

Supplementary Material

Experimental dynamic electron densities of multipole models at different temperatures

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1. Establishment of the strategy for multipole refinement

In order to have consistency, we decided to use a single multipole formalism to obtain aspherical models for all compounds. For this, we have chosen to use the multipolar formalism of Hansen and Coppens (Hansen & Coppens, 1978; Coppens, 1997) as implemented in the program XD2006 (Volkov *et al.*, 2006). During the process to determine the best possible strategy for multipole refinement using XD2006, we have faced difficulties to exactly reproduce the model of Destro and coworkers (Destro *et al.*, 2000); who have employed the software VALRAY (Stewart & Spackman, 1983). Eight different multipole refinements of α -Glycine have been carried out on the basis of different criteria as follows,

1. Local symmetry restrictions: Whether any restrictions for the refinement of the multipole parameters (on the basis of approximate 3-fold local symmetry of the ammonium nitrogen atom and mirror local symmetry for all other non-hydrogen atoms) have been made.

2. Chemical constraints: Whether the multipole parameters of hydrogen atoms from each groups (CH_2 and NH_3) were constrained to be the same (within the group).

3. Bond directed multipoles: For hydrogen atoms, whether only bond directed multipoles or all multipoles up to the level $l = 2$ (quadrupoles) were refined.

4. Hydrogen atom positions: The strategy used to refine/fix hydrogen atom positions.

5. Atomic displacement parameters (ADPs) for hydrogen atoms: The strategy for treating the thermal parameters of hydrogen atoms.

6. Observed criteria for reflections: Whether criteria for observed reflections were chosen as $F_{obs} > 0$ or $F_{obs} > 3\sigma(F_{obs})$. The second criteria is the default option of XD2006.

7. κ and κ' : The strategy for refining κ and κ' .

8. Extinction parameters: How the extinction parameters were refined.

Detailed comparisons of different strategies are given in Table 1, and the comparison of charge densities (ρ_{BCP}) and the Laplacians ($\nabla^2\rho_{BCP}$) at bond critical points (BCPs) are given in Table 2. None of these different methods were able to exactly reproduce the model of Destro *et al.* (2000). Small differences in topological properties from that of Destro *et al.* (2000) persisted for all models. This is not very surprising, because we have used a different multipole formalism according to Hansen and Coppens (Hansen & Coppens, 1978) and a different computer program (Volkov *et al.*, 2006), where as Destro *et al.* (2000) have used the multipolar formalism according to Stewart (Stewart, 1976; Flensburg *et al.*, 1995) as implemented in the computer program VALRAY (Stewart & Spackman, 1983). Besides, we have used the data bank of Su and Coppens (Su & Coppens, 1998) for the atomic scattering factors, which is more recent than what (Clementi & Roetti, 1974) Destro *et al.* have used. From Table 2, one can notice that the method 8, which is closest to the approach as Destro *et al.* (2000), also cannot reproduce exactly the same results. These small differences can be attributed to the use of different multipolar formalism, different software and different scattering factors. We do not concentrate much on these small differences in topological properties, as our primary goal is to compute static and dynamic densities directly from a sufficiently good multipole model. For this purpose, we choose the method 1, which is currently the state of art for performing multipole refinement using XD2006 with lowest number of refined parameters and minimum residual densities. Topological properties obtained from method 1 are similar to other amino acids and fall within the standard deviation limits for amino acids as reported by Mebs and coworkers (Mebs *et al.*, 2006).

Table 1. Comparison between different methods performed using different strategies for multipole refinements.

