

Voronoi Deformation Density (VDD) Charges: Assessment of the Mulliken, Bader, Hirshfeld, Weinhold, and VDD Methods for Charge Analysis

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Abstract: We present the Voronoi Deformation Density (VDD) method for computing atomic charges. The VDD method does not explicitly use the basis functions but calculates the amount of electronic density that flows to or from a certain atom due to bond formation by spatial integration of the deformation density over the atomic Voronoi cell. We compare our method to the well-known Mulliken, Hirshfeld, Bader, and Weinhold [Natural Population Analysis (NPA)] charges for a variety of biological, organic, and inorganic molecules. The Mulliken charges are (again) shown to be useless due to heavy basis set dependency, and the Bader charges (and often also the NPA charges) are not realistic, yielding too extreme values that suggest much ionic character even in the case of covalent bonds. The Hirshfeld and VDD charges, which prove to be numerically very similar, are to be recommended because they yield chemically meaningful charges. We stress the need to use spatial integration over an atomic domain to get rid of basis set dependency, and the need to integrate the deformation density in order to obtain a realistic picture of the charge rearrangement upon bonding. An asset of the VDD charges is the transparency of the approach owing to the simple geometric partitioning of space. The deformation density based charges prove to conform to chemical experience.

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Introduction

One of the most generally used concepts in chemistry is the atomic charge, which has the following intuitive meaning: when two noninteracting atoms A and B (**1**) form a chemical bond (**2**), the atomic charge of A resulting from the formation of the chemical bond is the amount of electronic density gained from (**2a**) or lost to (**2b**) atom B (Scheme 1). The definition can be made precise in some ideal cases. In an ideal ionic bond there is a complete transfer of electronic charge from one atom to the other (charges +1 and –1) and in the ideal covalent bond the electron pair is shared equally (charges 0). However, most molecules are not ideal cases and therefore chemists^{1–8} have tried to develop over the years methods to quantify the atomic charge. Quantification raises the problem: how can one partition the electronic density, which does not by definition belong to any atom, over the different atoms. Different ways of dividing lead to different numbers for the atomic charges and therefore possibly to different ways of interpreting the nature of the chemical bond. In this article we address the problem of assigning a value to the atomic charge, and we judge various methods for doing so in the light of the usefulness of the resulting

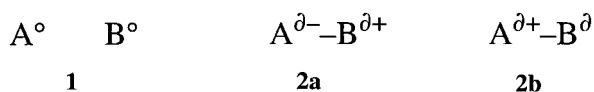
atomic charges for the characterization of the nature of the chemical bond.

The oldest and also the best known definition of the atomic charge is the Mulliken population analysis.¹ This method uses the basis functions, in terms of which the molecular wave function is expressed. Thus, the orbitals $\psi_i(\mathbf{r})$ are expanded in basis functions $\chi_\mu(\mathbf{r})$ centered on atoms A, that is, $\psi_i(\mathbf{r}) = \sum_A \sum_{\mu \in A} c_{\mu i} \chi_\mu(\mathbf{r})$. The total number of electrons N_e of the molecule is then given by $N_e = \sum_i^{\text{occ}} n_i \int |\psi_i(\mathbf{r})|^2 d\mathbf{r} = \sum_{A,B} \sum_{\mu \in A, \nu \in B} \sum_i^{\text{occ}} n_i c_{\mu i} c_{\nu i} \int \chi_\mu(\mathbf{r})^* \chi_\nu(\mathbf{r}) d\mathbf{r} = \sum_{A,B} \sum_{\mu \in A, \nu \in B} \mathbf{D}_{\mu, \nu} S_{\mu, \nu}$ with orbital occupations n_i , the elements of the density matrix \mathbf{D} defined as $\mathbf{D}_{\mu, \nu} = \sum_i^{\text{occ}} n_i c_{\mu i} c_{\nu i}$, and the overlap integral $S_{\mu, \nu}$ between $\chi_\mu(\mathbf{r})$ and

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Scheme 1

$\chi_\nu(\mathbf{r})$. The diagonal elements $\mathbf{D}_{\mu,\mu}S_{\mu,\mu}$ represent the net Mulliken population that basis functions χ_μ acquire in the molecule. The gross Mulliken population Q_μ of basis function $\chi_\mu(\mathbf{r})$ is obtained by assigning half of each total overlap population ($\mathbf{D}_{\mu,\nu}S_{\mu,\nu} + \mathbf{D}_{\nu,\mu}S_{\nu,\mu}$) to this basis function (and the other half to the corresponding other basis function) as shown in eq. (1):

$$Q_\mu = \mathbf{D}_{\mu,\mu}S_{\mu,\mu} + \sum_{\nu(\neq\mu)} \frac{1}{2} (\mathbf{D}_{\mu,\nu}S_{\mu,\nu} + \mathbf{D}_{\nu,\mu}S_{\nu,\mu}) \quad (1)$$

The Mulliken charge of atom A is obtained by summing up the gross populations Q_μ for all basis functions $\chi_\mu(\mathbf{r})$ centered on that atom ($\mu \in A$) and subtracting them from the corresponding nuclear charge Z_A , as shown in eq. (2):

$$Q_A^{\text{Mulliken}} = Z_A - \sum_{\mu \in A} Q_\mu \quad (2)$$

The half-and-half division of the overlap populations does not take into account the difference in electronegativity between the two atoms. Furthermore, this approach does not, in principle, converge with increasing basis set size. Unrealistic atomic charges can therefore result. Improvements^{2,3} have been proposed to overcome these types of problems associated with atomic charge schemes, such as the Mulliken method, that are based on populations of (atom-centered) basis functions. The most important is the Natural Population Analysis (NPA) developed by Reed et al.³

The above methods are all based on a representation of the molecular wave function using basis functions. We recognize a second class of methods, which is based directly on the electron density as a function of space. An example of such an atomic charge scheme, which is used in this article, is the Hirshfeld method.⁴ It makes use of the electronic density of the molecule and of a fictitious promolecule. The promolecule is defined as the sum over the (usually spherically averaged) ground-state atomic densities:

$$\rho_{\text{promolecule}}(\mathbf{r}) = \sum_B \rho_B(\mathbf{r}) \quad (3)$$

The electronic density ρ_{molecule} of the real molecule at each point in space is then distributed over the atoms A in the same ratio as the atomic densities $\rho_A(\mathbf{r})$ contribute at that point to the promolecule density: $\rho_A^{\text{molecule}}(\mathbf{r}) = (\rho_A(\mathbf{r})/\rho_{\text{promolecule}}(\mathbf{r}))\rho_{\text{molecule}}(\mathbf{r})$. The Hirshfeld atomic charge is then obtained by subtracting the integral of the density associated with atom A from the corresponding nuclear charge Z_A [eq. (4)]:

$$Q_A^{\text{Hirshfeld}} = Z_A - \int \frac{\rho_A(\mathbf{r})}{\rho_{\text{promolecule}}(\mathbf{r})} \rho_{\text{molecule}}(\mathbf{r}) d\mathbf{r} \quad (4)$$

We see that the Hirshfeld scheme accounts in a natural way for the fact that each atom has a certain characteristic size.

The Atoms in Molecules (AIM) approach of Bader⁵ is also based on the spatial function $\rho(\mathbf{r})$ and not on orbital coefficients or other basis function related quantities. This method uses the topology of the electron density to define an atomic domain. It starts with locating the bond critical points (bcps), which are the points of minimum charge density (zero gradient) along a bond path and a maximum in the normal direction to the bond. The bcps are used to determine the zero-flux surfaces, which then divide the molecule into atomic regions. Integrating the electronic density within an atomic region gives the charge assigned to that atom [eq. (5)]:

$$Q_A^{\text{Bader}} = Z_A - \int_{\text{atomic region determined with bcps}} \rho(\mathbf{r}) d\mathbf{r} \quad (5)$$

The present article deals with a new definition of atomic charge, the Voronoi Deformation density (VDD) method, which was first proposed by us in ref. 2a (for the concept of Voronoi cells, see ref. 9). Its three distinguishing features are:

1. It is based on direct spatial integration of the electron density function over an atomic domain; in particular it does not use projection in any form of the wave function on basis functions.
2. It defines the atomic domain as the Voronoi polyhedron of the atom, that is, the region of space closer to that atom (nucleus) than to any other atom.
3. It uses the deformation density $\rho_{\text{def}}(\mathbf{r}) = \rho(\mathbf{r}) - \rho_{\text{promolecule}}(\mathbf{r})$, so it focuses on the density *change* when going from the superposition of atomic densities to the final molecular density.

Thus, the definition of the VDD atomic charge Q_A^{VDD} of atom A is given by eq. (6):

$$Q_A^{\text{VDD}} = - \int_{\text{Voronoi cell of A}} [\rho(\mathbf{r}) - \rho_{\text{promolecule}}(\mathbf{r})] d\mathbf{r} \quad (6)$$

In the section VDD Method, the VDD method is presented and discussed in more detail, and the Hirshfeld method is reformulated in a way that exhibits its similarity with the VDD method. Then, the results of the VDD method are compared to the Mulliken, Hirshfeld, Bader, and NPA charges. Next, in the section Redefining the Promolecule in the Hirshfeld and VDD Methods, we discuss the possibility the VDD method offers of changing the definition of the reference systems, and their sum, and thus the use of an alternative promolecule. Instead of spherically symmetrized atoms, we may use an atomic charge density with lower symmetry, belonging to one state of a multiplet, or to a “valence state” atomic electron configuration, or to charged atoms. In the section VDD Charges as Bonding Analysis Tool, we introduce an extension of the VDD method that does not take atoms as basic units, but instead uses larger (molecular) fragments. This allows us to look at the redistribution of charge, when a molecule or complex (transition metal complex, molecular complex, hydrogen bonded com-

plex) is formed from subsystems. We will discuss how this allows one to avoid certain pitfalls in atom-based schemes when small charge redistributions are studied that arise from weak interactions between molecular fragments (the so-called front-atom problem), such as hydrogen bonds between nucleic acid bases. The last section offers an overall evaluation of the various methods. Here, we also discuss two other atomic charge methods that use the electron density in combination with a geometric partitioning of space, namely, the method of Politzer and coworkers¹⁰ and the method of Van Alsenoy and coworkers.¹¹ Politzer's method¹⁰ is based on a partitioning of the space into atomic regions that are similar in appearance to the Voronoi polyhedra but with the significant difference that they are chosen such that the integration of the density of the promolecule over the atomic region of atom A, Ω_A , yields a neutral atom A [eq. (7)]:

$$Q_A^{\text{Politzer}} = Z_A - \int_{\substack{\text{atomic region determined} \\ \text{with neutral atoms} \\ \text{in promolecule}}} \rho(\mathbf{r}) d\mathbf{r} \quad (7)$$

In a diatomic, proceeding from the Voronoi cell, this can be achieved by parallel displacement of the bond-perpendicular plane such that the above condition is satisfied. Van Alsenoy and coworkers¹¹ have recognized the problem of just electron density integration over the Voronoi cell and have addressed this problem by adjusting, in the spirit of Politzer's solution, the size of the cell. Thus, the perpendicular bisecting planes of a bond determining the Voronoi cell are displaced in proportion to the van der Waals radii [eq. (8)]:

$$Q_A^{\text{Van Alsenoy}} = Z_A - \int_{\substack{\text{atomic region} \\ \text{determined with} \\ \text{van der Waals radii}}} \rho(\mathbf{r}) d\mathbf{r} \quad (8)$$

We refer to refs. 6–8 for reviews and discussions of yet other charge analysis methods.

Furthermore, the last section contains our concluding remarks. The main conclusion is that a charge analysis method that avoids wave function projection on basis functions but uses direct spatial integration of the electronic density is by far the most trustworthy method to obtain stable charges. It is also a requirement that integration is performed of the deformation density, which gives the charging effects due to chemical bonding, and not just integration of the electron density itself. Integration of the deformation density over atomic domains proves to yield charges that conform to chemical intuition, that is, agree with deductions from the large and diverse body of chemical experimental knowledge. Both the VDD and Hirshfeld methods are of this type, and they yield charges that are usually quite close. They are recommended as the methods of choice to obtain atomic charges, with a preference for the VDD method in view of its simple and transparent definition of the atomic domain.

Computational Details

Almost all calculations were performed using the Amsterdam Density Functional (ADF) program¹² developed by Baerends et al.,^{12b–d} and parallelized^{12b} as well as linearized^{12f} by Fonseca Guerra et al. The numerical integration was performed using the procedure developed by te Velde et al.^{12g,h} The MOs were expanded in uncontracted sets of Slater type orbitals (STOs) containing diffuse functions: DZ, DZP, and TZ2P (no Gaussian functions were involved).¹²ⁱ The DZ and DZP basis set is of double- ζ quality for all atoms and the DZP basis set has been augmented with one set of polarization functions: 3d on Li, C, N, F, and Cl and 2p on H. The TZ2P basis set is of triple- ζ quality for all atoms and has been augmented with two sets of polarization functions: 2p and 3d on H and He, 3d and 4f on Li, B, C, N, O, F, Ne, Na, Si, P, S, Cl, Ar, and K, 4p and 4f on Ni, 4d and 4f on Cr, Fe, Ge, Br, Kr, and Rb, and 5d and 5f on Sn and I. Furthermore, an extra valence p function has been added to Li (2p), Na (3p), K (4p), and Rb (5p). The frozen-core (FC) approximation^{12j} was applied to the 1s core shell of Li, B, C, N, O, F, Ne, and Na, the 1s 2s 2p core shells of Si, P, S, Cl, Ar, K, Cr, Fe, and Ni, the 1s 2s 2p 3s 3p core shells of Ge and Br, the 1s 2s 2p 3s 3p 3d core shells of Kr and Rb, and the 1s 2s 2p 3s 3p 3d 4s 4p core shells of Sn and I.

