SUPPLEMENTARY MATERIAL

Critical examination of the radial functions in the Hansen-Coppens multipole model through topological analysis of primary- and refined-theoretical densities.

Anatoliy Volkov & Philip Coppens

Department of Chemistry, State University of New York at Buffalo,
Buffalo, NY 14260-3000, USA.

Abstract

A double-zeta (DZ) multipolar model has been applied to theoretical structure factors of four organic molecular crystals as a test of the ability of the multipole model to faithfully represent a theoretical charge density. The model leads to very significant improvement in the charge density along the covalent bonds and eliminates most of the bias introduced when a theoretical density is projected into the conventional multipole formalism.

The extended model may be too detailed for analysis of data sets of the accuracy and resolution typically achieved at present, but provides guidance for the type of algorithms to be adapted in future studies.

Net atomic charges and atomic volumes from AIM analysis of primary, and SZ and DZ multipole refined PHF and PDFT charge densities of *p*-nitroaniline, carbohydrazide and γ-aminobutyric acid

Table S.1. Net atomic charges derived from AIM analysis in PNA molecule.

ATOM (Ω)	**PHF/6-31G****				**PDFT(BPW91)/6-31G****		
	q(Ω)	*q(Ω)* ‡	*q(Ω)*††	*q(Ω)*‡‡	*q(Ω)*	*q(Ω)* ‡	*q(Ω)*‡‡
O1, O2	-0.60	-0.52	-0.54	-0.56	-0.56	-0.47	-0.52
N1 (amino)	-1.52	-1.16	-1.37	-1.37	-1.28	-1.02	-0.97
N2 (nitro)	+0.31	+0.27	+0.26	+0.29	+0.38	+0.32	+0.33
C1	+0.62	+0.43	+0.51	+0.52	+0.50	+0.32	+0.41
C2, C6	+0.08	-0.02	+0.06	+0.02	-0.02	-0.07	0.00
C3, C5	+0.07	-0.04	+0.02	+0.16	+0.02	-0.06	+0.07
C4	+0.30	+0.29	+0.28	+0.18	+0.21	+0.17	+0.21
H1A, H1B	+0.52	+0.47	+0.49	+0.48	+0.48	+0.44	+0.39
H2, H6	+0.01	+0.08	+0.06	+0.03	+0.08	+0.14	+0.02
H3, H5	+0.07	+0.12	+0.07	+0.06	+0.09	+0.13	+0.04
Σ $\lvert L(\Omega)\rvert$†††	2×10^{-4}	4×10^{-3}	6×10^{-3}	5×10^{-3}	4×10^{-3}	2×10^{-3}	6×10^{-3}
Σ $q(\Omega)$	-3×10^{-4}	4×10^{-3}	3×10^{-3}	3×10^{-3}	3×10^{-3}	1×10^{-3}	5×10^{-3}

† Primary theoretical density
‡ SZ multipole refinement of theoretical structure factors
†† SZ multipole refinement with $n_{1..3}$=4,4,6
‡‡ DZ multipole refinement of theoretical structure factors
††† Lagrangian integral

Table S.2. Net atomic charges derived from AIM analysis of carbohydrazide.

ATOM (Ω)	PHF/6-31G**			PDFT(B3LYP)/6-31G**		
	$q(\Omega)$†	$q(\Omega)$‡	$q(\Omega)$††	$q(\Omega)$†	$q(\Omega)$‡	$q(\Omega)$††
O1	-1.46	-1.30	-1.34	-1.32	-1.12	-1.26
N1	-1.14	-0.86	-1.00	-0.93	-0.76	-0.83
N2	-0.79	-0.65	-0.65	-0.77	-0.66	-0.66
N3	-1.14	-0.88	-1.00	-0.94	-0.75	-0.82
N4	-0.81	-0.66	-0.64	-0.79	-0.66	-0.62
C1	2.42	1.94	2.23	2.02	1.62	1.88
H1	0.54	0.45	0.46	0.48	0.42	0.42
H2, H3	0.46	0.37	0.37	0.44	0.36	0.38
H4	0.55	0.47	0.46	0.49	0.44	0.43
H5, H6	0.46	0.38	0.38	0.44	0.37	0.37
$\Sigma \lvert L(\Omega)\rvert$†††	1×10^{-2}	7×10^{-3}	8×10^{-3}	7×10^{-3}	7×10^{-3}	8×10^{-3}
$\Sigma\, q(\Omega)$	8×10^{-3}	6×10^{-3}	5×10^{-3}	3×10^{-3}	5×10^{-3}	6×10^{-3}

† Primary theoretical density
‡ SZ multipole refinement of theoretical structure factors
†† DZ multipole refinement of theoretical structure factors
††† Lagrangian integral

Table S.3. Net atomic charges derived from AIM analysis of γ-aminobutyric acid.

