Modeling hydroxyl and water H atoms

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Abstract

The coordinates of hydroxyl (alcohol, phenol, *etc.*) and water H atoms can be easily calculated, within acceptable approximation, by combined geometric and force-field calculations on the basis of hydrogen-bonding interactions. To perform this kind of calculation the computer program *HYDROGEN* has been developed.

1. Introduction

X-ray diffraction data are not always accurate enough to allow direct localization and refinement of H atoms. This is not a relevant problem when dealing with H atoms belonging to rigid groups of known geometry, such as methylene, methyne, benzene, *etc.*, for which the H-atom coordinates can be calculated on the basis of geometric considerations. But this is not possible in the case of hydroxyl groups and water molecules which assume orientations depending on their environments. Geometric considerations can help in finding the most suitable orientations which can be improved by energy calculations based on the fact that these groups are usually involved in moderate or weak hydrogen bonds involving energy which is mainly Coulombic in nature (Jeffrey & Saenger, 1994).

A computer program has been developed for application to small-molecule structures; it is based on the geometrical inspection of the environments of the OH and H_2O groups and on the analysis of the van der Waals and Coulomb nonbonded energy profiles. A fundamental aspect is that the OH group or the water molecule is under the influence of the electrostatic field created by the distribution of charges in the *entire* environment. So it is necessary to know the *entire* charge distribution for which the drastic approximation of assuming point atom charges is usually performed. This is one of the most difficult aspects of the treatment, as the values of the partial charges calculated by Mulliken population analysis vary quite relevantly with the type of molecular orbital (MO) calculation. *Ab initio* calculations on a suitable basis set certainly constitute the best approach, but it is found that the semiempirical 'extended Hückel' method gives reasonably acceptable values. In the case of ionic inorganic compounds, the partial charges on atoms can be evaluated on the basis of the bond-valence model (Brown, 1992; Brown & Altermatt, 1985). Another relevant approximation is performed assuming that the atom partial electric charge does not change when changing the reciprocal position of the groups involved.

2. Geometric criteria

To obtain starting coordinates for the hydroxyl H atom to be submitted to the force-field refinement, first all the atoms surrounding the O atom are considered and, according to their nature, the possible direction of the hydrogen-bond acceptor atom (A = O, N, F, Cl, S, Br, I) is defined, choosing the C—O$\cdots A$ angle nearest to 109.5°. Then the starting coordinates of H are calculated from the C1—C2—O—H$\cdots$O system (where C1 and C2 are not necessarily C atoms), the geometry of which is determined by the known positions of the non-H atoms, assuming for the O—H bond distance the value given by the user in the input file of the atomic partial charges.

The starting coordinates of the H atoms in the case of a water molecule are derived from the environment of its O atom, considering the couple of directions forming the shortest contacts and an angle nearest to 107.7°. This value for the water H—O—H angle is the average of those found by neutron diffraction in crystals; these values have been found to be dependent on the angle O$\cdots$O$w\cdots$O formed by the water with two acceptor O atoms (Chiari & Ferraris, 1982; Steiner, 1998). Then the water molecule is built up in the plane defined by the two directions; it is placed symmetrically with respect to the bisector of the angle formed by these directions. As for the hydroxyl, the O—H bond distance is given by the user in the input file of atom partial charges.

3. Force field

The atom–atom nonbonded potential-energy calculations are based on the function

$$E_{ij} = B_{ij}\exp(-C_{ij}r_{ij}) - A_{ij}r_{ij}^{-6},$$

with parameters A, B and C according to Mirsky (1978), and that for Coulomb energy

$$E_{C_{ij}} = q_i q_j r_{ij}^{-1}.$$

To increase the directional effects due to hydrogen bonding, the Coulomb energy is multiplied by the Gaussian function

$$F_h = 1.0 + y_0 \exp[-2.773(r_{ij} - 1.8)^2]$$

which exalts the Coulomb energy contributions when the atom–atom distance is near 1.8 Å. The y_0 parameter is given by the user in the input file of atom partial charges (the value of 5.0 for this parameter was found empirically to be proper in many cases). To eliminate unacceptable contacts, an additional contribution, $E_r = \exp[-10(r_{ij} - 1.7)] - 1$, is added to the total energy when the distance is less than 2.0 Å.

These functions make the calculated values of the energy unrealistic, so only differences of energy are considered, with the purpose of finding proper minima. In fact, the force-field refinement is carried out looking for the minima in the difference-energy profiles obtained by rotating the hydroxyl about the C—O bond, or about the two O—H bonds in the case of a water molecule.

Table 1. *Comparison of H-atom coordinates and hydrogen-bonding geometry for examples of hydroxyls taken from structures quoted in the literature*

For each entry, the first line gives the experimental data (with s.u.'s omitted to reduce overcrowding of data), the second line the calculated values. *d* is the displacement of the calculated H-atom site from the experimental one. The atom labels are those used in the literature. The equivalent position always refers to the acceptor. Only the shortest H···A contacts are considered. Distances are in Å, angles in °.

