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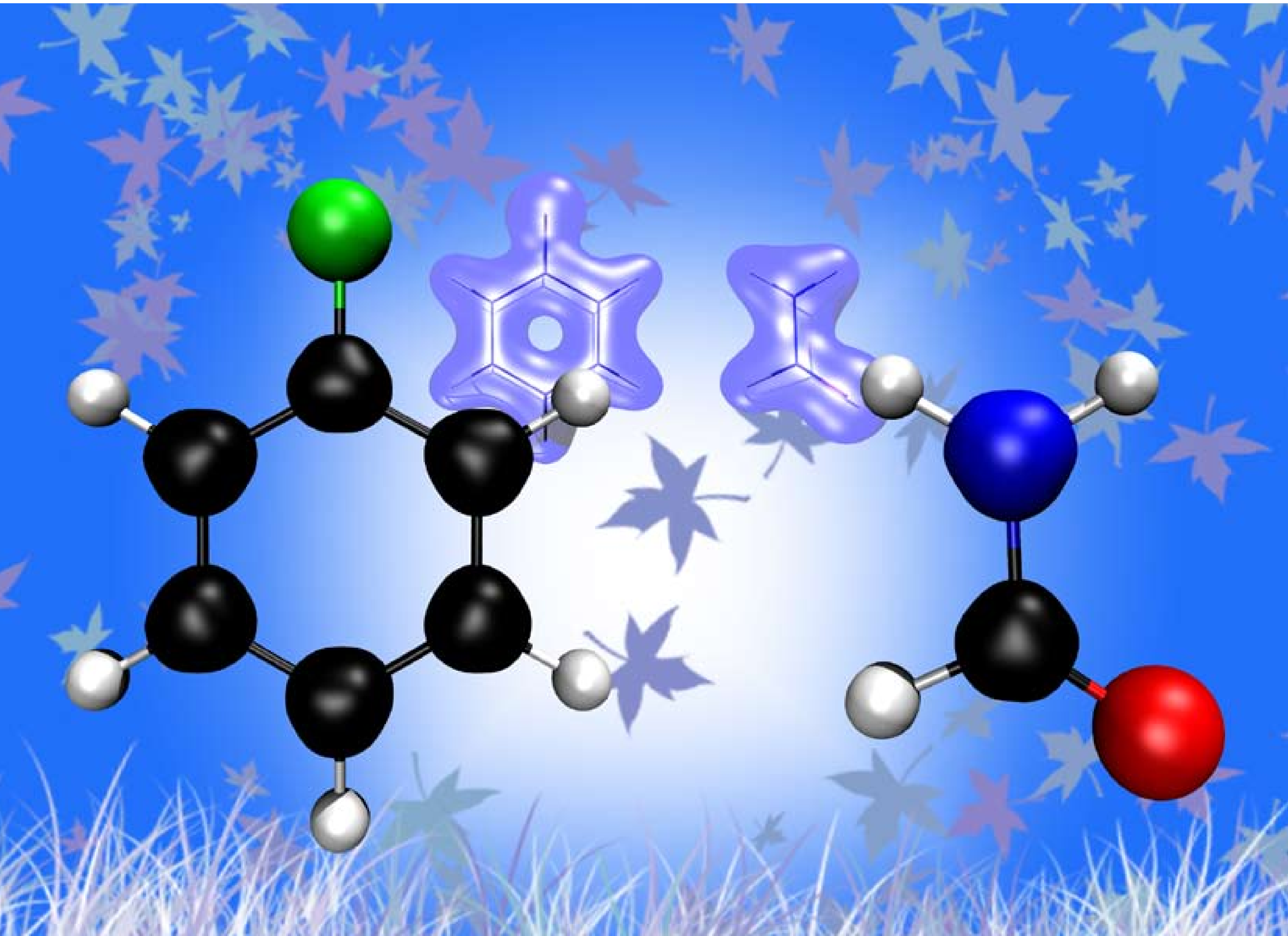

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FEATURE ARTICLE
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Redefining the atom: atomic charge densities produced by an iterative stockholder approach

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A new, simple, computational technique allows molecular electron densities to be divided into atoms which have intuitively correct shapes and charges.

