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CHARDI2015: charge distribution analysis of non-molecular structures

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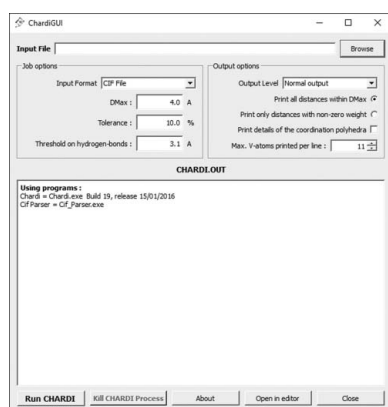
Keywords: bond weights; CHARDI; charge
 distribution; effective coordination numbers;
 computer programs.

The charge distribution method describes non-molecular crystal structures in a Madelung-type approach in which the formal oxidation number ('charge') of each atom is distributed among its neighbours. The sum of the distributed charges gives back the input charge when a structure is correctly refined and well balanced, so that the method can be used for structure validation and for the analysis of over- and underbonding effects. A new version of the software used to compute the charge distribution is presented, now with a CIF parser and graphical user interface.

1. Introduction

The charge distribution method, usually shortened as CHARDI, is the most recent extension of Pauling's (1929) concept of bond strength. Instead of empirical parameters used in the bond valence approach (Brown, 1978), it exploits the inter-atomic distances directly to assign a geometrically defined bond strength (called the 'bond weight') to each bond. CHARDI describes crystal structures in a Madelung-type approach in which each atom is treated as a point charge and forms a coordination polyhedron characterized by a real (as opposed to integer) coordination number ECoN (effective coordination number; Hoppe, 1979) which is a function not only of the number of atoms bonded but also of the strength of each bond.

CHARDI was introduced by Hoppe *et al.* (1989) as a method in which the formal oxidation number ('charge') of cations is distributed among the anions and the result is distributed back among the cations. A satisfactory agreement between the input and output charges confirms the reliability of the structural model. Nespolo *et al.* (1999) realized that the results of the forward (cation-to-anions) and backward (anions-to-cations) distributions bring complementary information (the former about the quality of the structural model, the latter on the presence of structural strains) and applied this analysis to a systematic evaluation of the pyroxene structures in the literature, as a function of chemistry and formation conditions. Nespolo *et al.* (2001) extended CHARDI to highly deformed polyhedra *via* an iterative calculation of ECoN, hydrogen bonds and heteroligand polyhedra. Eon & Nespolo (2015) showed that an anion-centred description may give better results for structures containing large cations or in which more regular polyhedra form around the anions. Finally, Nespolo (2016) introduced a new, more general, route to treat heteroligand polyhedra independent of the few parameters introduced in the previous version of the algorithm.



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The software used to perform the charge distribution analysis (*CHARDI-IT*) was presented by Nespolo *et al.* (2001), but following the recent developments it is now outdated. We present here a new version which exploits the new algorithm, offers a graphical interface and is also able to take CIFs as input.

2. CHARDI2015

CHARDI-IT was written in Fortran77 and was based on a bond-length calculation routine originally developed by G. Chiari, using as kernel a code called *POLCAL* written by S. J. Louisnathan. *CHARDI-IT* accepted three types of input: free-format (hand-written), the old ICSD (Allmann & Hinek, 2007) output format and a list of bond distances. The source code has now been rewritten in Fortran90, and a graphical user interface (GUI; Fig. 1), written in C++ on the basis of the Qt framework (version 4.8), has been implemented. The bond-distance input has been replaced by the CIF (crystallographic information file; Hall *et al.*, 1991), which is now the default input method. CIFs are interpreted *via* the CIF parser routine extracted from the *MoPro* package (Jelsch *et al.*, 2005) and must contain at least the following data blocks:

```
_cell_length_a
_cell_length_b
_cell_length_c
_cell_angle_alpha
_cell_angle_beta
_cell_angle_gamma
loop_
_space_group_symop_operation_xyz
[...]
loop_
_atom_type_symbol
_atom_type_oxidation_number
[...]
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
[...]
```

where [...] indicates the entries in each loop. All the other data blocks are ignored, with the exception of *_symmetry_space_group_name_H-M*, which, if present, is printed in the output file as additional information. The loop on the oxidation number is not always present in a CIF produced by structure refinement programs but this information is necessary: it can be added either by hand by the user or as a separate file (*oxidation.dat*), which will then be merged with the input provided by the CIF. If neither the loop in the CIF nor the requested external file is present, the execution halts with an error message. The CIF parser produces an inter-

mediate input file (*chardi.in*) in the free format already used by *CHARDI-IT* and from this point the data input proceeds as in the previous version.

