The Multipole Model and Refinement

Louis J Farrugia
Spherical Atom Scattering

The “standard” crystallographic refinement programs use a model of atomic scattering based on spherical atoms. The scattering from these atoms is isotropic. The example below is for Chromium ($Z = 24$)
The most commonly used formalism for describing aspherical atomic densities (and hence scattering) is the Hansen-Coppens pseudo-atom model. The total crystal density is modelled by the sum of pseudo-atoms at the atomic sites.

\[
\rho(\mathbf{r}) = P_{\text{core}}\rho_{\text{core}}(\mathbf{r}) + P_{\text{val}}k^3\rho_{\text{val}}(kr) + \sum_{l=0}^{l_{\text{max}}} k'^3 R_{l}(kr) \sum_{m=0}^{l} P_{lm\pm}Y_{lm\pm}(\Omega)
\]

The Pseudo-atom Multipole Representation

Core - (potentially) refinable population

Spherical valence - refinable monopole population \( P_v \) (charge) and kappa \( \kappa \)

Deformation valence - comprises a radial part and a spherical-harmonic part-refinable multipole populations \( P_{lm\pm} \) and kappa \( \kappa' \)

Real Spherical Harmonics

$Y^{-1}_1$  $Y^0_1$  $Y^1_1$  \[ \text{dipoles} \]

$Y^{-2}_2$  $Y^{-1}_2$  $Y^0_2$  $Y^1_2$  \[ \text{quadrupoles} \]

$Y^{-3}_3$  $Y^{-2}_3$  $Y^{-1}_3$  $Y^0_3$  $Y^1_3$  \[ \text{octupoles} \]

$Y^{-4}_4$  $Y^{-3}_4$  $Y^{-2}_4$  $Y^{-1}_4$  $Y^0_4$  $Y^1_4$  \[ \text{hexadecapoles} \]

Z axis is vertical, green is +ve, red is -ve
Real Spherical Harmonics

Spherical harmonics used in multipole models are \textit{density normalised}

\[
\int \mid d_{imp} \mid d\Omega = i \quad \text{for } l = 0, i = 1; \quad \text{for } l > 0, \ i = 2
\]

This normalisation means that for a spherically symmetric function, a population parameter of 1.0 denotes an electron population of 1.0

For the non-spherical functions, with \( l > 0 \), which have both positive and negative lobes, the population parameter represents the number of electrons shifted from the negative to the positive regions

In the special case of sites with cubic symmetry, the spherical-harmonic basis functions become mixed, and so-called \textit{Kubic Harmonics} are then required.

P. Coppens (1997), \textit{“X-ray Charge Densities and Chemical Bonding”}, IUCr Monograph, OUP, Oxford
Choice of the Radial Functions

The choice of the radial basis is in principle arbitrary, except that the analytical angular behaviour requires \( R_{nlm}r^{-1} \) to be finite at the origin. In practice either Gaussian or Slater type functions have been used.

The XD program uses (as one option - CSZD) these Slater-type functions:

\[
R_l(r) = \frac{a_l^{n(l)+3}}{(n(l)+2)!} r^{n(l)} \exp(-a_l r)
\]

Default values of the \( a_l \) and \( n(l) \) parameters for each atomic type are stored in databanks. Derived from atomic wavefunction calculations.

May be changed by user intervention.

Choice of the Radial Functions in XD

In the XD program, these radial functions are specified by the user in the MASTER FILE XD.MAS

The types of radial function may be individually selected for the core, spherical valence and deformation valence respectively.
Radial Functions for the Core Density

**CHFW** → Electron density from full HF expansion

\[
\psi(r) = |\phi_1 \phi_2 \ldots \phi_i \rangle = \sum_{j=1}^{m} \left[ \frac{(2n_j(l))!}{\left(\sum_{j=1}^{m}(2n_j(l))!\right)^{-1/2}} \right] (2\zeta_j)^{n_j(l)+1/2} c_{ji} r^{n_j(l)-1} \exp(-\zeta_j r) \]

\[
\rho_{\text{core}}(r) \propto \int \left| \psi_{\text{core}}(r) \right|^2 \quad \rightarrow \quad f_{\text{core}}
\]