Equilibrium structures were optimized using analytical gradient techniques.^{12k} Geometries, electron densities, and energies were calculated at the BP86 level of the generalized gradient approximation (GGA): exchange is described by Slater's $X\alpha$ functional^{12l} ($\alpha = \frac{2}{3}$), with self-consistent nonlocal corrections due to Becke,^{12m,n} and correlation is treated in the Vosko-Wilk-Nusair (VWN) parameterization^{12o} with nonlocal corrections due to Perdew^{12p} added, again, self-consistently (BP86).^{12q}

VDD and Hirshfeld charges use a promolecule charge density, which has been calculated at the $X\alpha$ /VWN level unless stated otherwise. It is possible to use a different functional in the calculation of the atoms that build the promolecule than in the SCF calculations on the molecule itself. Although this is not recommended, one may wonder whether the results for the final atomic charges are much affected. Tests to be discussed later in the article show that the VDD and Hirshfeld charges change very little when the reference atoms are calculated at the $X\alpha$ /VWN level instead of at BP86 level. It is therefore perfectly justified to use one set of reference atoms— $X\alpha$ /VWN atoms, say—and study molecules with a variety of functionals.

Bader's AIM atomic charges were computed with the program XAIM,¹³ which was interfaced to our ADF program. Weinhold's natural population analysis (NPA) atomic charges were obtained with the program Spartan.¹⁴

VDD Method

VDD Scheme for Calculating Atomic Charges

To which nucleus do the electrons go when a chemical bond is formed? In general, atomic charge schemes tackle this question by computing the amount of charge contained in an atomic volume. Here, we introduce a different approach and, instead, compute directly the *flow* of charge from one atom to another. Thus, we

define a fictitious promolecule in which all atoms occupy their final positions but any interaction between them is switched off, that is, the density of the promolecule is the superposition of atomic densities. Now, we rephrase the above question: when the chemical bond is switched on, how much charge that in the promolecule was closer to a particular nucleus than to any other nucleus has now shifted away from that particular nucleus and become closer to another nucleus (and vice versa). A natural and objective way to answer this question is to stand half-way between two atoms, and, when the chemical interaction is turned on, measure the amount of electronic density that crosses the bond midplane. For diatomics, this means that the space is divided by the bond midplane into two equal parts. The amount of electronic charge density flowing from one compartment of space to the other is defined as the VDD atomic charge. This definition of atomic charge is conceptually very simple and at the same time objective in the sense that it is unambiguous, i.e., not dependent on atomic properties with some degree of empiricism or arbitrariness (such as van der Waals radii or electronegativity).

The VDD charges can be further generalized to the case of poly-atomic molecules. The VDD method partitions the space into regions for each atom, which are defined to be the part of space closer to the nucleus of that atom than to any other nucleus. This particular compartment of space is called the Voronoi cell of an atom, and it is bounded by the bond midplanes on and perpendicular to all axes between nucleus A and its neighboring nuclei (cf. the Wigner-Seitz cells in crystals).^{9,12g} The VDD charge of an atom A is then calculated as the difference between the (numerical) integral over its Voronoi cell of the electron density ρ of the molecule and the superposition of atomic densities forming the promolecule density [eq. (9)]:

$$Q_A^{\text{VDD}} = - \int_{\text{Voronoi cell of A}} \left(\rho_{\text{molecule}}(\mathbf{r}) - \sum_B \rho_B(\mathbf{r}) \right) d\mathbf{r} \\ = - \int w_A^{\text{Voronoi}}(\mathbf{r}) \rho_{\text{def}}(\mathbf{r}) d\mathbf{r} \quad (9)$$

Thus, the VDD atomic charges are a way to quantify the deformation density $\rho_{\text{def}} = \rho - \sum_B \rho_B$ on an atomic basis using a simple geometric partitioning of space. The weight function $w_A^{\text{Voronoi}}(\mathbf{r})$ is 1 inside the Voronoi cell of atom A and zero everywhere else. Note that VDD atomic charges fulfill the basic requirements of adding up to exactly the total charge and being invariant to the choice of the origin of the molecular geometry. The VDD charge merely monitors if charge flows away or toward the space around a certain nucleus upon the formation of the molecule from its atoms. Therefore, the physical interpretation is rather simple and straightforward: a positive or negative atomic charge Q_A corresponds to the loss or gain of electrons in the Voronoi cell of atom A. It is interesting to observe that the VDD charges “cannot lie.” They do tell us how much charge flows into or out of an atomic Voronoi polyhedron. If the resulting charges would not conform to what chemists have agreed to, the question would become why the actual charge redistribution does not correspond to the inferences of the chemists.

The Hirshfeld and VDD methods are actually quite similar. This can easily be seen by rewriting eq. (4) with a substitution of Z_A by the integral over ρ_A , which yields eq. (10):

$$Q_A^{\text{Hirshfeld}} = \int \frac{\rho_A(\mathbf{r})}{\rho_{\text{promolecule}}(\mathbf{r})} \rho_{\text{promolecule}}(\mathbf{r}) d\mathbf{r} \\ - \int \frac{\rho_A(\mathbf{r})}{\rho_{\text{promolecule}}(\mathbf{r})} \rho_{\text{molecule}}(\mathbf{r}) d\mathbf{r} = - \int \frac{\rho_A(\mathbf{r})}{\sum_B \rho_B(\mathbf{r})} \\ \times \left(\rho_{\text{molecule}}(\mathbf{r}) - \sum_B \rho_B(\mathbf{r}) \right) d\mathbf{r} = - \int w_A^{\text{Hirshfeld}}(\mathbf{r}) \rho_{\text{def}}(\mathbf{r}) d\mathbf{r} \quad (10)$$

The Hirshfeld charge may thus be considered as an integration of the deformation density over the Hirshfeld “cell,” which is defined by the weight function $w_A^{\text{Hirshfeld}}(\mathbf{r})$ (see also refs. 4, 6j), which is practically 1 close to nucleus A and falls off to almost zero on neighboring nuclei. A comparison between VDD and Hirshfeld shows that the difference between the two methods lies in the choice of the weight factor. The Hirshfeld method defines a sort of fuzzy atom whereas the VDD method determines sharp boundaries between the atoms.

It may be considered an advantage that the Hirshfeld fuzzy cell takes into account the different sizes of atoms, while the Voronoi method is completely based on geometrical partitioning of space. We wish to caution, however, that the Hirshfeld cell may take an unexpected shape. In Figure 1, we have plotted the atomic cells of carbon in CH_4 and of germanium in GeH_4 through the HXH plane. The atomic cell of carbon is localized on carbon whereas the atomic cell of germanium encompasses the whole molecule and contains “holes” at the positions of the hydrogen atoms. Note in particular that the contour values of the Hirshfeld cell of Ge in a bond midplane of the H—H axis never drop below 0.6, but increase to 0.8 when going outwards (to 1.0 in the limit of large distance). This is due to the more diffuse nature of the Ge atomic density than the H density. The Ge cell contours are also quite high in the region between the hydrogen atoms. The Hirshfeld charge of Ge thus also counts electronic charge density (presumably small) in the outer regions of the molecule, which are in fact closer to the Hs, and in the region along and “behind” the H—H axis. The precise shape of a Hirshfeld fuzzy cell is not easily envisaged and needs this type of contour plot to be appreciated. So the Hirshfeld method has the “virtue” of taking the atomic size into account, but it is not *a priori* clear that the cell defined by $w_A^{\text{Hirshfeld}}(\mathbf{r})$ properly reflects the charge flows in the system upon bond formation. VDD utilizes a straightforward and much simpler method to visualize the atomic cell, but does not in any way take atomic size into account. We evaluate in the next section from many examples the actual differences and the relative advantages or disadvantages of the two cell definitions, if any.

Results and Discussion

In this section, we present the atomic charges for the four different methods (Mulliken, Hirshfeld, VDD, and Bader) and subject the

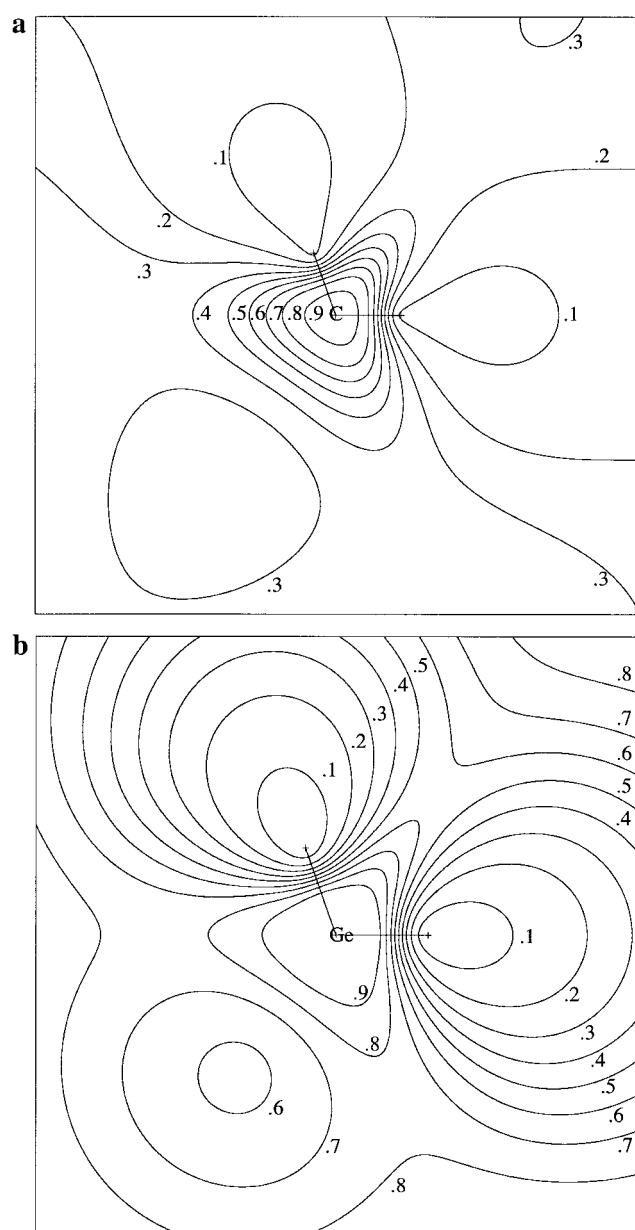


Figure 1. (a) Plot of the atomic cell of carbon in CH_4 ($\rho_{\text{C}}/\rho_{\text{CH}_4}^{\text{promolecule}}$) defined by Hirshfeld through H—C—H plane. (b) Plot of the atomic cell of germanium in GeH_4 ($\rho_{\text{Ge}}/\rho_{\text{GeH}_4}^{\text{promolecule}}$) defined by Hirshfeld through H—Ge—H plane (scan values for both plots: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9)

computed values to a thorough analysis. Our main goal is to evaluate if the charge values in this large variety of molecular systems are well defined and chemically meaningful. Well defined means that they are basis set independent, and in particular converge to a stable value with increasing basis set size. Chemically meaningful implies that the charges conform to our expectation (chemical intuition). “Chemical intuition” denotes expectations based on a large body of experimental data (e.g., dipole moments,

electrostatic effects showing up in solvation, protonation, charge control in reactions), which are summarized in, for instance, the electronegativities of the atoms. The electronegativity scale used throughout this article is the one by Allen (using Pauling units).¹⁵ For each molecular system or set of systems, these two criteria are tested, and furthermore, we carefully consider the values of the atomic charges and judge the chemical applicability of the four charge methods.

Methane, Methyl lithium, and Hydrogen Cyanide

The first systems to be studied are methane, methyl lithium, and hydrogen cyanide. We first consider the basis set dependence of the various methods. Figure 2 gives for the four methods the atomic charges of carbon in methane, methyl lithium, and hydrogen cyanide calculated with the three basis sets DZ, DZP, and TZ2P (for the exact values of all atoms see Table 1). The Mulliken charges are, as expected, heavily basis set dependent for the three molecules and therefore not useful. For instance, the values of $Q_{\text{C}}^{\text{Mulliken}}$ in methane range between -0.982 a.u. for DZ basis set to $+0.607$ a.u. for the TZ2P basis set (see Table 1). The VDD and Hirshfeld methods show, correctly, rather little basis set dependence for the three molecular systems. The Hirshfeld atomic charges are almost completely insensitive to improvement of the basis set (see also ref. 6), which is slightly surprising because the density $\rho(\mathbf{r})$ does change when the basis set is improved. The values of $Q_{\text{C}}^{\text{Hirshfeld}}$ are, for methane, -0.162 , -0.162 , and -0.167 a.u. for DZ, DZP, and TZ2P basis set, respectively, while the VDD method gives for the same basis sets -0.153 , -0.114 , and -0.095 a.u. (see Table 1). Apparently the use of the atomic density in the same basis, which enters the definition of the Hirshfeld fuzzy cell, has this equalizing effect on the Hirshfeld charges. The VDD charges are also stable but do reflect, with a small change in the value of the atomic charge, the improvement of the basis set used. Note that the basis set independence of both Hirshfeld and VDD charges and the fact that they are strictly defined for the “exact” (basis set limit) electronic charge densities imply that they will also be insensitive to the difference between Gaussian and Slater basis sets, if these basis sets are in both cases reasonably flexible. The basis set dependence of the charges calculated with the Bader method does not show the same trend for the three different molecules. For methyl lithium little basis set dependence is observed, but the Bader atomic charges of the carbon atom in methane and hydrogen cyanide are clearly basis set dependent (see Fig. 2), in particular in the step where polarization functions are added. The $Q_{\text{C}}^{\text{Bader}}$ of hydrogen cyanide is $+0.391$ a.u. for DZ basis set and $+0.716$ and $+0.817$ a.u. for the DZP and TZ2P basis sets. The addition of polarization functions to the DZ basis set causes, for some molecules, a dislocation of the bond critical point, which then leads to a modification of the atomic region and therefore to changes in the atomic charges. The dependence of the Bader atomic charges on the addition of polarization functions to a basis set that does not contain polarization functions was not found by Wiberg and Rablen,^{6a} because they used two basis sets (6-31G** and 6-31++G**) in their work, which have the same number of polarization functions. Basis set dependence for the Bader partitioning scheme was also found by Velders and Feil.^{6h} Of course, the basis set dependence of the Bader charges is of a different