	x	y	z	D—H	D···A/d	H···A	D—H···A	Equivalent position
C₃H₇NO₃.H₂O neutron (Frey *et al.*, 1973), LSE								
H3	0.2286	0.3813	0.5043	0.958	2.785	1.843	166.8	O1 at
	0.2281	0.3956	0.4952	0.938	0.180	1.891	158.4	x−1/2,1/2−y,1−z
C₃H₇NO₅S.H₂O neutron (Ramanadham *et al.*, 1973), LCY								
H7	0.3347	0.2932	0.3575	1.085	2.524	1.439	178.4	O1W at
	0.3868	0.2981	0.3477	0.938	0.376	1.674	148.9	x,y,z
C₄H₉ClN₂O₃.H₂O neutron (Koetzle *et al.*, 1972), GGL								
H9	0.89365	−0.14516	0.40306	1.003	2.644	1.658	166.8	O4W at
	0.89744	−0.13692	0.41267	1.003	0.122	1.688	158.0	x,y−1,z
[C₁₀H₃₀N₄][HPO₄].3H₂O neutron (Cohen *et al.*, 1997), SPH								
H4O	0.2956	0.2119	0.4598	1.004	2.637	1.650	166.8	O2 at
	0.2784	0.2138	0.4951	0.937	0.325	1.800	147.2	1/2+x,1/2−y,z
C₁₀H₁₂O₂ X-ray (Barcon *et al.*, 1997), TMB								
H2	0.4050	−0.1590	−0.0170	0.92	2.640	1.72	178	O1 at
	0.4060	−0.1484	−0.0048	0.850	0.121	1.799	169.5	1−x,−y,−z
C₁₄H₁₅NO₃ X-ray (Moreno-Fuquen *et al.*, 1997), POT								
H2	0.8216	0.3470	0.2413	0.90	2.528	1.65	164	O1 at
	0.8182	0.3427	0.2418	0.849	0.058	1.705	162.6	x,y,z
C₉H₁₀ClNO X-ray (Jerslev & Larsen, 1992), OXI								
H1O	0.421	0.562	−0.055	0.88	2.823	2.01	154	N at
	0.3906	0.5619	−0.0738	0.850	0.250	2.133	138.1	1−x,1−y,−z
C₄H₉NO₃ X-ray (Janczak *et al.*, 1997), THREO								
H6	0.1880	0.2240	0.5410	0.89	2.651	1.82	154	O1 at
	0.1879	0.2158	0.5406	0.850	0.062	1.841	158.8	x−1/2,1/2−y,1−z
C₁₀H₈O₃ X-ray (Lalancette *et al.*, 1997), IDCA								
H3	1.0200	0.8550	0.8580	1.03	2.635	1.65	159	O1 at
	0.9978	0.8470	0.8336	0.850	0.231	1.877	147.8	2−x,1/2+y,3/2−z
C₈H₉BN₂O X-ray (Robinson *et al.*, 1998), BZB								
H1	−0.0860	0.2643	0.9070	0.82	2.810	2.02	161	N3 at
	−0.0529	0.2646	0.9011	0.850	0.183	1.995	160.4	x+1/2,y+1/2,z+1/2
C₁₂H₁₂O₂ X-ray (Chinnakali *et al.*, 1998), DINA								
H1O2	0.2190	0.2740	0.8958	0.96	2.546	1.65	154	O1 at
	0.2311	0.2960	0.8971	0.850	0.227	1.813	143.2	x,y,z
C₆H₁₁NO₄ neutron (Noordik & Jeffrey, 1977), GLP								
H2O	0.7813	0.5645	0.5782	0.998	2.737	1.760	165.4	N at
	0.7822	0.5744	0.5702	0.938	0.154	1.860	154.4	3/2−x,1−y,1/2+z
H4O	0.6803	0.7556	0.3377	0.966	2.836	2.032	139.4	O5 at
	0.6826	0.7528	0.3307	0.938	0.063	2.059	139.2	1/2+x,3/2−y,1−z
Na₂B₄O₅(OH)₄.8H₂O neutron (Levy & Lisensky, 1978), NAB								
H4	0.2384	0.2597	0.2193	0.958	2.883	1.937	168.9	O9 at
	0.2364	0.2610	0.2244	0.964	0.074	1.932	168.2	1/2−x,y−1/2,1/2−z
H5	0.1127	0.5411	0.5379	0.982	2.731	1.755	172.8	O3 at
	0.1095	0.5581	0.5255	0.970	0.232	1.829	153.3	x,1−y,1/2+z
C₉H₉N₃O₉.H₂O neutron (Takusagawa *et al.*, 1979), NUC								
HO2′	−1.0188	−0.4785	−0.6895	0.974	2.775	1.874	152.5	O2 at
	−1.0140	−0.4753	−0.6951	0.976	0.066	1.904	147.2	−x−2,y−1/2,−z−1
HO3′	−1.1473	−0.5249	−0.3475	0.951	2.736	1.928	141.4	O5A at
	−1.1471	−0.5274	−0.3690	0.976	0.143	1.950	135.8	x−1,y,z
HO5′	−0.4991	−0.6984	−0.2114	1.014	2.570	1.566	169.8	OW at
	−0.5121	−0.7030	−0.2347	0.976	0.192	1.658	154.0	x,y,z

Table 1 (*cont.*)

