiansen and McCullough (1978) and for hyperpolarizabilities by Christiansen and McCullough (1979). Those properties depend increasingly on regions of $\rho^{mol}(r)$ far from the nuclei. The maps of $\rho^{mol}(r)$ in Fig. 2 contoured at logarithmic intervals illustrate this basis set dependence in a more graphic manner.

We believe that the sensitivity of the virial surfaces, and hence Δq^B , to fine details of the wavefunction is especially strong for Li containing compounds, where the electron density around the lithium nucleus is particularly diffuse, and hence is difficult to describe with a finite basis set optimized variationally. Indeed, the only other example of curious behaviour of a virial surface, among those listed in Table 1, was for LiCl, for which $\rho^{mol}(r)$ actually displayed local minima at ~ 7.5 a.u. from the Li nucleus. These minima, which make any partitioning of the electron density on the basis of topography difficult, coincide with a node in the 2π orbital located far beyond the Li atom. This is undoubtedly an artifact of the basis set used. The phenomenon does not affect the numerical values of charge transfer reported in Table 1 for LiCl in an obvious way. The indeterminacy of the surface beyond these minima is of minor consequence in estimating charges, since the regions beyond ~ 7.5 a.u. from the Li nucleus make a negligible contribution to the Δq values. This is not equivalent to stating that Δq^{B} values are totally insensitive to small changes in the wavefunction. Clearly they are likely to be sensitive for Li containing molecules.

In view of the general similarity of Δq^B and Δq^H values for the remaining molecules, and the sensitivity of the former to the quality of the wavefunction for Li compounds, further discussion relates to Δq^H values only. The fact that Hirshfeld's partitioning is computationally more tractable than Bader's, which in general requires the definition of three-dimensional boundary surfaces in polyatomic molecules with no symmetry, is a pleasant bonus.



Fig. 3. Plot of $\Delta q^{\rm H}$ against Pauling electronegativity differences $\Delta \chi$. The line through the data points is the best fit to the 31 points, excluding molecules containing fluorine (see Section 6*a*). The $\Delta q^{\rm H}$ values represent electron transfer from the heavy to the light atom.

6. Physical Meaning of Atomic Charges

Having established the close correlation between $\Delta q^{\rm H}$ and $\Delta q^{\rm B}$ values for a large number of heteronuclear diatomic molecules, and indicating our preference for those derived from Hirshfeld's scheme, we now demonstrate that these charges are physically sensible. They display the trends expected from known chemical behaviour, and their magnitudes are consistent with physical properties.

(a) Chemical Behaviour

Chemical behaviour of atoms may be summarized succinctly by using the concept of electronegativity. Pauling (1960) defined electronegativity as the power of an atom in a molecule to attract electrons to itself, although Pauling's scale is based on analyses of diatomic bond energies. A more obvious link is expected between electronegativity and the force of attraction between the atom and an electron at a distance comparable with the atomic covalent radius. Scales based on this approach have been reported by Allred and Rochow (1958) using empirical radii, and by Boyd and Markus (1981) using non-empirical radii. In general the values for these schemes differ little from those by Pauling.

We expect correlations between the charge transfer estimates described in the previous section and differences in electronegativities. In Fig. 3 the charge transfer values $\Delta q^{\rm H}$ are plotted against the electronegativity differences $\Delta \chi$ from Pauling's scale. In this diagram we define $\Delta q^{\rm H}$ in the sense of electron transfer from the heavy atom to the light atom, and $\Delta \chi$ is the electronegativity difference for the light atom minus the heavy atom. This classification enables us to better explore the correlation evident in Fig. 3. The correlation coefficient obtained for the 39 points in Fig. 3 (omitting the duplicate CO and LiF values) is 0.945, indicating that $\Delta q^{\rm H}$ is correlated strongly with $\Delta \chi$. Correlation coefficients obtained with other electronegativity scales are slightly lower (0.932 for the Allred and Rochow scale and 0.925 for that by Boyd and Markus).

