Acta Crystallographica Section B
**Structural
Science**
ISSN 0108-7681

Determination of covalent bond orders and atomic valence indices using topological features of the experimental electron density

Vladimir G. Tsirelson,[a]* Ekaterina V. Bartashevich,[b] Adam I. Stash[a,c] and Vladimir A. Potemkin[b]

[a]Mendeleev University of Chemical Technology, 9 Miusskaya Square, 125047 Moscow, Russia, [b]Chelyabinsk State University, 129 Br. Kashirinych Street, 454021 Chelyabinsk, Russia, and [c] Karpov Institute of Physical Chemistry, 10 Vorontsovo Pole, 105064 Moscow, Russia

Correspondence e-mail: tsirel@muctr.edu.ru

Received 14 September 2006
Accepted 1 November 2006

We present an approach for the determination of covalent bond orders from the experimental electron density and its derivatives at the bond critical points. An application of this method to a series of organic compounds has shown that it provides a bonding quantification that is in reasonable agreement with that obtained by orbital theory. The 'experimental' atomic valence indices are also defined and their significance for the characterization of chemical problems is discussed.

1. Introduction

Currently, the experimental electron density reconstructed from accurate X-ray diffraction data using the multipole model is widely used to obtain a wide spectrum of functions and quantities characterizing the electronic structure and properties of molecules and solids (Tsirelson & Ozerov, 1996; Popelier *et al.*, 2000; Koritsanszky & Coppens, 2001; Macchi & Sironi, 2003; Scherer & McGrady, 2004; Tsirelson & Stash, 2004; Gatti, 2005; Lecomte *et al.*, 2005), in good agreement with theory. Among them, a few density-based functions such as the electron localization function (Tsirelson & Stash, 2002*a*), localized-orbital locator (Tsirelson & Stash, 2002*b*) and Fermi hole density (Tsirelson & Stash, 2006) are closely related to the orbital notions of chemistry. Since orbital models play an important role in modern chemistry, the search for orbital-like characteristics, which might be expressed approximately in terms of the experimental electron density, deserves special attention.

The fundamental chemical notion of covalent bond order, which defines the number of electron pairs shared between two bonded atoms, is closely related to orbital representations of chemistry and is widely used for the characterization of bonding (Coulson, 1939, 1961; Mulliken, 1955*a*,*b*,*c*,*d*; Wiberg, 1968; Borisova & Semenov, 1973; Mayer, 1983, 1986; Angyan *et al.*, 1994; Reed & Schleyer, 1990; Bridgeman *et al.*, 2001; Angyan, 2000; Mayer *et al.*, 2004). The bond order can also be expressed in terms of the bond lengths and electron-density parameters. Pauling (1960) has quantitatively estimated the bond-order value for the different types of the covalent bonds using (1)

$$n_{\rm Pauling} = \exp[-(r - r_0)/a], \tag{1}$$

where r_0 is an idealized single-bond length and $a = 0.3$ for any type of bond. Lendvay (1994, 2000) and Howard & Lamarche (2003) confirmed this exponential relationship by non-empirical Hartree–Fock and DTF/B3LYP calculations. They reported that the a parameter depends on the atoms forming the bond and it varies from 0.29 to 0.41 Å for C—C, C—N, C—

doi:10.1107/S0108768106046003

Table 1
Summary of the three-parameter bond-order model $n_{\rm topo} = a_0 + a_1(\lambda_1 + \lambda_2) + a_2\lambda_3 + a_3\rho_{\rm BCP}$ (4).

Coefficients given by Howard & Lamarche (2003) for some covalent bonds are in italics.

Bonds	a_0	a_1	a_2	a_3	Correlation coefficient R	Fisher statistics $F(N)$†	R.m.s. error, S
C—C	*−0.522*	*0*	*−1.695*	*8.473*	*0.82*	*106.8 (55)*	*0.12*
	−1.004	2.839	0.634	17.633	0.98	458.7(55)	0.04
C—N	*−0.284*	*0.559*	*0.331*	*6.569*	*0.94*	*616.1 (82)*	*0.08*
	−0.851	0.715	0.221	8.561	0.95	221.2 (82)	0.07
C—O	*0.776*	*0*	*0.267*	*0*	*0.57*	*20.6 (45)*	*0.17*
	−0.668	0.567	−0.199	8.382	0.94	94.7 (45)	0.07
N—O	−0.628	0.448	0.505	5.275	0.97	297.1 (63)	0.02
N—N	−0.755	2.041	0.525	13.432	0.93	55.1 (28)	0.04
C—H	−0.153	0.983	0.481	8.087	0.75	42.0 (101)	0.02
N—H	−0.247	0.518	−0.025	7.020	0.96	115.3 (30)	0.02
O—H	0.908	−0.219	−1.005	0.086	0.98	138.6 (22)	0.01

† N is the number of bonds of a given type.

P and C—S bonds and has a value of 0.26 Å for the C—H bond.

Bader and co-workers (Bader *et al.*, 1983) proposed a simple exponential relationship between covalent bond order and the electron density at the bond critical point (BCP), $\rho_{\rm bcp}$

$$n_{\rm Bader} = \exp\lfloor a(\rho_{\rm bcp} - b)\rfloor. \qquad (2)$$

This expression was tested on a series of hydrocarbons and was used to estimate the C—C bond-order indices by using the two-parameter equation exploiting electron-distribution features. Matta & Hernandez-Trujillo (2003, 2005) suggested calibrating Bader's bond order (2) to reproduce the delocalization index between bonded atoms. This index counts the number of pairs shared between any two atoms in a molecule by integrating the exchange density once over each of the two atomic basins (Fradera *et al.*, 1999). Zhurova, Matta *et al.* (2006) have implemented this approach for C—C bonds using the experimental density of the estrone molecule.

Cioslowski & Mixon (1991) combined the orbital and topological descriptions of the electron density to describe covalent bond order. Their approach includes the following steps. First, the zero-flux surfaces in the electron-density gradient field are determined; these surfaces are identified with the atomic boundaries (Bader, 1990). Second, the elements of the atomic overlap matrix are computed by integrating the atomic orbital products over the corresponding atomic basins. Third, the unitary transformation among the occupied spin orbitals that maximizes the sum of the squared diagonal elements of each atomic overlap matrix is performed. Finally, the bond-order, $n_{\rm CM}$, is computed by summing corresponding contributions for A and B atoms

$$n_{\rm CM} = \sum_k n_k^2 \langle\varphi_k|\varphi_k\rangle_A \langle\varphi_k|\varphi_k\rangle_B. \qquad (3)$$

Here φ_k are the localized orbitals, k is the number of the orbital and n_k is the occupancy of kth orbital.

Howard & Lamarche (2003; hereafter H&L) used the Cioslowski–Mixon (1991) approach to generate the set of the covalent bond-order data and to model them using the topological BCP properties. They considered the C—C, C—N, C—O, C—P and C—S bonds and tested a few expressions which relate the covalent bond-order value with electron density, $\rho_{\rm BCP}$, the Laplacian of electron density, the eigenvalues of the Hessian of electron density (λ_1, λ_2 and λ_3), the bond ellipticity ($\lambda_1/\lambda_2 - 1$) and the kinetic energy density; all the quantities were taken at the BCP. It was found that the expression

$$n_{\rm topo} = a_0 + a_1(\lambda_1 + \lambda_2) + a_2\lambda_3 + a_3\rho_{\rm BCP} \qquad (4)$$

yields the best (from statistical point of view) bond-order description, based on the electron density and its derivatives at the BCPs. It is important that this expression is applicable to multiple bonds and has a simple physical interpretation. The values $\rho_{\rm BCP}$ and λ_3 measure the σ character of the covalent bond, while the curvatures of the electron density perpendicular to the bond line, λ_1 and λ_2, measure the degree of its π character. H&L have recommended applying expression (4) to the bond-order description for both the polar and non-polar covalent bonds mentioned above.

