SUPPLEMENTARY MATERIALS

Statistical analysis of multipole-model-derived structural parameters and charge-density properties from high-resolution X-ray diffraction experiments

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S1. Additional figures

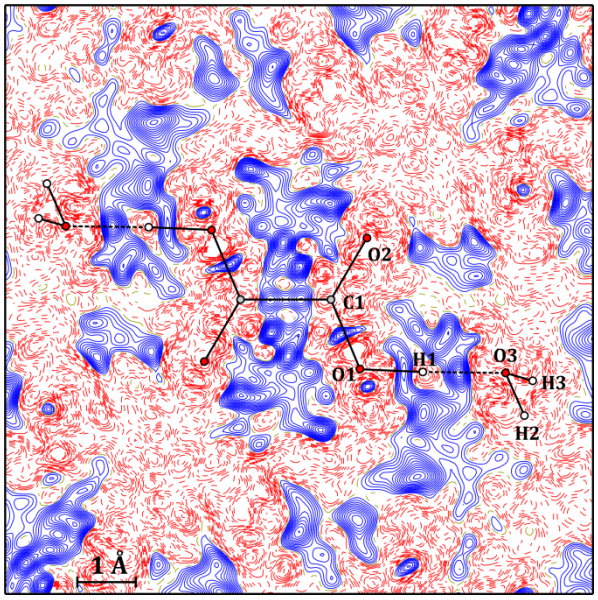
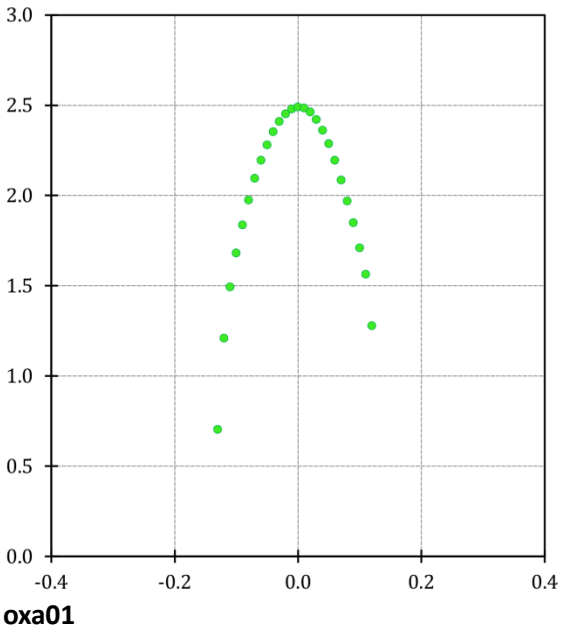
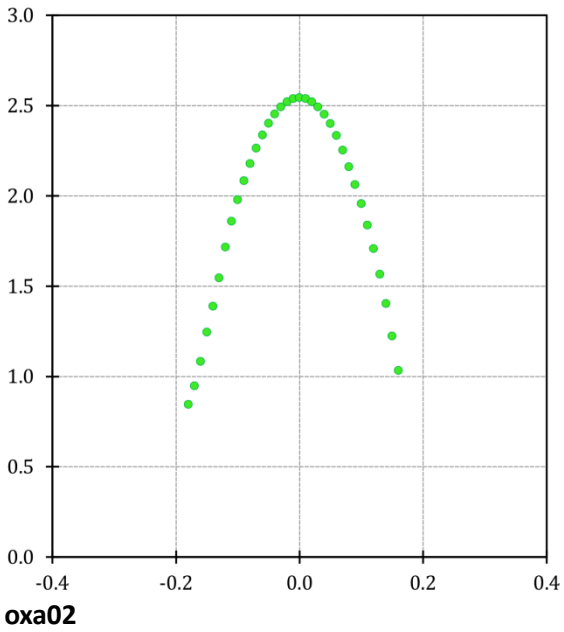


Figure S1. Sum of residual density maps across all 13 high-resolution measurements (C1-O2-C1$_{(1-x,\ 1-y,\ 1-z)}$ plane; contours at 0.05 e·Å^{-3}, blue lines – positive values, red – negative).



