

4.4. Electron density dictionary (rhoCIF)

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This is version 1.0.1 of the electron density CIF dictionary (rhoCIF). The data names defined in this dictionary complement those in the core CIF dictionary (Chapter 4.1).

Categories are described in alphabetical order; data items are arranged alphabetically within each category.

ATOM_LOCAL_AXES

This category allows the definition of local axes around each atom in terms of vectors between neighbouring atoms. High-resolution X-ray diffraction methods enable the determination of the electron density distribution in crystal lattices and molecules, which in turn allows for a characterization of chemical interactions (Coppens, 1997; Koritsanszky & Coppens, 2001). This is accomplished by the construction of a mathematical model of the charge density in a crystal and then by fitting the parameters of such a model to the experimental pattern of diffracted X-rays. The model on which this dictionary is based is the so-called multipole formalism proposed by Hansen & Coppens (1978). In this model, the electron density in a crystal is described by a sum of aspherical 'pseudoatoms' where the pseudoatom density has the form defined in the `_atom_rho_multipole_*` items. Each pseudoatom density consists of terms representing the core density, the spherical part of the valence density and the deviation of the valence density from sphericity. The continuous electron density in the crystal is then modelled as a sum of atom-centred charge distributions. Once the experimental electron density has been established, the 'atoms in molecules' theory of Bader (1990) provides tools for the interpretation of the density distribution in terms of its topological properties.

References: Bader, R. F. W. (1990). *Atoms in molecules: a quantum theory*. Oxford University Press. Coppens, P. (1997). *X-ray charge densities and chemical bonding*. Oxford University Press. Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921. Koritsanszky, T. S. & Coppens, P. (2001). *Chem. Rev.* **101**, 1583–1621.

Example 1 – This example shows how the local axes can be defined around each atom in terms of vectors between neighbouring atoms.

If necessary, dummy atoms can be introduced into the atom_site list for this purpose.

```
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
  Ni2+(1) DUM0 Z Ni2+(1) N(1) X

loop_
  _atom_site_label
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_occupancy
  DUM0 0.80000 0.80000 0.80000 0.0
```

`_atom_local_axes_atom_label` (char)

This item is used to identify an atom for which a local axis system is to be defined. Its value must be identical to one of the values given in the `_atom_site_label` list.

Appears in list as essential element of loop structure. **Must** match parent data name

`_atom_site_label`. [atom_local_axes]

`_atom_local_axes_atom0` (char)

Specifies 'atom0' in the definition of a local axis frame. The definition employs three atom-site labels, 'atom0', 'atom1' and 'atom2', and two axis labels, 'ax1' and 'ax2', having values '±X', '±Y' or '±Z'. For the atom defined by `_atom_local_axes_atom_label`, whose nuclear position is taken as the origin, local axis 'ax1' is the vector from the origin to atom0, axis 'ax2' is perpendicular to 'ax1' and lies in the plane of 'ax1' and a vector passing through the origin parallel to the vector atom1→atom2 (its positive direction making an acute angle with the vector parallel to atom1→atom2), and a right-handed orthonormal vector triplet is formed from the vector product of these two vectors. In most cases, atom1 will be the same as the atom specified by `_atom_local_axes_atom_label`. One or more 'dummy' atoms (with arbitrary labels) may be used in the vector definitions, specified with zero occupancy in the `_atom_site` description. The values of `*_atom0`, `*_atom1` and `*_atom2` must be identical to values given in the `_atom_site_label` list.

Appears in list containing `_atom_local_axes_atom_label`. **Must** match parent data name `_atom_site_label`. [atom_local_axes]

`_atom_local_axes_atom1` (char)

Specifies 'atom1' in the definition of a local axis frame. The definition employs three atom-site labels, 'atom0', 'atom1' and 'atom2', and two axis labels, 'ax1' and 'ax2', having values '±X', '±Y' or '±Z'. For the atom defined by `_atom_local_axes_atom_label`, whose nuclear position is taken as the origin, local axis 'ax1' is the vector from the origin to atom0, axis 'ax2' is perpendicular to 'ax1' and lies in the plane of 'ax1' and a vector passing through the origin parallel to the vector atom1→atom2 (its positive direction making an acute angle with the vector parallel to atom1→atom2), and a right-handed orthonormal vector triplet is formed from the vector product of these two vectors. In most cases, atom1 will be the same as the atom specified by `_atom_local_axes_atom_label`. One or more 'dummy' atoms (with arbitrary labels) may be used in the vector definitions, specified with zero occupancy in the `_atom_site` description. The values of `*_atom0`, `*_atom1` and `*_atom2` must be identical to values given in the `_atom_site_label` list.

