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Covalent bond orders and atomic anisotropies from iterated stockholder atoms

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Iterated stockholder atoms are produced by dividing molecular electron densities into sums of overlapping, near-spherical atomic densities. It is shown that there exists a good correlation between the overlap of the densities of two atoms and the order of the covalent bond between the atoms (as given by simple valence rules). Furthermore, iterated stockholder atoms minimise a functional of the charge density, and this functional can be expressed as a sum of atomic contributions, which are related to the deviation of the atomic densities from spherical symmetry. Since iterated stockholder atoms can be obtained uniquely from the electron density, this work gives an orbital-free method for predicting bond orders and atomic anisotropies from experimental or theoretical charge density data.

Introduction

One of the most useful concepts in chemistry, both quantitatively and qualitatively, is that of a molecule as a diffuse electron cloud surrounding nearly fixed nuclei. It is well known that the nuclei and inner electron shells change little when a molecule is formed from its constituent atoms, and this leads naturally to the question of whether molecular properties can be predicted from, or expressed as a superposition of, atomic properties. Such predictions would be very useful and powerful, because the number of known molecules is many orders of magnitude larger than the number of known atoms.

Much work has been devoted to this problem, and one of the most intensively studied properties is the electron density, from which many other properties can be derived or estimated. The seminal 'Atoms in Molecules' work of Bader[1] involves a division of the molecule into non-overlapping fragments. There are many advantages to this approach, but the resulting atoms are awkwardly shaped, and their sharp edges and discontinuous densities make them difficult to use in some applications. More recently, there has been a revival of interest[2] in 'fuzzy' or overlapping atoms, including two methods based on Hirshfeld's stockholder atoms.[3] These are the Hirshfeld-I[4] and iterated stockholder atoms (ISAs).[5] The atoms calculated using these two methods are surprisingly similar,[6] although the methods themselves are not closely related. The Hirshfeld-I method requires spherically averaged electron densities of the separate atoms, like Hirshfeld's original stockholder method, and also of their ions. The ISA method, which is used in this work, requires only the molecular electron density and the nuclear positions. Unlike the original stockholder method, it does not depend on an arbitrary choice of a 'promolecule'.

The ISA method divides the molecular density into atoms in a similar way to the stockholder method:

$$\rho_a = \frac{\rho_a^0 \rho}{\rho^0} \quad (1)$$

where ρ_a is the ISA density of atom a, ρ_a^0 is a spherically symmetrical 'weight function' assigned to atom a, which controls how the total electron density ρ is shared between the atoms, and ρ^0 is the sum of all the ρ_a^0 functions. In the stockholder method, ρ_a^0 is the spherically averaged density of the isolated gas-phase atom a, and the superposition of gas-phase atoms, ρ^0, is called the 'promolecule density'. In the ISA method, gas-phase atomic densities are not used, and ρ_a^0 is the spherical average of the atomic density ρ_a around the nucleus of a:

$$\rho_a^0 = \langle \rho_a \rangle_a. \quad (2)$$

Eqn (1) and (2) can be solved by iteration, starting from any positive weight functions (even an unphysical starting guess such as $\rho_a^0 = 1$ can be used), substituting them into eqn (1) to obtain the ISA densities, averaging the ISA densities using eqn (2), and repeating the process until the densities do not change significantly between iterations. The resulting atoms all have non-negative densities.

Alternatively, the solution of (1) and (2) is equivalent to minimising the functional

$$F = \int (\rho^0 - \rho - \rho \ln(\rho^0/\rho)) \mathrm{d}\mathbf{r} \quad (3)$$

with respect to ρ^0, subject to the condition that ρ^0, which can still be called the 'promolecule density', is a sum of spherically

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symmetrical atomic weight functions ρ_a^0, and provided that certain mathematical conditions are met. In particular, the weight functions that minimise the functional must all be non-negative. This condition has always been found to be satisfied for real molecules. At the minimum of the functional, which is known to be unique,

$$\langle \rho/\rho^0 \rangle_a = 1 \qquad (4)$$

for all a, and for the molecules considered in this paper, the iterative procedure given by eqn (1) and (2) gives this result at convergence.