	x	*y*	*z*	*D*−H	*D*··· *A*/*d*	H···*A*	*D*−H···*A*	Equivalent position
$C_6H_{12}O_5.H_2O$ neutron (Takagi & Jeffrey, 1978), RHA								
H1O	0.1725	−0.3467	−0.0092	0.979	2.715	1.740	174.0	O2 at
	0.1457	−0.3663	0.0230	0.969	0.352	1.826	151.0	−*x*,*y*−1/2,−*z*
H2O	−0.1897	0.0419	0.3359	0.974	2.784	1.814	173.2	O*W* at
	−0.1727	0.0620	0.3448	0.969	0.213	1.876	154.9	−*x*,*y*−1/2,1−*z*
H3O	0.1366	0.0227	0.7227	0.954	2.809	1.949	148.7	O5 at
	0.1413	0.0265	0.7206	0.969	0.051	1.962	144.6	*x*,*y*,1+*z*
H4O	0.3587	0.3040	0.4940	0.968	2.781	1.820	171.8	O*W* at
	0.3641	0.3042	0.4970	0.969	0.045	1.826	167.7	*x*,*y*,*z*
$C_5H_{10}O_5$ neutron (Longchambon *et al.*, 1985), ARAB								
H1O	−0.0938	−0.1361	0.5430	0.979	2.753	1.785	169.2	O5 at
	−0.1066	−0.1285	0.5401	0.938	0.098	1.821	172.0	−*x*,−*y*,1−*z*
H2O	−0.2630	−0.0844	0.7736	0.988	2.707	1.726	171.6	O3 at
	−0.2387	−0.0871	0.7718	0.938	0.150	1.809	159.3	−*x*−1,*y*−1/2,3/2−*z*
H3O	−0.5658	0.1655	0.7997	0.979	2.796	1.825	170.9	O4 at
	−0.5323	0.1747	0.8067	0.938	0.215	1.930	152.6	−*x*−1,*y*−1/2,3/2−*z*
H4O	−0.1460	0.4791	0.6494	0.981	2.769	1.817	163.0	O2 at
	−0.1548	0.4841	0.6369	0.938	0.169	1.900	153.1	−*x*,1/2+*y*,3/2−*z*
$C_{15}H_{22}O_4$ X-ray (Baures *et al.*, 1992), HYM								
H3O	0.175	1.487	0.115	0.99	2.894	1.97	155	O4′ at
	0.1848	1.4826	0.1199	0.850	0.153	2.081	160.3	*x*,1+*y*,*z*
H4O	0.173	1.212	0.029	0.96	2.751	1.86	154	O4′ at
	0.1734	1.1926	0.0281	0.850	0.147	1.978	150.8	*x*,1+*y*,*z*
H3O′	0.122	0.907	0.020	0.87	2.688	1.82	173	O4 at
	0.1185	0.8918	0.0317	0.850	0.202	1.891	155.6	*x*,*y*,*z*
H4O′	0.047	0.385	−0.002	0.79	2.684	1.90	177	O3′ at
	0.0421	0.3898	0.0056	0.850	0.129	1.841	171.0	−*x*,*y*−1/2,−*z*
$C_6H_{12}O_5$ X-ray (Szarek *et al.*, 1997), FRU								
H1	1.2480	0.2390	0.5330	0.71	2.748	2.04	175	O6 at
	1.2738	0.2303	0.5284	0.850	0.193	1.908	169.1	1/2+*x*,1/2−*y*,1−*z*
H2	0.9250	0.5740	0.3790	0.82	2.744	1.95	164	O5 at
	0.8789	0.5869	0.3932	0.850	0.363	1.931	159.8	3/2−*x*,1−*y*,*z*−1/2
H4	0.9550	0.7640	0.8080	0.77	2.783	2.03	168	O1 at
	0.9638	0.7429	0.8172	0.850	0.234	2.013	150.2	2−*x*,1/2+*y*,3/2−*z*
H5	0.8510	0.4560	0.7652	0.74	2.692	1.98	162	O4 at
	0.8569	0.4454	0.7617	0.850	0.114	1.869	162.8	2−*x*,*y*−1/2,3/2−*z*
$C_6H_{12}O_6$ neutron (Brown & Levy, 1979), GLU								
H8	0.27529	0.56742	−0.42998	0.970	2.849	1.915	160.9	O5 at
	0.29353	0.55646	−0.42915	0.938	0.250	1.970	155.3	1/2−*x*,1−*y*,*z*−1/2
H9	0.44860	0.77768	−0.20321	0.967	2.778	1.821	170.1	O6 at
	0.46340	0.78705	−0.13052	0.938	0.417	1.953	145.6	1−*x*,1/2+*y*,−1/2−*z*
H10	0.72463	0.71369	0.11783	0.975	2.708	1.758	164.9	O2 at
	0.72096	0.71029	0.11812	0.938	0.063	1.806	160.4	1/2+*x*,3/2−*y*,−*z*
H11	0.75171	0.50818	0.23235	0.972	2.777	1.819	167.7	O4 at 3/2−*x*,1−*y*,*z*+1/2
H11*c*	0.72821	0.52178	−0.11441	0.938	2.777	1.873	161.0	O4 at
H11···H11*c* 1.754 (see text)								3/2−*x*,1−*y*,*z*−1/2
H12	0.41270	0.28609	0.07009	0.966	2.714	1.758	169.7	O3 at
	0.39743	0.29402	0.06282	0.938	0.201	1.823	157.6	1−*x*,*y*−1/2,1/2−*z*
$C_{12}H_{22}O_{11}.H_2O$ neutron (Gress & Jeffrey, 1977), MLT								
H2O	0.5056	0.4519	0.0751	0.975	2.789	1.835	165.4	O3′ at
	0.5308	0.4496	0.0846	0.939	0.153	1.861	169.3	*x*,*y*,*z*
H3O	0.1695	0.3404	−0.2150	0.973	2.757	1.798	167.7	O*W* at
	0.1831	0.3430	−0.2148	0.938	0.077	1.848	162.9	*x*−1,*y*,*z*−1
H4O	0.0018	0.1806	−0.1874	0.961	2.801	1.927	150.0	O2′ at
	0.0188	0.1657	−0.1826	0.938	0.243	1.934	152.8	−*x*,*y*−1/2,−*z*
H6O	0.3797	0.0769	0.3118	0.971	2.807	1.846	169.9	O1′ at
	0.3667	0.0823	0.3118	0.938	0.103	1.902	161.3	1−*x*,*y*−1/2,1−*z*
H1′O	0.1151	0.5813	0.6628	0.976	2.768	1.812	165.6	O6 at
	0.1342	0.5750	0.6670	0.938	0.137	1.865	161.1	−*x*,1/2+*y*,1−*z*

Table 1 (*cont.*)

	x	y	z	$D-$H	$D\cdots A/d$	H$\cdots A$	$D-$H$\cdots A$	Equivalent position
H2′O	0.1767	0.6887	0.4140	0.968	2.800	1.849	166.6	O6′ at
	0.1525	0.6846	0.4195	0.938	0.151	1.921	155.2	$1-x,1/2+y,1-z$
H3′O	0.2303	0.5789	0.1346	0.962	2.769	1.824	166.7	O4 at
	0.2746	0.5893	0.1510	0.938	0.304	1.870	159.7	$-x,1/2+y,-z$
H6′O	0.7296	0.3299	0.5867	0.980	2.730	1.762	169.1	OW at
	0.7350	0.3383	0.5697	0.938	0.226	1.879	150.1	x,y,z