Appears in list containing `_atom_local_axes_atom_label`. **Must** match parent data name `_atom_site_label`. [atom_local_axes]

`_atom_local_axes_atom2` (char)

Specifies 'atom2' in the definition of a local axis frame. The definition employs three atom-site labels, 'atom0', 'atom1' and 'atom2', and two axis labels, 'ax1' and 'ax2', having values '±X', '±Y' or '±Z'. For the atom defined by `_atom_local_axes_atom_label`, whose nuclear position is taken as the origin, local axis 'ax1'

is the vector from the origin to atom0, axis 'ax2' is perpendicular to 'ax1' and lies in the plane of 'ax1' and a vector passing through the origin parallel to the vector atom1→atom2 (its positive direction making an acute angle with the vector parallel to atom1→atom2), and a right-handed orthonormal vector triplet is formed from the vector product of these two vectors. In most cases, atom1 will be the same as the atom specified by `_atom_local_axes_atom_label`. One or more 'dummy' atoms (with arbitrary labels) may be used in the vector definitions, specified with zero occupancy in the `_atom_site` description. The values of `*_atom0`, `*_atom1` and `*_atom2` must be identical to values given in the `_atom_site_label` list.

Appears in list containing `_atom_local_axes_atom_label`. Must match parent data name `_atom_site_label`. [atom_local_axes]

`_atom_local_axes_ax1` (char)

Specifies 'ax1' in the definition of a local axis frame. The definition employs three atom-site labels, 'atom0', 'atom1' and 'atom2', and two axis labels, 'ax1' and 'ax2', having values '±X', '±Y' or '±Z'. For the atom defined by `_atom_local_axes_atom_label`, whose nuclear position is taken as the origin, local axis 'ax1' is the vector from the origin to atom0, axis 'ax2' is perpendicular to 'ax1' and lies in the plane of 'ax1' and a vector passing through the origin parallel to the vector atom1→atom2 (its positive direction making an acute angle with the vector parallel to atom1→atom2), and a right-handed orthonormal vector triplet is formed from the vector product of these two vectors. In most cases, atom1 will be the same as the atom specified by `_atom_local_axes_atom_label`. One or more 'dummy' atoms (with arbitrary labels) may be used in the vector definitions, specified with zero occupancy in the `_atom_site` description. The values of `*_atom0`, `*_atom1` and `*_atom2` must be identical to values given in the `_atom_site_label` list.

Appears in list containing `_atom_local_axes_atom_label`.

The data value must be one of the following:

```
x  X  y  Y  z  Z +x +X +y +Y +z +Z -x -X -y
-Y -z -Z. [atom_local_axes]
```

`_atom_local_axes_ax2` (char)

Specifies 'ax2' in the definition of a local axis frame. The definition employs three atom-site labels, 'atom0', 'atom1' and 'atom2', and two axis labels, 'ax1' and 'ax2', having values '±X', '±Y' or '±Z'. For the atom defined by `_atom_local_axes_atom_label`, whose nuclear position is taken as the origin, local axis 'ax1' is the vector from the origin to atom0, axis 'ax2' is perpendicular to 'ax1' and lies in the plane of 'ax1' and a vector passing through the origin parallel to the vector atom1→atom2 (its positive direction making an acute angle with the vector parallel to atom1→atom2), and a right-handed orthonormal vector triplet is formed from the vector product of these two vectors. In most cases, atom1 will be the same as the atom specified by `_atom_local_axes_atom_label`. One or more 'dummy' atoms (with arbitrary labels) may be used in the vector definitions, specified with zero occupancy in the `_atom_site` description. The values of `*_atom0`, `*_atom1` and `*_atom2` must be identical to values given in the `_atom_site_label` list.