Covalent bond orders

Covalence, or the sharing of electrons between atoms, is the fundamental process involved in bond formation in most molecules. In light atoms, it is often possible to use valence rules to predict covalent bond orders (where a bond order of N indicates that $2N$ electrons are shared between the atoms). However, valence rules are often unsuitable for molecules containing heavy atoms or metal atoms, or for 'electron deficient' molecules. Several schemes have been devised for calculating or predicting bond orders, usually involving calculation of 'natural orbitals'.[7] However, orbitals are an arbitrary theoretical construct with no physical existence, and we therefore present here an alternative method for estimating bond orders, using only the electron density.

After subdivision of the electron density into atomic parts, each atom a can be taken to have N_a electrons, where N_a is the integral of the atomic density ρ_a over all space. Considering pairs of atoms a and b, the quantity

$$C_{ab} = \int \frac{\rho_a \rho_b}{\rho} \mathrm{d}\mathbf{r} \qquad (5)$$

can be interpreted as the number of electrons that atom a shares with atom b. Clearly $C_{ab} = C_{ba}$, and if the atomic densities sum to the molecular density, $\rho = \sum_a \rho_a$, then the number of electrons of atom a satisfies $N_a = \sum_b C_{ab}$. This sum includes $b = a$, and the quantity C_{aa} is the number of 'unshared' electrons of atom a. If the atoms are stockholder atoms, defined using eqn (1), then eqn (5) can be re-expressed in terms of the spherically symmetrical weight functions:

$$C_{ab} = \int \frac{\rho_a^0 \rho_b^0 \rho}{(\rho^0)^2} \mathrm{d}\mathbf{r}. \qquad (6)$$

When the quantities C_{ab} are calculated, they are found to be smaller than the number of electrons that are conventionally expected to be involved in a bond. For example, in a singly bonded molecule such as H_2, C_{ab} is less than 1 (approximately 0.3). This may be ascribed partly to the fact that a single-determinant wavefunction describing a 'covalent' bond is actually a mixture of ionic and covalent contributions, and partly to the localisation of electron density by the ISA scheme. However, it is found empirically that there is a rough proportionality between C_{ab} and the covalent bond order, such that the covalent bond order between atoms a and b is approximately kC_{ab}, where k is a constant scaling factor.

The quantity C_{ab} has also been calculated by Mayer and Salvador[8] (called the overlap population, q_{ab}) and by Vanfleteren *et al.*[9] (called the trace of the density, Tr ρ_{ab}^n). Mayer and Salvador used a partitioning scheme based on Becke's integration weights, which produced an overlap population that does not seem to be closely proportional to the bond order. Vanfleteren *et al.* used the Hirshfeld-I partitioning method, which is closer to the ISA method, and the results they presented for acrylonitrile are generally in line with the present work.

Table 1 shows calculated values of kC_{ab} for pairs of atoms in a number of molecules, including molecules with conventional single, double and triple bonds, molecules with bonds that are conventionally described using a non-integer bond order, two ionic molecules, a hydrogen-bonded molecule, and the electron-deficient borane molecule. The value of k is taken to be 3.32 to obtain the best correspondence between the calculations and the expected bond orders. Iterated stockholder atoms, densities, and hence the parameter k, are all calculated using the Hartree–Fock self-consistent field (SCF) method. The aug-cc-pVTZ basis set[10,11] is used for all molecules except B_2H_6 and C_6H_6, for which the aug-cc-pVDZ basis set[10,11] is used. Geometries are optimised at the second-order Møller–Plesset (MP2) level of theory with the same basis set using MOLPRO.[12] Iterated stockholder atoms are calculated on a large grid consisting of 300 radial shells of 600 angular points per atom. The calculation is performed by iterating eqn (1) and (2), with DIIS-type extrapolation using eqn (3). Convergence is achieved in a few tens of iterations.