oxa01



oxa02

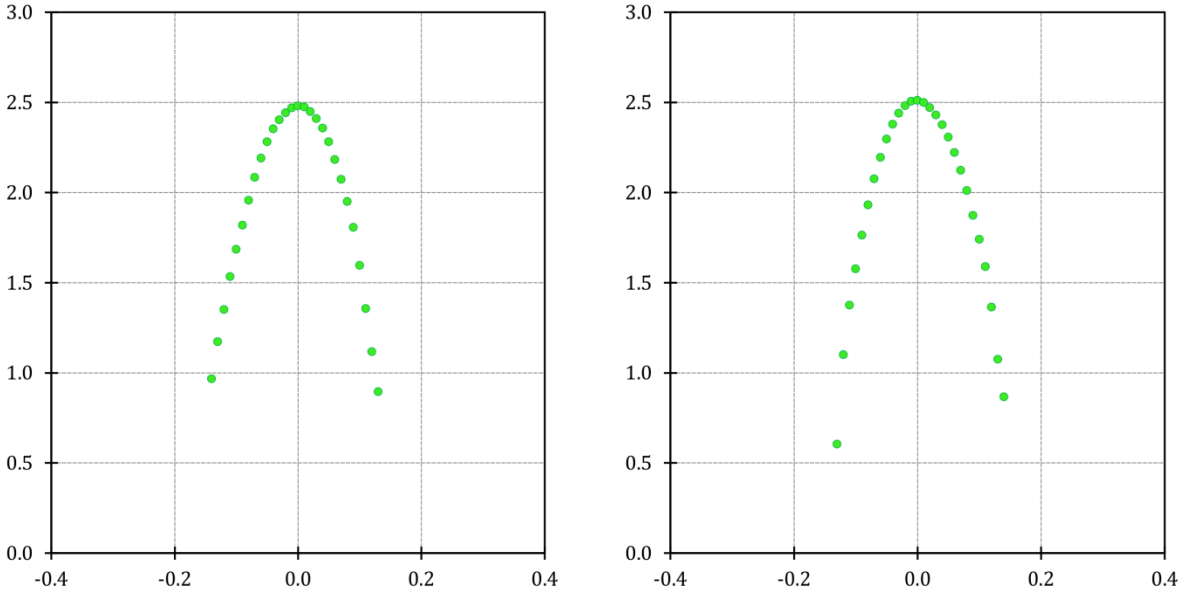
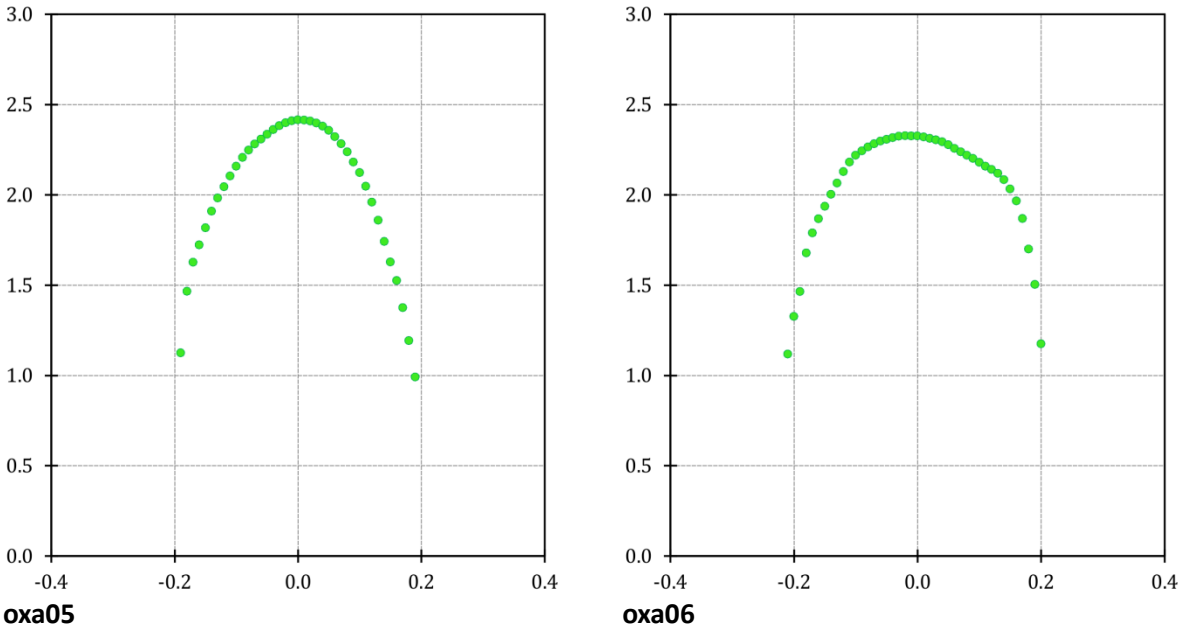