Appears in list containing `_atom_local_axes_atom_label`.

The data value must be one of the following:

```
x  X  y  Y  z  Z +x +X +y +Y +z +Z
-x -X -y -Y -z -Z. [atom_local_axes]
```

ATOM_RHO_MULTIPOLE

This category contains information about the multipole coefficients used to describe the electron density. High-resolution X-ray diffraction methods enable the determination of the electron density distribution in crystal lattices and molecules, which in turn allows for a characterization of chemical interactions (Coppens, 1997; Koritsanszky & Coppens, 2001). This is accomplished by the construction of a mathematical model of the charge density in a crystal and then by fitting the parameters of such a model to the experimental pattern of diffracted X-rays. The model on which this dictionary is based is the so-called multipole formalism proposed by Hansen & Coppens (1978). In this model, the electron density in a crystal is described by a sum of aspherical 'pseudoatoms' where the pseudoatom density has the form defined in the `_atom_rho_multipole_*` items. Each pseudoatom density consists of terms representing the core density, the spherical part of the valence density and the deviation of the valence density from sphericity. The continuous electron density in the crystal is then modelled as a sum of atom-centred charge distributions. Once the experimental electron density has been established, the 'atoms in molecules' theory of Bader (1990) provides tools for the interpretation of the density distribution in terms of its topological properties.

References: Bader, R. F. W. (1990). *Atoms in molecules: a quantum theory*. Oxford University Press. Coppens, P. (1997). *X-ray charge densities and chemical bonding*. Oxford University Press. Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921. Koritsanszky, T. S. & Coppens, P. (2001). *Chem. Rev.* **101**, 1583–1621.

Example 1 – Multipole coefficients for the nickel ion in $[Ni(H_3L)](NO_3)(PF_6)$. $[H_3L = N,N',N''\text{-tris}(2\text{-hydroxy-3-methylbutyl})\text{-1,4,7-triazacyclononane}]$ [G. T. Smith et al. (1997). *J. Am. Chem. Soc.* **119**, 5028–5034].

```
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
Ni2+ (1) 2.38 (4) 0.32 (4) 0.00 0.00 -0.02 (1)
0.00 (2) 0.00 0.00 0.00 0.00 -0.08 (1)
0.00 0.00 0.00 0.00 0.06 (1) -0.04 (1)
0.05 (1) 0.00 0.00 0.00 0.00 -0.20 (1)
0.08 (1) 0.00 0.00
1.04 (1) 0.44 (1) 0.44 1.15 (4) 0.44 1.15
```

`_atom_rho_multipole_atom_label` (char)
 This item is used to identify the atom whose electron density is described with an atom in the `ATOM_SITE` category. Its value must be identical to one of the values in the `_atom_site_label` list.
 Appears in list as essential element of loop structure. Must match parent data name
`_atom_site_label` [atom_rho_multipole]

`_atom_rho_multipole_coeff_Pc`
`_atom_rho_multipole_coeff_Pv`
`_atom_rho_multipole_coeff_P00`
`_atom_rho_multipole_coeff_P10`
`_atom_rho_multipole_coeff_P11`
`_atom_rho_multipole_coeff_P1-1`
`_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` (numb, su)

Specifies the multipole population coefficients $P(l, m)$ for the atom identified in `_atom_rho_multipole_atom_label`. The multipoles are defined with respect to the local axes specified in the `ATOM_LOCAL_AXES` category. The coefficients refer to the multipole formalism described by Hansen & Coppens [1978, equation (2)] which gives the electron density at position vector \mathbf{r} with respect to an atomic nucleus as

$$\rho(\mathbf{r}) = P_c \rho_{\text{core}}(\mathbf{r}) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum \{ \kappa'(l)^3 R(\kappa'(l), l, \mathbf{r}) \} \sum \{ P(l, m) d(l, m, \theta, \varphi) \},$$