**RDTB** → Also possible to construct core scattering from a table (seriously limits possibilities in analysis)

<table>
<thead>
<tr>
<th>K</th>
<th>RDTB</th>
<th>CHFW</th>
<th>CSZD</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.00000</td>
<td>17.64523</td>
<td>16.66577</td>
<td>15.27737</td>
</tr>
<tr>
<td>9.03673</td>
<td>8.38210</td>
<td>7.87046</td>
<td>7.45841</td>
</tr>
<tr>
<td>5.94559</td>
<td>5.66597</td>
<td>5.38698</td>
<td>5.11011</td>
</tr>
<tr>
<td>3.83114</td>
<td>3.60864</td>
<td>3.39964</td>
<td>3.20446</td>
</tr>
<tr>
<td>2.42940</td>
<td>2.31096</td>
<td>2.20308</td>
<td>2.10498</td>
</tr>
</tbody>
</table>
Radial Functions for Spherical Valence Density

**CHFW**  
Electron density from full HF expansion  
limited to the valence electrons defined in the SCAT table

\[
\psi(r) = |\varphi_1\varphi_2 \ldots \varphi_i> = \left[ \sum_{j=1}^{m} \frac{(2n_{ji}(l))!}{(2\zeta_{ji})^{n_j(l_i)+1/2}} c_{ji} r^{n_j(l_i)-1} \exp(-\zeta_{ji} r) \right]
\]

\[
\rho_{\text{valence}}(r) \propto \int |\psi_{\text{valence}}(r)|^2 \rightarrow f_{\text{valence}}
\]

<table>
<thead>
<tr>
<th>SCAT CORE SPHV DEFV</th>
<th>1S 2S 3S 4S 2P</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>chfw chfw cszd</td>
</tr>
</tbody>
</table>

\[
(2\langle j_0\rangle(2s2s) + 2\langle j_0\rangle2p2p))/4
\]
Radial Functions for Deformation Density

**CSZD**

A single-ζ Slater function will be used. The ζ exponent is constructed from the best single-ζ of the valence orbitals.

\[
\Phi_{nlm}(r) = \frac{\zeta^{n+1/2}}{(2n!)^{1/2}} r^{n-1} \exp(-\zeta r)
\]

Radial node-less function of an atomic orbital

\[
R_l(r) = \frac{a_l^{n(l)+3}}{(n(l) + 2)!} r^{n(l)} \exp(-a_l r)
\]

Radial node-less density function of an atomic orbital

\[
a_l = 2\zeta \\
n_l = 2(n-1)
\]

The \( n_l \) values must satisfy Poisson’s equation. The conditions are \( n_l \geq l \)

\[
\nabla^2 \varphi(r) = -4\pi \rho(r)
\]

Radial Functions for Deformation Density

**CHFW** → Electron density from full HF expansion

\[
\begin{align*}
C & \quad \text{CHFW CHFW CHFW CHFW} \quad 2 \quad -2 \quad 0 \quad 0 \quad 0 \quad -2 \quad \ldots \\
0 & \quad \text{CHFW (2s2s)+(2p2p)} \\
1 & \quad \text{CHFW (2s2s)} \\
2 & \quad \text{CHFW (2p2p)} \\
3 & \quad \text{RDSD} \quad 3 \quad 4.4 \\
4 & \quad \text{CSZD}
\end{align*}
\]

This defines the second monopole to be identical to the SPHV

Use the density of 2s orbital

Use the density of 2p orbital

Must define the form for all \( l \) values

Use a single-\( \zeta \), but with modified \( n_l \) and \( a \)

Use default single-\( \zeta \)

\[
\frac{1}{4} \left( 2\langle j_0 \rangle (2s2s) + 2\langle j_0 \rangle (2p2p) \right)
\]
Radial Functions for Deformation Density

CHFW - full expansion (5 Slater functions)
less sensitive to deformations, more adequate in describing
a molecular orbital which closely resembles an atomic orbital
(“low overlap regime”)  

CSZD - single Slater function
more expanded, therefore more sensitive to deformations, less adequate to describe a
“low overlap regime”

Radial Functions for Transition Metals

3d radial extension  (relatively contracted)

4s radial extension (highly diffuse)

scattering curve for density from 4s orbital

Only few reflections (often affected by extinction & absorption errors) contain information on 4s electrons.