One of the main unsolved problems in computational chemistry is the gap between the rigorously defined *molecular* properties which emerge from first-principles calculations and the more conceptual chemical properties which *atoms* and *functional groups* are known to possess, based on scientific experience. In particular, there is no unique method of dividing the electron density of a molecule into a sum of atomic parts.

Previous attempts to define atomic electron densities have been unsatisfactory for one or more reasons. Mulliken partitioning,[1] and the related Gaussian Multipoles method[2] based on Distributed Multipole Analysis (DMA),[3] give negative regions of electron density and depend strongly on the basis set used for the calculation. Bader's Atoms in Molecules (AIM)[4] have non-spherical shapes and discontinuous densities. A revised Distributed Multipole Analysis (here referred to as DFT–DMA),[5] or 'fuzzy atoms',[6] based on Density Functional Theory grid integration methods, also give highly non-spherical atoms and depend on arbitrarily chosen atomic radii. Stewart atoms[7] do not reproduce the molecular electron density, and have negative regions of density.

Atomic electron densities which are positive and which reproduce the molecular density can be obtained from the stockholder method,[8] by partitioning the molecular density according to spherically symmetrical weighting functions centred at the atomic nuclei:

$$\rho_a(\mathbf{r}) = \rho(\mathbf{r}) \frac{w_a(\mathbf{r})}{\sum_b w_b(\mathbf{r})} \tag{1}$$

where $\rho(\mathbf{r})$ is the molecular electron density at any position $\mathbf{r}$, ρ_a is the atomic electron density of atom a, and w_b is a weighting function which is spherically symmetrical around the nucleus of atom b. The sum on the denominator includes all atoms of the molecule.

The weighting functions w_b are obtained in the stockholder method by calculating the electron density of atom b in the gas phase, then spherically averaging it about the nucleus. This requires either an extra calculation on each atom or tables of precalculated densities. Furthermore the method of calculating the atomic density is not obvious when the gas-phase atom cannot be described by a single electron configuration, as is often the case.

In this work, weighting functions are defined without using gas-phase electron densities by *iterating* the stockholder procedure from an initial guess of the weighting functions, which can be as simple as $w_a = 1$. From these weighting functions, a first set of stockholder atoms is obtained from eqn (1). For the next iteration, the weighting functions are taken to be the spherical average of the stockholder atoms:

$$w_a(\mathbf{r}) = \langle \rho_a(\mathbf{r}) \rangle_a \tag{2}$$

where the angle brackets denote spherical averaging about the nucleus of atom a. These new weighting functions are inserted into eqn (1) to obtain new stockholder atoms, these are averaged *via* eqn (2), and the iteration procedure continues until the atomic densities converge, which means that eqns (1) and (2) are solved simultaneously. This procedure is similar to, but simpler than, that of Bultinck *et al.*[9]

Atomic electron densities ρ_a obtained from this process ('iterated stockholder atoms', or ISAs, for short), are clearly positive everywhere if the initial weighting functions are positive. They obey eqn (1), so their sum exactly reproduces the molecular electron density, and they do not depend explicitly on the basis set, only on the total electron density.

In order to demonstrate that atomic electron densities are of practical value, it is necessary to show that they are chemically reasonable. This should include features such as approximately spherical atoms, with smoothly decreasing electron density away from the nuclei, and negative net charges on electronegative atoms.

