The Multipole Model and Refinement

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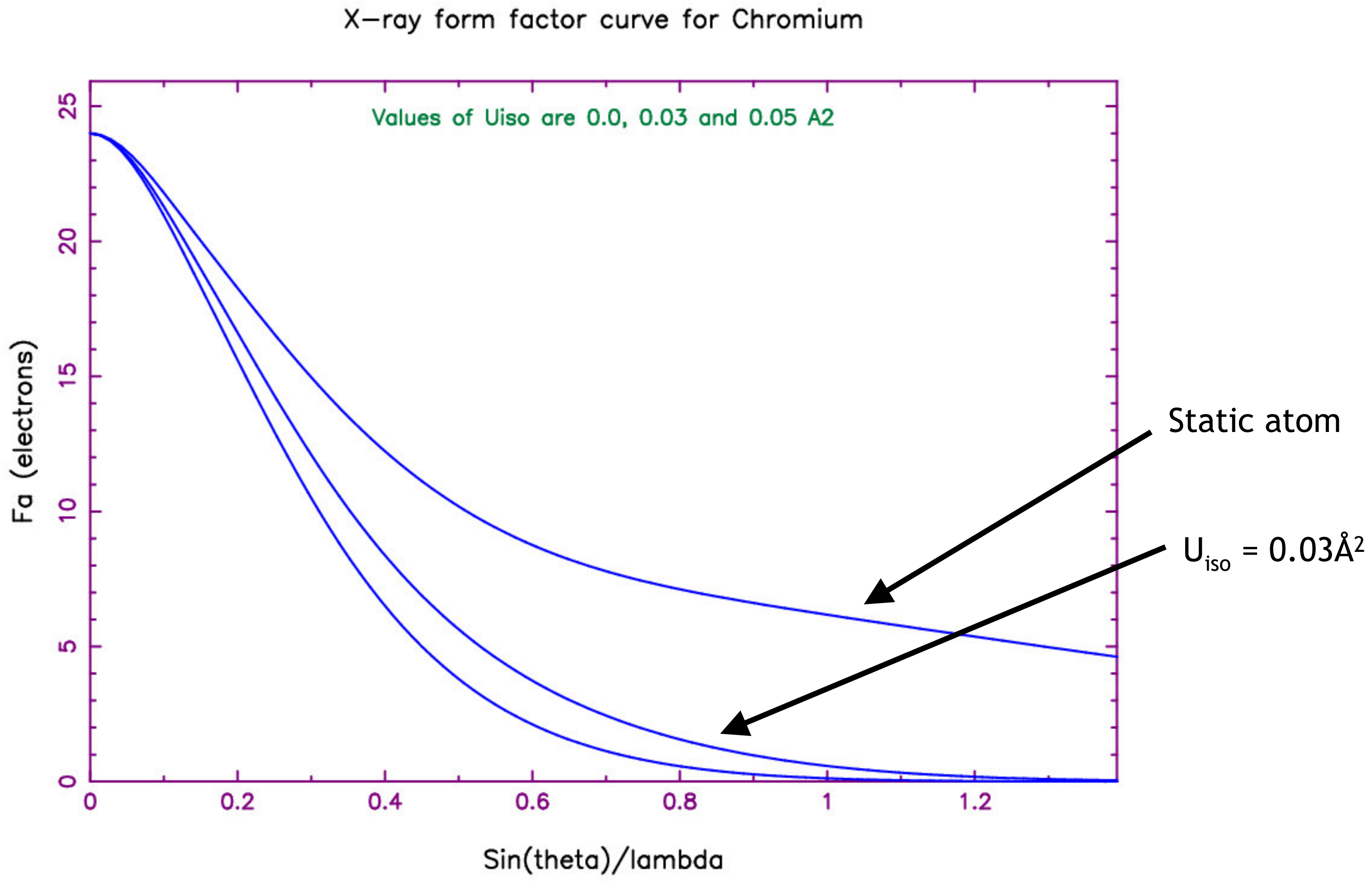
Spherical Atom Scattering

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)



Static atom

U_{iso} = 0.03Å^2

The Pseudo-atom Multipole Representation

$$\rho(\mathbf{r}) = \underset{\substack{\big\uparrow \\ \text{Spherical core}}}{P_{core}\rho_{core}(r)} + \underset{\substack{\big\uparrow \\ \text{Spherical valence}}}{P_{val}\kappa^{3}\rho_{val}(\kappa r)} + \sum_{l=0}^{l_{max}} \kappa'^{3} R_l(\kappa' r) \underset{\substack{\big\uparrow \\ \text{Deformation valence}}}{\sum_{m=0}^{l} P_{lm\pm} Y_{lm\pm}(\Omega)}$$

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.

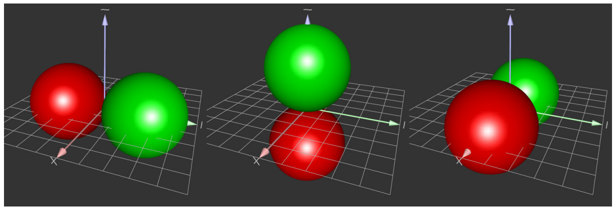
Core - (potentially) refinable population

Spherical valence - refinable monopole population *P*$_v$ (charge) and kappa κ

Deformation valence – comprises a radial part and a spherical-harmonic part- refinable multipole populations *P*$_{lm\pm}$ and kappa κ'

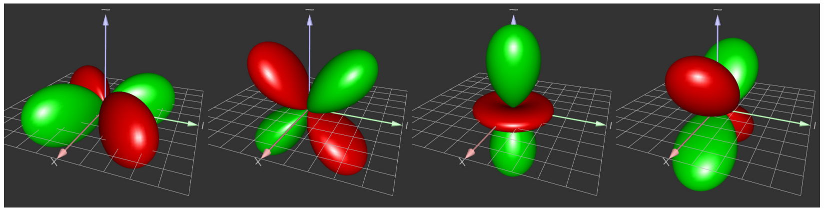
N.K. Hansen & P. Coppens (1978), *Acta Cryst*. **A34**, 909.