\[ \sin(\theta)/\lambda \]
Radial Functions for Transition Metals

<table>
<thead>
<tr>
<th>SCAT</th>
<th>CORE</th>
<th>SPHV</th>
<th>DEFY</th>
<th>1S</th>
<th>2S</th>
<th>3S</th>
<th>4S</th>
<th>2P</th>
<th>3P</th>
<th>4P</th>
<th>3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>CHFW</td>
<td>CHFW</td>
<td>CHFW</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>0</td>
<td>−6</td>
</tr>
<tr>
<td>0</td>
<td>CHWF</td>
<td>(3d3d)</td>
<td>1</td>
<td>RDSD 4 2.0</td>
<td>4s in “core”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>RDSD</td>
<td>4 2.0</td>
<td>2</td>
<td>CHWF (3d3d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CHWF</td>
<td>4 2.0</td>
<td>4</td>
<td>CHWF (3d3d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CHWF</td>
<td>(3d3d)</td>
<td>0</td>
<td>CHWF (3d3d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Entry for Fe atom in parameter file XD.INP

<table>
<thead>
<tr>
<th>Fe</th>
<th>3</th>
<th>2</th>
<th>12</th>
<th>5</th>
<th>0</th>
<th>3</th>
<th>3</th>
<th>4</th>
<th>1</th>
<th>0</th>
<th>0.489010</th>
<th>0.453599</th>
<th>0.063590</th>
<th>1.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.005450</td>
<td>0.005063</td>
<td>0.004324</td>
<td>−0.000270</td>
<td>0.000747</td>
<td>0.000968</td>
<td>6.0000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td></td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(starting) value for $P_v$, $P_{00}$ not refined
Radial Functions for Transition Metals

Even order multipoles are produced by \( d \) orbitals

Odd order multipoles are produced by \( s-d \) mixing

(should be small anyway) and therefore are more diffuse

Entry for Fe atom in parameter file XD.INP

Even order multipoles are produced by \( d \) orbitals

Odd order multipoles are produced by \( s-d \) mixing

(should be small anyway) and therefore are more diffuse

Entry for Fe atom in parameter file XD.INP

- Remove 4s from “core”
- Try refining 4s occupation....
- Only \( d \) orbitals in SPHV
Physical Importance of the $n_l$ Parameters

$$R_l(r) = \frac{a_l^{n(l)+3}}{(n(l) + 2)!} r^{n(l)} \exp(-a_l r)$$

For elements of the third period (Si, S, P, Cl), an improved agreement is often found when the radial exponents for higher multipoles are larger than those expected based on atomic orbitals. Increasing the value of $n_l$ moves the maximum further from the nucleus.

The higher multipoles model the density in the interatomic regions - the covalent electron density.
Physical Importance of the $\kappa$ parameters

\[ R_l(r) = \frac{\kappa a_l^{n(l)+3}}{(n(l)+2)!} r^{n(l)} \exp(-\kappa a_l r) \]

The kappa parameters are scaling parameters for the $a_l$ values. They are very important for obtaining a good fit (take into account differing effective atomic charges), but their refinement is difficult.
The Kappa Restricted Multipole Model

The problems experienced with the refinement of the kappa parameters has led to the concept of the Kappa Restricted Multipole Model (KRMM). In this model, the kappa parameters for the deformation valence ($\kappa'$) are derived from multipole refinements using theoretical (error-free) structure factors obtained from high quality wavefunctions. These (and more) parameters are now incorporated into databases.