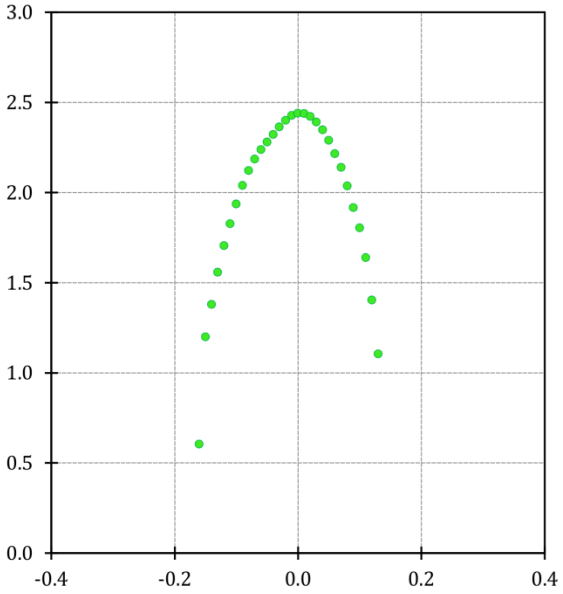
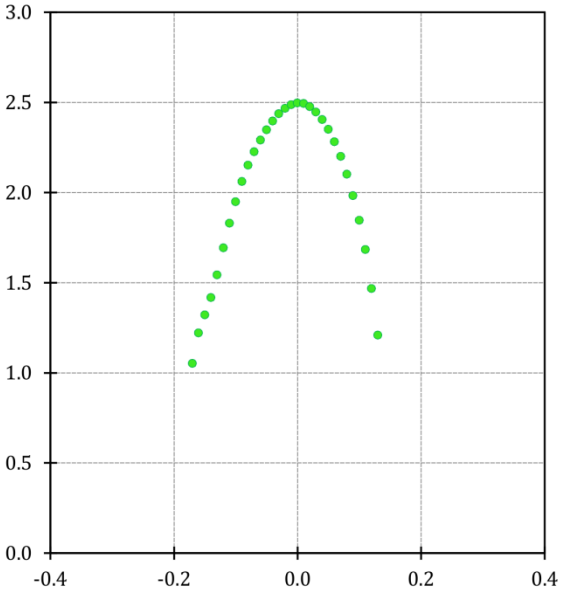