Real Spherical Harmonics



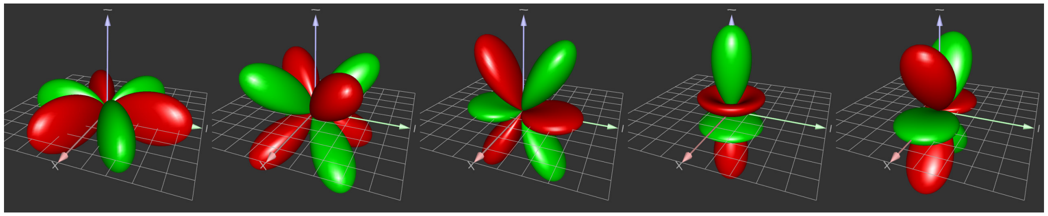
Y_1^{-1} Y_1^{0} Y_1^{1}

dipoles



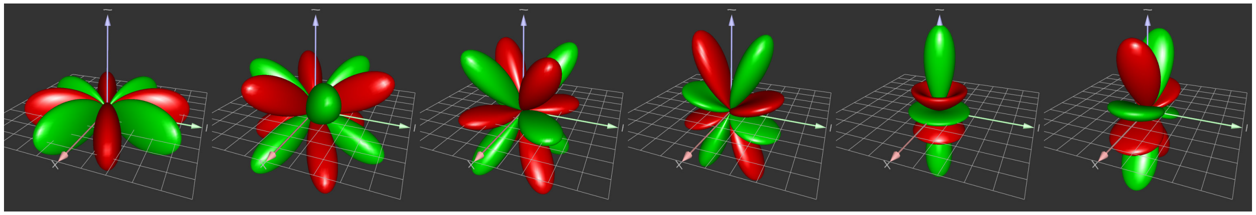
Y_2^{-2} Y_2^{-1} Y_2^{0} Y_2^{1}

quadrupoles



Y_3^{-3} Y_3^{-2} Y_3^{-1} Y_3^{0} Y_3^{1}

octupoles



Y_4^{-4} Y_4^{-3} Y_4^{-2} Y_4^{-1} Y_4^{0} Y_4^{1}

hexadecapoles

Z axis is vertical, green is +ve, red is -ve

Real Spherical Harmonics

Spherical harmonics used in multipole models are *density normalised*

$\int | d_{lmp} | d\Omega = i$ for $l = 0$, i = 1; 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 *Kubic Harmonics* are then required.

P. Coppens (1997), *"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.

K. Kurki-Suonio (1977) *Isr. J. Chemistry* **16**, 132.

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

```
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! <<< X D MASTER FILE >>> $Revision: 4.07 (Apr 25 2003)$           03-05-03 !
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
TITLE H2C2O4
CELL    6.1024    3.4973    11.9586    90.0000   105.7710    90.0000
WAVE    0.7107
LATT  C P
SYMM     0.5000 - X, 0.50000 + Y, 0.50000 - Z
BANK CR
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
    MODULE *XDLSM
SELECT   model 4 2 1 1 based_on F^2 test
SELECT  cycle 10 dampk 1. cmin 0.6 cmax 1. eigcut 1.d-09
SAVE  deriv lsqmat cormat
SOLVE  *inv diag *cond
!------------------------------------------------------------------------------
SCAT CORE SPHV DEFV   1S   2S   3S   4S   2P   3P   .... 6D   5F   DELF'   DELF''   NSCTL
O    CHFW CHFW CSZD    2   -2    0    0   -4    0   .... 0    0   0.0106  0.0060   0.580
C    CHFW CHFW CSZD    2   -2    0    0   -2    0   .... 0    0   0.0033  0.0016   0.665
H    CHFW CHFW CSZD   -1    0    0    0    0    0   .... 0    0   0.0000  0.0000  -0.374
END SCAT
```

The type of databank

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

limited to the core electrons defined in the SCAT table

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

$$\rho_{core}(r) \propto \int \left|\psi_{core}(r)\right|^2 \longrightarrow f_{core}$$

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

```
K     RDTB CHFW CSZD   2  2  2 -1  6  6  ....          0  0.1410  0.1580  0.371
   18.00000  17.64523  16.66577  15.27737  13.73497  12.24942  10.94846   9.88004
    9.03673   8.38210   7.87046   7.45841   7.11031   6.79966   6.50846   6.22570
    5.94559   5.66597   5.38698   5.11011   4.83746   4.57129   4.31370   4.06651
    3.83114   3.60864   3.39964   3.20446   3.02313   2.85543   2.70095   2.55916
    2.42940   2.31096   2.20308   2.10498   2.01590   1.93508   1.86179   1.79534
```

Radial Functions for Spherical Valence Density

CHFW ⟶ Electron density from full HF expansion

limited to the valence electrons defined in the SCAT table

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

$$\rho_{valence}(r) \propto \int\left|\psi_{valence}(r)\right|^2 \longrightarrow f_{valence}$$

```
SCAT CORE SPHV DEFV  1S 2S 3S 4S 2P
C    chfw chfw cszd   2 -2  0  0 -2
```

$$\big\downarrow$$

$$(2\overbrace{\langle j_0\rangle(2s2s) + 2\langle j_0\rangle 2p2p}))/4$$

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.