Table 1
Experimental $\kappa'$ parameters for oxygen atoms reported in the literature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional group</th>
<th>$\kappa'$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Dopa</td>
<td>Average in $-\text{CO}_2$</td>
<td>0.54</td>
<td>[1]</td>
</tr>
<tr>
<td>Ox-Histidine</td>
<td>$-\text{CO}_2$</td>
<td>0.84, 0.42</td>
<td>[7]</td>
</tr>
<tr>
<td>Ox-Proline-H$_2$O</td>
<td>Average in $-\text{CO}_2$</td>
<td>0.71</td>
<td>[7]</td>
</tr>
<tr>
<td>2-Methyl-4-nitroaniline</td>
<td>Average in $-\text{NO}_2$</td>
<td>0.95</td>
<td>[3]</td>
</tr>
<tr>
<td>p-Amino-p'-nitrobenzene</td>
<td>Average in $-\text{NO}_2$</td>
<td>0.85</td>
<td>[8]</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>Average in $-\text{NO}_2$</td>
<td>0.84</td>
<td>[8]</td>
</tr>
<tr>
<td>m-Nitrophenyl</td>
<td>Average in $-\text{NO}_2$</td>
<td>1.11</td>
<td>[2]</td>
</tr>
<tr>
<td>L-Dopa</td>
<td>$-\text{C-OH}$</td>
<td>0.80</td>
<td>[1]</td>
</tr>
<tr>
<td>m-Nitrophenyl</td>
<td>$-\text{C-OH}$</td>
<td>1.02</td>
<td>[2]</td>
</tr>
<tr>
<td>N-Acetyl-I-tyrosine</td>
<td>$-\text{C-OH}$</td>
<td>0.91</td>
<td>[5]</td>
</tr>
<tr>
<td>$\alpha$-Oxalic acid dihydrate</td>
<td>$-\text{C-OH}$</td>
<td>0.85</td>
<td>[6]</td>
</tr>
<tr>
<td>$\alpha$-Oxalic acid dihydrate</td>
<td>$-\text{C-OH}$</td>
<td>1.19</td>
<td>[9]</td>
</tr>
<tr>
<td>N-Acetyl-l-tryptophan methylamide</td>
<td>$-\text{C-O}$</td>
<td>0.64</td>
<td>[4]</td>
</tr>
<tr>
<td>N-acetyl-I-tyrosine</td>
<td>$-\text{C-O}$</td>
<td>0.88</td>
<td>[5]</td>
</tr>
<tr>
<td>$\alpha$-Oxalic acid dihydrate</td>
<td>$-\text{C-O}$</td>
<td>0.85</td>
<td>[6]</td>
</tr>
<tr>
<td>$\alpha$-Oxalic acid dihydrate</td>
<td>$-\text{C-O}$</td>
<td>1.00</td>
<td>[9]</td>
</tr>
<tr>
<td>(2S)-N-Acetyl-\alpha,\beta-dihydrophenylalanine methylamide</td>
<td>$-\text{C-O}$</td>
<td>1.01, 0.90</td>
<td>[10]</td>
</tr>
<tr>
<td>Ox-Proline-H$_2$O</td>
<td>H$_2$O</td>
<td>0.68</td>
<td>[7]</td>
</tr>
<tr>
<td>N-Acetyl-I-tyrosine</td>
<td>H$_2$O</td>
<td>0.76</td>
<td>[5]</td>
</tr>
<tr>
<td>$\alpha$-Oxalic acid dihydrate</td>
<td>H$_2$O</td>
<td>0.89</td>
<td>[6]</td>
</tr>
<tr>
<td>$\alpha$-Oxalic acid dihydrate</td>
<td>H$_2$O</td>
<td>1.01</td>
<td>[9]</td>
</tr>
</tbody>
</table>

The traditional choice is the databank derived from the Clementi-Roetti table. These were based on Roothan-Hartree Fock calculations on ground state isolated atoms and relevant ions. Each atomic orbital is expanded in a series of Slater functions

$$\varphi(r) = \sum_{j=1}^{m} \left[ (2n_j(l)!) \right]^{-1/2} (2\zeta_j)^{n_j(l)+1/2} c_j r_i^{n_j(l)-1} \exp(-\zeta_j r_i)$$

The use of analytical expressions to compute the scattering factors and the density means that all properties may be computed analytically as well.

Choice of the Databank

For the heavier elements \((Z > 36, \text{Kr})\) the effects of relativistic contractions cannot be neglected, especially for core electrons. For these elements, it is preferable to use a wave function that mimics the atomic relativistic density. In XD this is the SCM database (H to Xe), or the VM database (H to Cf).

### Graph

- **Relativistic**
- **Non-relativistic**
- **Difference**

**1s electron density of Xe**

**Difference is not large, but will have an effect on the refined thermal parameters**

Choice of the Databank

Discrepancies between the relativistic and non-relativistic scattering factors increase with the resolution of the data.

These scattering factors should be used for elements in the 5th period (2nd row transition metals).

The main advantages are
1. more accurate thermal parameters
2. better treatment of the core density

Choice of the Databank

**xd.bnk_RHF_CR: (BANK CR)**

CHFW Non relativistic wave functions (H-Kr, including ions)
Analytical Fit: *International Tables for Crystallography*

**xd.bnk_RHF_BBB: (BANK BBB)**

CHFW Non relativistic wave functions (H-Xe)
Analytical Fit: *International Tables for Crystallography*

**xd.bnk_RDF_SCM: (BANK SCM)**

CHFW Relativistic wave functions (H-Xe, including ions)

**xd.bnk_PBE-QZ4P-ZORA: (BANK VM)**

CHFW Relativistic wave functions (H-Cf) unpublished
Analytical Fit: Macchi, P.; Volkov, A. *unpublished*
The Refinable Atomic Parameters