Figure S2. Fractal dimension plots for all oxalic acid datasets (horizontal axis – residual density (ϱres) given in e·Å^{-1}; vertical axis – fractal dimension (df)).



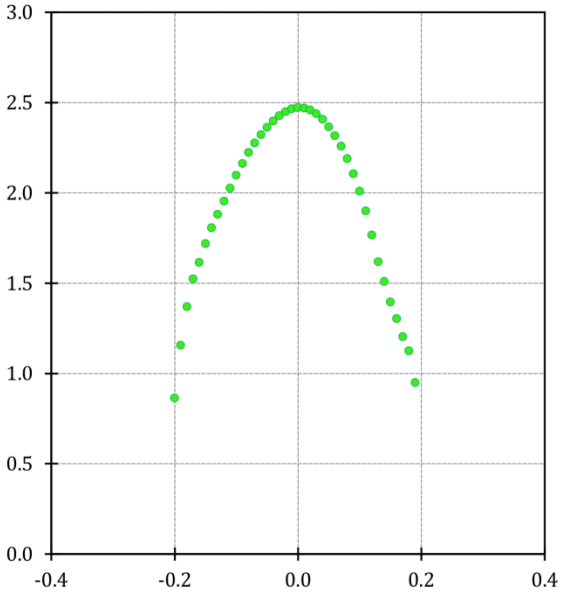


oxa07

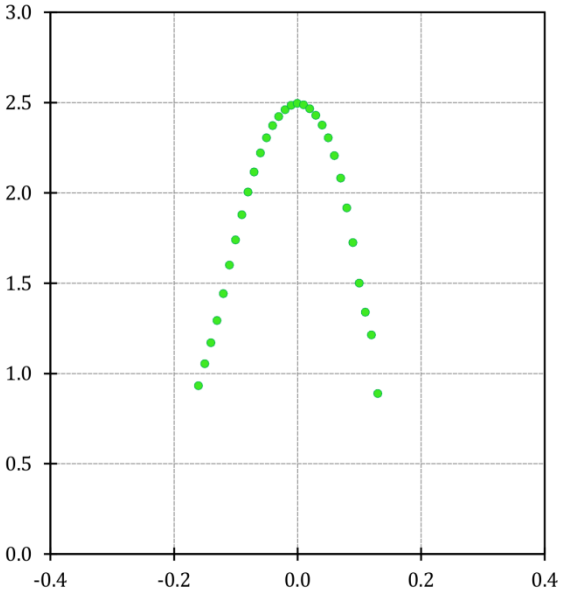


oxa08

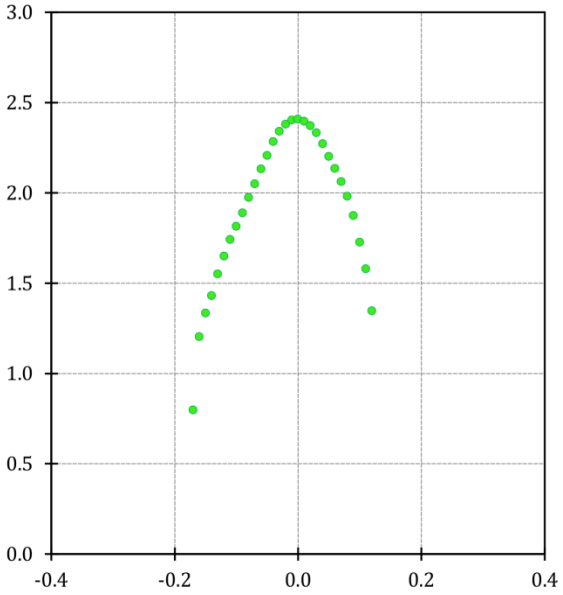
Figure S2 ***(continued)*****.** Fractal dimension plots for all oxalic acid datasets.

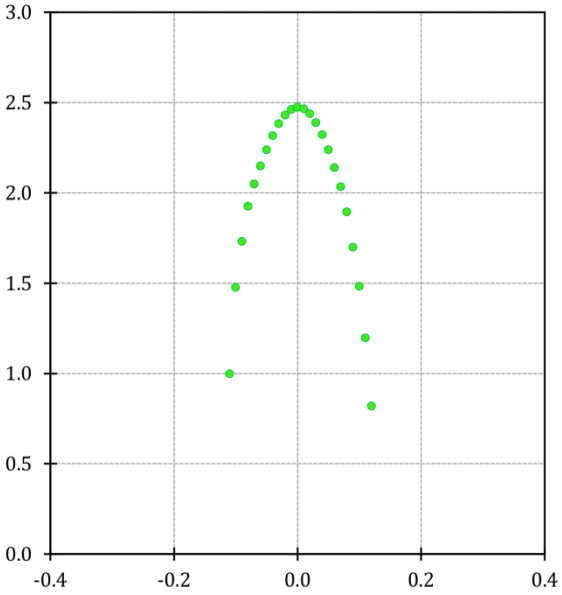


oxa09



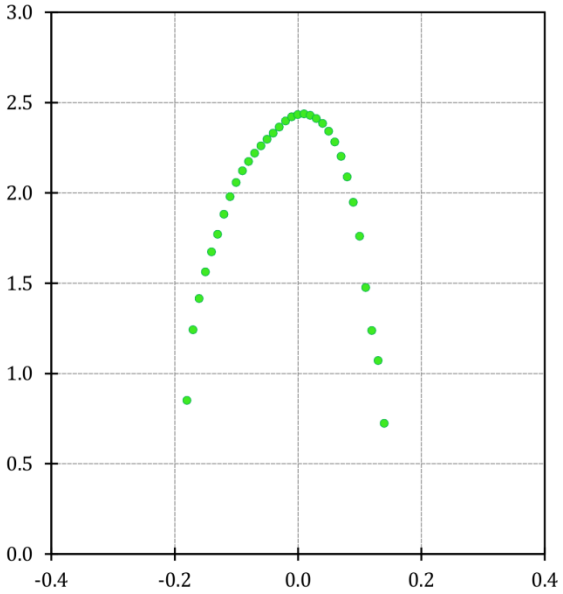
oxa10





oxa11 **oxa12**

Figure S3 ***(continued)*****.** Fractal dimension plots for all oxalic acid datasets.



oxa13

Figure S4 ***(continued)*****.** Fractal dimension plots for all oxalic acid datasets.