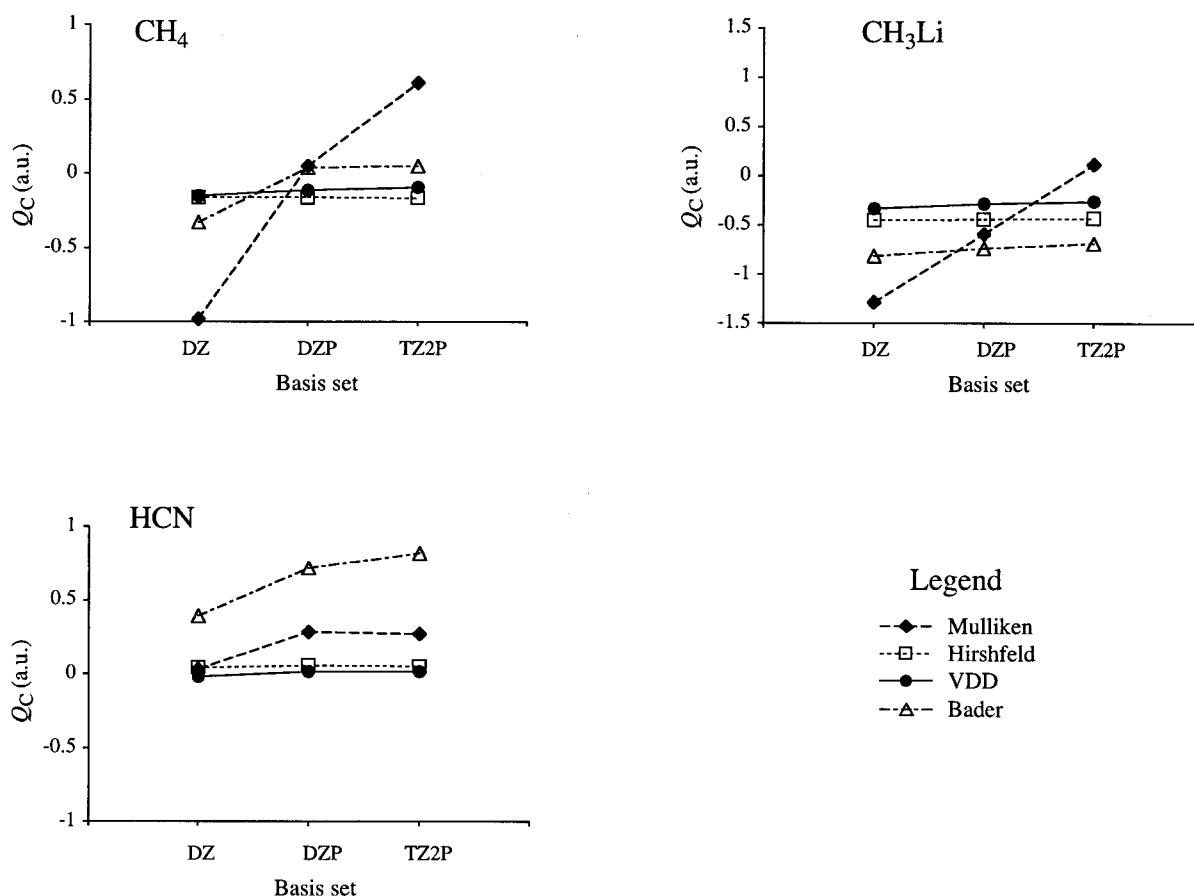


Figure 2. For methane, methyl lithium, and hydrogen cyanide, the Mulliken, Hirshfeld, VDD, and Bader charges of carbon are given at the BP86 level for three different basis sets: DZ, DZP, and TZ2P.

nature than for Mulliken charges. The Bader charges are well-defined values for the exact density $\rho(\mathbf{r})$. Thus, although they are quite sensitive to the choice of basis set and numerical precision, they will converge to those values with increasing basis set size.

Having established the basis set independence of the Hirshfeld and VDD methods, we now compare the charges obtained in the various methods. We start with the atomic charges of methane (for which we leave out Mulliken in view of the heavy basis set dependence mentioned above, which precludes obtaining a “true” Mulliken charge). Because the difference of electronegativity $\Delta\chi = \chi_{\text{C}} - \chi_{\text{H}}$ between carbon and hydrogen is small and positive (0.244), a small negative atomic charge for carbon and a small positive charge for hydrogen is expected. The Hirshfeld and VDD methods—which give values that are fairly close—show the proper trend (C negative, H positive) and the right order of magnitude, reflecting the formation of a covalent bond. The “converged” Bader values are small and *positive* for carbon (0.038 and 0.047 a.u. for DZP and TZ2P basis set). The same incorrect “bond polarization” was found by Wiberg and Rablen^{6a} and by Geerlings et al.^{6b} for the Bader charges of methane. Incidentally, the natural population analysis (see Table 2), gives a negative charge on C, but it is -0.88 (in a large Gaussian basis set) much too extreme, suggesting too much ionic character of the C—H bond.

We next turn to the results for methyl lithium and hydrogen cyanide. The difference in electronegativity between carbon and lithium amounts to 1.632 ($=\chi_{\text{C}} - \chi_{\text{Li}}$) and between nitrogen and carbon to 0.522 ($=\chi_{\text{N}} - \chi_{\text{C}}$). Therefore, the atomic charge of carbon in CH_3Li should be negative and in HCN positive and the absolute value of the carbon charge in HCN should be smaller than the absolute value of carbon in CH_3Li . This trend is correctly displayed by the Hirshfeld and VDD methods, where the C/Li charges in CH_3Li (TZ2P, see Table 1) are $-0.428/+0.494$ for Hirshfeld and $-0.259/+0.386$ for VDD, while the two methods yield C/N charges in HCN (TZ2P) of $+0.051/-0.180$ for Hirshfeld and $+0.015/-0.159$ for VDD. These charges indicate, as expected from the electronegativity differences, a nearly covalent C—N bond, and a considerably more ionic $\text{C}^{\delta-}-\text{Li}^{\delta+}$ bond of opposite polarity in CH_3Li . The Bader charges for these two molecules reveal an important flaw of the Bader method. The carbon charges of Bader have the correct sign, but their magnitudes are completely out of proportion. In CH_3Li the atomic Bader charges for C/Li are $-0.685/+0.890$ (TZ2P), and in HCN the C/N charges are $+0.817/-1.006$ a.u. (TZ2P). The bond polarities are pictured much stronger with the Bader charges. The Li charge is much more positive than in either the VDD or the Hirshfeld method. The C—N bond in HCN is even pictured as almost purely

Table 1. Basis Set Dependence of Atomic Charges (in a.u.) for CH₄, CH₃Li, and HCN.

Molecule	Atom	Basis set	Mulliken	Hirshfeld	VDD	Bader
CH ₄	C	DZ	−0.982	−0.162	−0.153	−0.329
		DZP	0.047	−0.162	−0.114	0.038
		TZ2P	0.607	−0.167	−0.095	0.047
	H	DZ	0.246	0.041	0.038	0.082
		DZP	−0.012	0.041	0.028	−0.009
		TZ2P	−0.152	0.042	0.024	−0.011
CH ₃ Li	C	DZ	−1.284	−0.447	−0.331	−0.814
		DZP	−0.592	−0.441	−0.284	−0.736
		TZ2P	0.118	−0.428	−0.259	−0.685
	Li	DZ	0.563	0.508	0.396	0.894
		DZP	0.436	0.512	0.406	0.898
		TZ2P	0.203	0.494	0.386	0.890
	H	DZ	0.240	−0.020	−0.022	−0.026
		DZP	0.052	−0.024	−0.040	−0.057
		TZ2P	0.107	−0.022	−0.042	−0.070
HCN	H	DZ	0.344	0.127	0.169	0.221
		DZP	0.159	0.128	0.153	0.191
		TZ2P	−0.017	0.129	0.144	0.188
	C	DZ	0.031	0.043	0.019	0.391
		DZP	0.282	0.054	0.014	0.716
		TZ2P	0.270	0.051	0.015	0.817
	N	DZ	−0.375	−0.170	−0.149	−0.617
		DZP	−0.441	−0.181	−0.167	−0.909
		TZ2P	−0.254	−0.180	−0.159	−1.006

Atomic charges were computed at BP86.

ionic. Similar Bader values have been found by others with large Gaussian basis sets: for instance, in HCN for C/N 0.919/−1.131 a.u. at the MP2/cc-pVDZ level^{6b} and for lithium in CH₃Li +0.902 a.u. at the HF/6-31G**//HF/6-31G* level.^{6a} Use of these atomic charges for interpretation of the chemical bond would indicate both bonds to be ionic, whereas the bond between C and N is known to be covalent, and the bond between C and Li in CH₃Li was shown to have some covalent character.^{2a} We conclude that the numbers produced by the Bader method can lead to a completely erroneous interpretation of the nature of a chemical bond.

The NPA charges calculated with SPARTAN at the BP86/6-31++//BP86/6-31G** level reveal similar erroneous values −1.471/0.839 a.u. for the C/Li pair in methyllithium. The NPA values at the same level of theory for the C/N pair in HCN (0.058/−0.296 a.u.) are more realistic.

Halomethanes

Series of halomethanes, such as CH₄, CH₃I, CH₃Br, CH₃Cl, CH₃F, and the series CH₄, CH₃X, CH₂X₂, CHX₃, CX₄ (X = F, Cl; see Table 2) lend themselves for the investigation of atomic charge methods. The order of electronegativity (H < I < Br < Cl < F, namely 2.300, 2.359, 2.685, 2.869, and 4.193, respectively) should be reflected in the atomic charges with, for instance, a corresponding displacement of electronic charge from the carbon atom towards the halogen atom in the series CH₄, CH₃I, CH₃Br, CH₃Cl, and CH₃F. In Table 2, we observe that the Hirshfeld and VDD charge on carbon display the expected regular behavior along the

series. The absolute charges are fairly small in both methods, and the largest change is, in both cases, from CH₃F to CH₃Cl. On the other hand, the Mulliken charge on C (apart from its unduly large positive value in this particular basis, TZ2P) shows irregular behavior along the series, the value for methane being out of line.

For the series of mono-, di-, tri-, and tetrafluoro- and chloromethanes, Figure 3 displays the Mulliken, Hirshfeld, and VDD charges of the carbon atom for two different basis sets, DZ and TZ2P. We first consider the basis set dependency. For the fluorine as well as for the chlorine substituted methanes the Mulliken charges reveal again their extreme basis set dependency. In the DZ basis set the Q_C^{Mulliken} charges for the chlorine substituted methanes are all about −1 a.u. and in the TZ2P they are all about +0.6 a.u. Figure 3 shows for the present series of molecules, as did Figure 2 for CH₄, CH₃Li, and HCN, that the Hirshfeld and VDD charges are practically basis set independent.

Now we subject the values of the atomic charges to chemical interpretation. The electronegativity of carbon (2.544) is known to be smaller than that of chlorine (2.869) and fluorine (4.193), the latter being the most electronegative of the three atoms. This implies that the carbon atoms become more positive as the number of substituted halogen atoms increases, and that the fluorine substituted methanes give more positive values for the carbon atom charges than the chlorine substituted methanes. We start with an examination of the Mulliken atomic charges. Q_C^{Mulliken} of the fluorine substituted methanes is, as it should be, always more positive than that of the chlorine substituted methanes (Fig. 3 and

Table 2. Atomic Charges (in a.u.) for Fluorine and Chlorine Substituted Methanes, CH₃X, CH₂X₂, CHX₃, and CX₄.

Atom	Molecule	Mulliken	Hirshfeld	VDD	Bader ^a	NPA ^b
C	CH ₃ F	1.076	−0.014	0.025	0.639	−0.095
	CH ₃ Cl	0.633	−0.076	−0.028	0.186	
	CH ₃ Br	0.599	−0.091	−0.041		
	CH ₃ I	0.482	−0.113	−0.062		
	CH ₄	0.607	−0.167	−0.095	0.081	−0.880
X	CH ₃ F	−0.594	−0.137	−0.141		−0.429
	CH ₃ Cl	−0.268	−0.083	−0.132		
	CH ₃ Br	−0.262	−0.066	−0.116		
	CH ₃ I	−0.192	−0.038	−0.093		
H	CH ₃ F	−0.161	0.050	0.039		0.175
	CH ₃ Cl	−0.122	0.053	0.053		
	CH ₃ Br	−0.113	0.052	0.052		
	CH ₃ I	−0.097	0.051	0.051		
	CH ₄	−0.152	0.042	0.024	−0.020	0.220
C	CH ₂ F ₂	1.199	0.112	0.132	1.221	0.562
	CHF ₃	1.887	0.220	0.230	1.844	1.120
	CF ₄	2.321	0.325	0.323	2.511	1.620
F	CH ₂ F ₂	−0.576	−0.113	−0.117		−0.429
	CHF ₃	−0.567	−0.095	−0.098		−0.421
	CF ₄	−0.580	−0.081	−0.081		−0.405
H	CH ₂ F ₂	−0.173	0.057	0.051		0.149
	CHF ₃	−0.186	0.066	0.063		0.142
C	CH ₂ Cl ₂	0.628	−0.012	0.031	0.268	
	CHCl ₃	0.568	0.041	0.081	0.335	
	CCl ₄	0.547	0.095	0.124	0.395	
Cl	CH ₂ Cl ₂	−0.214	−0.051	−0.089		
	CHCl ₃	−0.169	−0.033	−0.056		
	CCl ₄	−0.137	−0.024	−0.031		
H	CH ₂ Cl ₂	−0.100	0.057	0.074		
	CHCl ₃	−0.060	0.056	0.085		

^aMP2/6-311++G(3d,3p)//MP2/6-311++G(3d,3p) calculations of de Oliveira et al.^{6d}^bHF/6-31G**//HF/6-31G* calculations of Wiberg and Rablen^{6a}

Atomic charges were computed at BP86/TZ2P, unless stated otherwise.

see also for instance in Table 2, Q_C^{Mulliken} in CH₃F is 1.076 a.u. and in CH₃Cl 0.633 a.u.). The Mulliken charges of the fluorine substituted methanes also display a correct increase of positive charge on the carbon atom, but the behavior of the chlorine substituted methanes is incorrect: for instance, Q_C^{Mulliken} in CH₃Cl, CH₂Cl₂, CHCl₃, and CCl₄ are, in the TZ2P basis, 0.633, 0.628, 0.568, 0.547 a.u. respectively. Thus, we must draw the conclusion that the basis set dependence of the Mulliken charges not only renders the absolute values of the charges meaningless, but also distorts the trend of charges in a chemically related series so that it is not in accordance with chemical intuition. The Hirshfeld and VDD charges are of the same magnitude and display the same behavior (see Fig. 3 and Table 2). Both methods represent correctly the effects caused by increasing the number of halogen atoms and are therefore reliable indicators of the polarity of the bond.