Table 2. *Comparison of H-atom coordinates and hydrogen-bonding geometry for examples of water molecules taken from structures quoted in the literature*

For each entry, the first line gives the experimental data (with s.u.'s omitted to reduce overcrowding of data), the second line the calculated values. d is the displacement of the calculated H-atom site from the experimental one. The atom labels are those used in the literature. The equivalent position always refers to the acceptor. Only the shortest H$\cdots A$ contacts are considered. Distances are in Å, angles in °.

	x	y	z	$D-$H	$D\cdots A/d$	H$\cdots A$	$D-$H$\cdots A$	Equivalent position
$C_3H_7NO_3.H_2O$ neutron (Frey *et al.*, 1973), LSE								
H1W	0.0439	−0.0532	0.2199	0.946	2.809	1.868	173.2	O1 at
	0.0462	−0.0507	0.2148	0.938	0.045	1.882	169.3	$1/2-x,-y,z-1/2$
H2W	−0.0042	0.0334	0.4194	0.955	2.877	1.922	177.4	O3 at
	0.0013	0.0381	0.4149	0.938	0.080	1.947	170.4	$x-1/2,1/2-y,1-z$
$C_3H_7NO_5S.H_2O$ neutron (Ramanadham *et al.*, 1973), LCY								
H8	0.2877	0.2210	0.6559	0.930	2.814	1.887	174.3	O4 at
	0.2465	0.2211	0.6663	0.939	0.291	1.929	156.6	$x-1/2,1/2-y,1-z$
H9	0.1573	0.2879	0.6856	0.980	2.780	1.821	165.2	O5 at
	0.1924	0.2981	0.6874	0.938	0.311	1.863	164.7	$x-1,y,1+z$
$C_{12}H_{22}O_{11}.H_2O$ neutron (Gress & Jeffrey, 1977), MLT								
H1W	0.8039	0.4407	0.7304	0.965	2.832	1.871	173.4	O6 at
	0.8665	0.4373	0.7340	0.937	0.307	1.948	156.4	$1-x,1/2+y,1-z$
H2W	0.6652	0.3580	0.7782	0.968	2.791	1.834	169.1	O3 at
	0.6677	0.3718	0.7818	0.938	0.212	1.913	154.4	$x,y,1+z$
$C_6H_{12}O_5.H_2O$ neutron (Takagi & Jeffrey, 1978), RHA								
H1W	0.2584	0.5787	0.3480	0.967	2.909	1.981	160.4	O1 at
	0.2774	0.5760	0.3345	0.969	0.184	1.962	165.5	$x,1+y,z$
H2W	0.4359	0.5886	0.4693	0.975	2.744	1.771	175.2	O4 at
	0.4394	0.5785	0.4891	0.969	0.155	1.784	170.4	$1-x,1/2+y,1-z$
$C_4H_8N_2O_3.H_2O$ neutron (Verbist *et al.*, 1972), ASP								
H1W	0.18750	0.17421	0.07322	0.962	2.843	1.888	171.4	O1 at
	0.21442	0.18008	0.05617	0.959	0.258	1.939	156.1	x,y,z
H2W	0.35037	0.30200	0.06242	0.957	2.812	1.879	164.3	O1 at
	0.36796	0.30915	0.07590	0.959	0.200	1.853	177.2	$1/2+x,1/2-y,-z$
$C_4H_9ClN_2O_3.H_2O$ neutron (Koetzle *et al.*, 1972), GGL								
H10W	0.96048	0.68205	0.54917	0.972	2.728	1.764	170.7	O1 at
	0.95180	0.66382	0.54136	0.963	0.201	1.809	158.5	$2-x,1-y,1-z$
H11W	0.78286	0.71440	0.53722	0.954	3.086	2.168	161.1	Cl at
	0.78282	0.71193	0.53854	0.963	0.027	2.159	161.0	$1-x,1-y,1-z$
$C_6H_{10}N_3O_2Cl.H_2O$ neutron (Fuess *et al.*, 1977), HST								
H11	0.6113	0.3689	0.7067	0.988	3.217	2.233	174.2	Cl at
	0.6117	0.3675	0.7007	0.961	0.044	2.259	175.4	$1/2+x,1/2-y,1-z$
H12	0.5270	0.3500	0.5889	0.951	2.765	1.817	175.5	O2 at
	0.5231	0.3618	0.5925	0.961	0.124	1.810	172.4	x,y,z
$HgSeO_4.H_2O$ neutron (Stålhandske, 1978), MSE								
H1	0.20521	−0.01892	0.52118	0.983	2.734	1.756	172.9	O4 at
	0.20591	−0.01279	0.51917	0.938	0.051	1.804	171.0	$x,y-1,z$
H2	0.41584	0.06593	0.61734	0.984	2.706	1.738	167.3	O2 at
	0.40925	0.06972	0.59432	0.938	0.173	1.837	153.0	$1-x,y-1/2,3/2-z$

Table 2 (*cont.*)