It is very attractive to apply this approach to the determination of *topological bond-order indices* (4) from the experimental electron density derived by the accurate high-resolution X-ray diffraction experiment. First attempts to realise this idea have proved to be encouraging (Stash, Tanaka *et al.*, 2005; Tsirelson *et al.*, 2006). At the same time, the application of expression (4) with the original H&L coefficients to the wide range of organic compounds listed in the deposited Table D1[1] have shown that the correlation coefficients between the values $n_{\rm topo}$(H&L) (4) and $n_{\rm CM}$ (3) for the C—C and C—O bonds are only 0.84 and 0.57, respectively (r.m.s. errors 0.12 and 0.17). We also found that indices $n_{\rm topo}$(H&L) for C—O bonds in carboxyl groups as well as in carboxylate anions significantly deviate from $n_{\rm CM}$. The probable explanation lies in the fact that coefficients a_1 and a_3 in expression (4) were taken to be zero for the C—O bonds by H&L. Besides, $n_{\rm topo}$(H&L) for the C—C bonds appeared to be systematically higher than $n_{\rm CM}$ values computed from the same wavefunction, exhibiting reasonable correlation only in the limited range $1.1 < n_{\rm CM} < 1.4$.

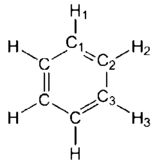
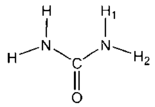
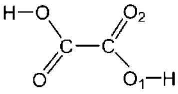
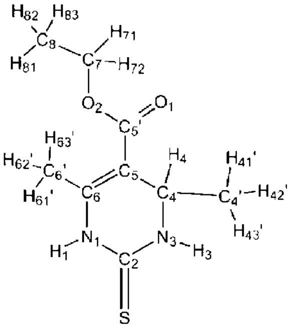
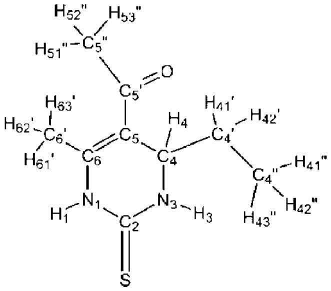
In this work we present a systematic study of the H&L approach for compounds consisting of the first-row atoms. We have made the training set more representative by including compounds with a wide spectrum of bonds. We have also

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5078). Services for accessing these data are described at the back of the journal.

Table 2

Observed values of covalent bond order, $n_{\rm CM}$ (3), theoretically calculated according to Cioslowski & Mixon (1991) and estimated values of the bond order $n_{\rm topo}$ (4) derived from the experimental electron density, as well as atomic valence indices, $V_{\rm A}$, calculated from these quantities.

Molecule	Bonds	$n_{\rm CM}$	$n_{\rm topo,exp}$	Atoms	$V_{\rm A,CM}$	$V_{\rm A,topo,exp}$
 Benzene	C1—C2	1.39	1.48	C1	3.74	4.00
	C1—C3	1.39	1.04	C2	3.74	3.98
	C2—C3	1.39	1.49	C3	3.74	3.98
	C1—H1	0.96	1.47	H1	0.96	1.04
	C2—H2	0.96	1.03	H2	0.96	1.03
	C3—H3	0.96	1.02	H3	0.96	1.02
 Urea	C—O	1.23	1.34	C	3.15	3.66
	C—N	0.96	1.16	O	1.23	1.34
	N—H1	0.82	0.80	N	2.62	2.75
	N—H2	0.84	0.79	H1	0.82	0.80
				H2	0.84	0.79
 Oxalic acid	C—C	0.79	0.78	C	2.69	3.48
	C—O1	0.74	1.29	O1	1.30	1.98
	C—O2	1.16	1.41	O2	1.16	1.41
	O1—H1	0.56	0.68	H1	0.56	0.68
 Ethyl 4,6-dimethyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (EDTTC)	S—C2	1.52	1.46	S	1.52	1.46
	O1—C5′	1.26	1.59	O1	1.26	1.59
	O2—C5′	0.87	1.10	O2	1.69	1.81
	O2—C7	0.82	0.71	N1	2.85	2.83
	N1—C2	1.02	1.09	N3	2.83	2.76
	N1—C6	1.06	1.00	C2	3.68	3.79
	N1—H1	0.77	0.74	C4	3.71	3.83
	N3—C2	1.14	1.23	C4′	3.82	3.94
	N3—C4	0.90	0.74	C5	3.53	3.67
	N3—H3	0.79	0.79	C5′	3.15	3.83
	C4—C4′	0.95	1.04	C6	3.60	3.53
	C4—C5	0.97	1.07	C6′	3.82	4.54
	C4—H4	0.90	0.98	C7	3.63	3.69
	C4′—H41′	0.95	0.97	C8	3.87	4.09
	C4′—H42′	0.96	0.96	H1	0.77	0.74
	C4′—H43′	0.96	0.97	H3	0.79	0.79
	C5—C5′	1.02	1.13	H4	0.90	0.98
	C5—C6	1.55	1.46	H41′	0.95	0.97
	C6—C6′	0.99	1.06	H42′	0.96	0.96
	C6′—H61′	0.94	1.20	H43′	0.96	0.97
	C6′—H62′	0.96	1.16	H61′	0.94	1.20
	C6′—H63′	0.93	1.12	H62′	0.96	1.16
	C7—C8	0.98	1.02	H63’	0.93	1.12
	C7—H71	0.91	0.98	H71	0.91	0.98
	C7—H72	0.91	0.98	H72	0.91	0.98
	C8—H81	0.96	1.04	H81	0.96	1.04
	C8—H82	0.96	1.01	H82	0.96	1.01
	C8—H83	0.96	1.01	H83	0.96	1.01
 5-Acetyl-4-ethyl-6-methyl-1,2,3,4-tetrahydropyrimidine-2-thione (AEMTT)	S—C2	1.52	1.54	S	1.52	1.54
	O—C5′	1.39	1.52	O	1.39	1.52
	N1—C2	1.02	1.13	N1	2.83	3.04
	N1—C6	1.04	1.01	N3	2.82	2.87
	N1—H1	0.77	0.91	C2	3.68	3.97
	N3—C2	1.14	1.31	C4	3.66	4.18
	N3—C4	0.89	0.77	C4′	3.76	4.36
	N3—H3	0.78	0.79	C4″	3.87	4.25
	C4—C4′	0.93	1.15	C5	3.52	4.02
	C4—C5	0.95	1.20	C5′	3.40	3.88
	C4—H4	0.89	1.07	C5”	3.80	4.22
	C4′—C4′	0.99	1.12	C6	3.55	3.82
	C4′—H41′	0.93	1.05	C6′	3.83	4.46
	C4′—H42′	0.94	1.04	H1	0.77	0.91
	C4″—H41″	0.96	1.04	H3	0.78	0.79
	C4″—H42″	0.96	1.04	H4	0.89	1.07
	C4″—H43″	0.96	1.05	H41′	0.93	1.05

undertaken an attempt to improve the coefficients in (4) for C—C and C—O bonds and we have expanded the coefficient set given by H&L to span the N—O and N—N bonds.