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

Radial node-less function of an atomic orbital

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

Radial node-less density function of an atomic orbital

$$\swarrow$$

$$\rho_{l,m(l)}(r)$$

$$a_l = 2\zeta \qquad n_l = 2(n-1)$$

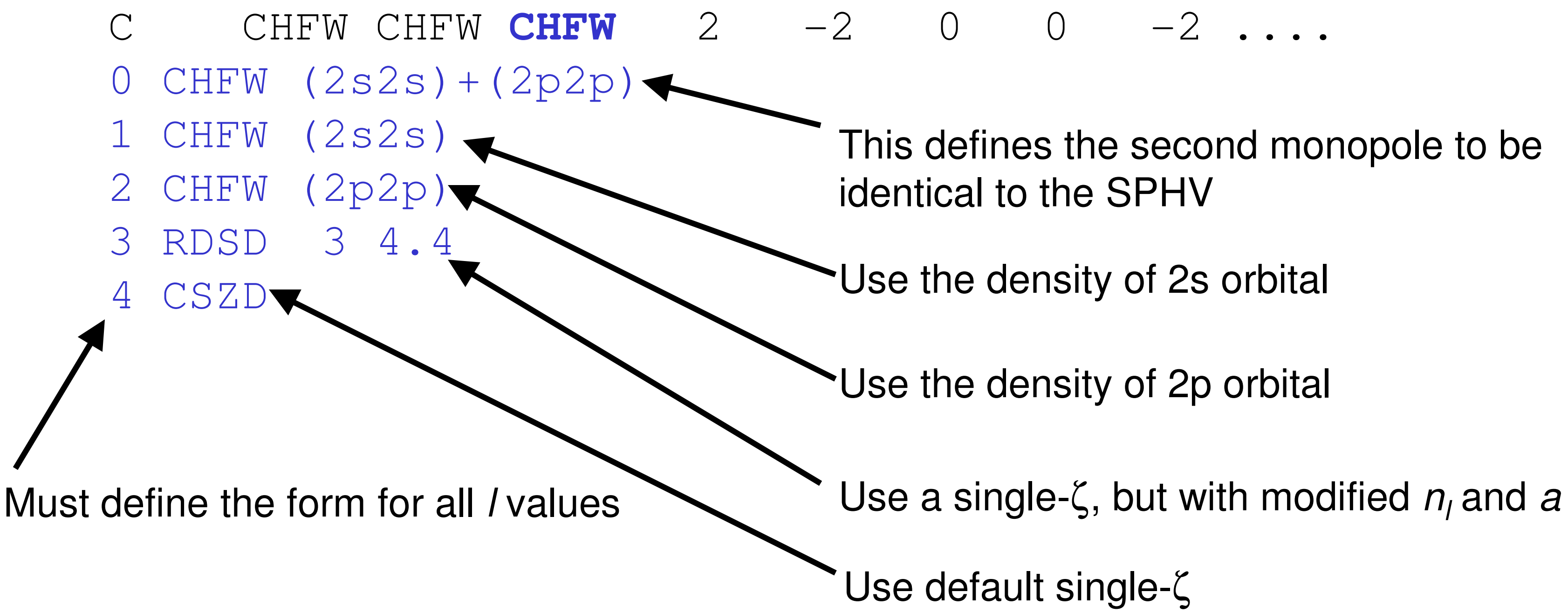
The n_l values must satisfy Poisson's equation.
The conditions are $n_l \geq l$

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

E. Clementi and D. L. Raimondi (1963) *J. Chem. Phys.* **38**, 2686.

Radial Functions for Deformation Density

CHFW → Electron density from full HF expansion



```
C     CHFW CHFW CHFW   2    -2    0    0    -2 ....
0 CHFW (2s2s)+(2p2p)
1 CHFW (2s2s)
2 CHFW (2p2p)
3 RDSD  3 4.4
4 CSZD
```