**SHELX**

- $x, y, z$, occupancy, $U_{iso}$ (or $U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}$) - maximum 10 parameters/atom

**XD**

- $x, y, z$, $U_{iso}$ (or $U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}$) (9 parameters/atom)
- Anharmonic Gram-Charlier coefficients $3^{rd} + 4^{th}$ order $C_{jkl}$ $D_{jklm}$ (25 parameters/atom)

<table>
<thead>
<tr>
<th>$P_v$</th>
<th>$P_{00}$</th>
<th>$P_{10}$</th>
<th>$P_{11\pm}$</th>
<th>$P_{20}$</th>
<th>$P_{21\pm}$</th>
<th>$P_{22\pm}$</th>
<th>$P_{30}$</th>
<th>$P_{31\pm}$</th>
<th>$P_{32\pm}$</th>
<th>$P_{33\pm}$</th>
<th>$P_{40}$</th>
<th>$P_{41\pm}$</th>
<th>$P_{42\pm}$</th>
<th>$P_{43\pm}$</th>
<th>$P_{44\pm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>26</td>
<td>9</td>
<td>= 26 multipoles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Maximum 60 parameters/atom

Neither possible nor desirable to refine 60 parameters/atom!

1. even with high resolution, usually results in a too low data/parameter ratio
2. least-squares refinement will not be stable - too strong correlations between parameters - e.g. between anharmonic thermal parameters and multipole populations

**Solution:** Start with a restricted model, and gradually increase the complexity.
Refinement strategy using XDLSM

Start from a refined model based on a spherical atom refinement (SHELX/CRYSTALS etc)

1. Refine scale factor

```
KEEP KAPPA 1 2 3
KEEP CHARGE GROUP1
WEIGHT -2.0000 0.0000 0.0000 0.0000 0.0000 0.3333
SKIP OBSMIN 0.  *SIGCUT 3. SNLMIN 0. SNLMAX 2.
DMSDA 1.0 1.8
FOUR FMOD1 4 2 0 0 FMOD2 -1 2 0 0
KEY  xyz  --U2--  ----U3----  ------U4-------  M-  --D--  --Q--  ---O---  -----H-----
O(1)  000 000000 0000000000 00000000000000 00 00 0000 000000 00000000
N(1)  000 000000 0000000000 00000000000000 00 00 0000 000000 00000000
C(1)  000 000000 0000000000 00000000000000 00 00 0000 000000 00000000
H(1)  000 000000 0000000000 00000000000000 00 00 0000 000000 00000000
H(2)  000 000000 0000000000 00000000000000 00 00 0000 000000 00000000
H(3)  000 000000 0000000000 00000000000000 00 00 0000 000000 00000000
KAPPA  000000
KAPPA  000000
KAPPA  000000
KAPPA  000000
EXTCN  0000000
OVTHP 0
SCALE 1
END KEY
```
Refinement strategy using XDLSM

Start from a refined model based on a spherical atom refinement (SHELX/CRYSTALS etc)

1. Refine scale factor
2. Refine scale factor and positional parameters (non-H atoms)

```
KEEP KAPPA 1 2 3
KEEP CHARGE GROUP1
WEIGHT       -2.0000  0.0000  0.0000  0.0000  0.0000  0.3333
SKIP OBSMIN 0.  *SIGCUT 3. SNLMIN 0.  SNLMAX 2.
DMSDA 1.0 1.8
FOUR FMOD1 4 2 0 0  FMOD2 -1 2 0 0
KEY     xyz --U2-- ----U3---- -------U4-------- M- -D- --Q-- ------O----- ------H-----
O(1)    111 000000 0000000000 0000000000000000 00 00 0000 000000 000000000
N(1)    111 000000 0000000000 0000000000000000 00 00 0000 000000 000000000
C(1)    111 000000 0000000000 0000000000000000 00 00 0000 000000 000000000
H(1)    000 000000 0000000000 0000000000000000 00 00 0000 000000 000000000
H(2)    000 000000 0000000000 0000000000000000 00 00 0000 000000 000000000
H(3)    000 000000 0000000000 0000000000000000 00 00 0000 000000 000000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
EXTCN   0000000
OVTHP   0
SCALE   1
END KEY
```
Refinement strategy using XDLSM

Start from a refined model based on a spherical atom refinement (SHELX/CRYSTALS etc)