The table shows a good correspondence between calculated and 'expected' bond orders. When the expected bond order is an integer, the calculated bond order always agrees with that value to within 0.4, and about half agree to within 0.1, with the biggest discrepancies being the calculated bond orders of 1.37 for Cl_2 and 2.61 for the C–N 'triple' bond in CH_3CN. The C–N bond order in formamide is calculated to be 1.49, but it would be expected to be more than 1 as a result of resonance. For bonds that are expected to have non-integer covalent bond orders (such as in borane and benzene), there is similarly good agreement between the calculated and expected bond orders. In general, the calculated orders of H–X bonds seem to be a little low, with most being between 0.9 and 1.0, although it is encouraging that bonds to acidic H atoms (which would be expected to have a partially ionic character) give some of the lowest calculated H–X covalent bond orders. Calculated covalent bond orders for the hydrogen bond and the two 'ionic' bonds are less than 0.3.

The results do not depend qualitatively on the basis set. Using CO, HF and Cl_2 as examples, calculated bond orders change by less than 0.01 when the basis set is changed to aug-cc-pVDZ or aug-cc-pVQZ. If 'relaxed' MP2 densities (defined as the analytical derivative of the MP2 energy) are used instead of SCF densities, a similarly negligible change occurs for CO, but the HF and Cl_2 bond orders both increase by 0.03–0.04, using the same value of k.

Atomic anisotropies

Atomic charge densities are deformed by the process of chemical bonding, and it can be useful to quantify the extent

Table 1 Theoretical covalent bond orders kC_{ab} for pairs of atoms in molecules, where C_{ab} is defined in the text for atoms a and b, and $k = 3.32$ is a proposed scaling constant. In C_4H_6, C2–C3 is the central C–C bond. In CH_3NH_2 and CH_3OH, the H2 atom is in the plane of symmetry, and the H1 atoms are not. In CH_2NH, H1 is *cis* to the H on N. In $HCONH_2$, H1 is *cis* to the H on C

Molecule	Bond	kC_{ab}
H_2	H–H	0.94
F_2	F–F	1.01
Cl_2	Cl–Cl	1.37
Br_2	Br–Br	1.30
N_2	N–N	2.70
CO	C–O	2.41
CO_2	C–O	1.96
HF	H–F	0.77
HCl	H–Cl	0.94
HBr	H–Br	0.96
HO^-	O–H	1.19
H_2O	O–H	0.88
H_2O_2	O–H	0.81
	O–O	1.23
NH_3	N–H	0.95
CH_4	C–H	1.03
C_2H_6	C–C	1.13
	C–H	0.99
C_2H_4	C–C	2.17
	C–H	0.97
C_2H_2	C–C	2.83
	C–H	0.91
C_4H_6	C1–C2	1.99
	C2–C3	1.37
	C1–H	0.97
	C2–H	0.92
C_6H_6	C–C	1.60
	C–H	0.94
CH_3F	C–H	0.95
	C–F	1.19
CH_3Cl	C–H	0.95
	C–Cl	1.18
CF_4	C–F	1.03
CCl_4	C–Cl	1.07
SiH_4	Si–H	0.97
$SiCl_4$	Si–Cl	1.24
CH_3NH_2	C–H1	0.92
	C–H2	0.96
	C–N	1.29
	N–H	0.95
CH_2NH	C–H1	0.98
	C–H2	0.95
	C–N	2.13
	N–H	0.89
CH_3CN	C–H	0.94
	C–C	1.29
	C–N	2.61
HCN	C–H	0.90
	C–N	2.69
CN^-	C–N	3.07
CH_3OH	C–H1	0.96
	C–H2	0.93
	C–O	1.26
	O–H	0.87
H_2CO	C–O	2.04
	C–H	0.94
HCO_2H	C–O	1.92
	C–O(H)	1.35
	O–H	0.77
	C–H	0.87
$HCONH_2$	C–H	0.85
	C–O	1.83
	C–N	1.49
	N–H1	0.87
	N–H2	0.83
NO_3^-	N–O	1.42
HNO_3	N–O	1.62
	N–O(H)	1.02
	O–H	0.64
CS_2	C–S	2.09
SO_2	S–O	2.01
SO_4^{2-}	S–O	1.42
H_2SO_4	S–O	1.87
	S–O(H)	1.24
	O–H	0.76
B_2H_6	B–H(B)	0.53
	B–H	1.00
LiF	Li–F	0.24
NaCl	Na–Cl	0.27
H_2CO–HF	O–H	0.12