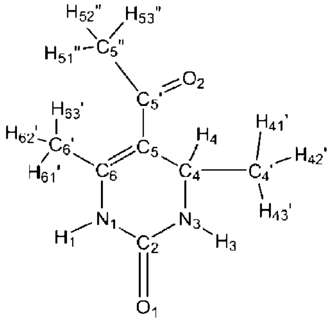
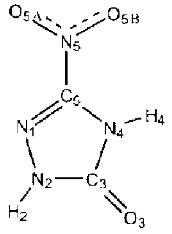
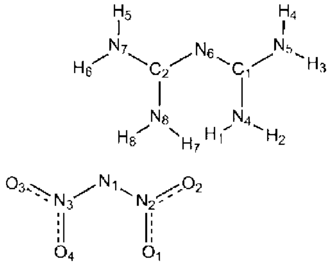
H&L did not consider X—H bonds (X is a non-H atom), which are important structural elements of both organic and organoelement compounds and their ensembles, as being responsible for forming hydrogen bonds. In addition, the X—H bonds are located on the periphery of the molecules. Hence, they define the molecular shape and consequently the features of the molecule packing in the condensed phases. Therefore, another aim of this work is an approximation of the X—H (X = C, O and N) covalent bond-order indices from expression (4).

Finally, we derived the bond-order indices and *atomic valence indices* defined below for a series of organic compounds using the topological features of the experimental electron density, and have discussed the chemical significance of these descriptors.

2. Computational

To produce the coefficients allowing the approximation of the ordinary and multiple covalent bond orders by expression (4) we have selected the following set of organic molecules: benzene, C_6H_6, formamide, CH_3NO, urea, CH_4N_2O, methanol, CH_4O, ethanol, C_2H_6O, propanol, C_3H_8O, ethylene glycol, $C_2H_6O_2$, glycerin, $C_3H_8O_3$, oxalic acid, $C_2H_2O_4$, malonic acid, $C_3H_4O_4$, lactic acid, $C_3H_6O_3$, α-D-ribopyranose, $C_5H_{10}O_5$, α-D-glucopyranose, $C_6H_{12}O_6$, asparagine, $C_4H_8N_2O_3$, histidine, $C_7H_{10}N_2O_2$, and tetrafluoroterephthalonitrile, $C_8F_4N_2$. Bridgeman *et al.* (2001) found that the quantity $n_{\rm CM}$ exhibits very little dependence on the DFT exchange and correlation functions, provided a middle-size basis set is used. Therefore, the geometries of the above-mentioned molecules have been optimized at the DFT B3LYP/6-311G(d,p) level of theory using the PC version of the program

Table 2 (continued)

Molecule	Bonds	$n_{\rm CM}$	$n_{\rm topo,exp}$	Atoms	$V_{\rm A,CM}$	$V_{\rm A,topo,exp}$
	C5—C5′	1.05	1.22	H42′	0.94	1.04
	C5—C6	1.52	1.61	H41″	0.96	1.04
	C5′—C5″	0.95	1.15	H42″	0.96	1.04
	C5″—H51″	0.95	1.01	H43″	0.96	1.05
	C5″—H52″	0.95	1.03	H51″	0.95	1.01
	C5″—H53″	0.94	1.04	H52″	0.95	1.03
	C6—C6′	0.99	1.20	H53″	0.94	1.04
	C6′—H61′	0.94	1.11	H61′	0.94	1.11
	C6′—H62′	0.95	1.08	H62′	0.95	1.08
	C6′—H63′	0.94	1.07	H63′	0.94	1.07
 5-Acetyl-4,6-dimethyl-1,2,3,4-tetrahydropyrimidin-2-one (ADT)	O1—C2	1.24	1.53	O1	1.24	1.53
	O2—C5′	1.39	1.52	O2	1.39	1.52
	N1—C2	0.89	1.06	N1	2.73	2.90
	N1—C6	1.05	1.00	N3	2.72	2.85
	N1—H1	0.79	0.84	C2	3.14	3.78
	N3—C2	1.02	1.19	C4	3.69	4.06
	N3—C4	0.90	0.77	C4’	3.82	4.11
	N3—H3	0.80	0.89	C5	3.53	3.82
	C4—C4′	0.94	1.06	C5′	3.40	3.79
	C4—C5	0.95	1.17	C5″	3.80	4.42
	C4—H4	0.89	1.06	C6	3.55	3.66
	C4′—H41′	0.96	1.04	C6′	3.82	4.48
	C4′—H42′	0.95	1.00	H1	0.79	0.84
	C4′—H43′	0.96	1.01	H3	0.80	0.89
	C5—C5′	1.06	1.15	H4	0.89	1.06
	C5—C6	1.52	1.51	H41′	0.96	1.04
	C5′—C5″	0.95	1.13	H42′	0.95	1.00
	C5″—H51″	0.95	1.09	H43′	0.96	1.01
	C5″—H52″	0.95	1.12	H51″	0.95	1.09
	C5″—H53″	0.95	1.08	H52″	0.95	1.12
	C6—C6′	0.99	1.15	H53″	0.95	1.08
	C6′—H61′	0.94	1.11	H61′	0.94	1.11
	C6′—H62′	0.95	1.11	H62′	0.95	1.11
	C6′—H63′	0.94	1.11	H63′	0.94	1.11
 β form of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO)	O3—C3	1.32	1.54	O3	1.32	1.54
	O5*B*—N5	1.63	2.03	O5*B*	1.63	2.03
	O5*A*—N5	1.66	1.96	O5*A*	1.66	1.96
	N1—C5	1.40	1.37	N1	2.71	2.79
	N2—H2	0.74	0.70	N2	3.00	3.11
	N2—N1	1.30	1.42	N4	2.71	2.73
	N2—C3	0.95	0.99	N5	4.15	4.83
	N4—H4	0.73	0.61	C3	3.22	3.55
	N4—C3	0.94	1.02	C5	3.30	3.31
	N4—C5	1.05	1.10	H2	0.74	0.70
	N5—C5	0.85	0.84	H4	0.73	0.61
 Biguanidinium dinitramide	O1—N2	1.61	1.82	O1	1.61	1.82
	O2—N2	1.47	1.81	O2	1.47	1.81
	O3—N3	1.56	1.79	O3	1.56	1.79
	O4—N3	1.61	1.81	O4	1.61	1.81
	N1—N2	1.25	1.50	N1	2.41	2.95
	N1—N3	1.16	1.45	N2	4.33	5.13
	N4—C1	1.09	1.12	N3	4.33	5.05
	N4—H1	0.76	0.75	N4	2.64	2.57
	N4—H2	0.80	0.70	N5	2.65	2.57
	N5—C1	1.06	1.24	N6	2.35	2.41
	N5—H3	0.82	0.68	N7	2.65	2.47
	N5—H4	0.78	0.66	N8	2.58	2.55
	N6—C1	1.19	1.22	C1	3.34	3.57
	N6—C2	1.15	1.19	C2	3.34	3.46
	N7—C2	1.06	1.14	H1	0.76	0.75
	N7—H5	0.79	0.67	H2	0.80	0.70
	N7—H6	0.81	0.65	H3	0.82	0.68
	N8—C2	1.12	1.13	H4	0.78	0.66
	N8—H7	0.66	0.69	H5	0.79	0.67
	N8—H8	0.79	0.73	H6	0.81	0.65
				H7	0.66	0.69
				H8	0.79	0.73

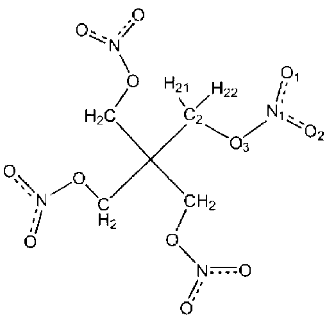
GAMESS(US) (Schmidt *et al.*, 1993; Granovsky, 2003). The vibration frequencies were checked to ensure that the energy minimum for each molecule was achieved.