where $P_c = \text{_atom_rho_multipole_coeff_Pc}$, $P_v = \text{_atom_rho_multipole_coeff_Pv}$, $P(0, 0) = \text{_atom_rho_multipole_coeff_P00}$, $P_c + P_v + P(0, 0) = Z$ (the atomic number) for a neutral atom, $\kappa = \text{_atom_rho_multipole_kappa}$, $\kappa'(l) = \text{_atom_rho_multipole_kappa_prime}[l]$ and $d(l, m, \theta, \varphi)$ is the spherical harmonic of order l, m at the position (θ, φ) with respect to spherical coordinates centred on the atom. The summations are performed over the index ranges $0 \leq l \leq l_{\text{max}}$, $-l \leq m \leq l$, respectively, where l_{max} is the highest order of multipole applied. The spherical coordinates are related to the local Cartesian axes defined in category `ATOM_LOCAL_AXES`, z is the polar axis from which the angle θ is measured, and the angle φ is measured from the x axis in the xy plane with the y axis having a value of $\varphi = +90^\circ$. $R(\kappa'(l), l, \mathbf{r})$ is defined in the `_atom_rho_multipole_radial_*` items. $\rho_{\text{core}}(\mathbf{r})$ and $\rho_{\text{valence}}(\kappa r)$ are the spherical core and valence 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`.

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478. Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921.

Appears in list containing `_atom_rho_multipole_atom_label`. [atom_rho_multipole]

`_atom_rho_multipole_configuration` (char)
 This item defines the electronic configuration of the atom given in `_atom_rho_multipole_atom_label` as free text.
 Appears in list containing `_atom_rho_multipole_atom_label`. [atom_rho_multipole]

`_atom_rho_multipole_core_source` (char),
 This item gives the source of the orbital exponents and expansion coefficients used to obtain the spherical core density of the atom defined in `_atom_rho_multipole_atom_label`. Alternatively, the core density may be obtained as described in the `_atom_rho_multipole_scat_core` item.

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478.

Appears in list containing `_atom_rho_multipole_atom_label`.
 Example:
 ; Clementi, E. & Roetti, C. (1974). At. Data Nucl. Data Tables, 14, 177-478.
 ; [atom_rho_multipole]

`_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` (numb, su)

Gives the radial function expansion-contraction coefficients ($\kappa = \text{_atom_rho_multipole_kappa}$ and $\kappa'(l) = \text{_atom_rho_multipole_kappa_prime}[l]$) for the atom specified in `_atom_rho_multipole_atom_label`. The coefficients refer to the multipole formalism described by Hansen & Coppens [1978, equation (2)], which gives the electron density at position vector \mathbf{r} with respect to an atomic nucleus as

$$\rho(\mathbf{r}) = P_c \rho_{\text{core}}(\mathbf{r}) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum \{ \kappa'(l)^3 R(\kappa'(l), l, \mathbf{r}) \} \sum \{ P(l, m) d(l, m, \theta, \varphi) \},$$

where $P_c = \text{_atom_rho_multipole_coeff_Pc}$, $P_v = \text{_atom_rho_multipole_coeff_Pv}$, $P(0, 0) = \text{_atom_rho_multipole_coeff_P00}$, $P_c + P_v + P(0, 0) = Z$ (the atomic number) for a neutral atom, $P(l, m) = \text{_atom_rho_multipole_coeff_P}[lm]$ and $d(l, m, \theta, \varphi)$ is the spherical harmonic of order l, m at the position (θ, φ) with respect to spherical coordinates centred on the atom. The spherical coordinates are related to the local Cartesian axes defined in category `ATOM_LOCAL_AXES`, z is the polar axis from which the angle θ is measured, and the angle φ is measured from the x axis in the xy plane with the y axis having a value of $\varphi = +90^\circ$. $R(\kappa'(l), l, \mathbf{r})$ is defined in the `_atom_rho_multipole_radial_*` items. $\rho_{\text{core}}(\mathbf{r})$ and $\rho_{\text{valence}}(\kappa r)$ are the spherical core and valence 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`. The order, l , of κ' refers to the order of the multipole function, $0 \leq l \leq 4$. The values of κ' are normally constrained to be equal.