For comparison, we have included Bader and NPA atomic charges from literature^{6a,d} into Table 2. We focus on the atomic charges for the carbon atom in the fluorine substituted methanes. In

the order CH₄, CH₃F, CH₂F₂, CHF₃, and CF₄, the Bader carbon charges are 0.081, 0.639, 1.221, 1.844, and 2.511 a.u. and the NPA carbon charges are −0.880, −0.095, 0.562, 1.120, and 1.620 a.u. Both methods show the correct trend, however, the absolute values are too large, which makes them both not suitable for interpretation of the nature of the chemical bond. Chemists do not classify the bond between carbon and fluorine as ionic, whereas the Bader method gives an increase of the atomic charge on carbon from +0.081 in CH₄ to +0.639 a.u. in CH₃F. With each additional F substitution a similar increase of the carbon charge with about +0.6 a.u. occurs. The NPA method also tends to give a too ionic view of the bonds. From a carbon charge of −0.880 a.u. calculated with NPA for CH₄ (which, as mentioned earlier, suggests an extremely ionic C—H bond), it apparently has the C—F bond too ionic because the total carbon charge drops very much in CH₃F, to −0.095 a.u. Subsequent F substitutions give, each time, an increase of the carbon charge by some +0.5 to +0.6 a.u. The NPA method has reduced the basis set dependency of the Mulliken

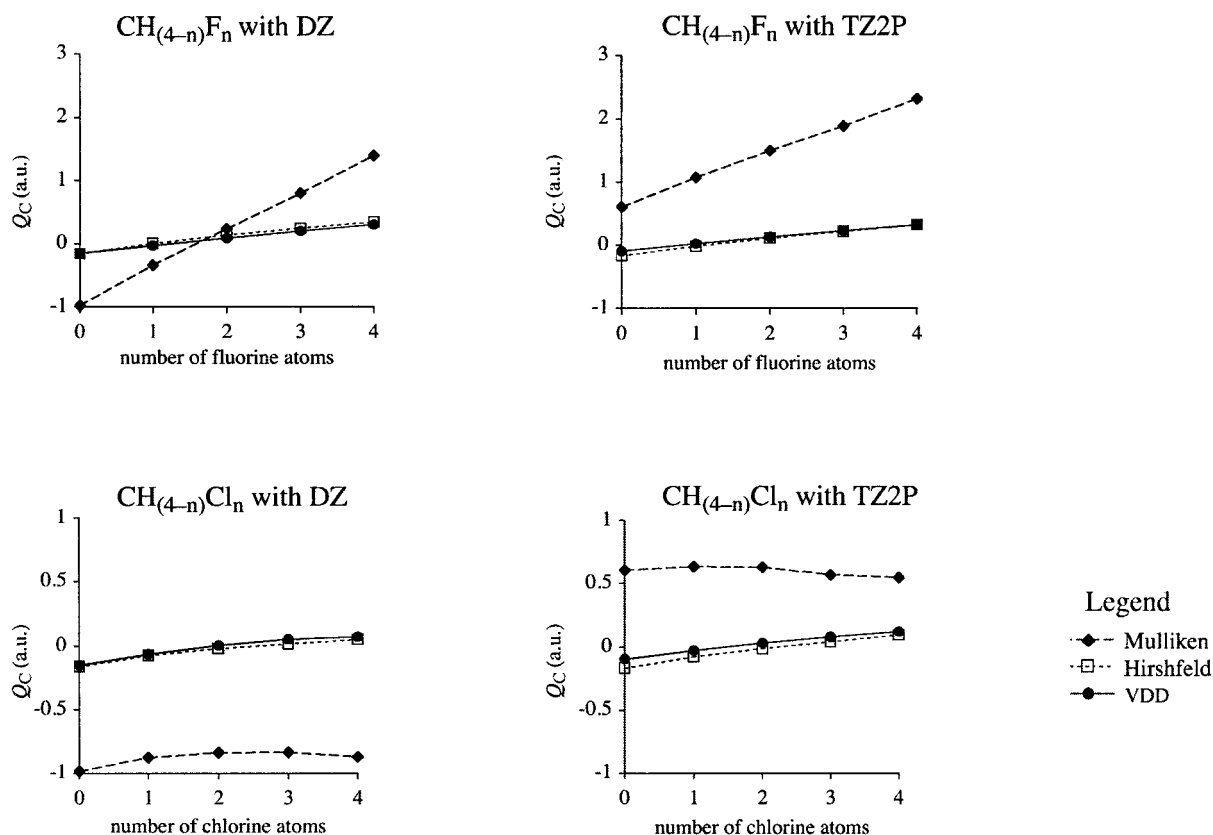


Figure 3. For methane, mono-, di-, tri-, and tetrafluoromethane as well as mono-, di-, tri-, and tetrachloromethane, the Mulliken, Hirshfeld, and VDD charges are given at the BP86 level for the DZ and TZ2P basis sets.

analysis, partly due to the disappearance of overlap terms in the NAO basis. It has not completely resolved the problem—which is probably inherent to any basis set based partitioning method—that populations associated with a certain atom can be spatially located on another atom, at least partly.³ It is clear that this problem gives serious errors in the Mulliken analysis, when AOs on atom A have large amplitude on neighboring atoms B. This problem has not completely disappeared in the NAOs of the NPA method. They are orthogonal onto each other, which makes them have amplitude (orthogonality tails) on neighboring atoms and therefore their population can include charge density, which is partially located on another atom. It is not known to us whether this feature causes, for example, the large negative NPA charge on C in CH_4 .

XH_4

We stay with the tetrahedral molecules and substitute the carbon atom of methane by Si, Ge, and Sn. The values of the electronegativity of the atoms involved are 2.300, 2.544, 1.916, 1.994, and 1.824 for H, C, Si, Ge, and Sn, respectively. Of the four central atoms only carbon is more electronegative than hydrogen. (The electronegativity of Ge is larger than that of Si due to an incomplete s,p valence shell screening by 3d electrons as one passes through the first transition series.¹⁵ This is reflected by the AO

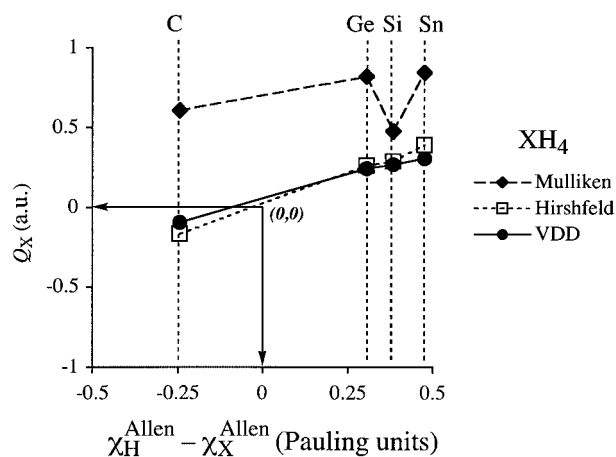


Figure 4. For the tetrahedral molecules CH_4 , SiH_4 , GeH_4 , and SnH_4 , the Mulliken, Hirshfeld, and VDD atomic charge of the central atom X is plotted against the difference in electronegativity (Allen's scale¹⁵) between X and H, computed at BP86/TZ2P.

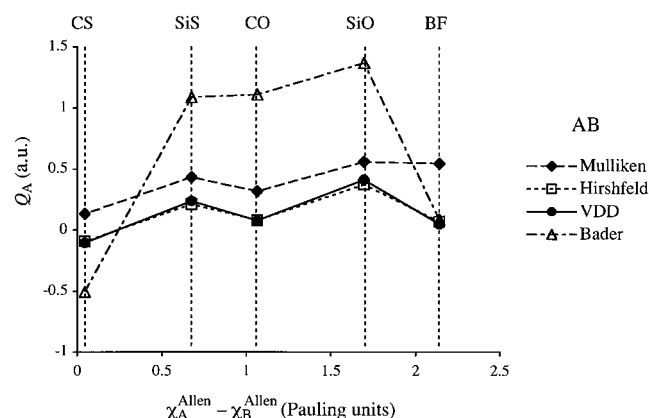


Figure 5. For the diatomic molecules, AB (CO, CS, SiO, SiS, and BF), the Mulliken, Hirshfeld, VDD, and Bader charges of A are plotted against the difference in electronegativity (Allen's scale¹⁵) between A and B, computed at BP86/TZ2P.

energies of Si and Ge in their ground state, s^2p^2 : -11.5 eV for 4s of Ge and -10.9 eV for 3s of Si.) The charge of the central atom X in CH_4 , SiH_4 , GeH_4 , and SnH_4 is -0.167 , $+0.289$, $+0.263$, and $+0.392$ a.u. according to Hirshfeld, and -0.095 , $+0.270$, $+0.246$, and $+0.307$ a.u. according to VDD. Figure 4 displays the atomic charge of the central atom X against the electronegativity difference between hydrogen and the atom X. The Hirshfeld and VDD charges follow precisely the electronegativity trend, the atomic charge of the central atom becoming more positive as it becomes more electropositive. The graph shows that, when interpolating between C and Ge, the Hirshfeld and VDD methods give properly an atomic charge of 0 when the difference in electronegativity with H would be 0. The Mulliken charges show again difficulties in following the electronegativity trend. The charge of silicon is too small and also the extrapolation of the graph shows an incorrect atomic charge for the hypothetical $\Delta\chi = 0$ case.

Series of Diatomics CO, SiO, CS, SiS, and BF

We extend our investigation to the diatomics AB and start with carbon monoxide, which is a ubiquitous ligand in organometallic and coordination chemistry. We investigate this molecule together with the neutral isoelectronic SiO, CS, SiS, and BF. Figure 5 displays the atomic charge of the more electropositive atom A

against the difference in electronegativity with B. The values of the atomic charges and the dipole moments are tabulated in Table 3. We focus on the Hirshfeld and VDD charges, which are again very similar. The charges do not correlate well with the electronegativity difference over the whole set of molecules. However, when we compare two molecules with one atom in common, the $\Delta\chi$ trend is always faithfully followed: both from CS to SiS and from CO to SiO the more electropositive Si gets a higher positive charge; both from CS to CO and from SiS to SiO the more electronegative O acquires more electron density, that is, the C or Si charge is more positive in the oxide than in the sulfide. But if there is no atom in common, the electronegativity difference does not correlate well with the charges, compare SiS and CO. Also BF, which shares no atom with the other molecules, does not properly fit in.

The Bader charges follow the trend of the VDD and Hirshfeld charges, however, the magnitude of the Bader charges (for instance, for carbon $+1.110$ a.u. in CO) is too large for the nature of the bond in these molecules. They falsely suggest an ionic bond in CO and the other isoelectronic diatomics. (These values have also been found by others.^{6b,c})

We list in Table 3 also the dipole moments. A definition of atomic charges in diatomics, which is sometimes advocated, is to assign charges to the atoms (i.e., put point charges at the nuclear positions) in such a way that the dipole moment is reproduced. It is apparent that the VDD (and Hirshfeld) atomic charges do not at all reproduce the dipole moment. (The latter can, however, be reproduced if one also takes the atomic dipole moments computed in the VDD or Hirshfeld cells into account, but this is not our purpose here.) We see that these charge methods even fail to reproduce the sign of the dipole moments for CO and BF. The dipole moment points, rather counterintuitively in view of the electronegativity difference, from a negative C (or B) to a positive O (or F), whereas the charge methods would give the opposite direction (Table 3). We stress that this is not a failure of the charge schemes. They are designed to represent correctly the flow of charge in these molecules, so essentially, in the Voronoi method, how much charge “moves” across the bond midplane. However, the dipole moment not only depends on how much charge flows across the bond midplane (i.e., if one goes from the promolecule, which has zero dipole moment, to the actual molecule), but also on how the charge is distributed within the cell. If, for instance, a large lone pair density develops in the molecule, as, for instance, happens at the C and B ends of CO and BF, this will create electron density with a large distance from the center of positive charge.

Table 3. Atomic Charges (in a.u.) of A and dipole moments μ (in D) for Diatomics AB.

Molecule	$\chi_B - \chi_A$	Mulliken	Hirshfeld	VDD	Bader	μ^a
CS	0.045	0.133	-0.094	-0.109	-0.507	-1.954
SiS	0.673	0.434	0.213	0.229	1.090	1.678
CO	1.066	0.317	0.080	0.071	1.110	-0.161
SiO	1.694	0.560	0.375	0.406	1.369	3.106
BF	2.142	0.546	0.069	0.045	0.881	-1.033

^a $\mu > 0$ points from negative B to positive A.
Atomic charges were computed at BP86/TZ2P.

Table 4. Charges (in a.u.) of the Metal Atoms in Metalhydrides and Metalfluorides.

Molecule	$\Delta\chi$ (X-M)	Mulliken	Hirshfeld	VDD	Bader
LiH	1.39	0.157	0.414	0.464	0.893
NaH	1.43	0.267	0.393	0.457	0.718
KH	1.57	0.716	0.463	0.521	0.738
HF	1.89	0.747	0.210	0.206	0.689
LiF	3.28	0.819	0.588	0.544	0.945
NaF	3.32	0.911	0.620	0.622	0.910
KF	3.46	0.868	0.656	0.601	0.883
RbF	3.49	0.868	0.666	0.596	^a

^aNo bcp found.

Charges were computed at BP86/TZ2P.