1. Refine scale factor
2. Refine scale factor and positional parameters (non-H atoms)
3. Refine scale factor, positional parameters & thermal parameters (non-H atoms)

```
KEEP KAPPA 1 2 3
KEEP CHARGE GROUP1
WEIGHT -2.0000 0.0000 0.0000 0.0000 0.0000 0.3333
SKIP OBSMIN 0.  *SIGCUT 3. SNLMIN 0. SNLMAX 2.
DMSDA 1.0 1.8
FOUR FMOD1 4 2 0 0 FMOD2 -1 2 0 0
KEY xyz --U2-- -----U3----- -------U4------ M- -D- --Q-- -----O---- -----H-----
O(1) 111 111111 0000000000 0000000000000000 00 00 0000 0000000000000000
N(1) 111 111111 0000000000 0000000000000000 00 00 0000 0000000000000000
C(1) 111 111111 0000000000 0000000000000000 00 00 0000 0000000000000000
H(1) 00 000000 0000000000 0000000000000000 00 00 0000 0000000000000000
H(2) 00 000000 0000000000 0000000000000000 00 00 0000 0000000000000000
H(3) 00 000000 0000000000 0000000000000000 00 00 0000 0000000000000000
KAPPA 000000
KAPPA 000000
KAPPA 000000
KAPPA 000000
KAPPA 000000
EXTCN 000000
OVTHP 0
SCALE 1
END KEY
```
Treatment of Hydrogen Atoms

The H atom positional parameters obtained from a spherical refinement will be incorrect.

(a) If neutron diffraction data are available, use the positional parameters for H atoms.
(b) Otherwise use the RESET BOND instruction to set X-H distances to standard neutron determined values, and refine an isotropic thermal parameter.

```
KEEP KAPPA 1 2 3
KEEP CHARGE GROUP1
WEIGHT -2.0000 0.0000 0.0000 0.0000 0.0000 0.3333
SKIP OBSMIN 0. *SIGCUT 3. SNLMIN 0. SNLMAX 2.
DMSDA 1.0 1.8
FOUR FMOD1 4 2 0 0 FMOD2 -1 2 0 0
RESET BOND N(1) H(1) 1.0 etc
KEY  x  y  z --U2-- -----U3----- --------U4--------- M--D--Q--O--H---
O(1) 111 111111 0000000000 0000000000000000 00 000 0000 00000000000000
N(1) 111 111111 0000000000 0000000000000000 00 000 0000 00000000000000
C(1) 111 111111 0000000000 0000000000000000 00 000 0000 00000000000000
H(1) 000 100000 0000000000 0000000000000000 00 000 0000 00000000000000
H(2) 000 100000 0000000000 0000000000000000 00 000 0000 00000000000000
H(3) 000 100000 0000000000 0000000000000000 00 000 0000 00000000000000
KAPPA 000000
KAPPA 000000
KAPPA 000000
KAPPA 000000
EXTCN 000000
OVTHP 0
SCALE 1
END KEY
```
Treatment of Hydrogen Atoms

The H atom isotropic thermal parameters are only poor approximations

(a) If neutron diffraction data are available, use the anisotropic thermal parameters
(b) They will need to be scaled to the adp’s of non-H atoms (using the UIJXN program)

---

Treatment of Hydrogen Atoms

The reason that the treatment of H atoms is very important is that the charge density parameters and thermal parameters are strongly correlated. It is impossible to obtain accurate multipole parameters without a reasonable estimate of the H atom thermal motion (Hirshfeld). H atoms have large amplitude anisotropic motion.

Welcome to the SHADE server
Updated 05 07 2006 [changes] SHADE publication just published

Simple Hydrogen Anisotropic Displacement Estimator
The shade program aims at providing an improved description of H atom thermal motion in molecular crystal structures by estimating an anisotropic description based on the displacements of the non-hydrogen atoms in the molecule.

Please upload a cif file containing the molecule for which anisotropic hydrogen atoms should be estimated.