Despite the high correlation between $\Delta q^{\rm H}$ and $\Delta \chi$, it is evident from Fig. 3 that the values for compounds containing fluorine deviate further from the mean distribution than those for other families. Omission of the molecules containing fluorine increases the correlation coefficient between $\Delta q^{\rm H}$ and $\Delta \chi$ to 0.977 for the remaining 31 points. The line drawn through the points in Fig. 3 is the best fit to these 31 molecules not containing fluorine. It is clear that the values of $\Delta q^{\rm H}$ obtained for the heteronuclear diatomic molecules are chemically consistent and sensible. They could be used to *define* an electronegativity scale, which would be essentially the same as that by Pauling, except that $\chi_{\rm F}$ would be reduced by ~0.8 from Pauling's value, with perhaps a smaller lowering for oxygen.

(b) Dipole Moments

The dipole moment of an uncharged molecule plays a dominant role in long range electrostatic interactions (Buckingham 1967). It is reasonable to expect that partitioning of $\rho^{\text{mol}}(r)$ into net atomic charges should reflect the polarity of the molecule, especially in cases where the atomic charges indicate a large amount of charge transfer. Jolly and Perry (1973) claimed that the correlation of dipole moments with atomic charges is a hopeless task, while Hirshfeld (1977) made a similar statement about attempts to derive atomic charges from dipole moments. Both works cited Coulson (1965), who discussed the importance of local polarizations of the electron density near each atomic nucleus (i.e. the contribution of the dipole moments of the atom-like fragments to the molecular dipole). Despite this pessimism, we plot in Fig. 4 Δq^{H} values (as in Fig. 3) against the charge transfer values predicted by the dipole moments μ , calculated from the molecular wavefunctions. The predicted values are obtained by assuming results from two point charges separated by a distance R, and hence $\Delta q = \mu/R$, with μ and R in atomic units.



Fig. 4. Plot of $\Delta q^{\rm H}$ against μ/R , the charge predicted by the molecular dipole moment. The line through the data points is the best fit to all 39 points. The $\Delta q^{\rm H}$ values represent electron transfer from the heavy to the light atom.

The lens shaped distribution of points in Fig. 4 belies the pessimism referred to above. There is a strong relationship between $\Delta q^{\rm H}$ and the molecular dipole moments. The correlation coefficient for the 39 points in Fig. 4 is 0.939, and the slope of the least squares line of best fit is 0.644, with an intercept of 0.019. In other words, $\Delta q^{\rm H}$ is generally ~65% of that which would be predicted from the assumption of point charges separated by the internuclear distance, satisfying μ .

The large spread of points with $|\Delta q^{\rm H}| < 0.4$ electrons reflects the fact that the fragment dipoles are important for systems such as BF, BN, CO, CF and many hydrides. These are commonly described as covalent, and for such molecules we expect fragment polarizations to be appreciable. On the other hand, more ionic species such as NaF, LiF, BeO and MgO display little deviation from the line of best fit. This suggests that these molecules are basically ion pairs with weaker local polarizations.

To test this assertion we constructed ion pairs from Hartree-Fock ionic wavefunctions (Clementi and Roetti 1974) for Li^+F^- and Na^+F^- . At the molecular internuclear separations, these 'ionic' density functions give Δq^{H} values of 0.600 and 0.665 electrons for electron transfer from cation to anion in Li^+F^- and Na^+F^- respectively. These are close to the values obtained from molecular wavefunctions (McLean and Yoshimine 1967) of 0.619 and 0.677 respectively. They follow precisely the pattern of the more ionic points in Fig. 4. Even the small difference between the Δq^H values for the two ion pairs is consistent with this trend, reflecting the longer internuclear separation for Na^+F^- since, as *R* increases, Δq^H must approach 1.0.