	x	*y*	*z*	*D*−H	*D*···*A/d*	H···*A*	*D*−H···*A*	Equivalent position
C$_9$H$_9$N$_3$O$_9$.H$_2$O neutron (Takusagawa *et al.*, 1979), NUC								
H1O*W*	−0.2496	−0.7255	−0.2399	0.967	2.796	1.853	164.1	O3′ at
	−0.2554	−0.7102	−0.2089	0.961	0.263	1.861	163.5	*x*+1,*y*,*z*
H2O*W*	−0.3375	−0.8589	−0.2120	0.955	2.846	1.956	154.2	O4 at
	−0.3075	−0.8550	−0.2054	0.961	0.272	2.109	132.2	*x*,*y*−1,*z*
C$_{10}$H$_{10}$O$_4$ X-ray (Lalancette *et al.*, 1997), IDCB								
H4*A*	−0.200	−0.040	0.024	0.77	2.845	2.18	144	O2 at
	−0.1947	−0.0685	0.0305	0.850	0.254	2.013	165.9	−*x*,−*y*,−*z*
H4*B*	−0.198	−0.021	0.152	0.90	2.754	1.86	172	O1 at
	−0.1746	0.0036	0.1626	0.850	0.212	1.923	165.6	*x*−1,*y*−1,*z*
C$_5$H$_7$Cl$_3$N$_2$O X-ray (Anagnostis & Turnbull, 1998), AMI								
H1O	0.4471	0.2532	−0.0412	0.82	3.178	2.37	170	Cl1 at
	0.4518	0.2542	−0.0313	0.850	0.083	2.343	167.5	*x*−1,1/2−*y*,1/2+*z*
H2O	0.4398	0.2034	−0.1578	0.76	3.144	2.38	172	Cl1 at
	0.4303	0.2009	−0.1642	0.850	0.090	2.297	175.0	*x*−1,*y*,*z*
C$_{16}$H$_{44}$Cl$_2$N$_4$O$_3$ X-ray (Simonov *et al.*, 1998), HXD								
H1*W*1	−0.0075	1.0754	0.7890	0.92	3.149	2.24	171	Cl1 at
	−0.0038	1.0660	0.7890	0.850	0.100	2.310	169.4	−*x*,1+*y*,3/2−*z*
H1*W*2	−0.1066	−0.0437	0.4505	0.93	3.241	2.33	167	Cl1 at
	−0.1040	−0.0408	0.4571	0.850	0.112	2.396	173.6	−*x*,−*y*,1−*z*
H2*W*2	−0.0771	0.0701	0.5243	0.94	3.308	2.37	175	Cl1 at
	−0.0836	0.0719	0.5201	0.850	0.115	2.462	173.6	*x*,*y*,*z*
C$_4$H$_{15}$N$_2$O$_2$Cl.2H$_2$O neutron (Koetzle, Lehmann *et al.*, 1972), LLY								
H7*W*	0.14675	0.36665	0.64829	0.953	3.220	2.273	172.7	Cl at
	0.13632	0.37569	0.61864	0.938	0.218	2.300	166.7	*x*,*y*,1+*z*
H8*W*	0.12653	0.25262	0.61130	0.960	2.805	1.857	169.2	O2 at
	0.10032	0.26407	0.63185	0.938	0.288	1.954	149.9	*x*,*y*,1+*z*
H9*W*	0.27647	0.34630	0.06455	0.936	3.254	2.329	169.7	Cl at
	0.27867	0.35073	0.07923	0.938	0.104	2.318	175.3	*x*,*y*,*z*
H10*W*	0.24346	0.30833	0.29135	0.957	2.718	1.775	167.9	O1*W* at
	0.28274	0.30196	0.31266	0.938	0.315	1.874	148.4	*x*,*y*,*z*
Ca(C$_3$H$_2$O$_4$).2H$_2$O neutron (Albertsson *et al.*, 1978), CAMA								
H11*W*	0.51486	0.78732	0.97641	0.977	2.815	1.842	173.0	O1 at
	0.52794	0.80842	0.97871	0.938	0.198	1.930	156.4	*x*,*y*,*z*
H12*W*	0.68181	0.73614	1.07428	0.988	2.724	1.764	163.0	O4 at
	0.67401	0.71409	1.06565	0.938	0.195	1.870	150.2	1+*x*,3/2−*y*,1/2+*z*
H21*W*	0.57893	0.37310	0.77223	0.974	2.791	1.820	174.3	O2 at
	0.56648	0.36171	0.80436	0.938	0.374	1.985	142.9	1−*x*,*y*−1/2,3/2−*z*
H22*W*	0.54405	0.54472	0.83962	0.947	3.021	2.078	173.1	O1*W* at
	0.53881	0.54847	0.83572	0.938	0.059	2.085	175.8	*x*,*y*,*z*
C$_6$H$_6$N$_2$O$_2$.2H$_2$O X-ray (Hawkinson, 1977), UAD								
H31	0.771	0.758	0.407	0.82	2.728	1.94	164	O4*W* at
	0.7812	0.7497	0.4190	0.850	0.166	1.885	171.7	1/2+*x*,3/2−*y*,1−*z*
H32	0.689	0.753	0.256	0.87	2.778	1.91	174	O2 at
	0.6878	0.7520	0.2646	0.850	0.060	1.929	175.8	1−*x*,1/2+*y*,1/2−*z*
H41	0.402	0.718	0.298	0.86	2.771	1.92	176	O2 at
	0.4056	0.7018	0.2774	0.850	0.253	1.972	156.2	1−*x*,1/2+*y*,1/2−*z*
H42	0.376	0.620	0.366	0.80	2.717	1.95	161	O1 at
	0.3548	0.6113	0.3572	0.850	0.240	1.868	175.6	*x*,*y*,*z*
C$_7$H$_7$KN$_2$O$_8$ X-ray (Paixão *et al.*, 1998), FRM								
H7*A*	0.9100	0.7778	0.6830	0.82	3.002	2.20	169	O1 at
	0.8983	0.7749	0.6789	0.850	0.106	2.152	177.9	*x*,1+*y*,*z*
H7*B*	0.8970	0.7347	0.8110	0.77	2.932	2.16	175	O1 at
	0.8972	0.7310	0.8206	0.851	0.103	2.083	176.1	*x*,1/2−*y*,1/2+*z*
H8*A*	0.4590	0.2826	0.8210	0.78	2.934	2.16	172	O1 at
	0.4522	0.2805	0.8322	0.850	0.108	2.084	178.3	1−*x*,1/2+*y*,3/2−*z*
H8*B*	0.4560	0.2352	0.7060	0.80	2.959	2.18	164	O1 at
	0.4594	0.2320	0.7016	0.849	0.076	2.139	162.1	1−*x*,−*y*,1−*z*