Refinement strategy for Multipoles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbolic name</th>
<th>Order number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractional Coordinates</td>
<td>X, Y, Z</td>
<td>1-3</td>
</tr>
<tr>
<td>Displacement Tensor Components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd order $U_i^j$</td>
<td>U11, U22, U33, U12, U13, U23</td>
<td>4-9</td>
</tr>
<tr>
<td>3rd order $C_{ijk}^j$</td>
<td>C111, C222, C333, C112, C122, C113, C133, C223, C233, C123</td>
<td>10-19</td>
</tr>
<tr>
<td>4th order $D_{ijkl}^j$</td>
<td>D1111, D2222, D3333, D1112, D1222, D1113, D1333, D2223, D2333, D1122, D1133, D2233, D1123, D1223, D1233</td>
<td>19-34</td>
</tr>
<tr>
<td>Multipole Populations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monopoles</td>
<td>M1, M2</td>
<td>35-36</td>
</tr>
<tr>
<td>Dipoles</td>
<td>D1+, D1-, D0</td>
<td>37-39</td>
</tr>
<tr>
<td>Quadrupoles</td>
<td>Q0, Q1+, Q1-, Q2+, Q2-</td>
<td>40-44</td>
</tr>
<tr>
<td>Octupoles</td>
<td>O0, O1+, O1-, O2+, O2-, O3+, O3-</td>
<td>45-51</td>
</tr>
<tr>
<td>Hexadecapoles</td>
<td>H0, H1+, H1-, H2+, H2-, H3+, H3-, H4+, H4-</td>
<td>52-60</td>
</tr>
<tr>
<td>Radial Screening</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\kappa$, $\kappa’(l)$</td>
<td>KS, K0, K1, K2, K3, K4</td>
<td>61-66</td>
</tr>
<tr>
<td>Isotropic and Anisotropic Extinction</td>
<td>EX11, EX22, EX33, EX12, EX13, EX23, RHOEX (for isotropic case ISOEX = EX11)</td>
<td>67-73</td>
</tr>
<tr>
<td>Overall U</td>
<td>OVTBP</td>
<td>74</td>
</tr>
<tr>
<td>Scale Factor</td>
<td>SCALE</td>
<td>75</td>
</tr>
</tbody>
</table>

H atoms - monopoles, one bond directed dipole (D0) (up to quadrupoles)
Second period elements (Li - F) - up to octupoles
Third period elements (Na - Cl) - possibly up to hexadecapoles
Heavier elements - up to hexadecapoles
Refinement strategy for Multipoles

Start with a simple model and gradually increase the complexity (flexibility). At each stage, check that any increase in flexibility results in a significant improvement.

Apply full chemical and symmetry restraints (often the symmetry will be/ needs be only approximate).

Think carefully about the local coordinate system which must be defined for all atoms.

Formamide HC(=O)NH₂
Refinement strategy for Multipoles

Need to consult Table in the XD manual, which gives site symmetry restrictions on multipoles.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Choice of coordinate axes</th>
<th>Indices of symmetric $\gamma_{imp}$ ($\lambda$, $\mu$ are integers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>any</td>
<td>all ($l,m,\pm$)</td>
</tr>
<tr>
<td>$\bar{1}$</td>
<td>any</td>
<td>($2\lambda,m,\pm$)</td>
</tr>
<tr>
<td>2</td>
<td>$2 \parallel z$</td>
<td>($i,2\mu,\pm$)</td>
</tr>
<tr>
<td>m</td>
<td>$m \perp z$</td>
<td>($l,-2\mu,\pm$)</td>
</tr>
<tr>
<td>2/m</td>
<td>$2 \parallel z$, $m \perp z$</td>
<td>($2\lambda,2\mu,\pm$)</td>
</tr>
<tr>
<td>222</td>
<td>$2 \parallel z$, $2 \parallel y$, ($2 \parallel x$)</td>
<td>($2\lambda,2\mu,+$), ($2\lambda+1,2\mu,-$)</td>
</tr>
<tr>
<td>mm2</td>
<td>$2 \parallel z$, $m \perp y$, ($m \perp x$)</td>
<td>($i,2\mu,+$)</td>
</tr>
<tr>
<td>mmm</td>
<td>$m \perp z$, $m \perp y$, $m \perp x$</td>
<td>($2\lambda,2\mu,+$)</td>
</tr>
</tbody>
</table>

Tells us that

(a) the local z-axis must be defined so it is perpendicular to the mirror plane
(b) the allowed multipoles are (0,0), (1,1±), (2,2±), (2,0), (3,3±), (3,1±), (4,4±), (4,2±), (4,0)

The allowed multipoles are merely those which are symmetric w.r.t. the symmetry elements.