This defines the second monopole to be identical to the SPHV

Use the density of 2s orbital

Use the density of 2p orbital

Use a single-ζ, but with modified n_l and a

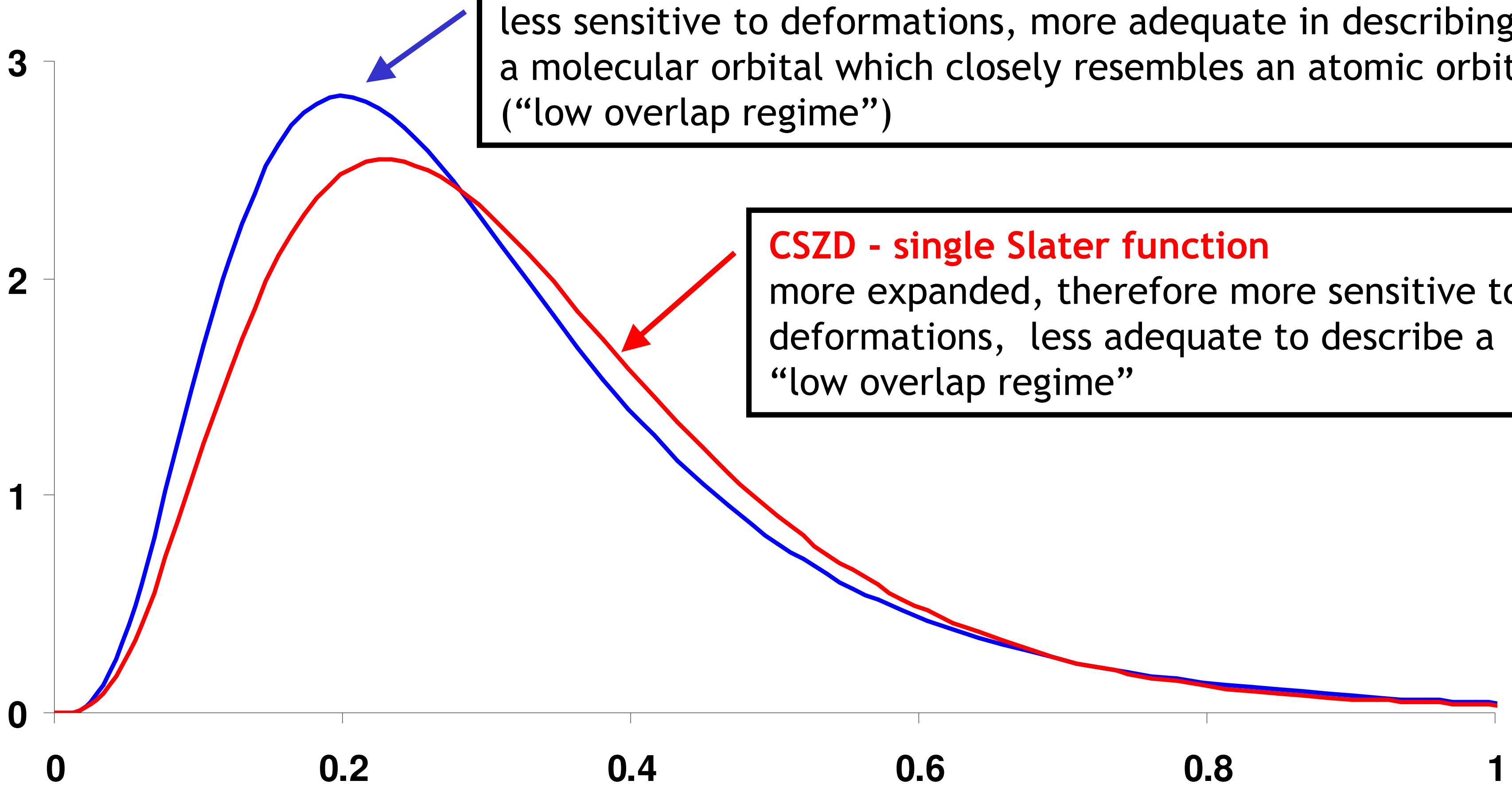
Use default single-ζ

Must define the form for all *l* values

$$(2\langle j_0\rangle(2s2s)\ +\ 2\langle j_0\rangle 2p2p))/4$$

Radial Functions for Deformation Density

3d orbital of Fe

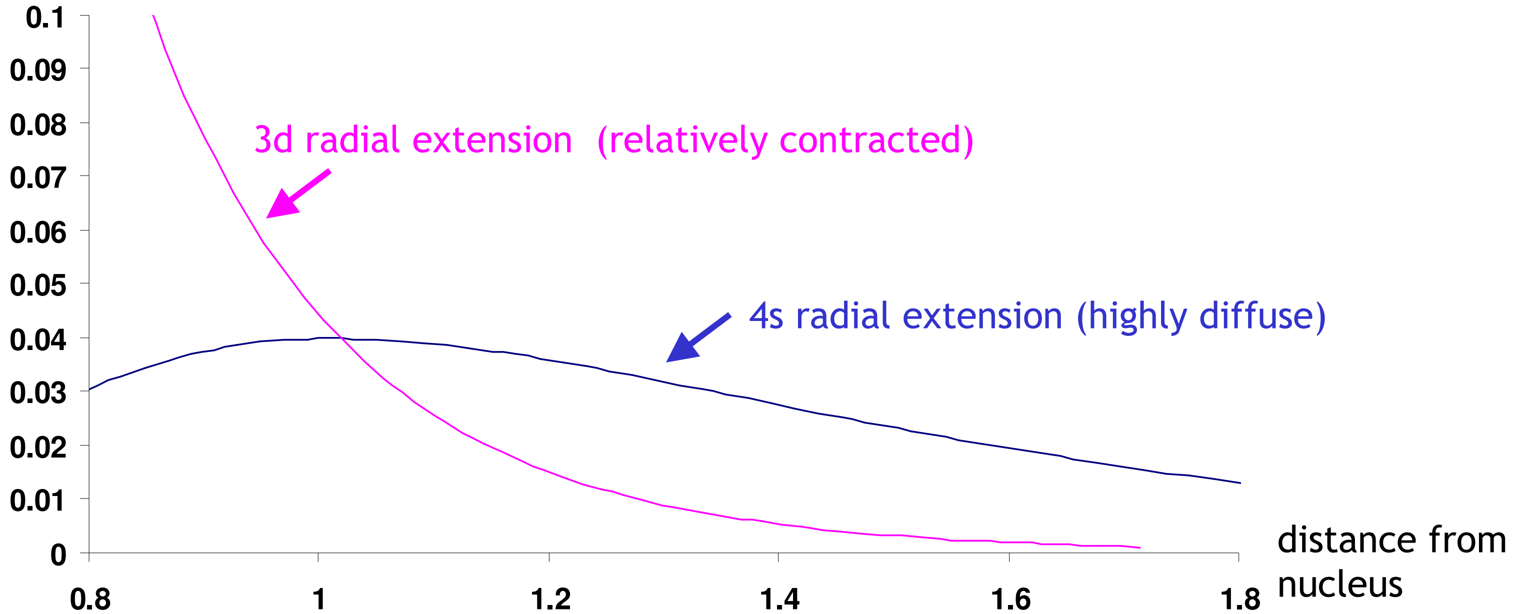


CHFW - full expansion (5 Slater functions)
less sensitive to deformations, more adequate in describing a molecular orbital which closely resembles an atomic orbital (“low overlap regime”)

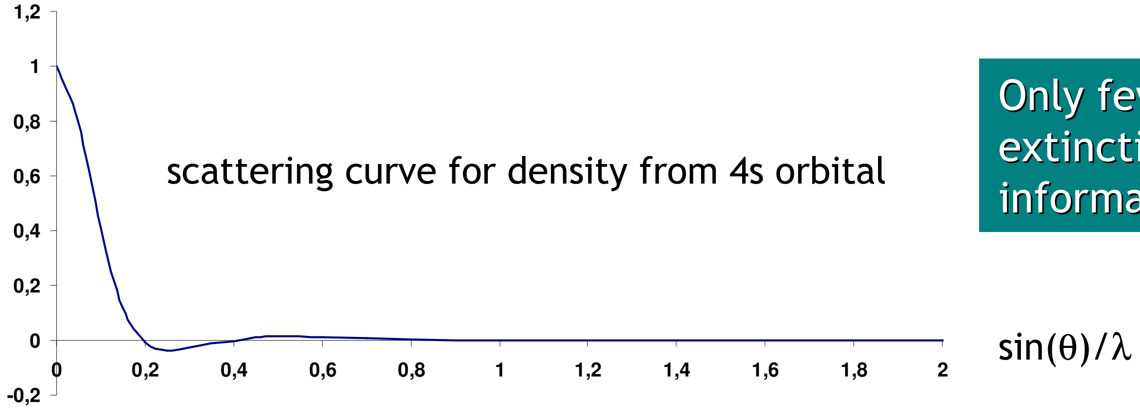
CSZD - single Slater function
more expanded, therefore more sensitive to deformations, less adequate to describe a “low overlap regime”

Tanaka *et al.*(1986) *J. Chem. Phys.* **12**, 6969.

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.

Radial Functions for Transition Metals

```
SCAT CORE SPHV DEFV   1S   2S   3S   4S   2P   3P   4P   3D
Fe   CHFW CHFW CHFW    2    2    2    2    6    6    0   -6
0 CHWF (3d3d)
1 RDSD 4 2.0
2 CHWF (3d3d)
3 CHWF 4 2.0
4 CHWF (3d3d)
```

4s in “core”

d orbitals in SPHV

Entry for Fe atom in parameter file XD.INP

```
Fe          3 2    2  12   5 0  3   3 4  1   0  0.489010  0.453599  0.063590 1.0000
  0.005450  0.005063  0.004324 -0.000270  0.000747  0.000968
  6.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
```

(starting) value for P_v

P_{00} not refined

Radial Functions for Transition Metals

```
SCAT CORE SPHV DEFV   1S   2S   3S   4S   2P   3P   4P   3D
Fe   CHFW CHFW CHFW    2    2    2    0    6    6    0   -8
0 CHWF (4s4s)
1 RDSD 4 2.0
2 CHWF (3d3d)
3 CHWF 4 2.0
4 CHWF (3d3d)
```

remove 4s from “core”

Try refining 4*s* occupation….

only *d* orbitals in SPHV

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

```
Fe          3 2    2  12   5 0   3   3 4   1    0  0.489010  0.453599  0.063590 1.0000
  0.005450  0.005063  0.004324 -0.000270  0.000747  0.000968
  8.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
```