In addition, calculations for the following compounds using accurate low-temperature X-ray diffraction geometries were carried out: 1-[(4,5-dihydroxymethyl-1,2,3-triazolyl)-1-methyl]-5-methyl-pyrimidine-2,4-dione (MTMT), $C_{10}H_{13}N_5O_4$ (Stash, Zavodnik *et al.*, 2005), ethyl-4,6-dimethyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-ethylcarboxylate (EDTTC), $C_9H_{14}N_2O_2S$ (Tsirelson *et al.*, 2006), ammonium dinitramide (ADN), $NH_4{\cdot}N_3O_4$ (Ritchie *et al.*, 2003), biguanidinium dinitramide (BIGH DN), $C_2H_8N_5{\cdot}N_3O_4$ (Zhurova *et al.*, 2002), β form of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (β-NTO), $C_2H_2N_4O_3$ (Zhurova & Pinkerton, 2001), pentaerythritol tetranitrate (PETN), $C_5H_8N_4O_{12}$ (Zhurova, Stash *et al.*, 2006), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (β-HMX), $C_2H_4N_4O_4$, (Chen, 2004), trinitrodiazapentalene (TNDAP), $C_6H_3N_5O_6$ (Chen *et al.*, 2007), 1,3,3-trinitroazetidine, $C_3H_4N_3O_6$ (TNAZ), hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX), $C_3H_6N_6O_6$ (Chen, 2004), and the γ and ε isomers of hexanitrohexaazaisowurtzitane (γ- and ε-HNIW), $C_6H_6N_{12}O_{12}$ (Bolotina *et al.*, 2004). The standard *X*—H bond distances tabulated in *International Tables for Crystallography* (1995) were employed in all structures used in this work.

The DFT B3LYP/6-311G(d,p) many-electron wavefunctions obtained were used to integrate the orbital products over the zero-flux atomic basins and the atomic overlap matrix elements were obtained. Then, the Cioslowski–Mixon bond orders $n_{\rm CM}$ in (3) were computed for each bond by summing the corresponding diatomic contributions. All the computations were performed using locally modified *AIMPAC* software (Biegler-Konig *et al.*, 1982) adapted to the PC.

The whole training set contains 182 C—*X* bonds, 63 N—O bonds,

Table 2 (continued)

Molecule	Bonds	$n_{\rm CM}$	$n_{\rm topo,exp}$	Atoms	$V_{\rm A,CM}$	$V_{\rm A,topo,exp}$
 Pentaerythritol tetranitrate	C1—C2	0.92	1.02	C1	3.68	4.09
	C2—O3	0.82	0.69	C2	3.52	3.66
	C2—H21	0.88	0.97	O1	1.66	1.93
	C2—H22	0.89	0.98	O2	1.68	1.96
	O1—N1	1.66	1.93	O3	1.85	1.86
	O2—N1	1.68	1.96	N1	4.36	5.06
	O3—N1	1.02	1.17	H21	0.88	0.97
				H22	0.89	0.98

82 C—N bonds, 28 N—N bonds and 163 X—H bonds (X = C, N, O). The BCP characteristics for all these bonds were computed and the multiple regression models (4) defining the topological bond-order indices, $n_{\rm topo}$, for these bonds were determined. These quantities are collected in Table D1 together with computed quantities, $n_{\rm CM}$, (3) and have been deposited. The model coefficients, as well as the statistical estimates characterizing the quality of the fit, are given in Table 1.

Then, the derived coefficients were used to calculate the bond-order indices using the topological features of the experimental density presented in terms of the Hansen & Coppens (1978) multipole model. We have selected for calculations a set of molecules with a wide spectrum of covalent bonds. Multipole parameters were taken from the following sources: benzene (Bürgi *et al.*, 2002), urea (Birkedal *et al.*, 2004; Stash, 2004), oxalic acid (in oxalic acid dihydrate) (Scherer, 2004), EDTTC (Tsirelson *et al.*, 2006), 5-acetyl-4-ethyl-6-methyl-1,2,3,4-tetrahydropyrimidine-2-thione (AEMTT), $C_9H_{13}N_2OS$ (Potemkin, Rykounov, Bartashevich *et al.*, 2006), 5-acetyl-4,6-dimethyl-1,2,3,4-tetrahydropyrimidin-2-one (ADT) $C_8H_{12}N_2O_2$ (Potemkin, Rykounov, Stash & Tsirelson, 2006), β-NTO (Zhurova & Pinkerton, 2001), BIGH DN (Zhurova *et al.*, 2002) and PETN (Zhurova, Stash *et al.*, 2006). The results are listed in Table 2.

3. Discussion

The electron-density features at the bond-critical points are widely used in theoretical and experimental studies of different aspects of the atomic and molecular interactions (Bader, 1990; Cremer & Kraka, 1984; Knop *et al.*, 1988; Cioslowski *et al.*, 1991; Tsirelson & Ozerov, 1996; Gibbs *et al.*, 1997; Martin Pendas *et al.*, 1998; Espinosa *et al.*, 1998; Rincon & Almeida, 1998; Tsirelson *et al.*, 1998; Popelier, 1999, 2005; Espinosa & Molins, 2000; Knop *et al.*, 2001; Exner & Schleyer, 2001; Downs *et al.*, 2002; Popelier & Aicken, 2003; Costales *et al.*, 2004; Gervasio *et al.*, 2004; Gatti, 2005; Stash, Tanaka *et al.*, 2005; Matta *et al.*, 2006; Zhurova, Matta *et al.*, 2006; Zhurova, Stash *et al.*, 2006). Determination of the bond-order indices using topological features of the experimental electron density at the BCP extends this approach and provides the information which is similar to the orbital description of bonding.

Let us analyze the efficiency of the application of model (4) to the covalent bonds formed by atoms in the organic compounds. Statistical estimates characterizing the quality of model (4) are given in Table 1. These are coefficients of correlation between the estimated bond-order indices $n_{\rm topo}$ (4) and observed values $n_{\rm CM}$ (3), equal to the fraction of variance accounted for by the model, R, the root-mean-square (r.m.s.) error, S, and Fisher's statistics, F, which represents the statistical significance of the model and is calculated as the ratio of variances derived by computation with a model under consideration (predicted values) and those of a corresponding model with zero-equaled parameters. The F statistics depend on both the number of variables in the regression equation and the number of points: the higher the F value, the more statistically significant the model under consideration (Jennrich, 1977)

Analyzing Table 1 we can conclude that model (4) with new coefficients for C—C and C—O bonds derived using more representative data sets yields much better statistics than the initial H&L coefficients. The data for the C—N bond show comparable statistics. However, they provide results in better agreement with the Cioslowski–Mixon bond order $n_{\rm CM}$. Fig. 1 presents results which confirm this conclusion, which is why hereafter we will consider the results of calculations based on the coefficients for covalent X—Y and X—H bonds (X, Y = C, N, O) derived in this work. For the C—S bonds, the original H&L parameters have been used.

