Anisotropic displacement parameters for hydrogen atoms using an ONIOM approach

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Synopsis *Ab initio* ONIOM cluster calculations are combined with TLS analysis of heavy atom ADPs from X-ray diffraction data to provide accurate estimates of hydrogen atom ADPs for charge density analysis.

Abstract X-ray diffraction data cannot provide anisotropic displacement parameters (ADPs) for hydrogen atoms, a major outstanding problem in charge density analysis of molecular crystals. Although neutron diffraction experiments are the preferred source of this information, for a variety of reasons they are possible only for a minority of materials of interest. To date, approximate procedures combine rigid body analysis of the molecular heavy atom skeleton, based on ADPs derived from the X-ray data, with estimates of internal motion provided by spectroscopic data, analyses of neutron diffraction data on related compounds, or *ab initio* calculations on isolated molecules. Building on these efforts, we present an improved methodology, incorporating information on internal vibrational motion from *ab initio* cluster calculations using the ONIOM approach implemented in *Gaussian03*. The method is tested by comparing model hydrogen atom ADPs with reference values, largely from neutron diffraction experiments, for a variety of molecular crystals: benzene, 1-methyluracil, α-glycine, xylitol and 2-methyl-4-nitroaniline. The results are impressive, and as the method is based on widely available software, and is in principle widely applicable, it offers considerable promise in future charge density studies of molecular crystals.

Keywords: anisotropic displacement parameters; hydrogen atoms; cluster calculations; charge density analysis; thermal motion

Supplementary material. TLS+ONIOM ADPs for H atoms (in units of 10^{-2} Å^2)

Table S1 1–methyluracil @ 21 K. First row: TLS+ONIOM results; second row: adjusted neutron reference results (McMullan & Craven, 1989); third row: differences.

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H3	ref.	1.56	1.06	2.53	–0.30	–	–
	calc.	1.58	1.07	2.65	–0.38	–	–
	Δ	*–0.02*	*–0.01*	*–0.12*	*0.07*	–	–
H5	ref.	1.99	1.17	3.42	0.34	–	–
	calc.	1.88	1.08	3.27	0.38	–	–
	Δ	*0.11*	*0.09*	*0.16*	*–0.05*	–	–
H6	ref.	1.60	1.20	2.84	–0.53	–	–
	calc.	1.61	1.23	3.32	–0.48	–	–
	Δ	*–0.01*	*–0.02*	*–0.48*	*–0.05*	–	–
H11	ref.	1.75	1.56	5.63	–0.58	–	–
	calc.	1.77	1.49	5.26	–0.48	–	–
	Δ	*–0.01*	*0.07*	*0.36*	*–0.11*	–	–
H12	ref.	2.28	4.10	3.21	0.33	–0.69	1.46
	calc.	2.01	3.80	2.70	0.40	–0.41	1.35
	Δ	*0.27*	*0.30*	*0.51*	*–0.07*	*–0.28*	*0.11*

Table S2 Benzene @ 110 K. First row: TLS+ONIOM results; second row: mass adjusted multi-temperature neutron reference results (Bürgi *et al.*, 2002); third row: differences.

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H1	ref.	4.94	2.56	5.50	0.93	0.29	0.12
	calc.	4.58	2.74	5.15	0.96	0.02	0.00
	Δ	*0.36*	*–0.18*	*0.35*	*–0.03*	*0.27*	*0.12*
H2	ref.	4.13	4.95	4.71	0.87	1.95	–0.32
	calc.	4.12	5.00	4.69	0.78	2.20	–0.46
	Δ	*0.01*	*–0.05*	*0.02*	*0.09*	*–0.25*	*0.14*
H3	ref.	4.86	4.00	4.45	–0.57	1.19	1.35
	calc.	4.47	4.18	4.05	–0.78	1.03	1.28
	Δ	*0.39*	*–0.18*	*0.40*	*0.21*	*0.16*	*0.07*

Table S3 α–glycine @ 23 K. First row: TLS+ONIOM results; second row: TLS + spectroscopy reference results (Destro *et al.*, 2000); third row: differences.

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H1	ref.	2.33	2.35	1.14	0.26	0.79	0.16
	calc.	2.33	3.77	1.16	0.70	0.95	0.43
	Δ	*0.00*	*–1.42*	*–0.02*	*–0.44*	*–0.16*	*–0.27*
H2	ref.	1.01	1.95	1.53	–0.16	0.43	–0.16
	calc.	1.28	2.03	1.63	–0.11	0.24	–0.14
	Δ	*–0.26*	*–0.08*	*–0.10*	*–0.05*	*0.19*	*–0.03*
H3	ref.	1.80	1.22	1.78	0.14	0.80	0.02
	calc.	2.21	1.34	2.39	0.13	0.78	0.09
	Δ	*–0.40*	*–0.12*	*–0.61*	*0.01*	*0.02*	*–0.07*
H4	ref.	2.78	1.25	2.25	0.24	1.32	0.35
	calc.	2.62	1.08	2.57	0.16	1.27	0.51
	Δ	*0.16*	*0.17*	*–0.32*	*0.08*	*0.04*	*–0.16*
H5	ref.	0.90	2.83	1.49	–0.16	0.24	–0.40
	calc.	1.17	2.76	1.52	–0.18	0.13	–0.47
	Δ	*–0.27*	*0.07*	*–0.04*	*0.03*	*0.11*	*0.07*

Table S4 Xylitol @ 123 K. First row: TLS+ONIOM results; second row: adjusted neutron reference results (Madsen *et al.*, 2003; Madsen *et al.*, 2004); third row: differences.