The charge distribution is computed in both the cation- and anion-centred descriptions, as detailed by Nespolo (2016) (*m*'s are indices on the cations, *n*'s on the anions):

(i) For stoichiometries of the type $A_m X_n$, *i.e.* when the structure is based on homoligand polyhedra in both descriptions, the cation-centred one is adopted first and the result is printed out directly.

(ii) For stoichiometries of the type $A_{m'} B_{n'} C_{m''} \dots X_n$, *i.e.* when the structure is based on homoligand polyhedra in the cation description, this description is adopted first because each cation receives a fraction of the charge of the only type of anion which forms its coordination shell. The same does not hold for the opposite description; therefore, the fraction of the formal charge an anion shares with each chemical species of cation is computed and used as charge to be distributed when the description is switched to anion centred.

(iii) For stoichiometries of the type $A_m X_n Y_{n'} Z_{n''} \dots$, *i.e.* when the structure is based on homoligand polyhedra in the anion description, the opposite situation occurs with respect to the previous case. The anion-centred description is adopted first and the fraction of the formal charge a cation shares with each chemical species of anion is computed. This result is then used as charge to be distributed when the description is switched to cation centred and the result is printed out directly.

(iv) For stoichiometries of the type $A_{m'} B_{n'} C_{m''} \dots X_n Y_{n'} Z_{n''} \dots$, *i.e.* when the structure is based on heteroligand polyhedra in both descriptions, we do not know *a priori* the

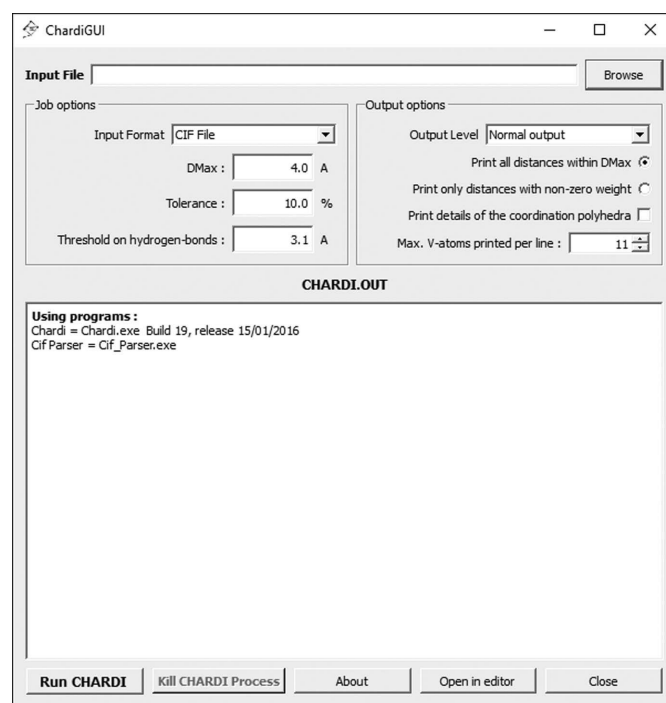


Figure 1
A screen shot showing the GUI for *CHARDI2015*.

fraction of charge that each atom shares with its neighbours in either description, and thus a recursive calculation is performed. The cation-centred description is adopted first, and the fraction of the formal charge the anions share with each chemical species of cation is initially set up simply as proportional to the fraction of ECoN. A recursive calculation is then started by switching back and forth between the cation- and anion-centred descriptions until convergence is reached on the fraction of the formal charge.

The user may choose three levels of output, which produce a number of separate files:

(i) The normal (minimal) output, which produces two files, `chardi.out` and `iterations.out`. These files have the same structure, presenting in a first section the bond distances for each coordination polyhedron in both descriptions (cation centred and anion centred), complemented by the fictive ionic radii (FIR) and bond weights, and the details of the ECoN calculation; and in a second section the computed charges for each atom as well as their distribution among each pair of atoms, again in both descriptions. The second section of `chardi.out` presents only the final result, after iteration, whereas `iterations.out` presents the result of each iteration.

```

***** Structure described as built on cation-centred polyhedra *****
===== COORDINATION POLYHEDRA =====
POLYHEDRON-CENTRING ATOM CORNER (VERTEX) ATOM
i j q*sof h(ij) r s q*sof h(rs) dist FIR BW
S 1 6.00 4 Se 1 -2.00 4 2.2562 0.138 1.000
O 3 -2.00 4 1.4387 0.130 1.032
O 2 -2.00 4 1.4499 0.131 0.985
O 1 -2.00 4 1.4511 0.131 0.981
S 2 6.00 4 Se 1 -2.00 4 2.2569 0.138 1.000
O 6 -2.00 4 1.4359 0.130 1.029
O 4 -2.00 4 1.4454 0.130 0.989
O 5 -2.00 4 1.4475 0.131 0.981
K 1 1.00 4 O 6 -2.00 4 2.6551 1.581 1.193
O 3 -2.00 4 2.6787 1.595 1.141
O 5 -2.00 4 2.7524 1.639 0.979
O 2 -2.00 4 2.7840 1.657 0.910
O 4 -2.00 4 2.7950 1.664 0.887
O 1 -2.00 4 2.8595 1.702 0.752
K 2 1.00 4 Se 1 -2.00 4 3.7556 1.847 1.000
O 3 -2.00 4 2.6606 1.584 1.370
O 5 -2.00 4 2.7706 1.649 1.134
O 5 -2.00 4 2.7923 1.662 1.088
O 1 -2.00 4 2.8237 1.681 1.021
O 4 -2.00 4 2.8787 1.714 0.905
O 2 -2.00 4 2.9548 1.759 0.751
O 4 -2.00 4 2.9588 1.761 0.743
O 1 -2.00 4 3.3554 1.998 0.172
O 1 -2.00 4 3.4249 2.039 0.120
ANALYSIS OF THE GEOMETRY OF THE COORDINATION POLYHEDRA
i j r n MEFIR n d(ij>r) ECoN(ij>r)
S 1 Se 1 0.138 1 2.256 1.00
S 1 O 1 0.131 2 1.446 3.00
S 2 Se 1 0.138 1 2.257 1.00
S 2 O 1 0.130 2 1.443 3.00
K 1 O 3 1.634 3 2.743 5.86
K 2 Se 1 1.847 1 3.756 1.00
K 2 O 5 1.687 6 2.833 7.30
DISTRIBUTION OF ECoN
Se 1 O 1 O 2 O 3 O 4 O 5 O 6
S 1 1.000 0.327 0.329 0.344 0.000 0.000 0.000
S 2 1.000 0.000 0.000 0.000 0.330 0.327 0.343
K 1 0.000 0.128 0.155 0.195 0.151 0.167 0.204
K 2 1.000 0.180 0.103 0.188 0.226 0.304 0.000
(a)
***** Structure described as built on anion-centred polyhedra *****
===== COORDINATION POLYHEDRA =====
POLYHEDRON-CENTRING ATOM CORNER (VERTEX) ATOM
i j q*sof h(ij) r s q*sof h(rs) dist FIR BW
Se 1 -2.00 4 S 1 6.00 4 2.2562 2.118 1.001
S 2 6.00 4 2.2569 2.119 0.999
O 1 -2.00 4 K 2 1.00 4 3.7556 1.909 1.000
S 1 6.00 4 1.4511 1.320 1.000
K 2 1.00 4 2.8237 1.143 1.222
K 1 1.00 4 2.8595 1.157 1.148
K 2 1.00 4 3.3554 1.358 0.286
K 2 1.00 4 3.4249 1.386 0.213
O 2 -2.00 4 S 1 6.00 4 1.4499 1.319 1.000
K 1 1.00 4 2.7840 1.127 1.146
K 2 1.00 4 2.9548 1.196 0.791
O 3 -2.00 4 S 1 6.00 4 1.4387 1.309 1.000
K 2 1.00 4 2.6606 1.077 1.020
K 1 1.00 4 2.6787 1.084 0.979
O 4 -2.00 4 S 2 6.00 4 1.4454 1.315 1.000
K 1 1.00 4 2.7950 1.131 1.153
K 2 1.00 4 2.8787 1.165 0.976
K 2 1.00 4 2.9588 1.197 0.813
O 5 -2.00 4 S 2 6.00 4 1.4475 1.317 1.000
K 1 1.00 4 2.7524 1.114 1.041
K 2 1.00 4 2.7706 1.121 1.001
K 2 1.00 4 2.7923 1.130 0.954
O 6 -2.00 4 S 2 6.00 4 1.4359 1.306 1.000
K 1 1.00 4 2.6551 1.074 1.000
ANALYSIS OF THE GEOMETRY OF THE COORDINATION POLYHEDRA
i j r n MEFIR n d(ij>r) ECoN(ij>r)
Se 1 S 1 2.118 1 2.257 2.00
Se 1 K 1 1.909 1 3.756 1.00
O 1 S 1 1.320 1 1.451 1.00
O 1 K 4 1.185 7 2.931 2.87
O 2 S 1 1.319 1 1.450 1.00
O 2 K 3 1.157 3 2.853 1.94
O 3 S 1 1.309 1 1.439 1.00
O 3 K 2 1.080 2 2.669 2.00
O 4 S 1 1.315 1 1.445 1.00
O 4 K 2 1.160 2 2.867 2.94
O 5 S 1 1.317 1 1.448 1.00
O 5 K 2 1.121 2 2.771 3.00
O 6 S 1 1.306 1 1.436 1.00
O 6 K 2 1.076 1 2.655 1.00
DISTRIBUTION OF ECoN
S 1 S 2 K 1 K 2
Se 1 0.500 0.500 0.000 1.000
O 1 1.000 0.000 0.400 0.600
O 2 1.000 0.000 0.592 0.408
O 3 1.000 0.000 0.490 0.510
O 4 0.000 1.000 0.392 0.608
O 5 0.000 1.000 0.347 0.653
O 6 0.000 1.000 1.000 0.000
(b)