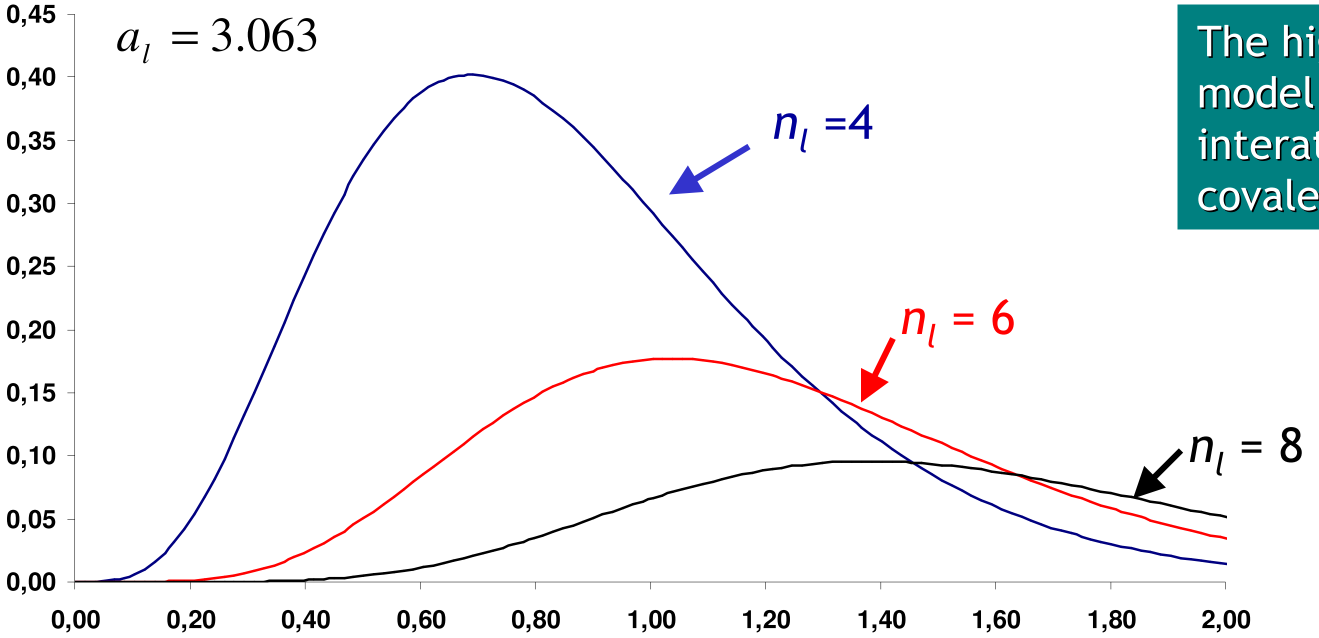
(starting) value for P_v

(starting) value for P_{00}

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.

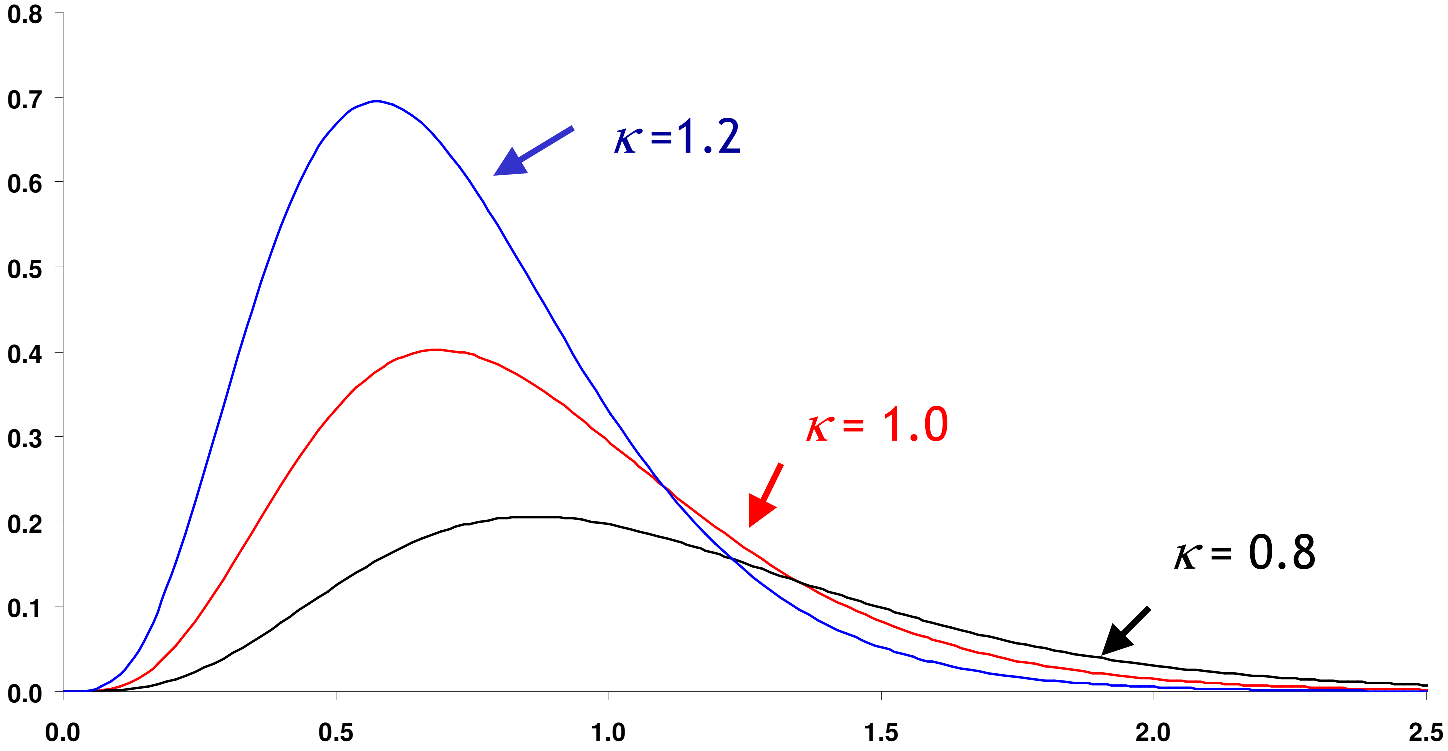


The higher multipoles model the density in the interatomic regions – the covalent electron density

Physical Importance of the κ 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 the deformation valence (κ′) are derived from mutipole refinements using theoretical (error-free) structure factors obtained from high quality wavefunctions. These (and more) parameters are now incorporated into databases.