Fig. 1 shows ISAs of formamide and fluorobenzene calculated at the B3LYP[10]/6-31G*[11] level of theory. The ISA atoms are calculated on a standard DFT grid using 175 radial points per atom with up to 434 angular points per radial shell. In both molecules, the atomic electron densities are approximately spherical and have a reasonable radial behaviour, decreasing near-exponentially from the nuclei. The atoms in Fig. 1 were obtained by the iterative procedure above, using DFT–DMA atoms as an initial guess. The DFT–DMA atoms are shown in Fig. 2. Comparison of the two figures illustrates the power of the iterative method, whereby unfavourable features of the DFT–DMA atoms are removed, producing the more chemically reasonable ISA atoms. The uniqueness of the method will be addressed in future work. It has been tested numerically for the molecules considered in this paper by using

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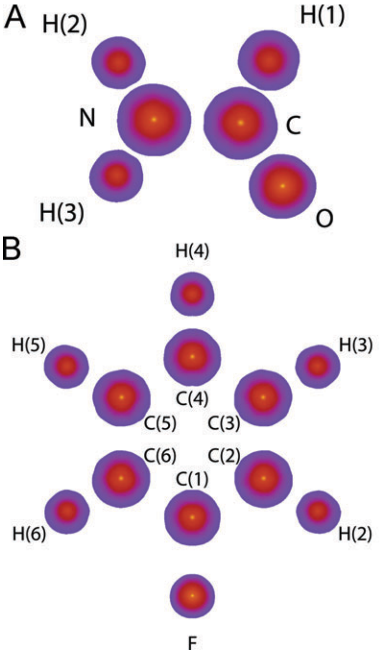

Fig. 1 Iterated stockholder atoms for formamide and fluorobenzene. The atomic electron density is plotted on a logarithmic scale between 10^{-4} and 10^{5} atomic units. Atoms in the molecules overlap but are separated for clarity in the figure by artificially lengthening the bonds.

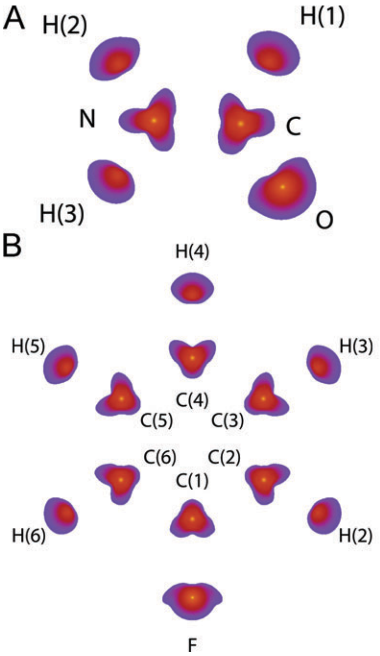

Fig. 2 DFT–DMA atoms for formamide and fluorobenzene. See caption of Fig 1.

weighting functions $w_a = 1$ as the initial guess as well as several different exponential and Gaussian functions. All initial guesses produce identical ISAs within the numerical precision of the calculations.

Table 1 Net Atomic Charges in units of fundamental charge e, obtained using several different methods. NAO refers to the Natural Atomic Orbital method,[12] and other abbreviations are defined in the text. Molecular dipole moments, μ, are shown with units e.a_0, where a_0 is the Bohr radius (1 e.$a_0 \approx 2.54$ Debye). Calculated molecular dipole moments are given in square brackets. Benzene has no dipole. The z-axis of formamide points from the N nucleus towards the C nucleus, and the molecule is in the x–z plane with the O nucleus located at $x > 0$