3.1. Bond orders based on theoretical electron density

Figs. 1 and 2 show the agreement of the estimated $n_{\rm topo}$ and computed $n_{\rm CM}$ bond orders, both quantities being derived from the same wavefunctions. The training set for the covalent bond used to derive $n_{\rm topo}$ (4) is dominated by the ordinary covalent bonds and bonds in aromatic systems with significant electron delocalization. In spite of this, the deviation, $\Delta = n_{\rm topo} - n_{\rm CM}$, for the C—C bonds is small and ranges from $\Delta = -0.11$ to 0.08. In general, the $n_{\rm topo}$(C—C) values are overestimated for bonds adjacent to nitro groups, while they are slightly underestimated in benzene.

The C—O bond sampling considered includes bonds in the hydroxyl and carbonyl groups, carboxylate anions, as well as bonds in heteroaromatic systems. Topological C—O bond orders reflect this diversity of C—O bonds and are in the range $0.72 < n_{\rm topo}$(C—O) < 1.36 with deviations $-0.25 < \Delta$(C—O) $<$ 0.10. The value of $n_{\rm topo}$(C—N) ranges from 0.65 to 2.19 with $-0.23 < \Delta$(C—N) < 0.20. We note that the deviations $|\Delta| >$

0.20 are observed for the C—O and C—N bonds in amino acids. The maximum underestimated value $n_{\rm topo}$(C—N) is observed for the triple C—N bond group in tetrafluoroterephthalonitrile.

The $n_{\rm CM}$ values for N—O bonds range from 1.47 to 1.69 with $0.05 < \Delta$(N—O) < 0.07. The deviations of $n_{\rm topo}$(N—N) are somewhat larger and are in the range $-0.15 < \Delta$(N—N) < 0.07. The only exception observed for the O—NO$_2$ group is pentaerythritol tetranitrate, where $n_{\rm CM}$(N—O) = 1.02 and $n_{\rm topo}$(N—O) = 1.03 are observed. The N—N bonds in the heterocyclic systems exhibit an average topological bond order of 1.40, with an r.m.s. error of $S = 0.09$; the majority of N—N bonds (90.3%) in nitroamines exhibit an $S(n_{\rm topo})$ value ≤ 0.03.

Covalent bonds C—H, N—H and O—H have satisfactory statistical indicators and low r.m.s. errors (Table 1). Even in the worst statistical case of the C—H bond, the deviations of $n_{\rm topo}$ from $n_{\rm CM}$ are in the narrow interval $-0.06 < \Delta$(C—H) < 0.04. For N—H and O—H bonds these deviations are even smaller: $-0.03 < \Delta$(N—H) < 0.04 and $-0.02 < \Delta$(O—H) < 0.02, respectively. Thus, the coefficients derived for model (4) listed in Table 1 satisfactorily describe the $n_{\rm topo}$ indices for X—H covalent bonds.

3.2. Bond orders based on the experimental electron density

Results of the application of model (4) to determine covalent bond order indices $n_{\rm topo}$(exp) from experimental electron density are given in Table 2 and Fig. 3. Before analyzing these data, we must mention the existence of a serious discrepancy in the multipole-model-based and wavefunction-based Laplacians of the electron density for the shared atomic interactions, which is repeatedly noted in the literature (Bianchi *et al.*, 1996; Iversen *et al.*, 1997; Spackman *et al.*, 1999; Volkov *et al.*, 2000; Volkov & Coppens, 2001; Flaig *et al.*, 2002; Volkov, Li *et al.*, 2004; Volkov, Koritsanszky *et al.*, 2004; Coppens & Volkov, 2004; Zhurova *et al.*, 2004; Henn *et al.*, 2004; Hibbs *et al.*, 2005; Tsirelson *et al.*, 2006; Zhurova, Matta *et al.*, 2006). The fact is that the flexibility of the current multipole models does not describe the experimental electron distribution both around the nuclei and in the middle-bond area simultaneously. The maximum discrepancy is observed for the electron density curvature along the bond line λ_3 for covalent and polar-covalent bonds (Flaig *et al.*, 2002; Volkov *et al.*, 2000; Tsirelson *et al.*, 2006). Therefore, we can anticipate that the 'experimental' bond-order indices will deviate from the theoretical ones owing to the presence of the λ_3 term in expression (4).

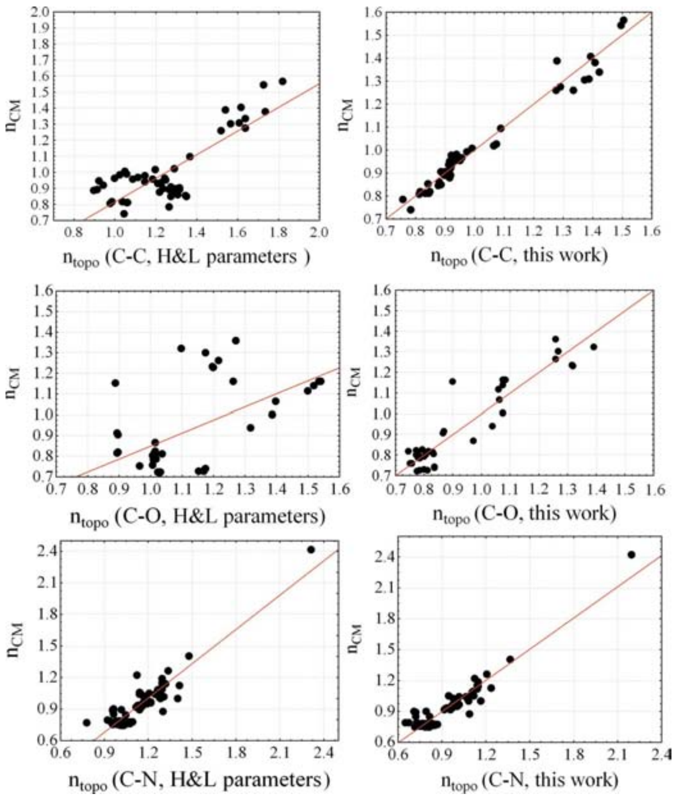


Figure 1
Plot of the Cioslowski–Mixon bond orders $n_{\rm CM}$ and topological bond orders $n_{\rm topo}$ for C—C, C—N and C—O covalent bonds computed using original H&L coefficients and coefficients derived in this work by the fit of model (4) to the theoretical electron density – see Table 1.