S2. Additional tables

Table S1. Equivalent of Table 6 for all datasets refined with no I/σI cut-off. Colour coding: yellow – no difference when compared to Table 6; green – the same mean value with slightly different standard deviation; grey – value not statistically different (*i.e.*, within 1σ).

Atom	*Local symmetry*	*Multipole populations*						
		κ	Pv	P10	P11+	P11-	P20	P21+
O1	*m*	0.993(7)	6.185(51)	0.001(6)	−0.054(5)	−0.044(7)	−0.008(13)	−0.003(19)
O2	*m*	0.993(8)	6.185(44)	−0.009(10)	−0.072(10)	−0.007(7)	−0.065(16)	−0.004(12)
C1	*m*	0.998(21)	4.055(102)	0.004(21)	0.115(21)	0.021(18)	−0.313(16)	−0.004(14)
O3	*mm*2	0.989(8)	6.286(61)	−0.069(6)	0.002(9)	0.0001(75)	−0.001(9)	0.004(14)
H1	∞	–	0.630(28)	0.087(6)	−0.002(15)	0.041(13)	0.109(15)	0.0004(104)
H2	∞	–	0.859(29)	0.157(10)	−0.006(27)	−0.004(34)	0.095(16)	−0.005(16)
H3	∞	–	0.801(26)	0.163(11)	−0.045(60)	−0.008(38)	0.072(25)	−0.011(32)
		P21-	P22+	P22-	P30	P31+	P31-	P32+
O1	*m*	0.002(8)	−0.039(14)	0.011(15)	−0.010(8)	0.016(6)	−0.018(5)	0.0001(53)
O2	*m*	0.004(11)	−0.045(10)	−0.003(11)	−0.009(6)	0.005(7)	−0.005(4)	−0.002(4)
C1	*m*	−0.009(13)	0.106(19)	−0.047(19)	0.010(10)	0.005(9)	−0.022(9)	0.006(15)
O3	*mm*2	−0.003(18)	0.053(7)	0.017(23)	−0.040(5)	0.012(5)	0.007(6)	−0.035(12)
H1	∞	0.018(11)	0.002(12)	−0.001(9)	–	–	–	–
H2	∞	0.008(22)	−0.003(6)	−0.004(8)	–	–	–	–
H3	∞	−0.012(26)	0.036(23)	0.005(13)	–	–	–	–
		P32-	P33+	P33-	P40	P41+	P41-	P42+
O1	*m*	0.003(3)	0.053(5)	0.009(5)	0.005(8)	−0.001(9)	−0.005(7)	−0.001(6)
O2	*m*	0.002(5)	0.030(4)	0.002(4)	−0.005(10)	0.001(9)	0.0002(66)	−0.001(11)
C1	*m*	0.0002(149)	0.473(16)	−0.057(15)	0.081(16)	0.007(17)	−0.008(10)	0.007(21)
O3	*mm*2	−0.013(8)	0.016(8)	−0.009(8)	−0.011(5)	−0.003(9)	0.007(10)	−0.006(12)
		P42-	P43+	P43-	P44+	P44-		
O1	*m*	0.009(8)	0.006(7)	−0.005(10)	0.011(13)	0.014(8)		
O2	*m*	0.001(4)	−0.002(9)	−0.001(10)	0.009(8)	−0.001(9)		
C1	*m*	−0.002(16)	−0.013(24)	−0.008(15)	−0.034(20)	0.021(21)		
O3	*mm*2	0.001(9)	−0.004(8)	−0.005(9)	0.008(5)	0.010(9)		

Table S2. Numerical values for plots presented in Figure 5. L denotes the sample mean of the Laplacian (L=2ϱ); d denotes distance from the BCP to the atomic centre (positive values indicate direction towards O1 atom, negative towards the C1 atom; BCP position is given in bold).