Table 2 (*cont.*)

	x	y	z	$D{-}H$	$D{\cdots}A/d$	$H{\cdots}A$	$D{-}H{\cdots}A$	Equivalent position
$(NH_4)_2[Ni(OH_2)_6](CrO_4)_2$ neutron (Hodgson *et al.*, 1978), NICR								
H15	0.2088	0.0835	0.3199	0.963	2.771	1.813	172.4	O5 at
	0.2075	0.0807	0.3213	0.977	0.039	1.799	172.5	*x,y,z*
H16	0.2422	0.1241	0.0996	0.996	2.840	1.848	174.2	O6 at
	0.2416	0.1284	0.1079	0.977	0.076	1.865	175.6	*x,y,z*−1
H17	−0.2572	0.0927	−0.0530	0.980	2.718	1.739	178.1	O4 at
	−0.2594	0.0917	−0.0404	0.977	0.088	1.745	173.5	*x*−1,*y,z*−1
H18	−0.1387	0.1816	0.0150	0.975	2.733	1.759	176.0	O6 at
	−0.1378	0.1816	0.0145	0.977	0.010	1.758	175.2	*x*−1/2,1/2−*y,z*−1
H19	−0.0925	−0.0529	0.3393	0.974	2.743	1.783	167.9	O5 at
	−0.0840	−0.0491	0.3584	0.977	0.133	1.817	157.0	−*x,*−*y,*1−*z*
H2O	0.0263	−0.1389	0.3314	0.974	2.720	1.750	173.0	O3 at
	0.0307	−0.1376	0.3391	0.977	0.057	1.744	176.9	1/2−*x,y*−1/2,1−*z*
$Na_3SbS_4.9H_2O$ neutron (Mereiter *et al.*, 1979), NSB								
H1	0.02163	0.30189	0.92121	0.967	3.343	2.379	175.4	S2 at
	0.02235	0.30375	0.92439	0.953	0.045	2.390	178.9	*x,y,z*
H2	−0.07326	0.36684	0.86187	0.947	2.807	1.874	167.7	O3 at
	−0.08365	0.35413	0.87154	0.953	0.228	1.928	152.4	*z*−1/2,1/2−*x,*1−*y*
H3	0.25114	0.66185	1.02221	0.959	3.358	2.403	173.9	S1 at
	0.25064	0.65750	1.01604	0.953	0.090	2.407	175.6	*x*−1/2,3/2−*y,*2−*z*
H4	0.16799	0.75864	1.03976	0.961	3.319	2.362	173.2	S2 at
	0.17247	0.75608	1.04322	0.953	0.074	2.372	172.4	*y,z,x*+1
H5	0.05069	0.22681	0.27323	0.957	3.293	2.338	175.9	S2 at
	0.04430	0.23354	0.27689	0.953	0.119	2.351	169.7	*z*−1,*x,y*
H6	0.06031	0.30690	0.37063	0.927	3.588	2.830	139.8	S1 at
	0.06907	0.31098	0.37668	0.953	0.136	2.738	148.9	1−*x,y*−1/2,3/2−*z*
H6	−	−	−	0.927	3.594	2.861	137.0	S2 at
	−	−	−	0.953	0.136	2.936	127.3	−*y,z*−1/2,1/2−*x*
$Na_2C_4H_{16}O_{10}$ X-ray (Montserrat *et al.*, 1998), SSH								
H3	0.5954	−0.1190	0.1785	0.827	2.781	1.960	171.7	O2 at
	0.5858	−0.0982	0.1834	0.850	0.171	1.940	169.8	1−*x,*−*y,*−*z*
H3*A*	0.6645	0.0490	0.2465	0.846	2.908	2.082	165.1	O2 at
	0.6837	0.0483	0.2531	0.850	0.170	2.102	158.0	*x,*1/2−*y,*1/2+*z*
H4	0.7602	−0.0050	−0.1234	0.873	2.798	1.940	167.3	O2 at
	0.7715	0.0049	−0.1135	0.850	0.144	1.951	174.8	*x,y,z*
H4*A*	0.7975	−0.1940	−0.1530	0.808	3.023	2.217	174.8	O3 at
	0.7921	−0.1962	−0.1561	0.850	0.054	2.174	177.6	*x,*−1/2−*y,z*−1/2
H5	0.9333	−0.4470	0.1211	0.845	2.770	1.937	168.5	O1 at
	0.9351	−0.4508	0.1215	0.850	0.029	1.928	170.4	*x,y*−1,*z*
H5*A*	1.0604	−0.3490	0.1082	0.815	2.863	2.051	174.0	O1 at
	1.0661	−0.3457	0.1091	0.850	0.054	2.022	170.1	2−*x,*−*y,*−*z*
$[C_{10}H_{30}N_4][HPO_4]_2.6H_2O$ neutron (Cohen *et al.*, 1997), SPH								
H3*W*1†	0.0361	0.0161	0.5162	0.926	2.760	1.836	177.2	O1*W* at
	0.0537	0.0218	0.6004	0.937	0.553	2.070	129.3	−*x,*−*y,*1−*z*
H2*W*1	0.0431	0.0822	0.4979	0.989	2.719	1.731	176.2	O3 at
	0.0571	0.0825	0.5198	0.939	0.147	1.804	164.1	*x,y,z*
H1*W*2	0.4932	0.0870	0.4877	0.970	2.839	1.875	172.9	O3*W* at
	0.4725	0.0810	0.5424	0.937	0.486	2.078	137.2	*x,y,z*
H2*W*2†	0.3110	0.0553	0.4731	0.964	2.758	1.803	170.2	O1*W* at
	0.3306	0.0332	0.4749	0.938	0.534	1.961	141.6	*x,y,z*
H1*W*3	0.7557	0.1460	0.5333	0.982	2.715	1.736	175.0	O3 at
	0.7386	0.1438	0.5194	0.938	0.141	1.782	172.6	1+*x,y,z*
H2*W*3	0.6056	0.1844	0.5632	0.980	2.822	1.845	175.1	O2 at
	0.6137	0.1836	0.5769	0.938	0.092	1.892	171.0	1/2+*x,*1/2−*y,z*
$Na_2B_4O_5(OH)_4.8H_2O$ neutron (Levy & Lisensky, 1978), NAB								
H6*A*	0.1997	0.8857	0.4633	0.963	2.842	1.891	168.6	O5 at
	0.2046	0.8622	0.4520	0.964	0.300	2.011	143.0	1/2−*x,*3/2−*y,*1−*z*
H6*B*	0.1338	0.7891	0.5125	0.964	2.865	1.940	160.1	O4 at
	0.1238	0.7840	0.5066	0.965	0.132	1.980	151.5	*x,*1−*y,*1/2+*z*
H7*A*	0.2016	−0.0245	0.1936	0.976	2.818	1.843	176.7	O2 at
	0.1959	−0.0419	0.1998	0.964	0.218	1.883	162.5	1/2−*x,y*−1/2,1/2−*z*