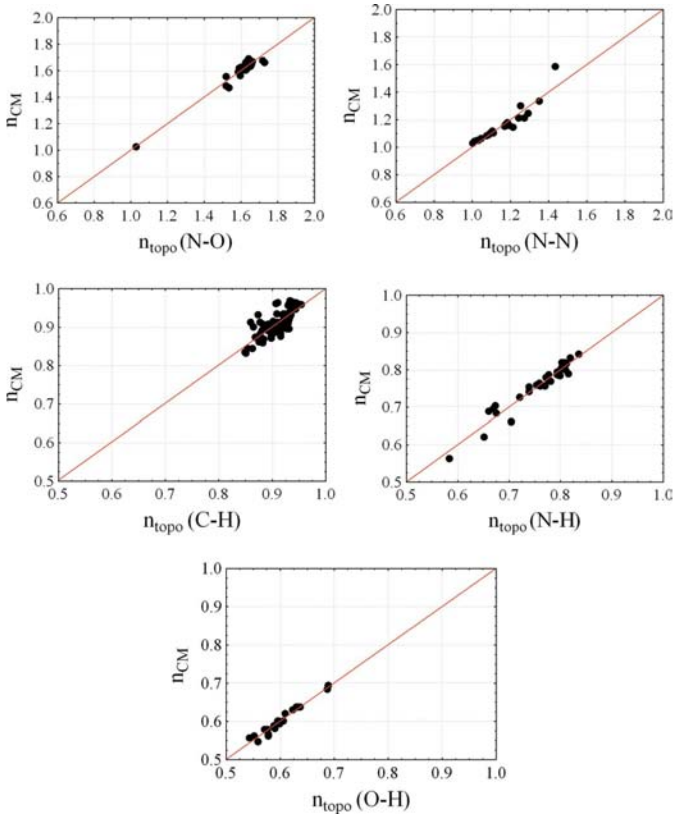


Figure 2
Plot of the Cioslowski–Mixon bond orders $n_{\rm CM}$ *versus* the estimated bond orders $n_{\rm topo}$ computed for 28 compounds listed in the text (see also Table D1) using coefficients derived by the fit of model (4) to the theoretical electron density for the N—O, N—N, C—H, N—H and O—H covalent bonds.

Table 2 and Fig. 3 show the values of $\Delta_{\rm exp}$ = $n_{\rm topo}$(exp) − $n_{\rm CM}$ for the C—C bond range from $\Delta_{\rm exp}$ = −0.08 to $\Delta_{\rm exp}$ = 0.24. The most overestimated $n_{\rm topo}$(exp) values are observed in the C4—C5 bonds in hydropyrimidines. The $\Delta_{\rm exp}$(C—O) values range from Δ = −0.14 to 0.33; in the case of the standard C—C bond in oxalic acid $\Delta_{\rm exp}$(C—O) = 0.55 owing to a significant distinction in the theoretical (λ_3 = 1.481 a.u.) and experimental (λ_3 = 0.494 a.u.) values of the electron-density curvature along the bond line. The experimental C—N bond orders are overestimated to a lesser degree compared with the C—O bond orders: the deviation scattering is $-0.16 < \Delta_{\rm exp} < 0.20$. In the case of the N—O bonds, the maximum deviation of $\Delta_{\rm max}$(N—O) = 0.39 is observed in the nitro group of β-NTO. For the three available N—N bonds, the average overestimation $n_{\rm topo}$(exp) is 0.25.

The values of $n_{\rm topo}$(exp) for C—H bonds are overestimated on average by 0.1 with $\Delta_{\rm max}$ = 0.16 in ADT. The $n_{\rm topo}$(exp) values for N—H bonds are slightly underestimated in nitroamines, but overestimated in hydropyrimidines.

The multipole-model parameters used in this work were derived from the accurate low-temperature (100–120 K) X-ray diffraction data by applying the same refinement strategy. Therefore, we suggest that these parameters are of approximately the same quality. The difference between experimental and theoretical electron-density values at the bond critical points is ≤ 0.1 e Å^{-3}. Thus, the main reason for the discrepancies observed for the bond orders of Cioslowski & Mixon (1991), $n_{\rm CM}$, and topological ones, $n_{\rm topo}$(exp), results from the above-mentioned insufficient flexibility of the mulipole model, which does not adequately describe the electron density curvature along the covalent bond lines. This shortcoming is the most noted in the case of the C—H bonds where it leads to $n_{\rm topo}$(exp) > 1 (as we already noted, the standard X—H bond distances were employed in the multipole-model refinements). Fortunately, we can anticipate that the deficiency mentioned can be overcome by using more sophisticated and flexible multipole models. What is remarkable is that a small systematic bias is observed for each type of bond. Therefore, the bond-order indices can be, in principle, empirically corrected, if necessary.

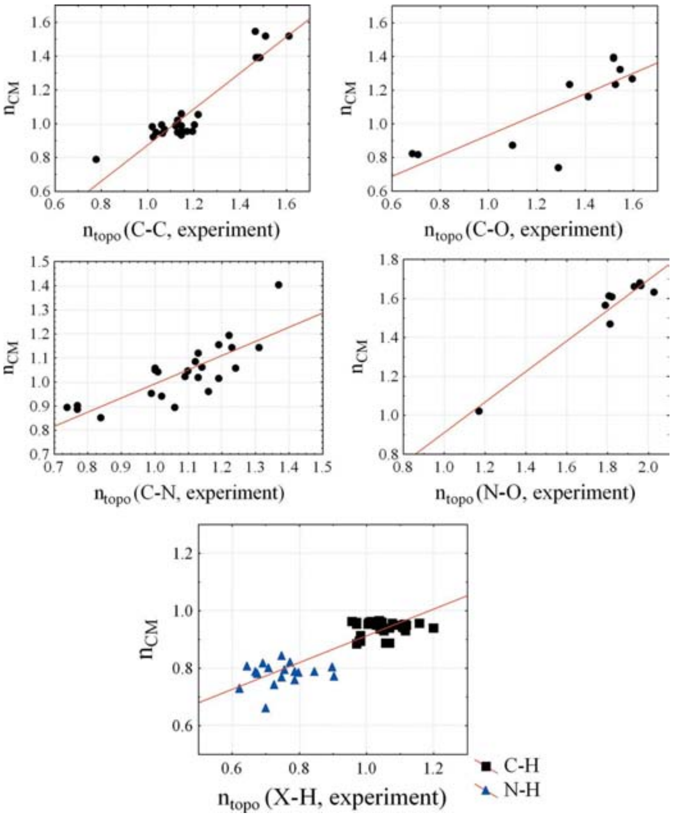


Figure 3
Plot of the theoretically computed Cioslowski–Mixon bond orders $n_{\rm CM}$ *versus* the bond orders $n_{\rm topo}$ estimated from the experimental electron density features for C—C, C—O, C—N, N—O and X—H covalent bonds (see Table 2 for detail).

3.3. Atomic valence indices

The sum of the bond-order values over the bonds formed by each A atom can be regarded as the atomic valence index, $V_{\rm A}$ (Tsirelson *et al.*, 2006), describing the degree of the atomic valence saturation. The corresponding experimental and theoretical values of $V_{\rm A}$ are listed in Table 2. The difference $V_{\rm A,max} - V_{\rm A}$, where $V_{\rm A,max}$ is the maximum valence of atom A, is an analogue of the atomic free valence: the larger the difference, the more additional interactions can be formed by this atom. This suggests that the atomic valence index can be useful to estimate the potential nucleophilic reactivity of compounds using density-derived quantities.

For example, among the typical reactions of hydropyrimidines are substitution, acylation, arylation and alkylation (Kappe, 2006). An increase in the atomic valence indexes $V_{\rm A}$ of the N atoms in hydropyrimidines must be accompanied by an increase of their activities in nucleophilic reactions such as N-acylation and N-arylation. Table 2 shows that the $V_{\rm A}$ indices for N atoms in the considered hydropyrimidines AEMTT, EDTTC and ADT are comparable in value. Therefore, we can expect a similar behaviour of these compounds in the mentioned nucleophilic reactions.