Methods	Destro <i>et al.</i> (2000)	Method1	Method2	Method3	Method4	Method5	Method6	Method7	Method8
Local symmetry restriction	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Chemical constraint	No	Yes	Yes	No	No	Yes	Yes	Yes	No
Bond directed MP for hydrogen atoms	No (all up to quadrupole were refined)	Yes (up to quadrupole)	Yes (up to quadrupole)	yes (up to quadrupole)	yes (up to quadrupole)	yes (up to quadrupole)	yes (up to quadrupole)	No (all up to quadrupole were refined)	No (all up to quadrupole were refined)
Hydrogen atom positions	Refined	Initially set to neutron distances, refined with $(\sin\theta/\lambda) \leq 0.5 \text{ \AA}^{-1}$ and then again fixed to neutron distances	Initially set to neutron distances, refined with $(\sin\theta/\lambda) \leq 0.5 \text{ \AA}^{-1}$ and then again fixed to neutron distances	Initially set to neutron distances, refined with $(\sin\theta/\lambda) \leq 0.5 \text{ \AA}^{-1}$ and then kept fixed to these new distances	Initially set to neutron distances, refined with $(\sin\theta/\lambda) \leq 0.5 \text{ \AA}^{-1}$ and then kept fixed to these new distances	Initially set to neutron distances, refined with $(\sin\theta/\lambda) \leq 0.5 \text{ \AA}^{-1}$ and then again fixed to neutron distances	Initially set to neutron distances, refined with $(\sin\theta/\lambda) \leq 0.5 \text{ \AA}^{-1}$ and then again fixed to neutron distances	Refined	Refined
ADPs of hydrogen atoms	Anisotropic (fixed)	Isotropic, (1.2 times of the parent)	Isotropic, (1.2 times of the parent)	Isotropic, (refined)	Isotropic, (refined)	Anisotropic (fixed, same as Destro)	Anisotropic (fixed, same as Destro)	Anisotropic (fixed, same as Destro)	Anisotropic (fixed, same as Destro)
κ and κ'	NA	Refined for non-H atoms	Refined for non-H atoms	Refined for non-H atoms	Refined for non-H atoms	Refined for non-H atoms	Refined for non-H atoms	Initially refined for non-H, and then kept fixed	Initially refined for non-H, and then kept fixed
Extinction	Anisotropic (fixed)	Anisotropic (refined)	Anisotropic (refined)	Anisotropic (refined)	Anisotropic (refined)	Anisotropic (refined)	Anisotropic (refined)	Anisotropic (fixed, same as Destro)	Anisotropic (fixed, same as Destro)
Observed criteria, observed reflections	$F^2(obs) > 0, 3789$	$F(obs) > 3\sigma, 3603$	$F(obs) > 0, 3789$	$F(obs) > 3\sigma, 3603$	$F(obs) > 0, 3789$	$F(obs) > 3\sigma, 3603$	$F(obs) > 0, 3789$	$F(obs) > 0, 3789$	$F(obs) > 0, 3789$
Number of parameters	216	131	131	145	145	131	131	189	216
$\Delta\rho_{min}/\Delta\rho_{max}$ ($e/\text{\AA}^3$)	–	–0.132/ 0.154	–0.144/ 0.164	–0.137/ 0.151	–0.153/ 0.167	–0.152/ 0.167	–0.162/ 0.170	–0.158/ 0.186	–0.167/ 0.191
$R_F(obs)$	0.0129	0.0124	0.0137	0.0123	0.0136	0.0128	0.0140	0.0138	0.0134
R_{F^2}	0.0172	0.0184	0.0184	0.0184	0.0185	0.0189	0.0190	0.0198	0.0194
wR_{F^2}	–	0.0293	0.0295	0.0287	0.0289	0.0303	0.0305	0.0292	0.0283
GoF	1.041	1.041	1.1588	1.1551	1.1376	1.2124	1.1930	1.1524	1.1234

Table 2. *Electron densities and Laplacians at the BCPs of covalent bonds of α -Glycine. Values are given for* *ρ_{bcp} ($e/\text{\AA}^3$; first line) and $\nabla^2 \rho_{bcp}$ ($e/\text{\AA}^5$; second line).*

Bond	Destro <i>et al.</i> (2000)	Method1	Method2	Method3	Method4	Method5	Method6	Method7	Method8
C1-O1	2.77(2) -32.8(9)	2.770 -36.57	2.770 -36.71	2.763 -35.94	2.763 -36.03	2.773 -36.40	2.773 -36.44	2.751 -32.81	2.758 -33.85
C1-O2	2.67(2) -30.5(9)	2.733 -35.07	2.727 -34.97	2.733 -35.06	2.728 -34.98	2.715 -34.43	2.710 -34.37	2.660 -30.84	2.693 -32.73
C1-C2	1.78(1) -15.6(4)	1.735 -12.80	1.736 -12.84	1.758 -13.50	1.759 -13.53	1.740 -13.08	1.741 -13.12	1.780 -14.76	1.774 -14.33
C2-N	1.69(1) -11.9(5)	1.691 -10.42	1.689 -10.45	1.693 -10.75	1.691 -10.76	1.698 -10.91	1.696 -10.93	1.673 -10.18	1.674 -10.12
C2-H4	1.99(1) -22.7(6)	1.940 -22.24	1.942 -22.32	1.892 -21.50	1.894 -21.59	1.969 -23.98	1.970 -24.05	1.980 -24.69	2.054 -25.55
C2-H5	1.91(2) -21.2(7)	1.907 -21.74	1.907 -21.79	1.891 -21.55	1.891 -21.59	1.863 -21.07	1.863 -21.11	1.855 -21.07	1.799 -20.05
N-H1	2.20(2) -35.4(13)	2.084 -35.78	2.083 -35.79	2.043 -35.47	2.040 -35.43	2.071 -35.65	2.070 -35.65	2.142 -4.07	2.185 -40.05
N-H2	2.21(2) -36.2(13)	2.086 -35.86	2.085 -35.86	1.989 -35.54	1.984 -35.50	2.072 -35.71	2.071 -35.71	2.074 -37.11	2.028 -40.39
N-H3	2.24(2) -33.0(11)	2.084 -35.76	2.083 -35.77	1.962 -34.10	1.961 -34.13	2.069 -35.60	2.069 -35.60	2.144 -40.93	2.189 -38.15