Table 2 (*cont.*)

	x	y	z	$D-H$	$D\cdots A/d$	$H\cdots A$	$D-H\cdots A$	Equivalent position
H7*B*	0.1276	0.0909	0.2021	0.962	2.950	2.031	159.2	O4 at
	0.1408	0.0684	0.2505	0.964	0.615	2.426	113.8	*x,y,z*
H8*A*	0.0840	0.1958	0.3842	0.975	2.790	1.823	170.4	O1 at
	0.0732	0.2001	0.3903	0.963	0.172	1.830	173.5	*x,y,z*
H8*B*	0.1936	0.1290	0.4636	0.951	3.148	2.259	155.4	O5 at
	0.1889	0.1283	0.4483	0.964	0.179	2.305	145.6	1/2−*x*,1/2−*y*,1−*z*
H9*A*	0.0996	0.6177	0.1638	0.951	3.097	2.164	166.6	O3 at
	0.0978	0.6177	0.1556	0.964	0.096	2.148	167.8	*x,y,z*
H9*B*	0.1152	0.7359	0.0967	0.969	2.927	1.974	167.2	O8 at
	0.1201	0.7442	0.1016	0.963	0.113	1.965	175.6	*x*,1−*y,z*−1/2
Na$_2$S$_2$O$_3$.5H$_2$O neutron (Lisensky & Levy, 1978), NATH								
H1	0.4817	0.2239	0.1339	0.965	2.822	1.864	171.7	O3 at
	0.4790	0.2287	0.1274	0.938	0.114	1.905	165.3	*x,y,z*
H2	0.7410	0.2133	0.1871	0.963	2.843	1.901	165.3	O2 at
	0.7352	0.2148	0.1895	0.938	0.054	1.933	163.1	*x,y,z*
H3	0.1364	0.2734	0.2453	0.962	2.803	1.843	176.0	O3 at
	0.1375	0.2757	0.2387	0.938	0.072	1.870	172.4	*x,y,z*
H4	0.1078	0.3117	0.4087	0.963	2.903	1.951	169.4	O3 at
	0.1069	0.3108	0.4051	0.938	0.032	1.976	169.5	*x*,1/2−*y,z*+1/2
H5	0.6100	0.3313	0.4287	0.964	2.863	1.905	172.1	O4 at
	0.6201	0.3289	0.4122	0.938	0.159	1.962	160.6	*x*,1/2−*y,z*+1/2
H6	0.7498	0.3899	0.4222	0.958	3.351	2.399	172.1	S1 at
	0.7336	0.3920	0.4289	0.938	0.128	2.437	165.0	1+*x*,1/2−*y*,1/2+*z*
H7	0.8499	0.4821	0.1879	0.960	3.337	2.390	168.4	S1 at
	0.7987	0.4709	0.1906	0.938	0.394	2.581	137.8	1−*x*,1/2+*y*,1/2−*z*
H8	0.7912	0.4618	−0.0126	0.967	2.855	1.889	177.4	O8 at
	0.7831	0.4582	−0.0095	0.938	0.097	1.920	173.9	*x*,1/2−*y,z*−1/2
H9	0.7491	0.0367	0.1885	0.956	3.336	2.418	160.8	S1 at
	0.7415	0.0501	0.2612	0.938	0.631	2.698	125.8	1+*x,y,z*
H10	0.4964	0.0336	0.2039	0.956	3.359	2.408	172.8	S1 at
	0.5024	0.0263	0.1699	0.938	0.310	2.489	154.1	*x,y,z*
NiSO$_4$.7H$_2$O neutron (Ptasiewicz-Bak *et al.*, 1997), NISO								
H51	0.1073	0.2327	0.2178	0.985	2.670	1.688	173.9	O3 at
	0.1028	0.2319	0.2140	0.938	0.055	1.735	175.1	1−*x,y*−1/2,1/2−*z*
H52	−0.1258	0.2354	0.1933	0.973	2.738	1.772	171.4	O4 at
	−0.1198	0.2346	0.1928	0.938	0.042	1.806	172.3	−*x,y*−1/2,1/2−*z*
H61	0.3017	0.4180	0.2701	0.987	2.742	1.764	170.6	O2 at
	0.2884	0.4248	0.2849	0.938	0.214	1.829	163.8	1−*x,y*−1/2,1/2−*z*
H62	0.2476	0.5449	0.2492	0.986	2.735	1.756	171.1	O4 at
	0.2182	0.5447	0.2623	0.938	0.252	1.837	159.5	*x,y,z*
H71	−0.3073	0.4215	0.2208	0.969	2.824	1.859	173.4	O2 at
	−0.3309	0.4267	0.2064	0.938	0.242	1.911	163.9	−*x,y*−1/2,1/2−*z*
H72	−0.2536	0.5451	0.1803	0.978	2.700	1.721	178.9	O3 at
	−0.2668	0.5408	0.1605	0.938	0.258	1.811	157.1	*x*−1,*y,z*
H81	0.1954	0.6219	0.0531	0.978	2.686	1.714	172.3	O1 at
	0.1738	0.6286	0.0660	0.938	0.226	1.807	155.0	*x,y,z*
H82	0.0143	0.6037	−0.0263	0.963	2.888	1.952	163.0	O2 at
	0.0151	0.6089	−0.0220	0.938	0.080	1.987	160.6	*x*−1/2,3/2−*y*,−*z*
H91	−0.0222	0.3634	−0.1087	0.975	2.824	1.860	169.4	O4 at
	−0.0454	0.3640	−0.1127	0.938	0.163	1.922	160.8	1/2−*x*,1−*y,z*−1/2
H92	−0.2197	0.4185	−0.0593	0.982	2.728	1.754	170.7	O11 at
	−0.2436	0.3699	−0.0521	0.938	0.601	2.051	127.7	−*x*−1/2,1−*y,z*−1/2
H101	0.3349	0.2840	0.0291	0.966	2.820	1.867	168.3	O9 at
	0.3534	0.2995	0.0012	0.938	0.400	2.076	135.1	*x*+1/2,1/2−*y*,−*z*
H102	0.4032	0.4090	0.0001	0.969	2.767	1.801	173.6	O11 at
	0.3996	0.4214	0.0312	0.938	0.401	1.928	147.9	1/2−*x*,1−*y,z*−1/2
H111	−0.0544	0.4274	0.4815	0.968	2.787	1.861	159.1	O1 at
	−0.0363	0.4196	0.4574	0.938	0.326	1.938	149.6	1/2−*x*,1−*y*,1/2+*z*
H112	−0.0010	0.4746	0.3650	0.964	2.825	1.887	163.6	O6 at
	−0.0606	0.4940	0.3550	0.938	0.476	2.125	130.5	*x,y,z*