Such density weighs heavily in the dipole moment. The dipole moment thus not only reflects the charge on the atoms, but also the redistribution of charge around the atoms due to bonding effects. The VDD charge only measures how much charge moves into or out of a Voronoi cell, not how it is distributed over the cell. When the charge is small, such as in CO, CS, and BF, the distribution within the atomic cell may even cause a dipole moment with an opposite sign to what would be expected on the basis of the charge alone.

Metal Hydrides and Metal Fluorides

The next two groups of diatomic molecules, subjected to our analysis, are the group I metal hydrides and fluorides (Table 4). We discuss both groups separately because the trend in electronegativity should be investigated while keeping one atom constant (*vide supra*). We start with the metal hydrides. The $\Delta\chi(\text{H-M})$ values are not very different for the different metals, in particular not for LiH and NaH. In agreement with this, the VDD and Hirshfeld charges do not show much variation; in particular, the charges for LiH and NaH are close. The difference in the Li and Na charges, although quite small, is actually against the $\Delta\chi$ trend. This effect can be understood by looking beyond the electronegativity difference at the composition of the main bonding orbital, the σ_{HOMO} of the metal hydrides. In the series Li, Na, and K the σ_{HOMO} becomes gradually more centered on the hydrogen atom, 59, 63, and 84%, respectively, which is in accordance with the increasing electronegativity difference down group I of the periodic table. This σ_{HOMO} is mainly formed between the 1s orbital of hydrogen and the valence s AO of the alkali metal, that is, 2s for Li, 3s for Na, and 4s for K. However, in LiH, there is also a considerable mixing of the $2p_z$ into the σ_{HOMO} (15% for the $2p_z$ of Li, 7% for the $3p_z$ of Na, and 0% for the $4p_z$ of K). The admixture of the $2p_z$ orbital of Li pushes some electronic density toward the hydrogen atom, which is reflected in the Li atomic charges of VDD and Hirshfeld. Clearly, a one-to-one correspondence between the electronegativity difference and the atomic charge is not always possible, as the definition of the electronegativity by Allen¹⁵ does not take into account admixture of unoccupied orbitals or effects caused by the repulsion between closed shells. The VDD and Hirshfeld charges on K are slightly larger, in agreement with the

slightly larger electronegativity difference for KH, which also shows up in the orbital composition mentioned above.

The Mulliken charges show a large variation, from a fairly small 0.157 and 0.267 a.u. for LiH and NaH to a large 0.716 a.u. for KH. These effects suggest many more bond polarity differences than there actually are, and must be ascribed to basis set effects on the Mulliken charge. The Mulliken charge on Li does not show the slightly larger charge of Li compared to Na that VDD and Hirshfeld exhibit. Of course Mulliken is insensitive towards the mixing of $2p_z$, which was invoked to explain this effect, because the $2p_z$ orbital is still located on the lithium atom. The Bader charges are again quite large compared to VDD and Hirshfeld, but now for all three of the molecules, even (against the $\Delta\chi$ trend) largest (0.893 a.u.) for Li.

Turning now to the fluorides, we note that the difference in electronegativity between the atom of group I and fluorine increases from H to Rb, with a large step from H to Li and small increments going further down the periodic table in this group. The positive atomic charge of the group I atoms is therefore expected to increase from H to Rb, with a large step from H to Li and smaller changes along Li–Rb. The Hirshfeld and VDD atomic charges behave correctly: they increase markedly by about one-third of an a.u. from H to Li, and are relatively constant afterwards with changes of only a few hundredths of an a.u. A more detailed look at the “plateau” of NaF, KF, and RbF shows that the Hirshfeld charges very slightly increase whereas the VDD charges very slightly decrease along this series (0.622, 0.601, and 0.596 a.u., see Table 4).

The Mulliken charges do not represent well the large increase in electronegativity difference $\Delta\chi$ from HF to LiF, and the charge on H is already quite high (0.747 a.u.). All Mulliken charges are rather high. Also, the Bader charges are again quite high.

Protonated Noble Gases

The protonated noble gases are listed in Table 5 according to their electronegativity and not to their position in the periodic table. Let us start with the VDD atomic charges, which for NeH^+ , HeH^+ , ArH^+ , and KrH^+ are 0.426, 0.431, 0.571, and 0.618 a.u., respectively. This represents properly the decrease of electronegativity of the noble gas atoms from Ne to Kr. Note that the total charge for

Table 5. Charges (in a.u.) of the Noble Gas Atoms in XH^+ .

Molecule	χ^x	Mulliken	Hirshfeld	VDD	Bader
NeH^+	4.787	0.399	0.482	0.426	0.113
HeH^+	4.160	0.708	0.406	0.431	0.088
ArH^+	3.242	0.584	0.653	0.571	0.358
KrH^+	2.966	0.671	0.706	0.618	^a

^aNo bcp found.

Atomic charges were computed at BP86/TZ2P.

each molecule is +1 a.u., and this is also the case for the VDD charge when one uses a promolecule with neutral atoms. The Hirshfeld charges are again not very different from the VDD charges and show the same trend. Only for He do we find with the Hirshfeld method an atomic charge (0.406 a.u.) that is smaller than that of Ne (0.482 a.u.). In this case the Mulliken charges do not have quantitatively very different values, except for He, for which the Mulliken atomic charge is much larger than the VDD or Hirshfeld ones, and is in fact *larger* than the charges for the other three noble gases. This breaks completely the correlation of the Mulliken charges with the electronegativities. For the Bader charges, it is difficult to give a judgment because the atomic charge for KrH^+ is missing. It was impossible to locate the bond critical point for this molecule, because the large electronic cloud of Kr overwhelms the much smaller hydrogen. The other Bader charges are in this case exceptionally small.

Other Substituted Methanes

Besides the fluorine and chlorine substituted methanes, we have also investigated CH_3BH_2 , CH_3NH_2 , CH_3PH_2 , CH_3OH , and CH_3SH . The atomic electronegativities of B, N, and so forth may not correspond well with the actual groups, the unsaturated hydrides, $-\text{BH}_2$, $-\text{NH}_2$, and so forth, but the atomic electronegativities are still used as a guide for our expectations. The charge of the methyl group is given in Table 6 for the Mulliken, Hirshfeld, and VDD methods. NPA and Bader charges for the methyl group in CH_3BH_2 , CH_3NH_2 , and CH_3OH can be found in ref. 6a. We have not listed the atomic charges of the carbon atom and hydrogen atoms separately, because the whole methyl group reacts to the substitution. The electronegativity increases along the first row of the periodic table. Therefore, the electronic density on the methyl group should diminish in the series CH_3BH_2 , CH_3NH_2 , and

CH_3OH . For CH_3BH_2 , Q_{CH_3} should be less than 0. All three methods meet our expectation (see Table 6). (Also, the NPA and Bader charges in ref. 6a follow this trend.) Furthermore, as the electronegativity of the second row elements is less than that of the first row, the charge of the methyl group should be less positive for CH_3PH_2 and CH_3SH than for CH_3NH_2 and CH_3OH , respectively. Only the Mulliken charge for the methyl group in CH_3PH_2 does not follow this trend, whereas the Hirshfeld and VDD charges correctly represent this difference in electronegativity.

The Bader and NPA charges show the same characteristics as in previous cases. The Bader charges exhibit the same trend as the VDD and Hirshfeld charges, but their absolute values are too extreme. Again, the Bader charges suggest a too ionic bond. The NPA charges have the same tendency to large bond polarity, but are less extreme than Bader charges.

Water, Formaldehyde, and Ammonia

We end this section with three small molecules, water, formaldehyde, and ammonia (see Table 7). We focus on the atomic charge of the most electronegative atom in each molecule. The methods for assigning an atomic charge behave as we expect after the previous examples. Hirshfeld and VDD are very close and exhibit moderate charge for these largely covalent compounds. The Bader charges are extreme, and also the NPA charges are rather large. For instance, all methods give a negative charge on the oxygen of water, but the Hirshfeld and VDD values (−0.302 and −0.266 a.u.) are much smaller than the large values −1.235 a.u. for Bader and −0.972 a.u. for NPA. The Bader and NPA charges are also large and negative on the O of formaldehyde (−1.297 and −0.577 a.u., respectively) and the nitrogen of ammonia (−1.113 and −1.133 a.u., respectively). The Bader and NPA methods clearly

Table 6. Methyl Group Charges (in a.u.) for Methyl Derivatives.

Molecule	χ	Mulliken	Hirshfeld	VDD	NPA ^a	Bader ^a
CH_3BH_2	$\chi_{\text{B}} = 2.051$	−0.103	−0.033	−0.003	−0.209	−0.741
CH_3NH_2	$\chi_{\text{N}} = 3.066$	0.132	0.032	0.036	0.174	0.444
CH_3OH	$\chi_{\text{O}} = 3.610$	0.289	0.074	0.077	0.315	0.647
CH_3PH_2	$\chi_{\text{P}} = 2.253$	0.147	−0.029	0.001		
CH_3SH	$\chi_{\text{S}} = 2.589$	0.232	0.021	0.056		

^aAtomic charges from ref. 6a.

Atomic charges were computed at BP86/TZ2P.

Table 7. Comparison of Various Charge Analysis Methods: Atomic Charges (in a.u.) for H₂O, CH₂O, and NH₃.

Molecule	Atom	Mulliken	Hirshfeld	VDD	Bader ^a	NPA ^a
H ₂ O	O	−0.600	−0.302	−0.266	−1.235	−0.972
	H	0.300	0.151	0.133	0.617	0.486
CH ₂ O	C	0.804	0.102	0.105	1.365	0.325
	O	−0.507	−0.199	−0.200	−1.297	−0.577
NH ₃	H	−0.148	0.048	0.047	−0.034	0.126
	N	−0.167	−0.300	−0.237	−1.113	−1.133
	H	0.056	0.100	0.079	0.371	0.378

^aHF/6-31G**//HF/6-31G* calculations of Wiberg and Rablen.^{6a}

Atomic charges were computed at BP86/TZ2P, unless stated otherwise.

suggest too much of an ionic bond in these compounds, while the Hirshfeld and VDD methods are in accordance with a covalent bond. The Bader and NPA charges obviously have to be treated with great caution. They may lead to an erroneous interpretation of the nature of the bond. The Mulliken charges (in the TZ2P basis) are considerably too large in CH₂O (and negative on H), and also too large in H₂O, but in this basis they are reasonable for NH₃ (actually much more realistic than either Bader or NPA charges).

In conclusion, Mulliken charges are not usable at all, because they are so strongly basis set dependent that, particularly in large basis sets, completely erratic results are obtained. The Bader and NPA charges reproduce more or less the difference in electronegativity between the atoms, but they overemphasize bond polarities, exhibiting large negative or positive charges for covalently bonded atoms. Therefore, these two methods should not be used to judge the polarity of a bond, or to estimate the charge on atoms, for instance, for electrostatic potentials or charge control effects in reactions. The Hirshfeld and VDD methods on the other hand are consistent with electronegativity values of elements, and conform to the chemical knowledge base for covalent and ionic character of bonds. Both appear to be good indicators for the nature of chemical bonds.

Redefining the Promolecule in the Hirshfeld and VDD Methods

A crucial feature of the Hirshfeld and VDD methods is that they measure changes of the charge density with respect to an initial charge density, the promolecule. As a corollary, the VDD and Hirshfeld methods offer the possibility to use a different reference density. This means that we can calculate flow of the electronic density from a different initial state to the final SCF converged molecule. As mentioned in the Introduction, the promolecule has been defined as a sum over the atoms, which are in their spherically average ground state calculated at the X α /VWN level. It is interesting to investigate various alternatives to this promolecule definition. First, we examine here, by changing to BP86 atoms, to what extent the approximation used for the exchange-correlation potential in the calculation of the atoms that constitute the promolecule will affect the VDD and Hirshfeld charges. In Table 8 the charges are given for CH₄ and CH₃Li for the cases of X α /VWN atoms and BP86 spherically averaged atoms. The differences in the

Hirshfeld and VDD atomic charges in the two cases are very small. This is to be expected because the atomic electron densities are not very sensitive to this change in the Kohn-Sham calculation. The largest deviation found for Hirshfeld is 0.010 electrons for the carbon atom in methane, and for VDD 0.004 electrons for Li in CH₃Li.

Next, we consider the possibility that we may not use spherically averaged atoms, but atoms brought into a “valence state.” In the valence state, we have set the occupation of the carbon atom to one electron in the 2s orbital and three electrons in the 2p orbitals. The carbon electrons are paired into bonding combinations with the 1s and 2s electron of hydrogen and lithium, respectively. (In the usual spherical spin-restricted reference atom, the carbon atom has two electrons in the 2s orbital and two electrons equally divided over the three 2p orbitals, with equal up and down spin density.) The effect of changing the valence state on the Hirshfeld and VDD charges is small. In the VDD method, the change is visible in the charges of the carbon atom [in methane −0.092 for s²p² BP86 reference atom and −0.120 a.u. for valence state (s¹p³) BP86 reference atom]. In the Hirshfeld method, this effect is masked by the weight function, which adapts the fuzzy atomic cell to the new situation. However, this conclusion is drastically changed when we compare for Ni(CO)₄ the Ni d⁸s² (ground state) to d¹⁰ (valence state). (Note that we have kept the C and O in the restricted ground state, see Table 8.) For Hirshfeld and VDD, we find, respectively, 0.165 and 0.181 a.u. for Ni in d⁸s² (ground state) and 0.424 and 0.536 a.u. for Ni in d¹⁰ (valence state). This is a direct consequence of the diffuse character of the 4s functions. The (4s)² charge density of Ni(d⁸s²) will significantly contribute to promolecule density outside the Voronoi cell of Ni. The positive charge on Ni when we start from Ni(d¹⁰) reflects backdonation out of 3d, but this is counteracted when, starting from Ni(d⁸s²), there is first a rearrangement of charge from the 4s density outside the Ni Voronoi cell to 3d density in that cell. This will happen because Ni is formally d¹⁰ in Ni(CO)₄.