The atomic valence indices of C5 and C6 atoms ($V_{\rm C5}$ and $V_{\rm C6}$) in the AEMTT, EDTTC and ADT hydropyrimidines can also be used to determine the regiospecificity of the addition processes with the participation of these compounds. Data given in Table 2 anticipate that an important feature of these hydropyrimidines is the domination of the C5 atom with respect to the C6 atom in such reactions.

4. Conclusions

This work develops the approach suggested by Howard & Lamarche (2003) for the determination of covalent bond orders from experimental electron density and its derivatives at the bond critical points. In the present form, this method is applicable to organic compounds with X—Y and X—H bonds (X, Y = C, O and N). The 'experimental' atomic valence indices characterizing the degree of atomic valence saturation have also been defined. It has been shown that these descriptors can be used to estimate the chemical reactivity properties of compounds under consideration.

The important feature of the approach given above consists of the determination of the bonding descriptors, which can be expressed both in terms of orbital representations and experimental electron-density characteristics. This unification of the theoretical and experimental methods enhances the information derived directly from X-ray diffraction data. At the same time, we found that the current problems with the adequate description of electron density in the case of the shared atomic interactions restrict the accuracy of the experimentally derived bond orders for the covalent bonds. Fortunately this problem can be overcome by using more sophisticated and flexible multipole models; work in this area is especially important.

Making an outline of the proposed approach presented above, we note that topological covalent bond orders can be related to the bond energies in the spirit of works by Grimme (1996) and Exner & Schleyer (2001).They can also be related to the bond valences of the Brown (1992) bond-valence model. Thus, the latter characteristics can be, in principle, estimated from the experimental electron density.

We thank Professor I. D. Brown for discussion. This work was supported by the Russian Foundation for Basic Research (grant 04-03-33053) and the Russian Federal Agency for Education (Program ‘Development of the Highest-School Scientific Potential, 2006–2008’, Project 2.1.1. 5051).

References

Angyan, J. (2000). *J. Mol. Struct. (Theochem.)* **501–502**, 379–388.

Angyan, J., Loos, M. & Mayer, I. (1994). *J. Phys. Chem.* **98**, 5244–5248.

Bader, R. F. W. (1990). *Atoms in Molecules: A Quantum Theory. The International Series of Monographs of Chemistry*, edited by J. Halpen & M. L. H. Green. Oxford: Clarendon Press.

Bader, R. F. W., Slee, T. S., Cremer, D. & Kraka, E. (1983). *J. Am. Chem. Soc.* **105**, 5061–5069.

Bianchi, R., Gatti, C., Adovasio, V. & Nardelli, M. (1996). *Acta Cryst.* B**52**, 471–478.

Biegler-Konig, F. W., Bader, R. F. W. & Tang, T.-H. (1982). *J. Comput.Chem.* **3**, 317–352.

Birkedal, H., Madsen, D., Mathiesen, R. H., Knudsen, K., Weber, H.-P., Pattison, P. & Schwarzenbach, D. (2004). *Acta Cryst.* A**60**, 371–381.

Bolotina, N. B., Hardie, M. J., Speer, R. L. Jr & Pinkerton, A. A. (2004). *J. Appl. Cryst.* **37**, 808–814.

Borisova, N. P. & Semenov, S. G. (1973). *Vestn. Leningrad University* pp. 119–124.

Bridgeman, A. J., Cavigliasso, G., Ireland, L. R. & Rothery, J. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2095–2108.

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.

Bürgi, H.-B., Capelli, S., Goeta, A. E., Howard, J. A. K., Spackman, M. A. & Yufit, D. S. (2002). *Chem. Eur. J. Chem.* **8**, 3512–3521.

Chen, Yu.-Sh. (2004). PhD Thesis. University of Toledo.

Chen, Yu-Sh., Stash, A. I. & Pinkerton, A. A. (2007). Submitted.

Cioslowski, J. & Mixon, S. T. (1991). *J. Am. Chem. Soc.* **113**, 4142–4145.

Cioslowski, J., Mixon, S. T. & Edwards, W. D. (1991). *J. Am. Chem. Soc.* **113**, 1083–1085.

Coppens, P. & Volkov, A. (2004). *Acta Cryst.* A**60**, 357–364.

Costales, A., Blanco, M. A., Martin Pendas, A., Mori-Sanchez, P. & Luana, V. (2004). *J. Phys. Chem. A*, **108**, 2794–2801.

Coulson, C. A. (1939). *Proc. R. Soc. London A*, **169**, 413.

Coulson, C. A. (1961). *Valence*, 2nd ed. Oxford University Press.

Cremer, D. & Kraka, E. (1984). *Croat. Chem. Acta*, **57**, 1259–1281.

Downs, R. T., Gibbs, G. V., Boisen, M. B. & Rosso, K. M. Jr (2002). *Phys Chem. Miner.* **29**, 369–385.

Espinosa, E. & Molins, E. (2000). *J. Chem. Phys.* **11**, 5686–5694.

Espinosa, E., Molins, E. & Lecomte, C. (1998). *Chem. Phys. Lett.* **285**, 170–173.

Exner, K. & Schleyer, P. von R. (2001). *J. Phys. Chem. A*, **105**, 3407–3416.

Flaig, R., Koritsanszky, T., Dittrich, B., Wagner, A. & Luger, P. (2002). *J. Am. Chem. Soc.* **124**, 3407–3417.

Fradera, X., Austen, M. A. & Bader, R. F. W. (1999). *J. Phys. Chem. A*, **103**, 304–314.

Gatti, C. (2005). *Z. Kristallogr.* **220**, 399–457.

Gervasio, G., Bianchi, R. & Marabello, D. (2004). *Chem. Phys. Lett.* **387**, 481–484.

Gibbs, G. V., Tamada, O. & Boisen, M. B. (1997). *Phys Chem Miner.* **24**, 432–439.

Granovsky, A. A. (2003). http://classic.Chem.msu.su/gran/gamess/index.html.

Grimme, S. (1996). *J. Am. Chem. Soc.* **118**, 1529–1534.

Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* A**34**, 909–921.

Henn, J., Ilge, D., Leusser, D., Stalke, D. & Engels, B. (2004). *J. Phys. Chem. A*, **108**, 9442–9452.

Hibbs, D. E., Overgaard, J., Howard, S. T. & Nguyen, Th. Ha. (2005). *Org. Biomol. Chem.* **3**, 441–447.

Howard, S. T. & Lamarche, O. (2003). *J. Phys. Org. Chem.* **16**, 133–141.

Iversen, B. B., Larsen, F. K., Figgis, B. N. & Reynolds, P. A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2227–2240.

Jennrich, R. I. (1977). *Stepwise Regression. Statistical Methods for Digital Computers*, edited by K. Enslein, A. Ralston & H. S. Wilf. New York: Wiley.

Kappe, C. O. (2006). MedChem Europe, 21–22 February 2006, Abstracts. Prague: Czech Republic, p. 9.

Knop, O., Boyd, R. J. & Choi, S. C. (1988). *J. Am. Chem. Soc.* **110**, 7299–7301.