d / Å	ϱ / e·Å^{-3}	sϱ / e·Å^{-3}	sϱ/ϱ / e·Å^{-3}	L / e·Å^{-5}	sL / e·Å^{-5}	sL/L / e·Å^{-5}
–0.39	581.81	97.42	0.17	–1621335.15	1257389.63	0.8
–0.36	297.47	49.04	0.16	–139347.46	68987.32	0.5
–0.33	153.54	24.95	0.16	–13211.02	10499.58	0.8
–0.30	79.99	12.79	0.16	5712.14	1247.51	0.2
–0.27	42.18	6.58	0.16	6529.53	393.04	0.1
–0.24	22.68	3.39	0.15	4573.64	505.86	0.1
–0.21	12.65	1.74	0.14	2801.75	367.59	0.1
–0.18	7.52	0.89	0.12	1607.87	231.07	0.1
–0.15	4.92	0.45	0.09	879.44	136.42	0.2
–0.12	3.63	0.23	0.06	456.29	77.68	0.2
–0.09	3.00	0.12	0.04	218.47	43.03	0.2
–0.06	2.71	0.08	0.03	88.90	23.21	0.3
–0.03	2.58	0.06	0.02	21.09	12.16	0.6
0.00	**2.50**	**0.06**	**0.02**	**–29.53**	**2.70**	**0.1**
0.03	2.52	0.06	0.02	–27.03	3.48	0.1
0.06	2.55	0.06	0.02	–23.06	4.09	0.2
0.09	2.60	0.06	0.02	–18.78	4.29	0.2
0.12	2.68	0.06	0.02	–14.86	4.23	0.3
0.15	2.77	0.06	0.02	–11.75	4.00	0.3
0.18	2.90	0.08	0.03	–9.82	3.65	0.4
0.21	3.07	0.09	0.03	–9.48	3.24	0.3
0.24	3.27	0.11	0.03	–11.16	2.88	0.3
0.27	3.52	0.14	0.04	–15.45	2.84	0.2
0.30	3.81	0.16	0.04	–22.97	3.52	0.2
0.33	4.14	0.20	0.05	–34.37	5.00	0.1
0.36	4.51	0.23	0.05	–49.90	6.96	0.1
0.39	4.92	0.26	0.05	–68.73	8.78	0.1
0.42	5.35	0.29	0.05	–87.16	9.43	0.1
0.45	5.80	0.32	0.06	–94.71	11.51	0.1
0.48	6.28	0.36	0.06	–65.67	33.92	0.5
0.51	6.82	0.43	0.06	59.07	100.76	1.7
0.54	7.60	0.62	0.08	410.35	260.44	0.6
0.57	9.05	1.14	0.13	1268.98	617.24	0.5
0.60	12.34	2.52	0.20	3211.42	1372.72	0.4
0.63	20.38	6.02	0.30	7317.73	2849.51	0.4
0.66	40.23	14.65	0.36	15124.00	5211.35	0.3
0.69	89.02	35.77	0.40	25932.98	6246.96	0.2
0.72	208.48	87.42	0.42	14857.36	22022.64	1.5
0.75	501.47	214.71	0.43	–264747.89	311371.42	1.2
0.78	1226.40	533.26	0.43	–14769727.38	27897210.07	1.9

Table S3. Definitions of parameters used to quantify electrostatic potential (ESP) mapped onto molecular surfaces (Murray & Politzer, 1998; Murray *et al.*, 2000).

Quantity	*Description*
VSri	ESP value on the molecular surface computed at point ri
n+	number of grid points corresponding to the positive value of ESP
n-	number of grid points corresponding to the negative value of ESP
VS,max	maximal value of the surface ESP value
VS,min	minimal value of the surface ESP value
VS+=1n+i=1n+VS+ri	positive average of the potential over the surface
VS-=1n-i=1n-VS-ri	negative average of the potential over the surface
VS=1n++n-i=1n+VS+ri+i=1n-VS-ri	overall average of the potential over the surface
Π=1n++n-i=1n++n-VSri-VS	average deviation of VSri
σ+2=1n+i=1n+VS+ri-VS+2	positive variance of VSri
σ-2=1n-i=1n-VS-ri-VS-2	negative variance of VSri
σtot2=σ+2+σ-2	total variance of VSri
ν=σ+2σ-2σtot22	degree of balance between the positive and negative surface potentials