Another possibility would be to use positively or negatively charged atoms to define the promolecule. As Davidson and Chakravorty⁶ⁱ pointed out this can give awkward values. One should keep in mind that intuitively we associate atomic charges as quantities that indicate a difference with respect to a *neutral* atom. Even when the molecule is charged, intuitively meaningful charges

Table 8. Atomic Charges (in a.u.) of Methane, Methyl lithium, and Ni(CO)₄ with the Promolecule Calculated with Restricted Spherical Ground-State Atoms at the X α VWN/TZ2P and BP86/TZ2P Level and with Valence State Atoms at the X α VWN/TZ2P and BP86/TZ2P Level.^a

Molecule	Atom	Level of promolecule	State of atoms in promolecule	Hirshfeld	VDD
CH ₄	C	X α VWN	Restricted ground state	-0.167	-0.095
		BP86	Restricted ground state	-0.157	-0.092
		BP86	C(2s ¹ 2p ³)H(1s ¹)	-0.157	-0.120
	H	X α VWN	Restricted ground state	0.042	0.024
		BP86	Restricted ground state	0.039	0.023
		BP86	C(2s ¹ 2p ³)H(1s ¹)	0.039	0.030
CH ₃ Li	C	X α VWN	Restricted ground state	-0.428	-0.259
		BP86	Restricted ground state	-0.422	-0.256
		BP86	Li(2s ¹)C(2s ¹ 2p ³)H(1s ¹)	-0.438	-0.295
	Li	X α VWN	Restricted ground state	0.494	0.386
		BP86	Restricted ground state	0.488	0.382
		BP86	Li(2s ¹)C(2s ¹ 2p ³)H(1s ¹)	0.500	0.397
	H	X α VWN	Restricted ground state	-0.022	-0.042
		BP86	Restricted ground state	-0.022	-0.042
		BP86	Li(2s ¹)C(2s ¹ 2p ³)H(1s ¹)	-0.021	-0.034
Ni(CO) ₄	Ni	X α VWN	Restricted ground states (Ni 3d ⁸ 4s ²)	0.1654	0.181
		X α VWN	Ni(3s ² 3p ⁶ 4d ¹⁰), C and O restricted ground state	0.4236	0.536
	C	X α VWN	Restricted ground states (Ni 3d ⁸ 4s ²)	0.0547	0.036
		X α VWN	Ni(3s ² 3p ⁶ 4d ¹⁰), C and O restricted ground state	-0.0012	-0.043
	O	X α VWN	Restricted ground states (Ni 3d ⁸ 4s ²)	-0.0960	-0.082
		X α VWN	Ni(3s ² 3p ⁶ 4d ¹⁰), C and O restricted ground state	-0.1047	-0.091

^aFinal molecule computed at BP86/TZ2P. See also text.

will result if we use neutral atoms for the promolecule. However, when we use charged atoms as reference, confusion may easily arise. In that case we calculate the amount of electronic density that flows into or away from the cell of the ion, compared to the sum of ion densities. These charge *shifts* will not take into account the original charges on the ions in the promolecule, and cannot be used as an indication of the charge on the atom in the final molecule. If for a neutral molecule a promolecule would be chosen with a net charge, the deformation density would not integrate to zero, that is, the sum of the charges on the atoms would not be zero. In the case of the Hirshfeld scheme, also spatially different fuzzy cells will result for the ion and the neutral atom.

We illustrate this for sodium chloride. In the standard approach, NaCl is built up from neutral (spherically averaged) ground-state atomic densities. The corresponding deformation density represents a shift of charge density from sodium to chlorine. This is monitored correctly by both VDD and Hirshfeld, which yield a positive charge for Na of +0.590 and +0.577 a.u., respectively. However, if the deformation density for NaCl is computed with respect to the superposition density of Na⁺ and Cl⁻, there is a shift of charge from the chloride anion to the sodium cation. This is correctly monitored by VDD, which yields a negative “charge” for Na of -0.130 a.u. Note that this “charge” is actually a charge shift. It reflects the difference with respect to the electron density of the Na⁺ ion, and cannot be interpreted as the actual charge of Na in NaCl. Nevertheless, one could add the charge change of -0.130 a.u. to the initial +1 charge of the Na⁺ ion, which would yield the reasonable value of +0.870 a.u. for the charge of the Na atom in NaCl.

In the case of Hirshfeld charges, the use of charged fragments has to be treated with even more caution. When the Hirshfeld charge is calculated according to eq. (4), as is actually the case in ADF and most other programs where it is evaluated (for exceptions, see ref. 6j), it will compare the total electron density in the final molecule that surrounds nucleus A, according to a weighting $\rho_A(\mathbf{r})/\rho_{\text{promolecule}}(\mathbf{r})$ that involves ionic densities, to the nuclear charge Z_A . The number should reflect the actual positive charge, and we find it to be +0.951 a.u. This is a meaningful number; it tells us that in the relatively small Hirshfeld atomic domain of Na⁺, $\Omega_{\text{Na}^+} = \rho_{\text{Na}^+}(\mathbf{r})/\rho_{\text{promolecule}}(\mathbf{r})$, there is one electron less than in the Na atom. It is more positive than the standard Hirshfeld value of +0.577 a.u., because the domain Ω_{Na^+} is smaller than the domain Ω_{Na} defined with neutral atoms in the promolecule. It is to be noted that this Hirshfeld charge is different from the VDD charge *change* of -0.130 a.u. (when ions are used in the promolecule). In fact, in this case, the Hirshfeld charge can no longer be interpreted as integration of the deformation density over a fuzzy cell according to eq. (10).

It is to be noted that confusion easily arises if one uses charged fragments. In our opinion, it is therefore better to refrain from using charged reference atoms (or fragments) in the promolecule. Note that this not only holds for neutral molecules. Also for charged molecules, neutral atoms in the promolecule are perfectly in order. A neutral promolecule will lead to atomic charges that sum up to the charge of the molecule and which will give an impression of where the positive or negative charge of the molecule is concentrated. The VDD and the Hirshfeld charges will be similar.

VDD Charges as Bonding Analysis Tool

VDD Charge Analysis for Bonding Between Molecular Fragments

We will consider in this section extensions of the VDD scheme that are suitable for the analysis of bonding between molecular fragments. We will also highlight a pitfall for the analysis of charge flow in the case of very weak interaction, and show that the extension of the VDD method to fragments as reference provides a natural solution. Examples of fragment based analysis (metal complexes) are given in the next section, and an example of the treatment of weak interaction (H-bonding in DNA base pairs) is given in the section after that.

Instead of measuring the flow of electronic density with the promolecule as initial density one can measure the charge rearrangements with the sum of poly-atomic subsystems ρ_i as initial density.

$$\Delta Q_A^{\text{VDD}} = - \int_{\text{Voronoi cell of A in molecule}} \left(\rho_{\text{molecule}}(\mathbf{r}) - \sum_{\text{subsystems}} \rho_i(\mathbf{r}) \right) d\mathbf{r} \quad (11)$$

Eq. (11) offers a direct insight into the redistribution of the electronic density caused by the formation of a bond between poly-atomic subsystems. The advantage, and even necessity, of using this definition of ΔQ_A^{VDD} may be understood by contrasting it with the seemingly plausible approach to simply compute for each atom A the difference between the atomic charge in the complex, $Q_{A,\text{complex}}^{\text{VDD}}$, and that in the separate molecule, $Q_{A,\text{molecule}}^{\text{VDD}}$ [eq. (12)]:

$$\begin{aligned} \Delta Q_A^{\text{VDD}} &= Q_{A,\text{complex}}^{\text{VDD}} - Q_{A,\text{molecule}}^{\text{VDD}} \\ &= - \int_{\text{Voronoi cell of A in complex}} \left(\rho_{\text{complex}}(\mathbf{r}) - \sum_{\text{atoms in complex}} \rho_C(\mathbf{r}) \right) d\mathbf{r} \\ &\quad + \int_{\text{Voronoi cell of A in molecule}} \left(\rho_{\text{molecule}}(\mathbf{r}) - \sum_{\text{atoms in molecule}} \rho_B(\mathbf{r}) \right) d\mathbf{r} \quad (12) \end{aligned}$$

However, the use of eq. (12) may lead to flagrant errors when A is an atom involved in the intermolecular bonding (a “front atom”) and the charge rearrangement due to the weak intermolecular interaction in the complex is small compared to the charge redistribution upon the formation of the strong bonds within the molecule. A good example is the hydrogen bonding between DNA base pairs, where one is interested in the charge rearrangement associated with the hydrogen bond formation, in particular that on the front atoms on each base, that is, the atoms pointing toward the other base.¹⁶ The effect of hydrogen bonding on the atomic charges is in this case about an order of magnitude smaller than the charge rearrangements due to the primary process of strong chemical bond formation within the individual molecules. ΔQ_A^{VDD} as

defined in eq. (12) is then not a reliable indicator of the charge flow due to hydrogen bonding. Note that $Q_{A,\text{complex}}^{\text{VDD}}$ and $Q_{A,\text{molecule}}^{\text{VDD}}$ differ in three respects: the different molecular densities ρ_{complex} and ρ_{molecule} ; the altered Voronoi cell; and different promolecules. For the front atoms, the second effect is important, and the third is as well. In a free molecule, the Voronoi cell of such an atom will extend to infinity in the direction where the second molecule will be located. In the complex, of course, the Voronoi cell of the front atom will have as one of its faces the bond midplane perpendicular to the bond to the other molecule and cutting that bond in half. This drastic change of the shape of the Voronoi cell has as much effect on the VDD charge as the subtle change of the density from ρ_{molecule} to ρ_{complex} , rendering eq. (12) useless in spite of the fact that the individual charges $Q_{A,\text{complex}}^{\text{VDD}}$ and $Q_{A,\text{molecule}}^{\text{VDD}}$ may be quite reasonable. This is the so-called front-atom problem. We wish to emphasize that other methods for the calculation of atomic charges (Mulliken, Hirshfeld, Bader), where the presence of the new neighbor atom in the other base directly affects the atomic charge evaluation on the front atom, are in principle subject to the same kind of problem when the small change in atomic charge due to hydrogen bonding would be calculated as the difference of the “large” charges in the pair and in the base.

With the use of eq. (11), the calculation of a small difference of two large numbers that are not completely comparable, as in eq. (12), is now avoided. Only one Voronoi cell is used, the one in the complex, which eliminates the problem identified above. This method for “measuring” the charge rearrangement due to the weak hydrogen bonding is of course in the spirit of the VDD calculation of atomic charges resulting from chemical bond formation because it integrates the relevant density difference over an appropriate atomic part of space. The example of hydrogen bonding between base pairs is discussed as an illustration in the section Charge Transfer in Hydrogen-Bonded Systems.

VDD Charge Decomposition Complementary to Bond Energy Decomposition

The VDD scheme offers wider analysis possibilities, by integrating density differences other than just the deformation density over the Voronoi cell of an atom. This is particularly useful when combined with bond energy decomposition methods, which usually break a total interaction up into steps that are each characterized by a density change. Interactions are then often considered between larger fragments than just atoms. It is customary to distinguish steps in the bond formation.¹⁷ The first is Pauli repulsion, corresponding to a wave function $\Psi^0 = N A[\Psi^A \Psi^B]$, which only incorporates antisymmetrization and renormalization of the product of ground state wave functions of fragments A and B. In an orbital model (Hartree-Fock or Kohn-Sham) the formation of the density ρ^0 corresponding to Ψ^0 can be accomplished by orthogonalization of the occupied orbitals. The next step is relaxation towards the final ground state wave function of the complete system, which in an orbital model is accomplished by mixing in of the virtual orbitals, describing charge transfer between and mutual polarization of the fragments. So the deformation density of the complex $\Delta\rho_{\text{complex}}$ is divided into a Pauli-repulsion component:

Table 9. Atomic Charges (in a.u.) for the Transition Metal Complexes Cr(CO)₆ and Fe(CO)₅.^a

Molecule	Symmetry	Atom	Mulliken	Hirshfeld atoms	VDD atoms	VDD fragments	Bader
Cr(CO) ₆	O _h	Cr	−0.719	0.222	0.261	0.406	1.123
		C	0.501	0.063	0.038	−0.058	0.893
		O	−0.381	−0.100	−0.081	−0.010	−1.077
Fe(CO) ₅	D _{3h}	Fe	−0.833	−0.071	−0.118	0.026	0.748
		C _{ax}	0.561	0.131	0.126	0.026	0.951
		O _{ax}	0.387	−0.088	−0.072	0.000	−1.064
		C _{eq}	0.552	0.099	0.092	−0.012	0.907
		O _{eq}	−0.390	−0.103	−0.089	−0.015	−1.076

^aSee also text.

Atomic charges were computed at BP86/TZ2P.

$$\Delta\rho_{\text{Pauli}} = \rho_{\text{complex}}^0 - \sum_{\text{subsystems}} \rho_i \quad (13)$$

and an orbital interaction component

$$\Delta\rho_{\text{oi}} = \rho_{\text{complex}} - \rho_{\text{complex}}^0 \quad (14)$$

The atomic charge change caused by the Pauli repulsion upon formation of the complex from the subsystems is defined as follows [eq. (15)]:

$$\Delta Q_{\text{Pauli},A} = - \int_{\text{Voronoi cell of A in complex}} \left[\rho_{\text{complex}}^0(\mathbf{r}) - \sum_{\text{subsystems}} \rho_i(\mathbf{r}) \right] d\mathbf{r} \quad (15)$$

The changes brought about by the charge transfer between and polarization of the subsystems are given by

$$\Delta Q_{\text{oi},A} = - \int_{\text{Voronoi cell of A in complex}} [\rho_{\text{complex}}(\mathbf{r}) - \rho_{\text{complex}}^0(\mathbf{r})] d\mathbf{r} \quad (16)$$

This definition parallels the energy decomposition¹⁷ used in the ADF program, offering the possibility not only to quantify the energetic terms of the interaction but also to calculate the charge rearrangements associated with it. Eqs. (15) and (16) are able to measure quantitatively and separately the charge redistributions associated with the energy component ΔE_{Pauli} and with the orbital interaction component ΔE_{oi} of the interaction energy.