```

Figure 2

Coordination polyhedra for $K_2SeS_2O_6$ in (a) the cation-centred and (b) the anion-centred description: screen shots of the output.

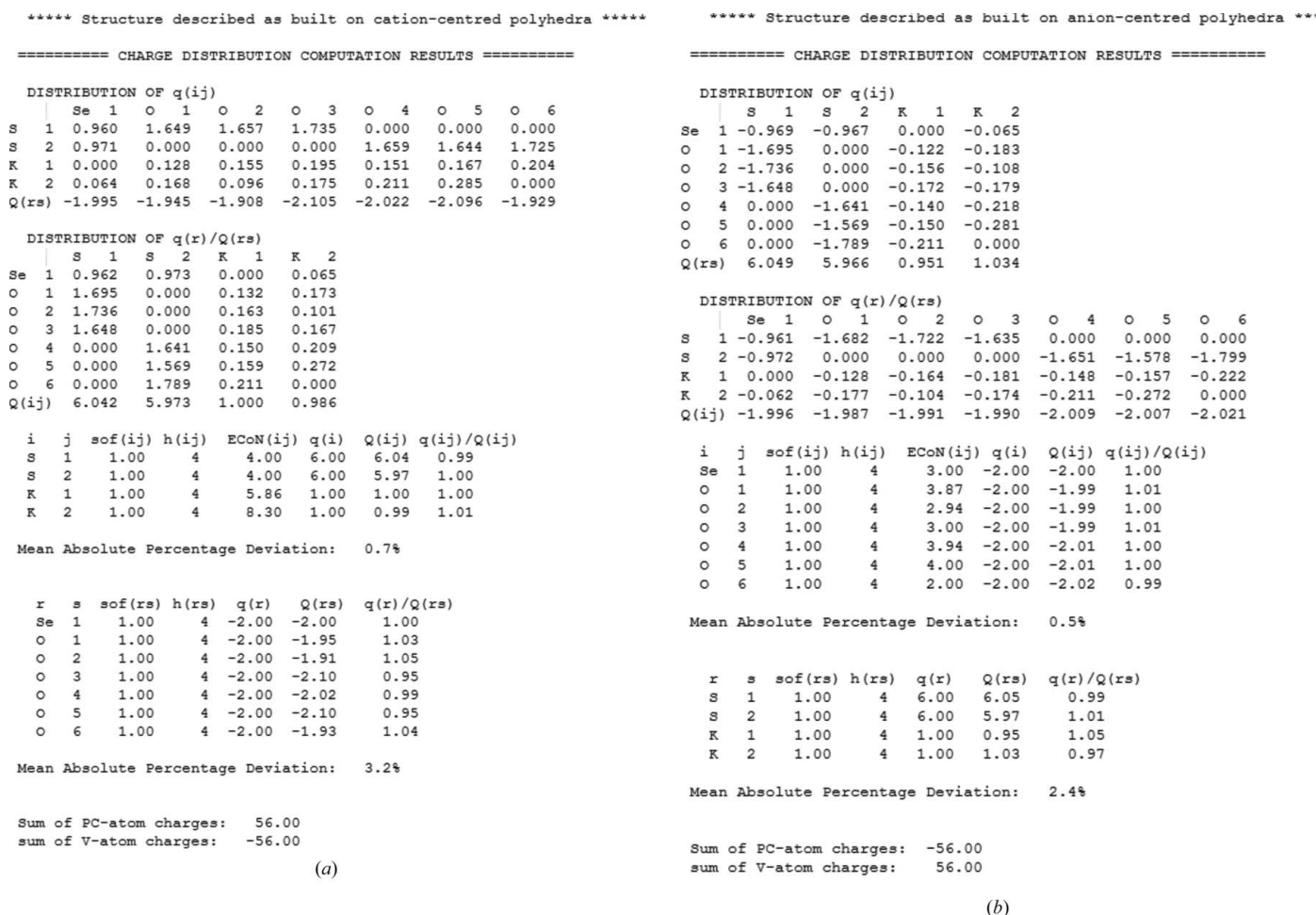


Figure 3 Charge distribution results for $K_2SeS_2O_6$ in (a) the cation-centred and (b) the anion-centred description: screen shots of the output.