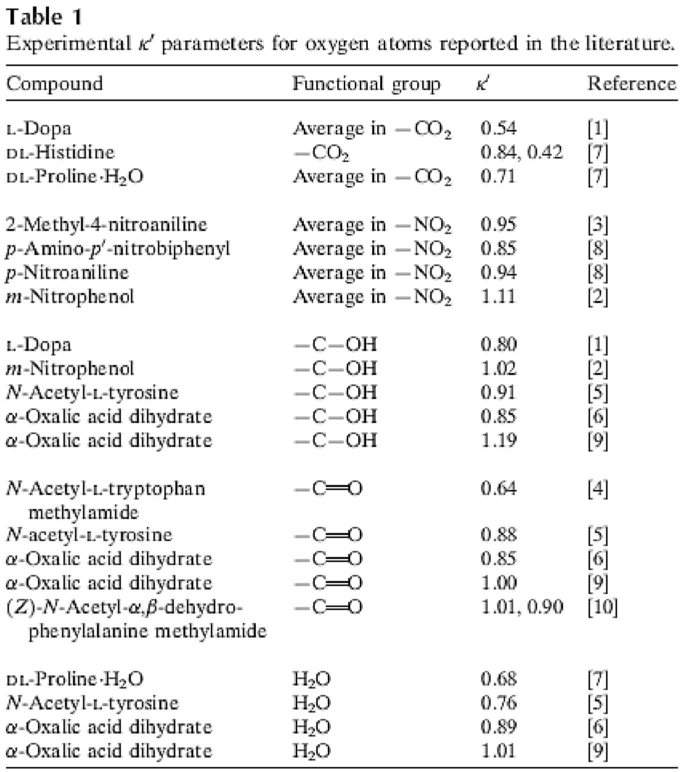
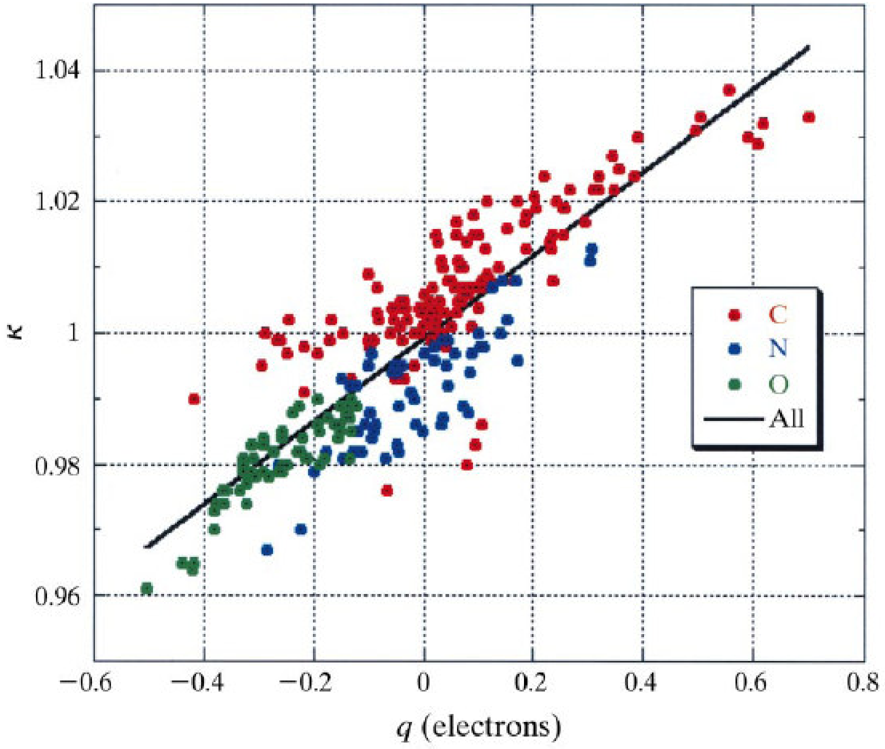


Table 1

Experimental κ' parameters for oxygen atoms reported in the literature.

Compound	Functional group	κ'	Reference
L-Dopa	Average in $-CO_2$	0.54	[1]
DL-Histidine	$-CO_2$	0.84, 0.42	[7]
DL-Proline·H_2O	Average in $-CO_2$	0.71	[7]
2-Methyl-4-nitroaniline	Average in $-NO_2$	0.95	[3]
p-Amino-*p*′-nitrobiphenyl	Average in $-NO_2$	0.85	[8]
p-Nitroaniline	Average in $-NO_2$	0.94	[8]
m-Nitrophenol	Average in $-NO_2$	1.11	[2]
L-Dopa	$-C-OH$	0.80	[1]
m-Nitrophenol	$-C-OH$	1.02	[2]
N-Acetyl-L-tyrosine	$-C-OH$	0.91	[5]
α-Oxalic acid dihydrate	$-C-OH$	0.85	[6]
α-Oxalic acid dihydrate	$-C-OH$	1.19	[9]
N-Acetyl-L-tryptophan methylamide	$-C{=}O$	0.64	[4]
N-acetyl-L-tyrosine	$-C{=}O$	0.88	[5]
α-Oxalic acid dihydrate	$-C{=}O$	0.85	[6]
α-Oxalic acid dihydrate	$-C{=}O$	1.00	[9]
(*Z*)-*N*-Acetyl-α,β-dehydro-phenylalanine methylamide	$-C{=}O$	1.01, 0.90	[10]
DL-Proline·H_2O	H_2O	0.68	[7]
N-Acetyl-L-tyrosine	H_2O	0.76	[5]
α-Oxalic acid dihydrate	H_2O	0.89	[6]
α-Oxalic acid dihydrate	H_2O	1.01	[9]