As a further analysis tool, which parallels the breakdown of the interaction energy into components belonging to irreducible representations, which was originally proposed by Ziegler and Rauk,^{17d,e} the $\Delta Q_{\text{Pauli},A}$ and $\Delta Q_{\text{oi},A}$ can also be decomposed into contributions of different irreducible representations Γ of the complex:

$$\Delta Q_{\text{Pauli},A}^{\Gamma} = - \int_{\text{Voronoi cell of A in complex}} \left[\rho_{\text{complex}}^{0,\Gamma}(\mathbf{r}) - \sum_{\text{subsystems}} \rho_i^{\Gamma}(\mathbf{r}) \right] d\mathbf{r} \quad (17)$$

$$\Delta Q_{\text{oi},A}^{\Gamma} = - \int_{\text{Voronoi cell of A in complex}} [\rho_{\text{complex}}^{\Gamma}(\mathbf{r}) - \rho_{\text{complex}}^{0,\Gamma}(\mathbf{r})] d\mathbf{r} \quad (18)$$

This decomposition of the VDD charge rearrangements has been implemented for planar molecules such as the DNA base pairs AT and GC, and affords a distinction to be made between σ and π components. The division of ΔQ_A^{Γ} into a Pauli and orbital interaction component, particularly the use of ΔQ_A^{σ} , makes it possible to differentiate small charge-transfer rearrangements from the charge redistribution caused by the Pauli repulsion (*vide infra*).

Metal Complexes: Cr(CO)₆ and Fe(CO)₅

The first systems to which we apply eq. (11) are some metal complexes, which are built up from a transition metal atom and ligands. The Mulliken, Hirshfeld, VDD, and Bader atomic charges for the metal complexes, Cr(CO)₆ and Fe(CO)₅, are listed in Table 9. Also the values for the change in atomic charges, where we build up the molecule from poly-atomic fragments (metal atom and CO molecules), are given for the VDD method. First, we focus on the “normal” atomic charges [i.e., eq. (9)]. The coordination bond in the neutral Cr(CO)₆ and Fe(CO)₅ is formed by a donation of the lone pair on C of CO to the unoccupied *d* atomic orbitals of the metal and also by the back donation from the occupied *d* orbitals on the metal to the π^* orbitals on the CO ligands.¹⁸ The charge on the metal atom depends on which of the two interactions is strongest. The VDD and Hirshfeld method name for Cr(CO)₆ the back donation as winner and for Fe(CO)₅ it is, with a smaller margin, the donation from the lone pair of CO to metal. The atomic charge of Cr is +0.222 and +0.261 a.u. for Hirshfeld and VDD, respectively, and the atomic charge of Fe is −0.071 and −0.118 a.u. for the two methods (see Table 9). These moderate charges basically confirm the covalent metal-ligand bond in the transition

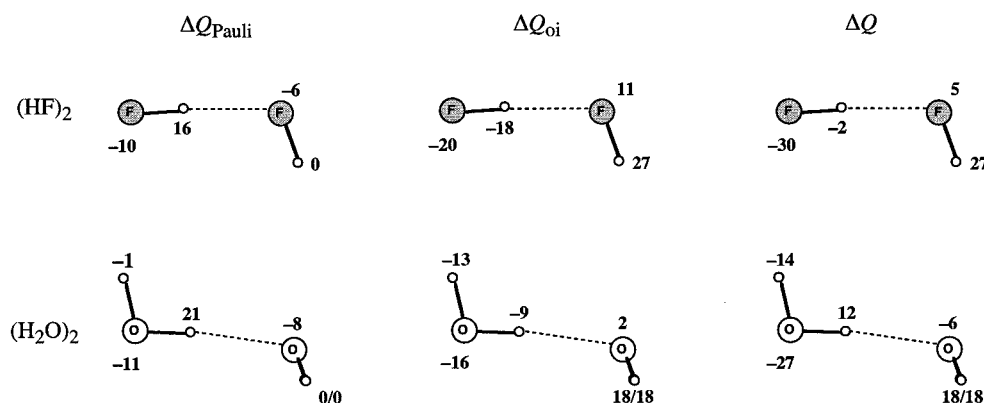


Figure 6. Changes in total VDD charges (in milli-a.u.) caused by the Pauli repulsion and the orbital interaction on forming the hydrogen bonds in $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$, computed at BP86/TZ2P.

metal complexes. The Bader charges calculated for the CO ligands in the metal complexes are too large: an almost +1 charged C atom and more than −1 charged O atom. Also, the charge of the metal atoms (+1.123 for Cr and +0.748 a.u. for Fe) implies too much ionic bond character between the metal and its ligands. The Mulliken method suggests an opposite ionic character with large negative values for the metal atoms, −0.719 and −0.833 a.u. for Cr and Fe, respectively.

Let us now consider the effect of calculating the VDD charges as charge rearrangements due to the formation of a molecule from (poly-atomic) fragments (in this case CO molecules). The “normal” charges [“VDD(atoms)”] on C and O are fairly small, and in fact are of the same order of magnitude as in the free CO molecules [0.038 a.u. on C in $\text{Cr}(\text{CO})_6$, to be compared to +0.071 a.u. in free CO]. This means that the charge changes upon complex formation are potentially not well represented by the VDD charge with respect to atoms, for the reasons explained previously (see also next paragraph). The charge changes are much more reliably represented by the VDD charge with respect to the CO fragments (plus the Cr atom). The VDD(fragments) charge on C has the opposite sign (−0.058 a.u.), indicating there has been a net increase of electron density in the C Voronoi cell due to the combined effect of π -backdonation and σ -donation. The VDD(atoms) charge on O (−0.081 a.u.) is in an absolute sense larger than on C, but this should not be interpreted as meaning that complexation causes more charging up of O. Rather, the VDD(fragments) charge of −0.010 a.u. on O shows that the change in electron density around O is actually much smaller than around C, which fits in with the fact that both the donor orbital (σ lone pair) and the acceptor orbital (π^*) are mostly located on C. The negative charge on C indicates larger backbonding charge transfer, in keeping with the positive metal charge.

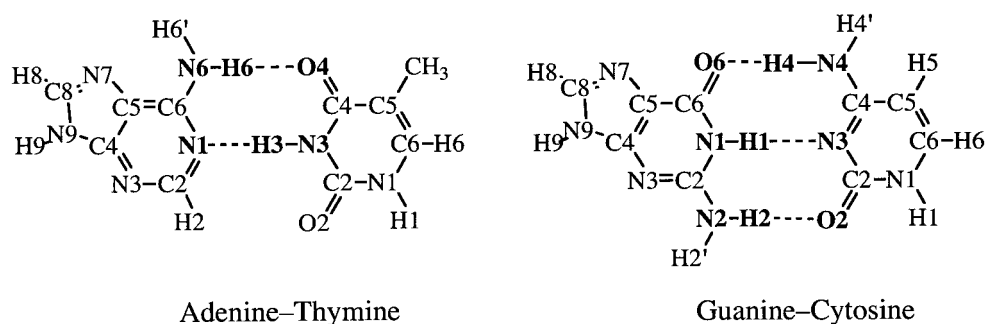
In the $\text{Cr}(\text{CO})_6$ case the VDD(fragments) charges give the same qualitative picture as the VDD(atoms) charges, when the values in the complex are compared to the free CO ones. For instance, the diminishing of the VDD(atoms) charge on C from +0.071 a.u. (C in free CO) to +0.038 a.u. [C in $\text{Cr}(\text{CO})_6$] has at least the same sign as the −0.058 VDD(fragments) charge. This is not always the case. When the changes become smaller the conclusions from

VDD(atoms) charges may even be qualitatively wrong. For CO_{eq} in $\text{Fe}(\text{CO})_5$, we see that the VDD(atoms) charge of C is slightly more positive in the complex than in free CO (+0.092 compared to +0.071 a.u.), but the VDD(fragments) charge of −0.012 a.u. reveals that again the electron density on C increases. The effect of the change in the Voronoi cell of C when going from free CO to $\text{Fe}(\text{CO})_5$ is so large—it would already yield a different charge on C in the free CO molecule—that its effect obscures the charge rearrangement we are after. This is the front-atom problem discussed previously. In the next section we will further substantiate this failure of VDD(atoms), and indeed any other charge analysis that does not work with fragments, to faithfully represent very small charge redistributions due to weak interactions, with examples from hydrogen bonding.

Charge Transfer in Hydrogen-Bonded Systems

In our work on the DNA base pairs,¹⁶ we have established with our MO analysis and the decomposition of the energy the occurrence of charge transfer in hydrogen-bonded systems (the BSSE in these computations was shown^{16c} to be less than 1 kcal/mol). This can be verified and quantified with the charge rearrangements calculated with eqs. (15) and (16). Figure 6 contains for the HF dimer and H_2O dimer the total charge rearrangements ΔQ calculated with eq. (11). The division of ΔQ into a Pauli-repulsion and an orbital interaction term gives a clear picture of what happens due to the formation of the hydrogen bond. The Pauli repulsion causes the density to flow away from the overlap region towards the sides, resulting in a depopulation around the central hydrogen atom and an increase of density on the proton-donor and proton-acceptor atoms (see Fig. 6). The orbital interactions account for the donation of density from the proton-acceptor molecule to the proton-donating molecule.

The difficulties encountered if one computes the *change* in atomic charges with eq. (12) can be illustrated with a numerical example for the water dimer. We can rewrite eq. (12) to the following form [eq. (19)]:



Scheme 2

$$\Delta Q_A^{\text{VDD}} = - \int_{\text{Voronoi cell of A in complex}} \rho_{\text{complex}}(\mathbf{r}) d\mathbf{r} + \int_{\text{Voronoi cell of A in molecule}} \rho_{\text{molecule}}(\mathbf{r}) d\mathbf{r} + \int_{\text{Voronoi cell of A in complex}} \sum_{\text{atoms in complex}} \rho_C(\mathbf{r}) d\mathbf{r} - \int_{\text{Voronoi cell of A in molecule}} \sum_{\text{atoms in molecule}} \rho_B(\mathbf{r}) d\mathbf{r} \quad (19)$$

and fill in the numbers for the proton-accepting oxygen atom of the water dimer: $\Delta Q_O^{\text{VDD}} = (-7.179 + 7.286) + (6.944 - 7.021) = 0.030$ a.u. This number shows properly a decrease of density on the

proton-accepting atom. However, when we look at how this number is obtained, we see that the difference between the two first terms of eq. (19) is $(-7.179 + 7.286) = 0.107$ a.u. and between the last two is $(6.944 - 7.021) = -0.077$. These numbers, which are determined by the difference in Voronoi cell and the final or initial density, are very close in absolute value and are also of the same order of magnitude as the actual charge transfer. Therefore, ΔQ_O obtained with eq. (12) is unreliable as we do not know if we are dealing with a real charge transfer or an artifact caused by the difference in Voronoi cell.

The results obtained for the hydrogen-bonded DNA base pairs (Scheme 2) are given in Figures 7 and 8. ΔQ_s are the atomic charge rearrangements acquired with eq. (11). We see here again that the total

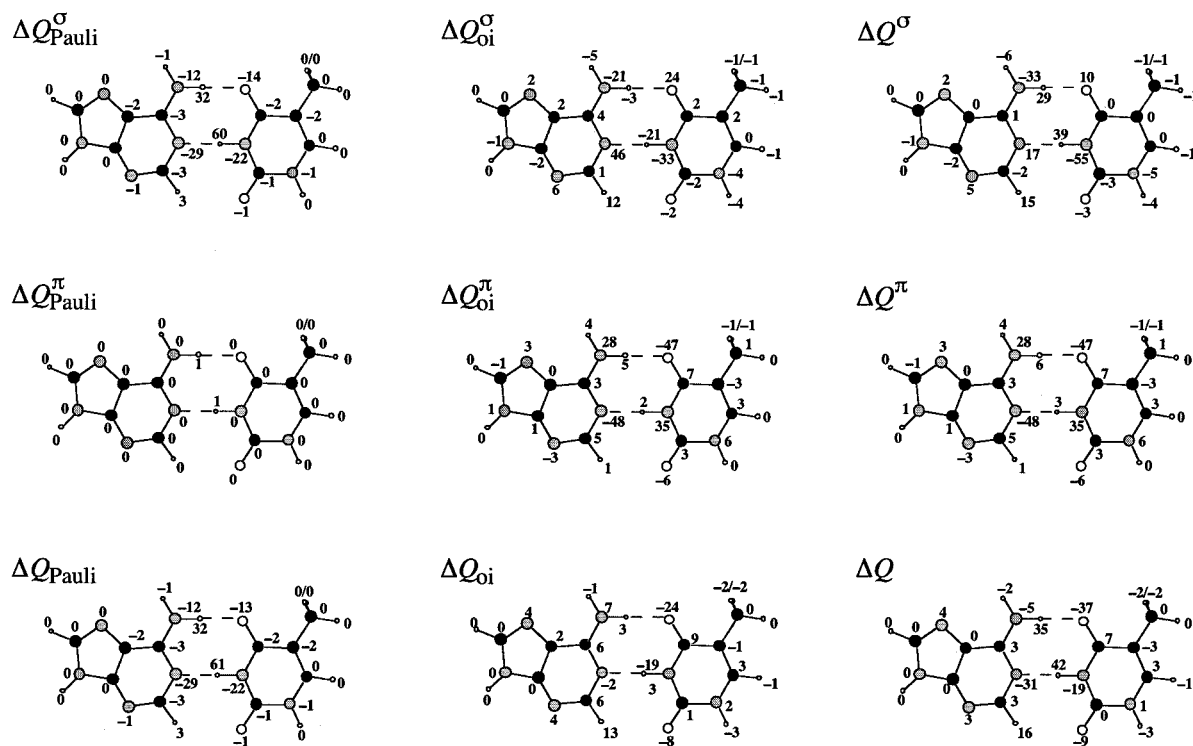


Figure 7. Changes in σ , π , and total VDD charges (in milli-a.u.) caused by the Pauli repulsion and the orbital interaction on forming the $\text{N6(H)} \cdots \text{O4}$ and $\text{N1} \cdots (\text{H})\text{N3}$ hydrogen bonds between adenine and thymine in AT (see Scheme 2), calculated at BP86/TZ2P.