to which an atom in a molecule is anisotropic. For example, force fields describing non-bonded interactions between atoms may need to include dipole, quadrupole or higher multipole contributions if the interacting atoms are anisotropic.[13] The accuracy of molecular geometries obtained from high-resolution X-ray diffraction experiments can be improved if the atoms are not assumed to be spherical.[14]

The functional F, defined by eqn (3), is a measure of the total anisotropy of all the atoms within a molecule. If the molecule can be described exactly as a superposition of spherical densities, then $\rho = \rho^0$ and $F = 0$. If not, then $F > 0$.

Individual atomic anisotropies F_a can be defined for atoms a within a molecule by analogy with eqn (3):

$$F_a = \int \rho_a^0 - \rho_a - \rho_a \ln(\rho_a^0/\rho_a)\mathbf{dr}, \qquad (7)$$

where $F = \sum_a F_a$, provided that the atoms obey eqn (1). If the atomic densities are non-negative, each atomic anisotropy is also non-negative, and equals zero only if the atom is exactly spherical.

Table 2 shows the anisotropies calculated for H, Li, B, C, N, O, F, Na, Si, S, Cl and Br atoms in different molecules, arranged in increasing order of anisotropy for each atom. The anisotropies vary in size from about 0.002 to 0.07 of the elementary charge. The positive ions, Li in LiF and Na in NaCl, have the smallest anisotropies, as might be expected. However, the F and Cl ions in these molecules have anisotropies comparable to those found in covalent molecules, showing that the anisotropy caused by polarization of negative ions in an ionic bond, and that caused by covalent bonding, are roughly similar in size. The hydrogen atom usually has the smallest anisotropy of atoms involved in covalent bonding, and acidic hydrogen atoms are amongst the least anisotropic of these. Hydrogen atoms attached to carbonyl groups are amongst the most anisotropic. Anisotropy generally decreases along the series C, N, O, F, which may be related to the atoms becoming 'smaller', as the electrons are more strongly held by the nuclei along the series. Although there are fewer data, the anisotropy of S similarly appears to be larger than that of Cl, and the anisotropies of these two atoms are generally larger than those of the lighter atoms in the same group, O and F respectively. Atoms in tetrahedral environments, such as C in CH_4 and Si in SiH_4, have significant anisotropies, even though the atoms cannot have dipoles or quadrupoles by symmetry.

Table 2 Theoretical atomic anisotropies F_a for atoms in molecules, where F_a is defined in the text and is quoted as a multiple of the elementary charge, e, for the atom shown in bold type. Atoms are identified using the same notation as in Table 1. In B_2H_6, H_b is a 'bridging' hydrogen atom and H_t is a 'terminal' hydrogen atom