2. Effects of shifts in bond critical points on topological properties

Comparative analysis of static and dynamic multipole densities has revealed that BCPs in static densities ($\text{BCPs}^{\text{static}}$) slightly differ in position from the corresponding BCPs in dynamic densities ($\text{BCPs}^{\text{dynamic}}$). Magnitudes of these differences increase with temperature, as is found for *D, L*-Serine (Dittrich *et al.*, 2005) at three different temperatures (Tables 3, 4 and 5). A maximum shift of 0.0795 Å between $\text{BCPs}^{\text{static}}$ and $\text{BCPs}^{\text{dynamic}}$ has been observed for C1–O1 bond at 298K (Table 5). To find the effects of these shifts, topological properties of static densities in *D, L*-Serine at the positions of $\text{BCPs}^{\text{static}}$ and of $\text{BCPs}^{\text{dynamic}}$ have been calculated and compared. These topological properties of static densities have been further compared with the corresponding properties of dynamic densities at $\text{BCPs}^{\text{dynamic}}$. We have found that, below 100K, static properties at positions of $\text{BCPs}^{\text{static}}$ as well as at $\text{BCPs}^{\text{dynamic}}$ are almost equal (Tables 6 & 7), with a maximum difference of $0.003 \text{ e}/\text{\AA}^3$ for the ρ_{BCP} and $3.15 \text{ e}/\text{\AA}^5$ for the Laplacian of the C1–O1 bond at 100K. Larger differences have been observed at 298 K (Tables 8), however properties of static densities are still reasonable within the scope of the quantum theory of atoms in molecules (QTAIM) (Bader, 1990). Corresponding properties (especially Laplacians) of dynamic densities at same positions are clearly different.

These results indicate that up to 100K, the differences in topological properties of static and dynamic densities are not due to the differences in the positions of BCPs, but due to the fact that, dynamic densities indeed possess different characteristics than the static densities. This is also evidenced by the fact that the topological properties of dynamic densities at BCPs are not just uniformly smaller than the corresponding properties of static densities with increasing temperature, but basically different.

At 298K, Laplacians of static densities at BCPs of C–O bonds are already different for the $\text{BCPs}^{\text{dynamic}}$ position than for the real position, but the difference with the

Laplacians of dynamic densities at the same position is even larger. This indicates that, differences in the positions of BCPs might play a part behind the difference between properties of static and dynamic densities at room temperature. However, different positions of BCPs are not sufficient to fully explain the differences between the static and the dynamic densities.

Table 3. *Coordinates of BCPs for D, L-Serine from static and dynamic densities at 20K.*

Covalent bonds	coordinates of BCPs ^{static}	coordinates of BCPs ^{dynamic}	Distance (Å)
C1-O1	0.71242 0.40949 0.57309	0.711978 0.409521 0.572458	0.0049
C1-O2	0.77919 0.45022 0.70047	0.779159 0.450022 0.700500	0.0019
C3-O3	0.90562 0.19860 0.86703	0.905430 0.198843 0.869956	0.0149
C1-C2	0.75123 0.34592 0.77428	0.751245 0.346113 0.774225	0.0018
C2-C3	0.82110 0.24942 0.92130	0.821600 0.249377 0.922031	0.0055
C2-N1	0.71039 0.23563 0.82015	0.711017 0.236348 0.821271	0.0098
Hydrogen bonds	coordinates of BCPs ^{static}	coordinates of BCPs ^{dynamic}	Distance (Å)
O1...H4-O3	0.61988 0.51909 0.36079	0.619486 0.519025 0.361269	0.0054
O3...H11-N1	0.52040 0.26122 0.71670	0.519808 0.261055 0.714965	0.0090
O2...H12-N1	0.66031 0.07084 1.02780	0.660410 0.069911 1.027448	0.0088
O2...H13-N1	0.66631 0.08088 0.45373	0.666745 0.080841 0.453148	0.0061
O1...H2-C2	0.70033 0.35666 1.20523	0.701021 0.356350 0.207473	0.0115