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478. Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921.

Appears in list containing `_atom_rho_multipole_atom_label`.

[`_atom_rho_multipole`]

`_atom_rho_multipole_radial_function_type` (char)

Specifies the function $R(\kappa'(l), l, \mathbf{r})$ used for the radial dependence of the valence electron density in the multipole formalism described by Hansen & Coppens [1978, equation (2)] which gives the electron density at position vector \mathbf{r} with respect to the nucleus of the atom specified in `_atom_rho_multipole_atom_label` as

$$\rho(\mathbf{r}) = P_c \rho_{\text{core}}(\mathbf{r}) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum \{ \kappa'(l)^3 R(\kappa'(l), l, \mathbf{r}) \} \sum \{ P(l, m) d(l, m, \theta, \varphi) \},$$

where $P_c = \text{_atom_rho_multipole_coeff_Pc}$, $P_v = \text{_atom_rho_multipole_coeff_Pv}$, $P(0, 0) = \text{_atom_rho_multipole_coeff_P00}$, $P_c + P_v + P(0, 0) = Z$ (the atomic number) for a neutral atom, $\kappa = \text{_atom_rho_multipole_kappa}$, $\kappa'(l) = \text{_atom_rho_multipole_kappa_prime}[1]$, $P(l, m) = \text{_atom_rho_multipole_coeff_P}[lm]$ and $d(l, m, \theta, \varphi)$ is the spherical harmonic of order l, m at the position (θ, φ) with respect to spherical coordinates centred on the atom. The summations are performed over the index ranges $0 \leq l \leq l_{\text{max}}$, $-l \leq m \leq l$, respectively, where l_{max} is the highest order of multipole applied. The spherical coordinates are related to the local Cartesian axes defined in category `ATOM_LOCAL_AXES`, z is the polar axis from which the angle θ is measured and the angle φ is measured from the x axis in the xy plane with the y axis having a value of $\varphi = +90^\circ$. $\rho_{\text{core}}(\mathbf{r})$ and $\rho_{\text{valence}}(\kappa r)$ are the spherical core and valence 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_scatter_core` and `_atom_rho_multipole_scatter_valence`.

This item need not be given if a Slater function is used. The parameters of the Slater function should be given using the `_atom_rho_multipole_radial_slater_*` items.

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478. Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921.

Appears in list containing `_atom_rho_multipole_atom_label`.

[`_atom_rho_multipole`]

`_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` (numb, su)

These items are used when the radial dependence of the electron density, $R(\kappa'(l), l, \mathbf{r})$, of the atom specified in `_atom_rho_multipole_atom_label` is expressed as a Slater-type function [Hansen & Coppens (1978), equation (3)]:

$$R(\kappa'(l), l, \mathbf{r}) = \{ \zeta(l)^{n(l)+3} / [n(l) + 2]! \} (\kappa'(l)r)^{n(l)} \exp(-\kappa'(l)\zeta(l)r),$$

where $\kappa'(l) = \text{_atom_rho_multipole_kappa_prime}[1]$, $n(l) = \text{_atom_rho_multipole_radial_slater_n}[1]$ and $\zeta(l) =$

`_atom_rho_multipole_slater_zeta[1]`. $R(\kappa'(l), l, \mathbf{r})$ appears in the multipole formalism described by Hansen & Coppens [1978, equation (2)] which gives the electron density at position vector \mathbf{r} with respect to an atomic nucleus as

$$\rho(\mathbf{r}) = P_c \rho_{\text{core}}(\mathbf{r}) + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) + \sum \{ \kappa'(l)^3 R(\kappa'(l), l, \mathbf{r}) \} \sum \{ P(l, m) d(l, m, \theta, \varphi) \},$$