A. Volkov, Y. A. Abramov & P. Coppens (2001) *Acta Cryst.* **A57**, 272.

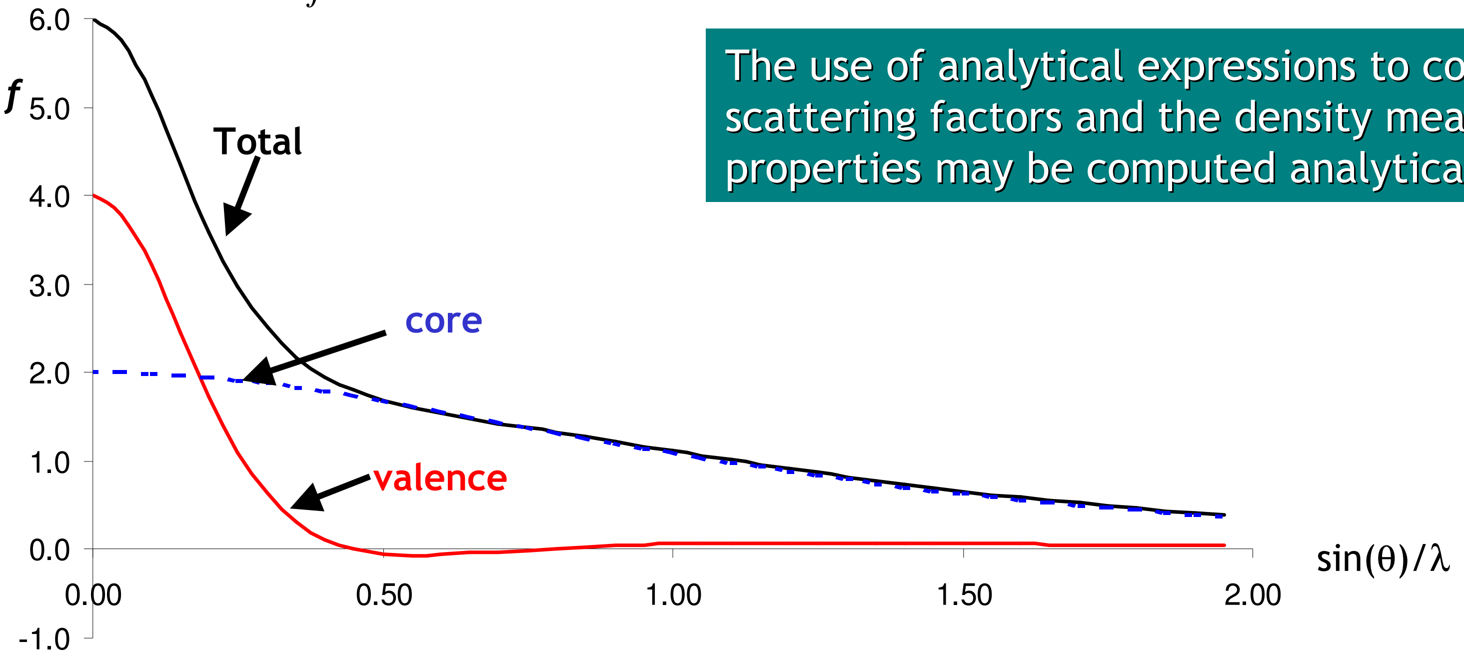
P. M. Dominiak, A. Volkov, X. Li, M. Messerschmidt, P. Coppens (2007) *J. Chem. Theory Comp.* **3**, 232

Choice of the Databank

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

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

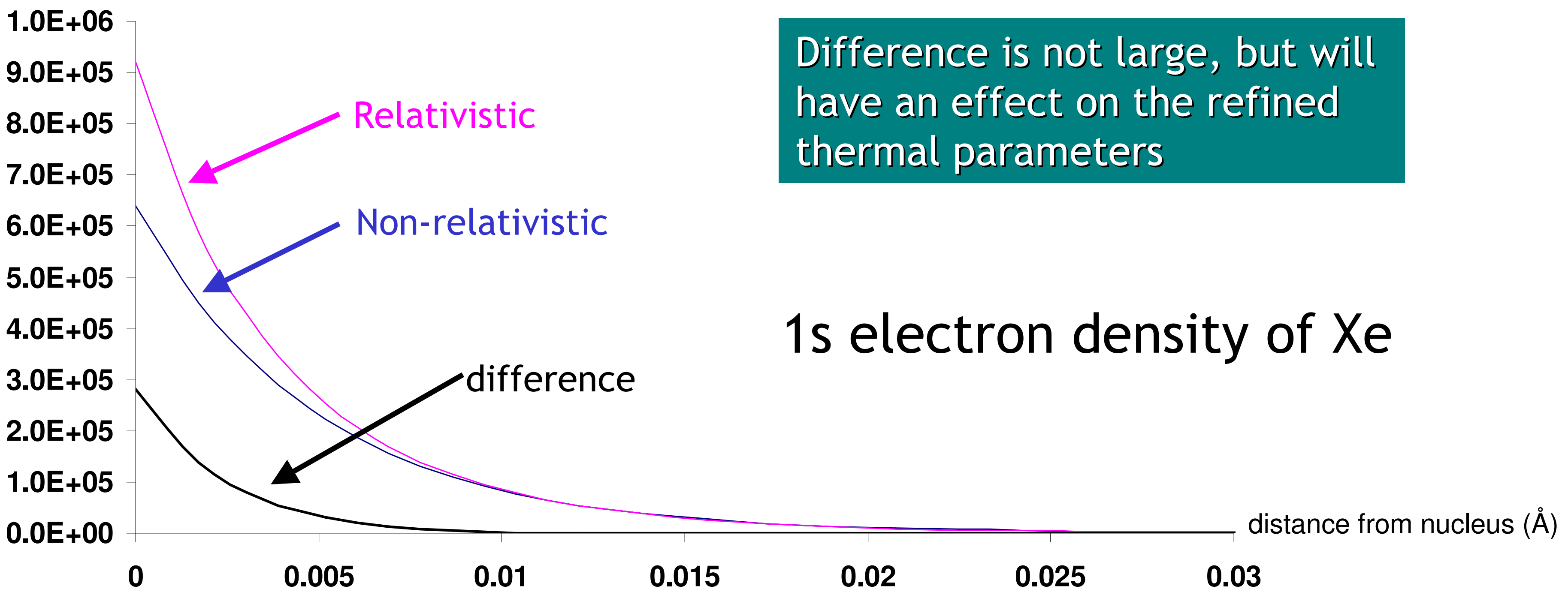
The use of analytical expressions to compute the scattering factors and the density means that all properties may be computed analytically as well



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

Choice of the Databank

For the heavier elements (*Z* > 36, Kr) the effects of relativistic contractions cannot be neglected, especially for core electrons. For these elements, it is prefereable 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)