Table 4. *Coordinates of BCPs D, L-Serine from static and dynamic densities at 100 K.*

Covalent Bonds	coordinates of BCPs ^{static}	coordinates of BCPs ^{dynamic}	Distance (Å)
C1-O1	0.71330 0.40837 0.57365	0.711612 0.408511 0.570543	0.0199
C1-O2	0.77988 0.44903 0.70061	0.780750 0.449716 0.701396	0.0110
C3-O3	0.90574 0.19703 0.86823	0.905862 0.196956 0.870873	0.0124
C1-C2	0.75143 0.34497 0.77460	0.751487 0.345354 0.774502	0.0036
C2-C3	0.82108 0.24817 0.92105	0.821968 0.248093 0.922336	0.0098
C2-N1	0.71035 0.23463 0.81999	0.711214 0.235654 0.821724	0.0141
Hydrogen bonds	coordinates of BCPs ^{static}	coordinates of BCPs ^{dynamic}	Distance (Å)
O1...H4-O3	0.62100 0.51790 0.35979	0.620374 0.517923 0.360353	0.0079
O3...H11-N1	0.52082 0.26222 0.71670	0.520033 0.262037 0.713981	0.0134
O2...H12-N1	0.66036 0.07017 1.02917	0.660646 0.069085 1.028519	0.0111
O2...H13-N1	0.66565 0.07989 0.45386	0.666192 0.079970 0.453431	0.0068
O1...H2-C2	0.70088 0.35533 1.20560	0.702068 0.354944 0.208145	0.0153

Table 5. *Coordinates of BCPs D, L-Serine from static and dynamic densities at 298 K.*

Covalent Bonds	coordinates of BCPs ^{static}	coordinates of BCPs ^{dynamic}	Distance (Å)
C1-O1	0.71670 0.40466 0.57587	0.710262 0.405263 0.562817	0.0795
C1-O2	0.78214 0.44494 0.70141	0.787042 0.449350 0.705637	0.0648
C3-O3	0.90631 0.19188 0.87140	0.909128 0.189420 0.866709	0.0482
C1-C2	0.75294 0.34132 0.77458	0.753060 0.342489 0.774094	0.0111
C2-C3	0.82110 0.24369 0.92052	0.823344 0.243527 0.924057	0.0253
C2-N1	0.71038 0.23147 0.81935	0.709279 0.231005 0.820112	0.0140
Hydrogen bonds	coordinates of BCPs ^{static}	coordinates of BCPs ^{dynamic}	Distance (Å)
O1...H4-O3	0.62170 0.51350 0.36113	0.619588 0.514534 0.362896	0.0280
O3...H11-N1	0.52133 0.26324 0.72013	0.519976 0.262383 0.714268	0.0290
O2...H12-N1	0.65827 0.06677 1.02774	0.659001 0.065158 1.025061	0.0224
O2...H13-N1	0.66399 0.07617 0.45410	0.664909 0.076327 0.455122	0.0098
O1...H2-C2	0.70300 0.35183 1.20569	0.706058 0.351153 0.208417	0.0323

Table 6. *Topological properties of static and dynamic densities at different points for D,L-Serine at 20 K. ρ ($e/\text{\AA}^3$) is given in the first line and $\nabla^2\rho$ ($e/\text{\AA}^5$) in the second line*

Bonds	from static densities at the position of BCPs^{static}	from static densities at the position of $\text{BCPs}^{dynamic}$	from dynamic densi- ties at the position of $\text{BCPs}^{dynamic}$
C1-O1	2.810 -32.18	2.810 -31.50	2.723 -23.40
C1-O2	2.791 -35.32	2.791 -35.59	2.693 -24.15
C3-O3	1.869 -16.64	1.871 -18.39	1.807 -9.02
C1-C2	1.710 -11.77	1.710 -11.78	1.670 -11.23
C2-C3	1.726 -12.29	1.726 -12.32	1.684 -13.60
C2-N1	1.684 -10.06	1.685 -10.70	1.664 -12.20
O1...H4-O3	0.258 4.29	0.258 4.29	0.279 3.91
O3...H11-N1	0.219 3.89	0.219 3.91	0.237 4.10
O2...H12-N1	0.200 3.47	0.200 3.49	0.218 3.71
O2...H13-N1	0.185 3.42	0.185 3.43	0.202 3.84
O1...H2-C2	0.075 1.53	0.075 1.53	0.086 1.97