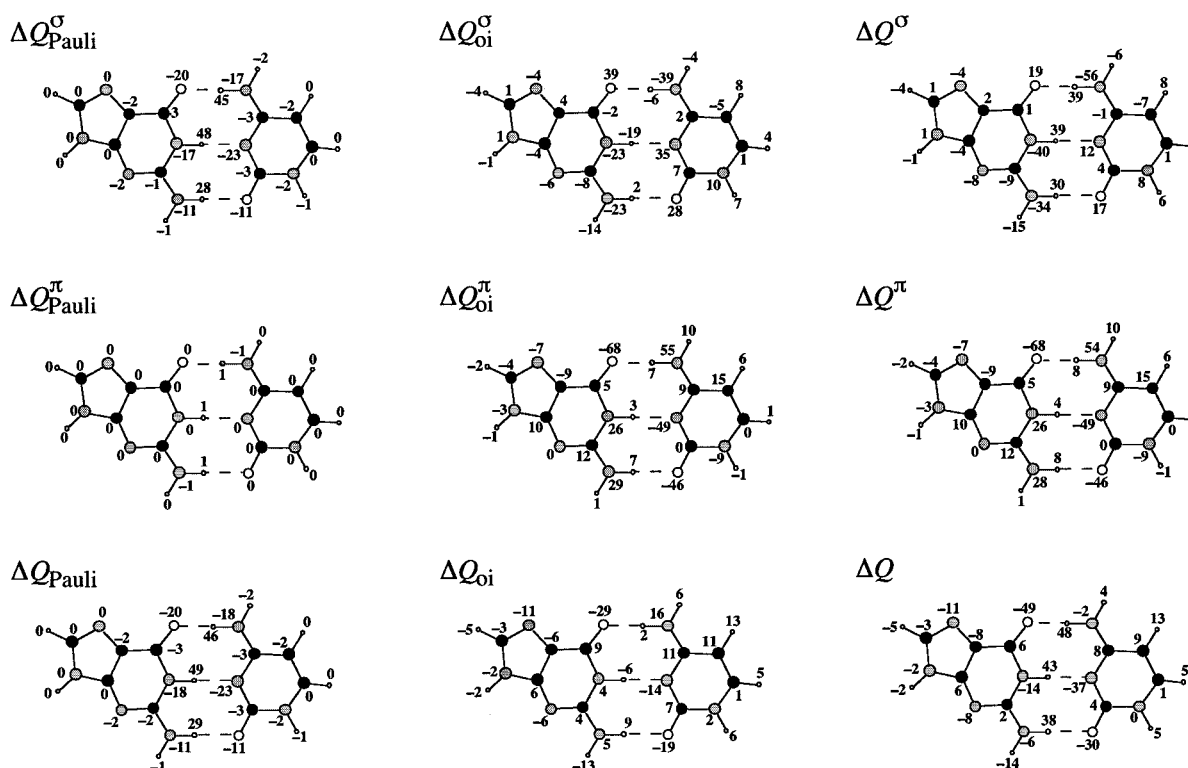


Figure 8. Changes in σ , π , and total VDD charges (in milli-a.u.) caused by the Pauli repulsion and the orbital interaction on forming the O6...N4, N1(H)...N3, and N2(H)...O2 hydrogen bonds between guanine and cytosine in GC (see Scheme 2) calculated at BP86/TZ2P.

atomic charge rearrangements are difficult to interpret because the donor-acceptor interactions, which have been established in our previous work,^{16a} are not visible. For instance, the oxygen and nitrogen atoms with lone pairs should lose electronic density instead of gaining it. A decomposition of these charge rearrangements as proposed in eqs. (17) and (18), shows how the total charge redistributions are built up. We discuss here the situation of the proton-accepting atoms, that is the oxygen and nitrogen atoms with lone pairs. For a complete discussion we refer to our work¹⁶ on the DNA base pairs. The net accumulation of electronic density on the proton-accepting atoms, as for instance the O4 of thymine (-0.037 a.u.), is caused by the Pauli repulsion (-0.013 a.u.) and the orbital interactions (-0.024 a.u.). A division of the charge rearrangements due to the orbital interactions into a σ component and a π component reveals a charge transfer of 0.024 electrons from the O4 of thymine to adenine and a gain of -0.047 a.u. on O4 due to π polarization. Also for the GC pair (see Fig. 8), we see that charge transfer interactions, which are masked by Pauli repulsion and π polarization, can be revealed by exploiting the symmetry analysis feature of the VDD method given in eqs. (17) and (18).

Concluding Remarks

To assess the results obtained for the VDD charge method, let us briefly reconsider the definitions of atomic charges used in

this and other work. We divide the methods into two major groups: methods based on representation of the molecular wave function with the help of basis functions and methods based on the electron density as a function in space. The Mulliken charges¹ and also its improvements^{2,3} are based on the wave function representation with basis functions and therefore inevitably suffer from the problems of: the spatial extent of the basis functions—they are usually centered on a nucleus but will extend over other atomic domains; and the existence of overlap terms, which have to be partitioned over the atoms. When the overlap populations become large, which is the case in large basis sets with diffuse basis functions, the half-half partitioning of the Mulliken population analysis¹ yields totally unphysical charges, which do not properly converge with increasing basis set size. Attempts to circumvent this problem have not given the desired results.^{2,3} The NPA charges³ employ explicitly orthogonalized (natural) atomic orbitals, and thus solve the overlap population problem. Nevertheless, we have found the NPA analysis to yield still unphysically large charges, giving a too ionic picture of covalent bonds. Presumably, the extension of the basis functions over a much larger region of space than one atom, either due to the orthogonality tails on other atoms, or due to the diffuse character of the primitive basis functions, hampers a realistic charge analysis. The use of basis set dependent methods as a tool to analyze the atomic charges is therefore questionable.

The other group of charge methods is based on the electronic density. To facilitate a convenient and direct comparison, we summarize in eq. (20) the definitions of the atomic charge according to VDD, Hirshfeld, Politzer and coworkers,¹⁰ Bader, and Van Alsenoy and coworkers¹¹:

$$Q_A^{\text{VDD}} = - \int_{\text{Voronoi cell of A}} [\rho(\mathbf{r}) - \rho_{\text{promolecule}}(\mathbf{r})] d\mathbf{r} \quad (20a)$$

$$Q_A^{\text{Hirshfeld}} = - \int \frac{\rho_A}{\rho_{\text{promolecule}}} [\rho(\mathbf{r}) - \rho_{\text{promolecule}}(\mathbf{r})] d\mathbf{r} \quad (20b)$$

$$\begin{aligned} Q_A^{\text{Politzer}} &= Z_A - \int_{\substack{\text{atomic region determined} \\ \text{with neutral atoms} \\ \text{in promolecule}}} \rho(\mathbf{r}) d\mathbf{r} \\ &= \int_{\substack{\text{atomic region determined} \\ \text{with neutral atoms} \\ \text{in promolecule}}} [\rho(\mathbf{r}) - \rho_{\text{promolecule}}(\mathbf{r})] d\mathbf{r} \quad (20c) \end{aligned}$$

$$Q_A^{\text{Bader}} = Z_A - \int_{\substack{\text{atomic region} \\ \text{determined with bcps}}} \rho(\mathbf{r}) d\mathbf{r} \quad (20d)$$

$$Q_A^{\text{Van Alsenoy}} = Z_A - \int_{\substack{\text{atomic region} \\ \text{determined with} \\ \text{van der Waals radii}}} \rho(\mathbf{r}) d\mathbf{r} \quad (20e)$$

Politzer's method¹⁰ is based on a partitioning of the space into regions in such a way that the integration of the density of the promolecule over the atomic region of atom A, Ω_A , does not yield charge transfer but yields a neutral atom A. In a diatomic this can be achieved by parallel displacement of the bond-perpendicular plane used for the Voronoi partitioning. Politzer thus determines the region Ω_A in such a way that $\int_{\Omega_A} \rho_{\text{promolecule}}(\mathbf{r}) d\mathbf{r} = Z_A$, which means that we can rewrite his charge definition according to the first line of eq. (20c) in the form of the second line of eq. (20c). This exhibits its analogy with the VDD and Hirshfeld definitions, that is, it can be conceived as being based on the deformation density. Atomic charges for some diatomics are given in the literature (HF 0.27; LiF 0.52; NaF 0.62; CO 0.14; SiO 0.42).¹⁰ These are actually not very different from the Hirshfeld and VDD charges (compare the above values of ref. 10 with those in Tables 3 and 4). The method, however, lacks generality. For nonlinear molecules it cannot be used because the atomic cells cannot be defined uniquely. It is, however, remarkable, that, as long as one integrates over the deformation density, the precise size and shape of the atomic regions do not seem to be very critical. This was already apparent from the closeness of the VDD and Hirshfeld

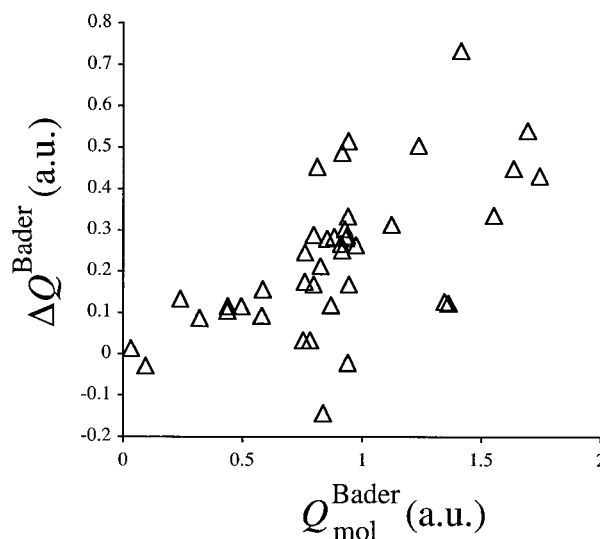


Figure 9. The “normal” Bader charges Q^{Bader} plotted against the Bader redistribution of electronic charge ΔQ^{Bader} computed as the deformation density integrated over the volume defined by the zero-flux surfaces determined by the final SCF-converged molecule (data from ref. 19b).

charges, and appears also from the similarity of the Politzer charges to VDD and Hirshfeld charges.

This finding is further substantiated by the early results of Spackman and Maslen.¹⁹ Spackman and Maslen recognized the importance of working with the deformation density for determining meaningful charges. They demonstrated that the Bader partitioning scheme into atomic regions yields atomic charges for the promolecule that suggest a considerable charge-transfer for this situation in which there is actually no chemical interaction at all. This is an unphysical result, which suggests the presence of a sizeable dipole moment whereas the dipole moment of the promolecule (composed of dipoleless atomic charge distributions) is zero. The same problem occurs, in fact, when integrating the promolecule density over the atomic Voronoi cells. As a matter of fact, the promolecule density does not differ very much from the final molecular density, and the “charge transfer” that is seemingly present in the promolecule density when integrated over an atomic domain (either Bader or Voronoi) persists in the atomic domain integration of the molecular density. This is why a Voronoi charge definition of the same form as a Bader charge, $Q_A^{\text{Voronoi}} = Z_A - \int_{\text{V-cell}} \rho(\mathbf{r}) d\mathbf{r}$, would yield similar erroneous charges. The Hirshfeld weighting factor (“cell”) by definition avoids this problem for the promolecule density. As in the Politzer definition it obeys $\int_{\Omega_A} \rho_{\text{promolecule}}(\mathbf{r}) d\mathbf{r} = Z_A$, which is why the Hirshfeld charge can be written as an integration over the deformation density. Spackman and Maslen clearly recognized this problem for the Bader charges and proposed to integrate the deformation density over the Bader atomic regions, yielding ΔQ^{B} . These ΔQ^{B} values (LiH 0.267; NaH 0.454; HF 0.174; LiF 0.287; NaF 0.516; CO 0.126; SiO 0.449) make much more sense than the Bader charges and are in fact very much in line with the VDD and Hirshfeld charges (see Table 3 and 4). No correlation (or a very poor one at best) between

the Bader charges of the molecule $Q_{\text{mol}}^{\text{Bader}}$ and the Bader charges of the deformation density ΔQ^{B} could be found for the molecules calculated by Spackman and Maslen^{19b} (see Fig. 9). Spackman and Maslen do, however, stress the difficulties that are sometimes experienced when determining the zero-flux surfaces of Bader's method, and the sensitivity of these surfaces to the quality of the wave function.

Van Alsenoy and coworkers have recognized the problem of just electron density integration over the Voronoi cell and have addressed this problem by adjusting, in the spirit of Politzer's solution, the size of the cell. The perpendicular bisecting planes of a bond determining the Voronoi cell are displaced in proportion to the van der Waals radii.¹¹ In molecules that can be treated with this method, the charges change strongly with respect to the "pure" Voronoi ones (C in CO 0.253 \rightarrow 0.165; O in H₂O +0.715 \rightarrow -0.396; N in NH₃ +1.274 \rightarrow -0.330), and become indeed fairly close to the VDD and Hirshfeld ones (cf. Tables 3 and 7). This method, like Politzer's, does not appear to be generally applicable, because of geometric conflicts in molecules of general shape.

We conclude from the results in this article that methods based on spatial integration of the deformation density over an atomic domain provide meaningful charges that conform to chemical experience. The spatial integration avoids the problems inherent to basis set based schemes. The use of the deformation density is necessary, otherwise unrealistic atomic charges are obtained for the promolecule density. It appears that the shape of the atomic domain, although it should of course be reasonable, is not very critical. Although the Hirshfeld fuzzy cell, and the Voronoi hard cell, look rather different (cf. Fig. 1), the VDD and Hirshfeld charges are very similar. The Hirshfeld cell may have a counter-intuitive shape (see Fig. 1 for GeH₄). Charge accumulation at the outer edge of GeH₄ would not be ascribed to the hydrogens, but fully to Ge. The Voronoi cell has a simpler and purely geometric definition. There is no ambiguity as to where the charge flow it measures is going to. The fact that the Voronoi cell does not in any way take atomic size into account does not seem to impair the VDD atomic charges. We feel that the Hirshfeld and VDD methods are both very suitable for the determination of atomic charges, and can be recommended as the methods of choice, with a preference for VDD because of the simplicity of its atomic domain definition.

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