ATOM (Ω)	PHF/6-31G**			PDFT(B3LYP)/6-31G**		
	q(Ω)†	*q*(Ω)‡	*q*(Ω)††	*q*(Ω)†	*q*(Ω)‡	*q*(Ω)††
O1	-1.48	-1.34	-1.39	-1.32	1.16	-1.23
O2	-1.48	-1.36	-1.41	-1.31	-1.18	-1.26
N1	-1.45	-1.16	-1.23	-1.20	-1.05	-1.11
C1	0.54	0.43	0.61	0.34	0.26	0.43
C2	0.18	0.22	0.22	0.03	0.05	0.07
C3	0.13	0.08	0.12	-0.04	-0.05	-0.03
C4	1.97	1.82	1.94	1.79	1.60	1.73
H1	0.60	0.54	0.53	0.52	0.50	0.48
H2	0.58	0.53	0.51	0.52	0.49	0.48
H3	0.60	0.55	0.53	0.52	0.50	0.48
H4	-0.01	-0.05	-0.06	0.04	0.03	-0.01
H5	-0.04	-0.06	-0.09	0.02	-0.01	-0.03
H6	-0.03	-0.07	-0.08	0.03	0.00	-0.01
H7	-0.07	-0.09	-0.09	0.00	-0.01	-0.03
H8	-0.01	-0.01	-0.04	0.04	+0.03	0.01
H9	-0.03	-0.03	-0.05	0.03	+0.03	0.01
$\Sigma\lvert L(\Omega)\rvert$†††	5×10^{-2}	9×10^{-3}	1×10^{-2}	4×10^{-2}	4×10^{-3}	7×10^{-3}
$\Sigma\, q(\Omega)$	7×10^{-3}	7×10^{-3}	9×10^{-3}	4×10^{-3}	2×10^{-3}	5×10^{-3}

† Primary theoretical density
‡ SZ multipole refinement of theoretical structure factors
†† DZ multipole refinement of theoretical structure factors
††† Lagrangian integral

Table S.4. Atomic volumes (in Å^3) in PNA molecule from AIM analysis.
Calculated volume of the unit cell from cell parameters is 612.3 Å^3.

ATOM	PHF/6-31G**				PDFT(BPW91)/6-31G**		
	V(Ω)†	*V*(Ω)‡	*V*(Ω)††	*V*(Ω)‡‡	*V*(Ω)†	*V*(Ω)‡	*V*(Ω)‡‡
O1	17.2	16.9	16.8	16.9	17.1	16.7	16.8
O2	17.5	17.2	17.2	17.4	17.4	17.1	17.2
N1 (amino)	19.8	18.6	18.8	19.1	18.7	17.9	16.8
N2 (nitro)	7.2	7.3	7.8	7.3	7.3	7.3	7.9
C1	7.7	8.2	8.2	8.0	8.1	8.5	8.3
C2	10.9	11.5	11.4	11.1	11.0	11.6	11.0
C3	10.6	11.4	11.3	10.3	10.8	11.4	10.2
C4	9.0	9.0	8.8	9.3	8.8	9.1	8.8
C5	10.2	10.6	10.6	9.9	10.4	10.8	9.9
C6	11.4	12.1	12.2	11.7	11.6	12.0	11.5
H1A	3.5	3.3	3.2	3.4	3.6	3.5	4.2
H1B	2.8	2.8	2.5	2.5	3.2	3.1	3.5
H2	6.4	5.7	5.5	6.2	6.2	5.5	6.4
H3	6.7	6.5	6.8	7.0	6.6	6.6	7.2
H5	5.3	5.2	5.2	5.5	5.4	5.2	5.6
H6	6.8	6.6	6.5	7.1	6.5	6.6	7.3
$V_{AIM\ molecule}$ (Å^3)	152.9	152.7	152.6	152.9	152.8	152.8	152.9
$V_{AIM\ unit\ cell}$ (Å^3)	611.8	610.9	610.5	611.7	611.3	611.3	611.4
$V_{AIM\ unit\ cell}$ / V_{calc} (%)	99.9	99.8	99.7	99.9	99.8	99.8	99.9