† Disordered with site occupancy factor 0.5.

4. Structure of the *HYDROGEN* program

The program considers two possibilities: that of the hydroxyl and that of water, which are run independently. Details of the calculations and energy-profile data can be obtained from the program on request. The input is that of *PARST97* (Nardelli, 1995), without the H atoms to be calculated, and a file containing the atom partial charges, with the following structure:

```
Title
N,YO,HD
FRT
000000 x.xxx
000000 x.xxx
...
AAAAAA y.yyy
AAAAAA y.yyy
...
```

where N is the number of hydroxyls or waters to be considered, YO is the coefficient for the Gaussian factor (suggested value 5.0), HD is the O—H distance (*e.g.* 0.938 Å for neutron, 0.850 Å for X-ray), FRT is the format of the data to be read [*e.g.* (6A1,F7.3)], 000000 is the label of the hydroxyl or water O atom, with atomic partial charge x.xxx of the attached H atom (N entries), and AAAAAA is the atom label, with associated atomic partial charge y.yyy (these atom labels *must* be equal to those of the *PARST* input).

The output gives the hydroxyl or water H-atom coordinates and the hydrogen bonds. On request, output of geometric data and nonbonded energy profiles is also given. The program asks for the problem – hydroxyl or water – and for the names of the input and output files.

5. Comments and remarks

In Tables 1 and 2, experimental and calculated data are compared, showing that the treatment gives, in general, quite acceptable results. Relevant differences are sometimes observed in the values of the D—H$\cdots A$ angle, but it is important to note that this angle is strongly influenced both by the length of the D—H bond and the angle C—O—H for hydroxyl or H—O—H for water.

Probably, the parameters most responsible for the observed differences between the calculated and experimental data are the partial atomic charges, but it is not so easy to determine values of general validity for them. Moreover, it must be kept in mind that the distribution of the electric charge of a molecule in a crystal depends not only upon the nature of the atoms and the bonds they form, but also on the conformation of the molecule and its environment. Another point to be considered is that when there are several hydroxyls and/or water molecules, the results can be dependent on the sequence assumed in the treatment of the missing H atoms, as the acceptable directions and the energy profiles can be dependent on them.

In all cases listed in the two tables there is correspondence between the observed and calculated directions of interaction, with only one exception: that of H11 of α-D-glucose (labeled GLU in Table 1), for which observed C4—O4$\cdots$O4^i = 99.01°, O4$\cdots$O4^i = 2.777 Å [symmetry code: (i) 3/2 − x, 1 − y, z + 1/2], while calculated C4—O4$\cdots$O4^{ii} = 118.53°, O4$\cdots$O^{ii} = 2.777 Å [symmetry code: (ii) 3/2 − x, 1 − y, z − 1/2].

This is a very particular case where the calculated acceptor atom, O4^{ii}, is shifted with respect to the observed one, O4^i, by one translation period along the z axis, with an exactly equal value of the donor–acceptor distance and C4—O4$\cdots$O4′ angles differing from the ideal value of 109.5° by 9.03 and 10.49° (difference only 1.46°) for the calculated and observed directions, respectively. It is worthy of note that no unacceptable contacts with the calculated H11c atom are found.

It is important to consider that the results calculated by the program must be considered critically before assuming them, particularly by checking (by *PARST*) that the calculated H atoms are not involved in unacceptable contacts and, if possible, checking them by structure-factor calculations. In any case, the program is useful for a better understanding of the hydrogen bonds in a crystal structure.

In the case of disorder causing more than one orientation of the hydroxyl or water molecule, the program gives only one orientation in agreement with one of those possible, or intermediate between them. An example is given by the SPH compound in Table 2, where the disordered atoms are indicated.

The atomic partial charges for the examples quoted in Tables 1 and 2 were calculated using the 'extended Hückel' semiempirical MO routine of the *HYPERCHEM* package (Autodesk, 1992).

6. Availability of the program

The Fortran 77 source code and some executable files of the program can be downloaded from the World Wide Web site http://www.unipr.it/~nardelli/software.html.

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