

3. CIF DATA DEFINITION AND CLASSIFICATION

Example 3.5.3.1. Definition of the local Cartesian axis system for the atoms in a proton sponge complex.

```

loop_
_atom_local_axes_atom_label
_atom_local_axes_atom0
_atom_local_axes_ax1
_atom_local_axes_atom1
_atom_local_axes_atom2
_atom_local_axes_ax2
N(1) C(1) X N(1) N(2) Y
N(2) C(8) X N(2) N(1) Y
C(1) N(1) X C(1) C(2) Y
C(2) C(1) X C(2) C(3) Y
C(3) C(2) X C(3) C(4) Y
C(4) C(10) X C(4) C(3) Y
C(5) C(10) X C(5) C(6) Y
C(6) C(5) X C(6) C(7) Y
C(7) C(8) X C(7) C(6) Y
C(8) C(9) X C(8) N(2) Y
C(9) C(10) X C(9) C(1) Y
C(10) C(9) X C(10) C(5) Y
C(11) N(1) X C(11) H(111) Y
C(14) N(2) X C(14) H(141) Y
CL(1A) C(2A) X CL(1A) CL(2A) Y
CL(2A) C(3A) X CL(2A) CL(1A) Y
O(1A) C(1A) X O(1A) H(100) Y
O(2A) C(1A) X O(2A) CL(1A) Y
O(3A) C(4A) X O(3A) CL(2A) Y
O(4A) C(4A) X O(4A) H(100) Y
C(1A) O(1A) X C(1A) O(2A) Y
C(2A) C(1A) X C(2A) CL(1A) Y
C(3A) C(2A) X C(3A) CL(2A) Y
C(4A) O(3A) X C(4A) O(4A) Y
H(1NN) N(1) X H(1NN) N(2) Y
H(100) O(1A) X H(100) O(4A) Y
H(111) C(11) X H(111) H(112) Y
H(112) C(11) X H(112) H(111) Y
H(113) C(11) X H(113) H(111) Y
H(141) C(14) X H(141) H(142) Y
H(142) C(14) X H(142) H(141) Y
H(143) C(14) X H(143) H(141) Y
H(2) C(2) X H(2) H(3) Y
H(3) C(3) X H(3) H(2) Y
H(4) C(4) X H(4) H(3) Y
H(5) C(5) X H(5) H(4) Y
H(6) C(6) X H(6) H(7) Y
H(7) C(7) X H(7) H(6) Y

```

The ATOM_LOCAL_AXES category is used to define a local Cartesian axis system for each atom. Data items in this category are looped, with the category key (`_atom_local_axes_atom_label`) being a pointer to the `_atom_site_label` defined in the ATOM_SITE category of the core CIF dictionary. The orientation of the Cartesian basis is defined in terms of vectors between atoms, and any arbitrary orientation can be described by including dummy atoms if necessary. The spherical coordinate system used in the description of the multipoles is defined in terms of the local Cartesian basis: z is the polar axis from which the angle θ is measured, φ is measured from the x axis in the xy plane with the y axis having a value of $\varphi = +90^\circ$.

Example 3.5.3.1 shows how the category is used in part of an electron density CIF relating to a charge density study of the complex of 1,8-bis(dimethylamino)naphthalene with 1,2-dichloromaleic acid (a ‘proton sponge’) (Mallinson *et al.*, 1997).

3.5.3.2. Atom-centred multipole expansion functions

Data items in this category are as follows:

```

ATOM_RHO_MULTIPOLE
• _atom_rho_multipole_atom_label
  → _atom_site_label
  _atom_rho_multipole_coeff_Pc
  _atom_rho_multipole_coeff_Pv
  _atom_rho_multipole_coeff_P00