† Primary theoretical density
‡ SZ multipole refinement of theoretical structure factors
†† SZ multipole refinement with $n_{1..3}$=4,4,6
‡‡ DZ multipole refinement of theoretical structure factors

Table S.5. Atomic volumes (in Å^3) in 1,3-diaminourea from AIM analysis.
Calculated volume of the unit cell from cell parameters is 380.9 Å^3.

ATOM	PHF/6-31G**			PDFT(B3LYP)/6-31G**		
	V(Ω)†	*V(Ω)*‡	*V(Ω)*††	*V(Ω)*†	*V(Ω)*‡	*V(Ω)*††
O1	17.1	16.3	16.3	16.7	15.6	16.4
N1	13.9	13.3	13.6	13.2	12.8	12.9
N2	14.7	14.1	14.1	14.5	13.9	13.9
N3	13.5	12.9	13.1	12.7	12.4	12.4
N4	15.1	14.5	14.3	14.8	14.3	14.1
C1	3.0	3.6	3.2	4.1	4.5	4.1
H1	2.6	3.1	3.0	2.9	3.4	3.2
H2	2.8	3.0	3.2	3.0	3.2	3.3
H3	3.1	3.6	3.6	3.3	3.6	3.6
H4	2.6	3.0	3.0	3.1	3.3	3.2
H5	3.2	3.6	3.7	3.3	3.8	3.8
H6	3.7	4.0	4.1	3.8	4.1	4.2
$V_{AIM\ molecule}$ (Å^3)	95.4	95.0	95.1	95.4	95.0	95.0
$V_{AIM\ unit\ cell}$ (Å^3)	381.7	380.0	380.3	381.8	380.1	380.1
$V_{AIM\ unit\ cell}$ / V_{calc} (%)	100.2	99.8	99.8	100.2	99.8	99.8

† Primary theoretical density
‡ SZ multipole refinement of theoretical structure factors
†† DZ multipole refinement of theoretical structure factors

Table S.6. Atomic volumes (in Å^3) in γ-aminobutyric acid from AIM analysis. Calculated volume of the unit cell from cell parameters is 554.24 Å^3.

ATOM	PHF/6-31G**			PDFT(B3LYP)/6-31G**		
	V(Ω)†	*V*(Ω)‡	*V*(Ω)††	*V*(Ω)†	*V*(Ω)‡	*V*(Ω)††
O1	20.2	19.6	19.8	19.8	19.0	19.2
O2	19.6	19.6	19.9	19.1	19.0	19.2
N1	16.7	15.4	15.5	15.2	14.7	14.7
C1	7.0	7.4	7.0	7.5	8.2	7.6
C2	8.2	7.8	7.8	8.7	8.5	8.5
C3	9.4	9.4	9.1	9.8	10.0	9.9
C4	4.6	4.7	4.6	5.4	5.7	5.5
H1	1.9	2.0	2.0	2.3	2.3	2.3
H2	2.1	2.3	2.3	2.6	2.6	2.6
H3	2.1	2.0	2.0	2.6	2.3	2.4
H4	7.0	7.3	7.3	6.8	7.0	7.2
H5	8.0	8.1	8.2	7.8	7.9	8.0
H6	7.4	7.6	7.8	7.1	7.5	7.5
H7	7.1	7.3	7.3	6.8	7.0	7.0
H8	8.8	8.6	8.9	8.6	8.6	8.6
H9	8.2	8.2	8.2	7.8	7.8	7.9
$V_{AIM\ molecule}$ (Å^3)	138.4	138.0	137.8	137.8	138.0	138.1
$V_{AIM\ unit\ cell}$ (Å^3)	553.6	551.8	551.3	551.1	551.9	552.4
$V_{AIM\ unit\ cell}$ / V_{calc} (%)	99.9	99.6	99.5	99.4	99.6	99.7

† Primary theoretical charge density
‡ SZ multipole refinement of theoretical structure factors
†† DZ multipole refinement of theoretical structure factors