(ii) A verbose output, which produces two additional files, cations.out and anions.out, where all the details of the intermediate calculations in each description are provided.

(iii) An optional output produces a file polyhedra.out where the atomic coordinates of all the atoms in the coordination sphere are given.

The content of the file chardi.out is also presented in the GUI.

3. Example: potassium selenotriothionate, $K_2SeS_2O_6$

This compound has been presented and analysed in detail by Nespolo (2016) and is therefore a suitable example for illustrating the use of the new version of the software.

The input file was obtained from the ICSD (Inorganic Crystal Structure Database; <http://icsd.fiz-karlsruhe.de/icsd/>) with code 25027. The data used by CHARDI2015 are the following:

```

_cell_length_a 9.5032(12)
_cell_length_b 5.9375(10)
_cell_length_c 15.3132(21)
_cell_angle_alpha 90

```

```

_cell_angle_beta 110.418(12)
_cell_angle_gamma 90
_symmetry_space_group_name_H-M 'P 1 21/c 1'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 'x, -y+1/2, z+1/2'
2 '-x, -y, -z'
3 '-x, y+1/2, -z+1/2'
4 'x, y, z'
loop_
_atom_type_symbol
_atom_type_oxidation_number
K1+ 1
O2- -2
S6+ 6
Se2- -2
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x

```



```

_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_attached_hydrogens
Se1 Se2- 4 e 0.87403(4) 0.16812(6) 0.20090(2) 1. 0
S1 S6+ 4 e 0.66132(9) 0.29083(13) 0.09046(5) 1. 0
S2 S6+ 4 e 0.80887(9) 0.23982(15) 0.32647(5) 1. 0
O1 O2- 4 e 0.53971(25) 0.2315(4) 0.12288(16) 1. 0
O2 O2- 4 e 0.66425(31) 0.1642(5) 0.01018(16) 1. 0
O3 O2- 4 e 0.67639(28) 0.5301(4) 0.08192(16) 1. 0
O4 O2- 4 e 0.73423(29) 0.4558(4) 0.31300(15) 1. 0
O5 O2- 4 e 0.70942(27) 0.0579(4) 0.32970(16) 1. 0
O6 O2- 4 e 0.95016(31) 0.2345(6) 0.40221(18) 1. 0
K1 K1+ 4 e 0.22067(9) 0.23520(13) 0.03267(5) 1. 0
K2 K1+ 4 e 0.44688(9) 0.27813(13) 0.31912(5) 1. 0

```

The fields `_atom_site_Wyckoff_symbol` and `_atom_site_attached_hydrogens` are not used and so are ignored. Because the compound is of the type $A_n B_m C_m \dots X_n Y_n Z_n \dots$, the recursive calculation procedure is adopted, the results being in the `iterations.out` file. Figs. 2 and 3 are screen shots of the `chardi.out` file showing, respectively, the first and second sections of the output described above and can be compared with the tables of Nespolo (2016); in particular, the information in Tables 13–15 in that paper is presented here in Figs. 2(a) and 2(b), and the ‘Step 3’ (convergence reached) data in Table 17 are presented in Figs. 3(a) and 3(b). The intermediate results obtained at each iteration (Table 16, as well as ‘Step 1’ and ‘Step 2’ in Table 17) are printed in the other files described above; the screen shots are omitted here for reasons of space but are easily obtained by running the software.

Now suppose that the loop on the oxidation numbers is absent from the CIF above. *CHARDI2015* then asks for these data in the `oxidation.dat` file, which should be written in the following self-evident format:

```

K1 K1+ 1
K2 K1+ 1
O1 O2- -2

```

```

O2 O2- -2
O3 O2- -2
O4 O2- -2
O5 O2- -2
O6 O2- -2
S1 S6+ 6
S2 S6+ 6
Se1 Se2- -2

```

The content of this file is then merged with the original CIF to produce the example reported above.

4. Software availability

CHARDI2015 is available for download from the CMR2 laboratory web site (<http://www.crystallography.fr/chardi>) compiled for Microsoft Windows. Detailed instructions on the input methods and the level of output are provided with the installer.

Acknowledgements

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