```

```

_atom_rho_multipole_coeff_P1-1
_atom_rho_multipole_coeff_P10
_atom_rho_multipole_coeff_P11
_atom_rho_multipole_coeff_P2-2
_atom_rho_multipole_coeff_P20
_atom_rho_multipole_coeff_P21
_atom_rho_multipole_coeff_P22
_atom_rho_multipole_coeff_P3-3
_atom_rho_multipole_coeff_P3-2
_atom_rho_multipole_coeff_P3-1
_atom_rho_multipole_coeff_P30
_atom_rho_multipole_coeff_P31
_atom_rho_multipole_coeff_P32
_atom_rho_multipole_coeff_P33
_atom_rho_multipole_coeff_P4-4
_atom_rho_multipole_coeff_P4-3
_atom_rho_multipole_coeff_P4-2
_atom_rho_multipole_coeff_P4-1
_atom_rho_multipole_coeff_P40
_atom_rho_multipole_coeff_P41
_atom_rho_multipole_coeff_P42
_atom_rho_multipole_coeff_P43
_atom_rho_multipole_coeff_P44
_atom_rho_multipole_configuration
_atom_rho_multipole_core_source
_atom_rho_multipole_kappa
_atom_rho_multipole_kappa_prime0
_atom_rho_multipole_kappa_prime1
_atom_rho_multipole_kappa_prime2
_atom_rho_multipole_kappa_prime3
_atom_rho_multipole_kappa_prime4
_atom_rho_multipole_radial_function_type
_atom_rho_multipole_radial_slater_n0
_atom_rho_multipole_radial_slater_n1
_atom_rho_multipole_radial_slater_n2
_atom_rho_multipole_radial_slater_n3
_atom_rho_multipole_radial_slater_n4
_atom_rho_multipole_radial_slater_zeta0
_atom_rho_multipole_radial_slater_zeta1
_atom_rho_multipole_radial_slater_zeta2
_atom_rho_multipole_radial_slater_zeta3
_atom_rho_multipole_radial_slater_zeta4
_atom_rho_multipole_scat_core
_atom_rho_multipole_scat_valence
_atom_rho_multipole_valence_source

```

The bullet (•) indicates a category key. The arrow (→) is a reference to a parent data item.

Data items in this category are also looped. The category key (`_atom_rho_multipole_atom_label`) is also a child of `_atom_site_label` in the ATOM_SITE category, thereby linking the electron density multipole coefficients to a specific atom site in the list of atom coordinates. This category contains all the parameters of the Hansen & Coppens (1978) function

$$\rho(\mathbf{r}) = P_c \rho_{\text{core}}(\mathbf{r}) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum_{0 \leq l \leq l_{\text{max}}} \{ \kappa^l(l)^3 R(\kappa^l(l), l, \mathbf{r}) \} \sum_{-l \leq m \leq l} \{ P(l, m) d(l, m, \theta, \varphi) \},$$

where \mathbf{r} is a position vector with respect to the atomic nucleus, and $\rho_{\text{core}}(\mathbf{r})$ and $\rho_{\text{valence}}(\kappa r)$ are the spherical core and valence electron densities, respectively. They are obtained from atomic orbital analytic wavefunctions such as those tabulated by Clementi & Roetti (1974). They are also the Fourier transforms of the X-ray scattering factors given in `_atom_rho_multipole_scat_core` and `_atom_rho_multipole_scat_valence`.

P_c is the weight applied to the free-atom core (`_atom_rho_multipole_coeff_Pc`), P_v is the weight applied to the free-atom valence shell (`_atom_rho_multipole_coeff_Pv`), $P(0, 0)$ is the number of remaining electrons (`_atom_rho_multipole_coeff_P00`) and $P_c + P_v + P(0, 0) = Z$ (the atomic number) for