where $P_c = \text{_atom_rho_multipole_coeff_Pc}$, $P_v = \text{_atom_rho_multipole_coeff_Pv}$, $P(0, 0) = \text{_atom_rho_multipole_coeff_P00}$, $P_c + P_v + P(0, 0) = Z$ (the atomic number) for a neutral atom, $\kappa = \text{_atom_rho_multipole_kappa}$, $\kappa'(l) = \text{_atom_rho_multipole_kappa_prime}[1]$, $P(l, m) = \text{_atom_rho_multipole_coeff_P}[lm]$ and $d(l, m, \theta, \varphi)$ is the spherical harmonic of order l, m at the position (θ, φ) with respect to spherical coordinates centred on the atom. The spherical coordinates are related to the local Cartesian axes defined in category `ATOM_LOCAL_AXES`, z is the polar axis from which the angle θ is measured, and the angle φ is measured from the x axis in the xy plane with the y axis having a value of $\varphi = +90^\circ$. $\rho_{\text{core}}(\mathbf{r})$ and $\rho_{\text{valence}}(\kappa r)$ are the spherical core and valence 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_scatter_core` and `_atom_rho_multipole_scatter_valence`.

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478. Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* **A34**, 909–921.

Appears in list containing `_atom_rho_multipole_atom_label`.

[`_atom_rho_multipole`]

`_atom_rho_multipole_scatter_core` (char)

This item gives the scattering factor for the core electrons of the atom specified in `_atom_rho_multipole_atom_label` as a function of $\sin(\theta)/\lambda$. The text should contain only a table of two columns, the first giving the value of $\sin(\theta)/\lambda$, the second giving the X-ray scattering factor at this point in reciprocal space. The atomic core scattering factors are used in least-squares fitting of the items in `_atom_rho_multipole_coeff_*` and `_atom_rho_multipole_kappa_*` to experimental X-ray structure factors [see for example Coppens (1997)]. This item enables them to be supplied in the form of a numerical table. Normally, they originate from atomic orbital analytic wavefunctions such as those tabulated by Clementi & Roetti (1974).

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478. Coppens, P. (1997). *X-ray charge densities and chemical bonding*. Oxford University Press.

Appears in list containing `_atom_rho_multipole_atom_label`.

[`_atom_rho_multipole`]

`_atom_rho_multipole_scatter_valence` (char)

This item gives the scattering factor for the valence electrons of the atom specified in `_atom_rho_multipole_atom_label` as a function of $\sin(\theta)/\lambda$. The text should contain only a table of two columns, the first giving the value of $\sin(\theta)/\lambda$, the second giving the X-ray scattering factor at this point in reciprocal space. The atomic valence scattering factors are used in least-squares fitting of the items in `_atom_rho_multipole_coeff_*` and `_atom_rho_multipole_kappa_*` to experimental X-ray structure factors [see for example Coppens (1997)]. This item enables them to be supplied in the form of a numerical table. Normally, they originate from atomic orbital analytic wavefunctions such as those tabulated by Clementi & Roetti (1974).

References: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478. Coppens, P. (1997). *X-ray charge densities and chemical bonding*. Oxford University Press.

Appears in list containing `_atom_rho_multipole_atom_label`.

`[atom_rho_multipole]`

`_atom_rho_multipole_valence_source` *(char)*

This item gives the source of the orbital exponents and expansion coefficients used to obtain the spherical valence density of the atom defined in `_atom_rho_multipole_atom_label`. Alternatively, the valence density may be obtained as described in the `_atom_rho_multipole_scatter_valence` item.

Reference: Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177–478.

Appears in list containing `_atom_rho_multipole_atom_label`.

Example:

```
; Clementi, E. & Roetti, C. (1974). At. Data Nucl. Data
  Tables, 14, 177-478.
```

```
; [atom_rho_multipole]
```

ATOM_SITE

Data items in the ATOM_SITE category record details about the atom sites in a crystal structure, such as the positional coordinates, atomic displacement parameters, magnetic moments and directions.

`_atom_site_label` *(char)*

The `_atom_site_label` is a unique identifier for a particular site in the crystal, and is fully defined in the core CIF dictionary. The child data names itemized here are in addition to those in the core dictionary.

Appears in list as essential element of loop structure. May match child data name(s):

```
_atom_local_axes_atom0, _atom_local_axes_atom1,
  _atom_local_axes_atom2, _atom_local_axes_atom_label,
  _atom_rho_multipole_atom_label. [atom_site]
```