Table 7. *Topological properties of static and dynamic densities at different points for D, L-Serine at 100 K. ρ ($e/\text{\AA}^3$) is given in the first line and $\nabla^2\rho$ ($e/\text{\AA}^5$) in the second line*

Bonds	from static densities at the position of BCPs^{static}	from static densities at the position of $\text{BCPs}^{dynamic}$	from dynamic densi- ties at the position of $\text{BCPs}^{dynamic}$
C1-O1	2.814 -32.30	2.817 -29.15	2.716 -12.04
C1-O2	2.795 -35.50	2.796 -33.49	2.661 -13.22
C3-O3	1.874 -16.80	1.874 -18.09	1.791 -2.16
C1-C2	1.713 -11.84	1.713 -11.85	1.649 -11.25
C2-C3	1.730 -12.36	1.730 -12.42	1.662 -13.41
C2-N1	1.686 -10.09	1.688 -11.03	1.661 -11.19
O1...H4-O3	0.259 4.31	0.259 4.31	0.288 3.79
O3...H11-N1	0.217 3.83	0.217 3.86	0.238 4.02
O2...H12-N1	0.200 3.51	0.200 3.52	0.224 3.74
O2...H13-N1	0.183 3.40	0.183 3.41	0.207 3.81
O1...H2-C2	0.075 1.53	0.075 1.54	0.090 2.03

Table 8. *Topological properties of static and dynamic densities at different points for D, L-Serine at 298 K. ρ ($e/\text{\AA}^3$) is given in the first line and $\nabla^2\rho$ ($e/\text{\AA}^5$) in the second line*

Bonds	from static densities at the position of BCPs^{static}	from static densities at the position of $\text{BCPs}^{dynamic}$	from dynamic densi- ties at the position of $\text{BCPs}^{dynamic}$
C1-O1	2.831 -32.82	2.896 -18.75	2.793 8.03
C1-O2	2.814 -36.28	2.855 -23.79	2.648 8.90
C3-O3	1.888 -17.30	1.900 -12.34	1.874 18.63
C1-C2	1.716 -11.87	1.716 -11.95	1.568 -10.09
C2-C3	1.735 -12.46	1.737 -12.70	1.584 -11.10
C2-N1	1.690 -10.17	1.690 -9.58	1.669 -2.62
O1...H4-O3	0.252 4.20	0.252 4.15	0.305 3.00
O3...H11-N1	0.209 3.71	0.208 3.75	0.248 3.71
O2...H12-N1	0.187 3.29	0.187 3.30	0.233 3.40
O2...H13-N1	0.175 3.27	0.174 3.27	0.221 3.58
O1...H2-C2	0.074 1.52	0.074 1.52	0.104 2.19

References

- Bader, R. F. W. (1990). *Atoms in Molecules - A Quantum Theory*. New York: Oxford University Press.
- Clementi, E. & Roetti, C. (1974). *Atomic Data and Nuclear Data Tables*, **14**(3–4), 177–478.
- Coppens, P. (1997). *X-Ray Charge Densities and Chemical Bonding*. New York: Oxford University Press.
- Destro, R., Roversi, P., Barzaghi, M. & Marsh, R. E. (2000). *J. Phys. Chem. A*, **104**(5), 1047–1054.
- Dittrich, B., Hübschle, C. B., Messerschmidt, M., Kalinowski, R., Girnt, D. & Luger, P. (2005). *Acta Cryst.* **A61**(3), 314–320.
- Flensburg, C., Larsen, S. & Stewart, R. F. (1995). *J. Phys. Chem.* **99**(25), 10130–10141.
- Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**(6), 909–921.
- Mebs, S., Messerschmidt, M. & Luger, P. (2006). *Z. Kristallogr.* **221**, 656–664.
- Stewart, R. F. (1976). *Acta Cryst.* **A32**(4), 565–574.
- Stewart, R. F. & Spackman, M. A., (1983). VALRAY Users Manual. Department of Chemistry, Carnegie-Mellon University: Pittsburgh.
- Su, Z. & Coppens, P. (1998). *Acta Cryst.* **A54**(5), 646–652.
- Volkov, A., Macchi, P., Farrugia, L. J., Gatti, C., Mallinson, P. R., Richter, T. & Koritsanszky, T., (2006). *XD2006, A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental or Theoretical Structure Factors*.