Example 3.5.3.2. Multipole expansion for an atom in the proton sponge complex of Example 3.5.3.1.

```

loop_
_atom_rho_multipole_atom_label
_atom_rho_multipole_coeff_Pv
_atom_rho_multipole_coeff_P00
_atom_rho_multipole_coeff_P11
_atom_rho_multipole_coeff_P1-1
_atom_rho_multipole_coeff_P10
_atom_rho_multipole_coeff_P20
_atom_rho_multipole_coeff_P21
_atom_rho_multipole_coeff_P2-1
_atom_rho_multipole_coeff_P22
_atom_rho_multipole_coeff_P2-2
_atom_rho_multipole_coeff_P30
_atom_rho_multipole_coeff_P31
_atom_rho_multipole_coeff_P3-1
_atom_rho_multipole_coeff_P32
_atom_rho_multipole_coeff_P3-2
_atom_rho_multipole_coeff_P33
_atom_rho_multipole_coeff_P3-3
_atom_rho_multipole_coeff_P40
_atom_rho_multipole_coeff_P41
_atom_rho_multipole_coeff_P4-1
_atom_rho_multipole_coeff_P42
_atom_rho_multipole_coeff_P4-2
_atom_rho_multipole_coeff_P43
_atom_rho_multipole_coeff_P4-3
_atom_rho_multipole_coeff_P44
_atom_rho_multipole_coeff_P4-4
_atom_rho_multipole_kappa
_atom_rho_multipole_kappa_prime0
_atom_rho_multipole_kappa_prime1
_atom_rho_multipole_kappa_prime2
_atom_rho_multipole_kappa_prime3
_atom_rho_multipole_kappa_prime4
_atom_rho_multipole_configuration
_atom_rho_multipole_radial_slater_n0
_atom_rho_multipole_radial_slater_zeta0
_atom_rho_multipole_radial_slater_n1
_atom_rho_multipole_radial_slater_zeta1
_atom_rho_multipole_radial_slater_n2
_atom_rho_multipole_radial_slater_zeta2
_atom_rho_multipole_radial_slater_n3
_atom_rho_multipole_radial_slater_zeta3
_atom_rho_multipole_radial_slater_n4
_atom_rho_multipole_radial_slater_zeta4
_atom_rho_multipole_core_source
_atom_rho_multipole_valence_source
N(1) 2.63(5)
  0.00 -0.037(17) 0.062(14) 0.00 -0.084(18)
  0.00 0.00 -0.027(15) -0.048(13) 0.00
-0.098(16) -0.063(14) 0.00 0.00 0.082(14)
-0.037(14) 0.00 0.00 0.00 0.00
  0.00 0.00 0.00 0.00 0.00
0.992(8) 0.80(4) 0.80 0.80 0.80 0.80
;
1S 2S 3S 4S 2P 3P 4P 3D 4D 4F 5S 5P 6S 6P 5D 7S 6D 5F
2 -2 0 0 -3 0 0 0 0 0 0 0 0 0 0 0 0 0
;
  2 7.2553 2 7.2553 2 7.2553 3 7.2553
  4 7.2553
' Clementi & Roetti, 1974 '
' Clementi & Roetti, 1974 '
# Data for other atoms have been omitted for brevity

```

a neutral atom. κ is the valence electron expansion factor (`_atom_rho_multipole_kappa`), $R(\kappa'(l), l, \mathbf{r})$ is the radial function (Slater or equivalent) (`_atom_rho_multipole_radial_*`), $\kappa'(l)$ is the multipole function expansion factor (`_atom_rho_multipole_kappa_prime[1]`), $P(l, m)$ are the spherical harmonic coefficients (`_atom_rho_multipole_coeff_P[1m]`) and

$d(l, m, \theta, \varphi)$ is the spherical harmonic of order l, m at the angle (θ, φ) . The summations are performed over the index ranges $0 \leq l \leq l_{\max}$, $-l \leq m \leq l$, where l_{\max} is the highest order of multipole applied.

Example 3.5.3.2 demonstrates how the category is used in the proton sponge complex of Example 3.5.3.1. Only the first atom is shown in the example.

3.5.4. Development of the dictionary and supporting software

The first implementation of the dictionary appeared in a version of the *XD* program package (Koritsanszky *et al.*, 2003). Thus *XD* can read and write CIFs which include data items in the two categories described above (as well as, of course, items in the core CIF dictionary). It is envisaged that future developments to the rhoCIF dictionary will add features that are relevant to other widely used program packages. In the *XD* implementation, use was made of the *CIFtbx* library of Fortran functions for programming CIF applications (Hall & Bernstein, 1996).

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