Molecule	Atom	$F_a/10^{-3}$
HNO_3	H	3.3
OH$^-$	H	3.5
$\mathbf{H_2}O$	H	5.2
HCO_2**H**	H	5.3
HF	H	5.4
$\mathbf{NH_3}$	H	5.4
$\mathbf{H_2}SO_4$	H	5.4
$HCONH_2$	H2	5.5
CH_3**OH**	H	5.6
$HCONH_2$	H1	5.6
$\mathbf{CH_4}$	H	6.8
$\mathbf{H_2}O_2$	H	7.3
$C_2\mathbf{H_6}$	H	8.2
$B_2\mathbf{H_6}$	H_b	8.2
CH_3**C**N	H	8.3
HCl	H	8.4
HBr	H	8.8
$C_2\mathbf{H_4}$	H	9.6
$C_6\mathbf{H_6}$	H	10.3
CH_3**C**l	H	10.4
CH_3**O**H	H1	11.5
$C_2\mathbf{H_2}$	H	11.7
CH_3**O**H	H2	12.0
CH_3**F**	H	12.5
$B_2\mathbf{H_6}$	H_t	13.5
HCN	H	15.4
$\mathbf{H_2}CO$	H	15.8
$\mathbf{H_2}$	H	16.4
Si$\mathbf{H_4}$	H	18.0
H$CONH_2$	H	20.5
HCO_2H	H	22.2
LiF	Li	2.0
$\mathbf{B_2}H_6$	B	36.9
CF_4	C	16.1
CCl_4	C	20.4
$\mathbf{C_2}H_6$	C	28.3
CH_4	C	31.3
CO_2	C	32.2
$\mathbf{C_6}H_6$	C	33.4
CH_3CN	C	34.4
CH_3**C**N	C	34.9
CONH_2	C	37.2
CH_3**O**H	C	39.3
CH_3**C**l	C	39.5
CO_2H	C	39.9
$\mathbf{CS_2}$	C	43.1
CN	C	44.1
$\mathbf{C_2}H_4$	C	44.7
$\mathbf{C_2}H_2$	C	46.9
CH_3**F**	C	47.8
H_2**C**O	C	47.8
CN$^-$	C	51.9
CO	C	72.9
NO_3^-	N	18.0
NHO_3	N	20.3
CN$^-$	N	29.6
$\mathbf{N_2}$	N	31.7
$HCONH_2$	N	32.5
NCN	N	33.0
CH_3**C**N	N	33.6
NH_3	N	35.1
NHO_3	O(H)	14.4
SO_4^{2-}	O	14.6
SO_2	O	15.8
CO	O	16.5
H_2**S**O_4	O	17.9
CO_2	O	18.0

Table 2 (*continued*)

Molecule	Atom	$F_a/10^{-3}$
$HCONH_2$	O	18.2
HCO_2**H**	O(H)	19.0
HCO_2**H**	O	19.3
OH$^-$	O	19.7
HNO_3	O	22.6
H_2SO_4	O(H)	23.1
ONO_3^-	O	23.6
H_2**C**O	O	24.3
CH_3**O**H	O	25.3
H_2**O**	O	25.6
H_2O_2	O	50.8
CF_4	F	12.1
CH_3**F**	F	13.5
HF	F	15.3
Li**F**	F	17.3
$\mathbf{F_2}$	F	49.3
NaCl	Na	3.0
SiCl_4	Si	38.7
SiH_4	Si	59.2
CS_2	S	23.6
SO_4^{2-}	S	30.3
H_2**S**O_4	S	37.8
SO_2	S	66.5
SiCl_4	Cl	19.0
Na**Cl**	Cl	24.3
CH_3**Cl**	Cl	27.9
CCl_4	Cl	28.5
HCl	Cl	30.2
$\mathbf{Cl_2}$	Cl	45.1
HBr	Br	33.7
$\mathbf{Br_2}$	Br	42.8

The calculated atomic anisotropies depend moderately on the basis set, which suggests that they are more sensitive to the tail of the charge density than the calculated bond orders. For example, the anisotropy of Cl in Cl_2 is $54.1\text{x}10^{-3}$ with the aug-cc-pVDZ basis set, $45.1\text{x}10^{-3}$ with the aug-cc-pVTZ basis set and $46.0\text{x}10^{-3}$ with the aug-cc-pVQZ basis set. If MP2 densities are used instead of SCF densities, the atomic anisotropies decrease. This is most noticeable for C in CO, which has an anisotropy of $72.9\text{x}10^{-3}$ at the SCF/aug-cc-pVTZ level and $47.3\text{x}10^{-3}$ at the MP2/aug-cc-pVTZ level.

In conclusion, an orbital-free method based on iterated stockholder atoms has been proposed for estimating covalent bond orders (using one scaling parameter) and atomic anisotropies within molecules. The methodology described here can be applied, in principle, to calculated or experimentally measured charge densities. It can also be applied to atoms calculated from Hirshfeld's original stockholder method, and from all related methods that obey eqn (1), not just from iterated stockholder atoms.

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