Supporting information

VALTOPO: A program for the determination of atomic and molecular properties from experimental electron densities

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Table S1 Experimental and theoretical third moments $\mu_{\alpha\beta\gamma}$ (DebyeÅ^2) in L-alanine.[†]

	μ_{xxx}	μ_{yyy}	μ_{zzz}	μ_{xyy}	μ_{xxy}	μ_{xxz}	μ_{xzz}	μ_{yzz}	μ_{yyz}	μ_{xyz}
Experiment (from QTAIM)										
crystal	−26.5	−3.2	−2.3	−9.9	−10.0	−2.4	−3.9	−3.2	−1.6	2.1
'molecule'	−28.8	−3.3	−2.6	−10.5	−10.3	−2.9	−4.5	−3.1	−1.7	2.3
Experiment (from multipole populations)										
	−29.4(27)	−3.7(15)	−2.5(6)	−10.8(8)	−10.5(13)	−2.6(5)	−4.6(4)	−3.0(4)	−1.4(5)	2.2(4)
Theory[‡]										
RHF/6-311++G**	−33.3	−9.1	−3.8	−14.1	−15.5	−3.0	−3.8	−4.9	−3.8	3.2
B3LYP/6-311++G**	−28.5	−8.5	−3.5	−12.5	−14.6	−2.9	−2.8	−4.7	−3.7	2.8
MP2/6-311++G**	−29.8	−9.1	−3.6	−12.6	−14.9	−3.3	−3.0	−4.9	−3.7	2.8

[†] The results are given with respect to the inertial axes frame, with the centre of mass chosen as origin.
[‡] Experimental geometry.

Table S2 Experimental and theoretical fourth moments $\mu_{\alpha\beta\gamma\delta}$ (DebyeÅ^3) in L-alanine, bpe and F_4dIb.[†]

	μ_{xxxx}	μ_{yyyy}	μ_{zzzz}	μ_{xxxy}	μ_{xxxz}	μ_{yyyx}	μ_{yyyz}	μ_{zzzx}	μ_{zzzy}	μ_{xxyy}	μ_{xxzz}	μ_{yyzz}	μ_{xxyz}	μ_{yyxz}	μ_{zzxy}
							L-ALANINE								
Experiment (from QTAIM)															
crystal	–289.0	–178.7	–60.7	8.9	17.2	15.6	4.7	0.9	–4.8	–89.5	–64.0	–40.6	2.7	1.0	5.3
'molecule'	–310.1	–189.5	–68.9	8.7	18.3	16.9	5.5	1.6	–5.3	–94.1	–69.1	–45.6	3.1	1.9	5.7
Experiment (from multipole populations)															
	–310.0(67)	–188.7(36)	–68.7(10)	9.1(31)	17.7(11)	17.8(14)	5.7(10)	1.2(7)	–4.9(5)	–93.6(19)	–68.7(6)	–45.4(5)	3.3(6)	1.6(5)	5.6(4)
Theory[a]															
RHF/6-311++G**	–365.3	–231.1	–91.3	19.3	18.2	23.0	7.3	4.0	0.2	–107.1	–79.4	–52.5	6.0	1.9	8.0
DFT/6-311++G**	–375.9	–238.6	–95.6	18.8	16.1	21.7	7.4	3.7	0.3	–108.8	–81.3	–54.7	5.4	2.2	7.6
MP2/6-311++G**	–376.7	–240.4	–96.6	20.6	16.8	22.7	7.3	3.9	0.2	–109.5	–81.8	–55.1	5.4	2.3	8.0
							BPE								
Experiment (from QTAIM)															
	–5569	–526	–104	44	11	52	17	0	2	–783	–946	–128	73	3	6
Experiment (from multipole populations)															
	–5601(327)	–528(27)	–104(1)	52(146)	15(15)	53(40)	17(2)	0(1)	2(1)	–788(73)	–946(4)	–129(1)	73(6)	3(3)	7(1)
Theory															
RHF/MIDI![b]	–6267	–513	–89	–161	4	6	0	3	–1	–784	–923	–122	1	1	0
DFT/MIDI![b]	–6226	–531	–85	–150	4	6	–1	3	–1	–804	–917	–122	1	1	1
MP2/MIDI![b]	–6438	–549	–97	–160	25	3	–2	2	–5	–824	–940	–126	12	0	–1
MP2/MIDI![a]	–6271	–533	–87	–157	–5	4	1	0	0	–801	–905	–120	7	–1	2
							F_4DIB								
Experiment (from QTAIM)															
	–5332	–963	–139	–30	–21	–4	–1	0	0	–987	–853	–184	–4	0	0
Experiment (from multipole populations)															
	–5348(115)	–965(12)	–140(1)	–31(3)	–22(3)	– 4(5)	–1(1)	0(1)	0(1)	–988(9)	–854(6)	–184(1)	–4(1)	0(1)	0(1)
Theory															
RHF/MIDI![b]	–4130	–965	–124	–2	–1	–4	0	–1	0	–962	–814	–169	0	0	–1
DFT/MIDI![b]	–4164	–941	–120	–3	–1	–4	0	–1	0	–950	–808	–169	0	0	–1
MP2/MIDI![b]	–4275	–974	–124	–3	–1	–4	0	–1	0	–975	–827	–173	0	0	–1
MP2/MIDI![a]	–4269	–953	–123	–1	–1	0	0	0	0	–971	–827	–170	0	0	0

[†]Axes frame as in Table 4; [a] Experimental geometry; [b] Optimised geometry