	ISA	Mulliken	DMA	DFT–DMA	NAO
H_2O					
O	−0.80	−0.79	−0.75	−0.42	−0.93
H	0.40	0.40	0.37	0.21	0.47
μ [−0.82]	−0.90	−0.90	−0.84	−0.47	−1.06
H_2CO					
C	0.34	0.07	0.68	0.14	0.23
O	−0.37	−0.31	−0.60	−0.30	−0.50
H	0.01	0.12	−0.04	0.08	0.13
μ [−0.86]	−0.85	−0.98	−1.28	−0.86	−1.42
$HCONH_2$					
C	0.62	0.34	0.88	0.16	0.51
N	−0.83	−0.70	−0.80	−0.25	−0.86
O	−0.53	−0.42	−0.76	−0.38	−0.61
H(1)	−0.02	0.10	−0.05	0.09	0.14
H(2)	0.37	0.34	0.36	0.18	0.41
H(3)	0.38	0.35	0.36	0.20	0.41
μ_z [−0.95]	−1.02	−1.03	−1.43	−0.93	−1.50
μ_x [−0.85]	−0.92	−0.97	−1.31	−0.85	−1.40
CH_3Cl					
C	−0.04	−0.52	−0.02	−0.33	−0.65
Cl	−0.23	−0.09	−0.18	0.09	−0.08
H	0.09	0.20	0.07	0.08	0.24
μ [−0.82]	−0.96	−0.70	−0.75	0.15	−0.74
C_6H_6					
C	−0.10	−0.13	−0.09	−0.09	−0.23
H	0.10	0.13	0.09	0.09	0.23
C_6H_5F					
F	−0.19	−0.32	−0.31	−0.24	−0.34
C(1)	0.37	0.41	0.46	0.14	0.43
C(2)	−0.27	−0.20	−0.19	−0.08	−0.31
C(3)	−0.04	−0.12	−0.08	−0.08	−0.22
C(4)	−0.16	−0.13	−0.11	−0.10	−0.25
H(2)	0.14	0.15	0.11	0.12	0.25
H(3)	0.10	0.14	0.10	0.10	0.24
H(4)	0.12	0.13	0.09	0.10	0.24
μ [−0.71]	−0.56	−1.00	−0.77	−0.97	−1.27

Table 1 shows atomic charges in units of the fundamental charge e, obtained by integrating the atomic electron density over all space and subtracting the result from the nuclear charge. The atomic charges have converged to 10^{-3} e after about 30–50 iterations. Molecular dipoles calculated with the same B3LYP/6-31G* method are listed in square brackets, and the molecular dipoles calculated using the atomic charges are shown in units of e.a_0, where a_0 is the Bohr radius. The Gaussian 03[13] package was used to calculate the Mulliken and Natural Atomic Orbital (NAO) charges.

A number of desirable chemical features are displayed by the ISAs. Electronegative atoms have negative charges, and hydrogens bonded to electronegative atoms have positive charges. Hydrogens bonded to carbon have small charges and the two NH_2 hydrogens in formamide have similar charges. In fluorobenzene, the *ortho* (C(2)) and *para* (C(4)) carbons are the most negatively charged of the carbons, as expected from the electron withdrawing substituent. A comparison of the dipole moments calculated using the atomic charges with the B3LYP/6-31G* molecular dipoles in square brackets further illustrates the utility of the ISAs. The ISA charges reproduce the molecular dipoles to within 0.2 atomic units in all cases. The ISA atomic dipoles (not shown) are never larger than 0.15 atomic units.

For comparison, the Mulliken, DMA, DFT–DMA and NAO charges are also shown in Table 1. All of the methods shown have charges that are qualitatively similar to the ISA charges, but the Mulliken and NAO methods place a larger negative charge on the carbon atom than the chlorine atom in chloromethane while the DFT–DMA method places a positive charge on the chlorine atom. The NAO method also places larger charges on the hydrogens than the ISA method, and therefore overestimates several of the molecular dipole moments. The DMA charges significantly overestimate the polarity of formaldehyde and formamide. The DFT–DMA method significantly underestimates the polarity of water and chloromethane.

In conclusion, iterated stockholder atoms are recommended as a simple and intuitive way of analysing molecular charge densities. The algorithm is rapid to use and straightforward to implement in a quantum chemistry computer program. The atoms that emerge from the procedure are in accord with informed expectations of atomic shapes and charges.

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