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H1A	ref.	3.19	2.73	2.59	0.77	–0.23	–1.08
	calc.	2.81	2.69	2.19	0.46	–0.07	–0.67
	Δ	*0.38*	*0.03*	*0.40*	*0.32*	*–0.16*	*–0.41*
H1B	ref.	1.93	3.93	2.77	–0.68	0.17	1.17
	calc.	1.92	3.27	2.67	–0.48	0.20	0.89
	Δ	*0.01*	*0.66*	*0.10*	*–0.19*	*–0.03*	*0.29*
H2	ref.	1.99	2.04	2.60	0.12	0.11	–0.70
	calc.	2.33	1.97	2.05	0.17	0.03	–0.50
	Δ	*–0.34*	*0.07*	*0.55*	*–0.05*	*0.08*	*–0.20*
H3	ref.	2.33	1.98	2.21	0.22	–0.04	–0.64
	calc.	2.35	2.10	2.17	0.20	0.02	–0.67
	Δ	*–0.02*	*–0.12*	*0.04*	*0.02*	*–0.05*	*0.03*
H4	ref.	2.37	2.85	1.59	–0.04	–0.07	0.45
	calc.	2.26	2.58	1.55	–0.01	0.03	0.23
	Δ	*0.11*	*0.27*	*0.04*	*–0.03*	*–0.11*	*0.23*
H5A	ref.	2.46	2.66	4.64	0.23	0.36	–1.74
	calc.	2.35	2.51	2.94	0.26	0.12	–1.08
	Δ	*0.12*	*0.15*	*1.71*	*–0.03*	*0.24*	*–0.66*
H5B	ref.	2.35	3.21	2.79	–0.01	–0.51	1.07
	calc.	2.42	3.01	1.94	0.17	–0.15	0.32
	Δ	*–0.07*	*0.20*	*0.85*	*–0.18*	*–0.35*	*0.75*
H11	ref.	1.70	3.15	2.10	–0.12	0.43	0.32
	calc.	1.90	3.71	2.24	0.14	0.46	0.15
	Δ	*–0.20*	*–0.56*	*–0.14*	*–0.26*	*–0.03*	*0.17*
H12	ref.	2.70	3.00	2.17	–0.46	0.68	–0.19
	calc.	2.94	3.31	1.71	–0.60	0.76	–0.20
	Δ	*–0.24*	*–0.30*	*0.46*	*0.15*	*–0.07*	*0.01*
H13	ref.	3.01	1.79	2.24	–0.10	0.10	0.21
	calc.	4.27	1.75	2.70	–0.27	–0.23	0.24
	Δ	*–1.25*	*0.03*	*–0.46*	*0.17*	*0.33*	*–0.02*
H14	ref.	3.17	1.97	2.73	0.82	–0.28	0.13
	calc.	3.46	2.03	2.35	0.83	–0.62	0.22
	Δ	*–0.30*	*–0.06*	*0.38*	*–0.01*	*0.33*	*–0.09*
H15	ref.	2.61	2.77	2.23	–0.62	0.02	–0.68
	calc.	2.82	3.31	2.53	–0.82	–0.29	–0.71
	Δ	*–0.21*	*–0.53*	*–0.30*	*0.20*	*0.32*	*0.03*

Table S5 MNA @ 100 K. First row: TLS+ONIOM results; second row: adjusted neutron reference results (Whitten, Turner *et al.*, 2006); third row: differences.

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
HNA	ref.	2.55	2.46	3.98	–0.19	–0.69	0.18
	calc.	2.02	3.08	5.47	–0.36	–0.89	–0.43
	Δ	*0.53*	*–0.62*	*–1.49*	*0.16*	*0.20*	*0.61*
(NB	ref.	3.06	1.95	4.95	0.33	–0.84	0.51
	calc.	2.92	2.15	5.19	0.40	–0.54	0.72
	Δ	*0.13*	*–0.19*	*–0.24*	*–0.07*	*–0.30*	*–0.21*
H3	ref.	2.59	1.53	3.95	0.30	–0.81	0.09
	calc.	2.91	1.67	4.08	0.16	–0.74	0.27
	Δ	*–0.31*	*–0.14*	*–0.14*	*0.14*	*–0.07*	*–0.17*
H5	ref.	2.05	1.96	4.12	–0.40	–0.72	0.16
	calc.	2.29	2.35	4.20	–0.61	–0.87	–0.12
	Δ	*–0.24*	*–0.39*	*–0.08*	*0.21*	*0.15*	*0.28*
H6	ref.	2.85	1.79	4.55	0.09	–0.25	0.33
	calc.	2.97	1.66	4.59	0.15	–0.81	0.24
	Δ	*–0.13*	*0.13*	*–0.03*	*–0.06*	*0.56*	*0.09*
H7A	ref.	3.75	3.76	2.56	–0.78	–0.84	0.12
	calc.	3.77	4.13	2.48	–0.80	–1.06	0.11
	Δ	–0.02	–0.37	0.08	0.01	0.22	0.01
H7B	ref.	2.44	4.46	4.06	–0.82	0.50	–0.33
	calc.	2.19	4.37	4.20	–0.69	0.55	–0.42
	Δ	*0.25*	*0.10*	*–0.14*	*–0.13*	*–0.06*	*0.10*
H7C	ref.	3.53	1.94	5.98	0.01	–1.31	0.24
	calc.	3.62	1.94	5.22	–0.14	–1.02	0.17
	Δ	*–0.09*	*0.01*	*0.76*	*0.16*	*–0.29*	*0.07*