Knop, O., Rankin, K. N. & Boyd, R. J. (2001). *J. Phys. Chem. A*, **105**, 6522–6566.

Koritsanszky, T. & Coppens, P. (2001). *Chem. Rev.* **101**, 1583–1627.

Lecomte, C., Guillot, B., Jelsch, C. & Podjarny, A. (2005). *Int. J. Quant. Chem.* **101**, 624–634.

Lendvay, G. J. (1994). *Phys. Chem.* **98**, 6098–6104.

Lendvay, G. J. (2000). *J. Mol. Struct. (Theochem.)* **501–502**, 389–393.

Macchi, P. & Sironi, A. (2003). *Coord. Chem. Rev.* **238–239**, 383–412.

Martin Pendas, A., Costales, A. & Luana, V. (1998). *J. Phys. Chem. B*, **102**, 6937–6948.

Mayer, I. (1983). *Chem. Phys. Lett.* **97**, 270–274.

Mayer, I. (1986). *Int. J. Quant. Chem.* **29**, 477–483.

Matta, C. F., Castillo, N. & Boyd, R. J. (2006). *J. Phys. Chem. B*, **110**, 563–578.

Matta, C. F. & Hernandez-Trujillo, J. (2003). *J. Phys. Chem. A*, **107**, 7496–7504.

Matta, C. F. & Hernandez-Trujillo, J. (2005). *J. Phys. Chem. A*, **109**, 10798.

Mayer, I., Knapp-Mohammady, M. & Suhai S. (2004). *Chem. Phys. Lett.* **389**, 34–38.

Mulliken, R. S. (1955*a*). *J. Chem. Phys.* **23**, 1833–1840.

Mulliken, R. S. (1955*b*). *J. Chem. Phys.* **23**, 1841–1846.

Mulliken, R. S. (1955*c*). *J. Chem. Phys.* **23**, 2338–2342.

Mulliken, R. S. (1955*d*). *J. Chem. Phys.* **23**, 2343–2346.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca, NY: Cornell University Press.

Popelier, P. L. A. (1999). *J. Phys. Chem. A*, **103**, 2883–2890.

Popelier, P. L. A. (2005). *Structure and Bonding*, Vol. 115, *Intermolecular Forces and Clusters I*, edited by D. J. Wales, pp. 1–56. Berlin and Heidelberg: Springer.

Popelier, P. L. A. & Aicken, F. M. (2003). *J. Am. Chem. Soc.* **125**, 1284–1292.

Popelier, P. L. A., Aicken, F. M. & O'Brien, S. E. (2000). *Specialist Periodical Report, Chemical Modeling Applications and Theory A*, Vol. 1, pp. 143–198. The Royal Society of Chemistry.

Potemkin, V. A., Rykounov, A. A., Bartashevich, E. V., Pereyaslavskaya, E. S., Stash, A. I. & Tsirelson, V. G. (2006). IV National Crystal Chemistry Conference, 26–30 June 2006, Russia, Chernogolovka: Book of Abstracts, p. 75.

Potemkin, V. A., Rykounov, A. A., Stash, A. I. & Tsirelson, V. G. (2006). IV National Crystal Chemistry Conference, 26–30 June 2006, Russia, Chernogolovka: Book of Abstracts, p. 130.

Reed, A. & Schleyer, P. von R. (1990). *J. Am. Chem. Soc.* **112**, 1434–1445.

Rincon, L. & Almeida, R. (1998). *J. Phys. Chem. A*, **102**, 9244–9254.

Ritchie, J. P., Zhurova, E. A., Martin, A. & Pinkerton, A. A. (2003) *J. Phys. Chem. B*, **107**, 14576–14589.

Scherer, W. (2004). Personal communication.

Scherer, W. & McGrady, G. S. (2004). *Angew. Chem. Int. Ed. Engl.* **43**, 1782–1806.

Schmidt, M. W., Baldridge, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S. J., Windus, T. L., Dupuis, M. & Montgomery, J. A. (1993). *J. Comput. Chem.* **14**, 1347–1363.

Spackman, M. A., Byrom, P. G., Alfredsson, M. & Hermansson, K. (1999). *Acta Cryst.* A**55**, 30–47.

Stash, A. I. (2004). Unpublished work.

Stash, A. I., Tanaka, K., Shiozawa, K., Makino, H. & Tsirelson, V. G. (2005). *Acta Cryst.* B**61**, 418–428.

Stash, A. I., Zavodnik, V. E., Zavgorodny, S. G., Gurskaya, G. V. & Tsirelson V. G. (2005). *Acta Cryst.* E**61**, o1721–o1723.

Tsirelson, V. G., Abramov, Yu. A., Zavodnik, V. E., Stash, A. I., Belokoneva, E. L., Stahn, J., Pietsch, U. & Feil, D. (1998). *Struct. Chem.* **9**, 249–254.

Tsirelson, V. G. & Ozerov, R. P. (1996). *Electron Density and Bonding in Crystals.* Bristol/Philadelphia: Institute of Physics.

Tsirelson, V. G. & Stash, A. I. (2002*a*). *Chem. Phys. Lett.* **351**, 142–148.

Tsirelson, V. G. & Stash, A. I. (2002*b*). *Acta Cryst.* B**58**, 780–785.

Tsirelson, V. G. & Stash, A. I. (2004). *Acta Cryst.* A**60**, 418–426.

Tsirelson, V. & Stash, A. (2006). *Exchange Hole and Pair Function from Experimental Electron Density*. European-Charge Density Meeting, Brandenburg, Germany, 26–29 January, 2006, p. 62.

Tsirelson, V. G., Stash, A. I., Potemkin, V. A., Rykounov, A. A., Shutalev, A. D., Zhurova, E. A., Zhurov, V. V., Pinkerton, A. A., Gurskaya, G. V. & Zavodnik, V. E. (2006). *Acta Cryst.* B**62**, 676–688.

Volkov, A., Abramov, Y., Coppens, P. & Gatti, C. (2000). *Acta Cryst.* A**56**, 332–339.

Volkov, A. & Coppens, P. (2001). *Acta Cryst.* A**57**, 395–405.

Volkov, A., Li, X., Koritsanszky, T. & Coppens, P. (2004). *J. Phys. Chem. A*, **108**, 4283–4300.

Volkov, A., Koritsanszky, T., Li, X. & Coppens, P. (2004). *Acta Cryst.* A**60**, 638–639.

Wiberg, K. (1968). *Tetrahedron*, **24**, 1083–1089.

Zhurova, E. A., Martin, A. & Pinkerton, A. A. (2002). *J. Am. Chem. Soc.* **124**, 8741–8750.

Zhurova, E. A., Matta, C. F., Wu, N., Zhurov, V. V. & Pinkerton, A. A. (2006). *J. Am. Chem. Soc.* **128**, 8849–8862.

Zhurova, E. A. & Pinkerton, A. A. (2001). *Acta Cryst.* B**57**, 359–365.

Zhurova, E. A., Stash, A. I., Tsirelson, V. G., Zhurov, V. V., Bartashevich, E. V., Potemkin, V. A. & Pinkerton, A. A. (2006). *J. Am. Chem. Soc.* **128**, 14728–14734.

Zhurova, E. A., Tsirelson, V. G., Stash, A. I., Yakovlev, M. V. & Pinkerton, A. A. (2004). *J. Phys. Chem. B*, **108**, 20173–20179.