Sometimes crystallographic site symmetry mandates the use of these restrictions.
Refinement strategy for Multipoles

ATOM table

| ATOM | ATOM0 | AX1 | ATOM1 | ATOM2 | AX2 | R/L | TP | TBL | KAP | LMX | SITESYM | CHEMCON | O(1)     | C(1)       | X | O(1)      | N(1)      | R   | 1  | 4   | 4   | 1 cyl              |
|------|-------|-----|-------|-------|-----|-----|----|-----|-----|-----|---------|----------| O(1)     | C(1)       | Z | N(1)      | O(1)      | Y   | R | 2  | 2   | 2   | 4 mm2             |
| N(1) | C(1)  | Z   | N(1)  | O(1)  | Y   | R   | 2  | 3   | 3   | 4   | m       |          | N(1)     | C(1)       | X | C(1)      | O(1)      | Y   | R | 2  | 3   | 3   | 4 mm2             |
| C(1) | N(1)  | X   | C(1)  | O(1)  | Y   | R   | 2  | 3   | 3   | 4   | m       |          | C(1)     | H(1)       | Z | H(1)      | C(1)      | Y   | R | 1  | 4   | 4   | 1 cyl             |
| H(2) | N(1)  | Z   | H(2)  | C(1)  | Y   | R   | 1  | 4   | 4   | 1   | cyl     |          | H(2)     | H(3)       | O | O(1)      | O(1)      | Y   | R | 1  | 4   | 4   | 1 cyl             |
| H(3) | C(1)  | Z   | H(3)  | O(1)  | Y   | R   | 1  | 4   | 4   | 1   | cyl     |          | H(3)     | H(1)       | O | O(1)      | O(1)      | Y   | R | 1  | 4   | 4   | 1 cyl             |

KEY table

| RESET BOND | N(1) H(1) 1.0 etc |
| KEY | xyz --U2-- -----U3----- -------U4------- M- -D- --Q-- ----O---- -----H----- |
| O(1) | 111 111111 0000000000 000000000000000 10 110 10011 0110011 100110011 |
| N(1) | 111 111111 0000000000 000000000000000 10 100 10010 0100010 100100010 |
| C(1) | 111 111111 0000000000 000000000000000 10 110 10011 0110011 100110011 |
| H(1) | 000 000000 0000000000 000000000000000 10 001 10000 000000 000000000 |
| H(2) | 000 000000 0000000000 000000000000000 10 001 10000 000000 000000000 |
| H(3) | 000 000000 0000000000 000000000000000 10 001 10000 000000 000000000 |

. .
| SCALE 1 |
| END KEY |
Verification of refinement strategy

The refined parameters need to be checked to see if they represent a physically sensible density. This can be done through

(a) **Low residual indices, R values and GOF**. This is a necessary but not sufficient condition - many deficiencies in the model and data do not manifest in high residual indices.

(b) **Difference Fourier maps**. This is an essential test - an ideal map is featureless. Deficiencies in the model often manifest in spurious features.

(c) **Anisotropic thermal parameters**. The rigid bond test proposed by Hirshfeld should be checked at each stage. Typically we wish to see all \( \Delta \text{dmsa} < 0.001 \, \text{Å}^2 \) for the covalently bonded pairs of atoms (except H atoms) - the DMSDA command in XDLSM.

<table>
<thead>
<tr>
<th>ATOM---&gt;</th>
<th>ATOM</th>
<th>/ DIST</th>
<th>DMSDA</th>
<th>ATOM</th>
<th>/ DIST</th>
<th>DMSDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>C(1)</td>
<td>*</td>
<td>1.2405</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>C(1)</td>
<td>*</td>
<td>1.3193</td>
<td>-4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Deficiencies of the Multipole Model

The deficiencies of the multipole model have been much discussed in recent years. Mostly shows up as discrepancies in topological parameters when comparing experimental and theoretically derived densities. One well known case concerns polar covalent bonds.

Possible reasons for discrepancies include
(a) inadequate basis sets in theoretical studies
(b) neglect of electron correlation
(c) neglect of crystal environment (calculations mostly in gas phase)
(d) deficiencies in multipole model, particularly the radial functions.

Quantum calculations are usually undertaken using Gaussian basis sets. Coppens has noted that discrepancy between theory and experiment is less when Slater bases are used in theoretical calculations (ADF).

The KRMM was one proposed way of reducing the influence of kappa refinement.

Deficiences of the Multipole Model

“for chemically bound atoms, theoretically derived RDF’s are superior to those obtained from calculations on isolated atoms, even if differences … do not manifest themselves in the usual figures of merit”