An examination of the ion pair model explains why the charge transfer obtained is less than 1.0. The $\Delta\rho(r)$ for the ion pair is the sum of the two component deformation densities. That for the cation is negative in the valence region, whereas the anion deformation is positive (see Figs 1 and 2 of Boyd and Choi 1983). The overlap of the component deformations leads to a cancellation in $\Delta\rho(r)$, and hence the total deformation density is less pronounced than that of the components separately. In a sense, information about the deformation of the atoms to form ions is lost, which no method of partitioning ρ or $\Delta\rho$ can adequately retrieve. Hirshfeld's scheme must therefore yield charge transfers lower than the ionic values, even for a purely ionic model. The deviation of the charges from 1.0 is a simple function of the internuclear distance, with an almost linear relationship between $\Delta q^{\rm H}$ and R, with R between 1.5 and 4.5 a.u. for Li⁺F⁻. Even at R = 8.0 a.u., $\Delta q^{\rm H}$ is still less than 0.95 electrons.

From this analysis it is evident that partitioning will not yield the charges expected from ionicity arguments directly: it simply sets lower bounds. The fact that lithium fragments in Bader's virial partitioning of LiF and LiH yield Δq^{mol} close to $1 \cdot 0$ (see Table 1) may correspond with an intuitive concept of an ionic fragment (Bader 1981). It does not imply charge transfer of one electron, as the promolecule yields values of similar magnitude. The only satisfactory way to describe the ionicity of an electron distribution is to compare it with an ionic model, as shown above for LiF and NaF, and as discussed by Bader and Henneker (1965).

It is possible to analyse the deviations of points from the line of best fit in Fig. 4 on the basis of atomic fragment dipole moments, calculated in a manner similar to that used for $\Delta q^{\rm H}$ (Hirshfeld 1977). However, these fragment dipoles are, to an extent, an artifact of the partitioning and, in the same manner that the sum of fragment electron densities retrieves the molecular electron density, summed contributions from fragment charges and dipoles necessarily yield the correct dipole moment. Since the ion pair model yields charges too small to satisfy μ , the fragments must have nonzero dipole moments in order to retrieve μ , despite the fact that the ions comprising the model are spherical. In view of this, we conclude the discussion on dipole moments, having established the existence of a relationship between $\Delta q^{\rm H}$ values and the charge transfer estimates from molecular dipole moments, and demonstrated that the $\Delta q^{\rm H}$ values are sensible in magnitude, since they are always less than those predicted by an ionic model.

7. Conclusions

Despite the widespread pessimism about the virtue of calculating atomic charges, they are nevertheless a powerful tool for explaining chemical and physical properties. We have therefore attempted to restore some credibility to these quantities. Two dissimilar methods of partitioning the electron density yield estimates of charge transfer which agree with each other for a wide range of atoms in different bonding environments. Although our study is restricted to diatomic molecules, it is clear that the conclusions will be valid for polyatomic systems, including solids.

We do not intend here to justify all atomic charge estimates: clearly some are less valid than others. The principal reason why the atomic charges derived from the two methods agree with each other is that both partition $\Delta \rho$. We expect that any sensible means of partitioning the deformation density will yield similar results. By virtue of the fact that the charges are relative to the promolecule, for which the charge transfer and dipole moment are zero, these charges show sensible correlations with chemical behaviour (as exemplified by electronegativities) and dipole moments.

Hirshfeld's (1977) method should be applicable to the determination of atomic charge estimates from X-ray diffraction data for crystals. Charges calculated by this method should avoid problems associated with methods which partition $\rho(r)$ by pseudo-atom multipole expansions (Stewart and Spackman 1981; Baert et al. 1982). Hirshfeld and associates have determined atomic charges from multipole expansions of $\rho(r)$ for molecular crystals (Hirshfeld and Hope 1980). These results have also been applied to the calculation of molecular crystal packing energies (Berkovitch-Yellin and Leiserowitz 1980, 1982). We expect that the partitioning will apply to crystalline solids in general. In this manner, relationships between electron distributions in chemically related families of solids (e.g. silicates) can be explored, using the atomic charge as a simple indication of the loss or gain of electrons in the vicinity of the atom. Atomic charges derived from diffraction data by some current methods appear to be too large, based on the considerations of the ionic pair model (see e.g. Sasaki et al. 1980). It would be a worthwhile exercise to apply Hirshfeld's partitioning scheme to the data sets to test whether silicon and oxygen are charged as highly as the original results suggest.

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