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

1s electron density of Xe

Su, Z.; Coppens, P. *Acta Cryst* **1997**, *A53*, 749, Su, Z.; Coppens, P. *Acta Cryst* **1998**, *A54*, 646, Macchi, P.; Coppens, P. *Acta Cryst.*, **2001**, *A57*, 656

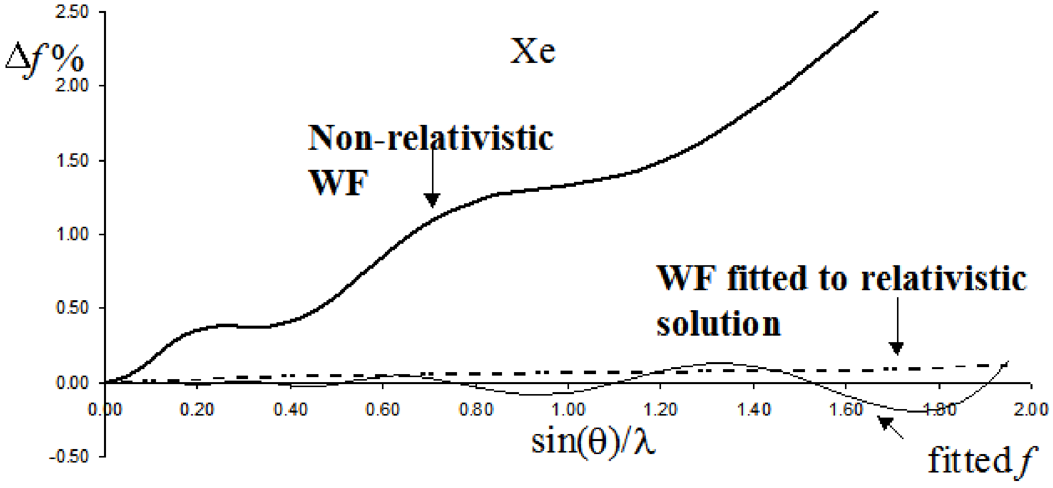
Choice of the Databank

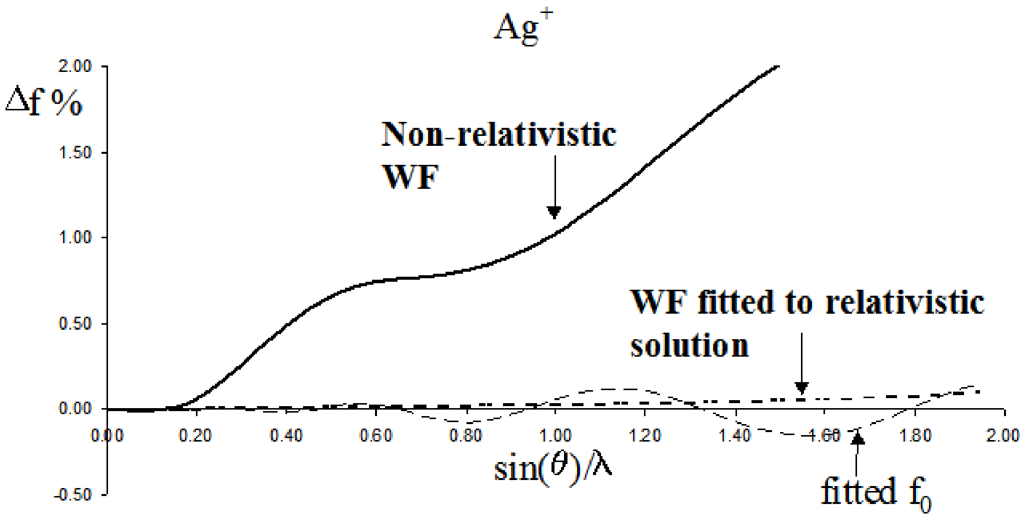
Discrepancies between the relativistic and non-relativistic scattering factors increase with the resolution of the data.

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





P. Macchi & P. Coppens (2001) *Acta Cryst.*, **A57**, 656

P. Macchi *et al* (2001) *J. Phys. Chem. A.* **105**, 9231

Choice of the Databank

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

CHFW Non relativistic wave functions (**H-Kr,** including ions)
Clementi, E. & Roetti, C. (1974). *At. Data Nucl. Data Tables*, **14**, 177-478
RDSD E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686-2689 (1963).
Analytical Fit : *International Tables for Crystallography*

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

CHFW Non relativistic wave functions **(H-Xe)**
C. F. Bunge, J. A. Barrientos, A. V. Bunge *At. Data Nucl. Data Tables*, **53**, 113-162 (1993).
RDSD E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686-2689 (1963).
Analytical Fit : *International Tables for Crystallography*

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

CHFW Relativistic wave functions (**H-Xe**, including ions)
Z. Su and P. Coppens *Acta Cryst.*, ***A54***, 646 (1998):
P. Macchi and P. Coppens *Acta Cryst.*, ***A57***, 656 (2001).
RDSD E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686-2689 (1963).
Analytical Fit : Su, Z.; Coppens, P. *Acta Cryst* **1997,** *A53*, 749,
Macchi, P.; Coppens, P. *Acta Cryst.*, **2001**, *A57*, 656

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

CHFW Relativistic wave functions (**H-Cf**) unpublished
RDSD E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686-2689 (1963).
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 3rd + 4th order C_{jkl} D_{jklm} (25 parameters/atom)

P_v	P_{00}	P_{10} $P_{11\pm}$	P_{20} $P_{21\pm}$ $P_{22\pm}$	P_{30} $P_{31\pm}$ $P_{32\pm}$ $P_{33\pm}$	P_{40} $P_{41\pm}$ $P_{42\pm}$ $P_{43\pm}$ $P_{44\pm}$
1	1	3	5	7	9 = 26 multipoles

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 000000000000000 00 000 00000 0000000 000000000
N(1)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
C(1)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(1)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(2)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(3)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
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 000000000000000 00 000 00000 0000000 000000000
N(1)    111 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
C(1)    111 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(1)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(2)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(3)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
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 000000000000000 00 000 00000 0000000 000000000
N(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
C(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
H(1)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(2)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(3)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
EXTCN   0000000
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     xyz --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
N(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
C(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
H(1)    000 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(2)    000 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(3)    000 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
EXTCN   0000000
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)

```
KEY     xyz --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
N(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
C(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
H(1)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
.
.
END KEY
```

If using neutron parameters, they must be *fixed*, i.e. not refined

XD.INP parameter file

Replace these with the *exact* neutron parameters

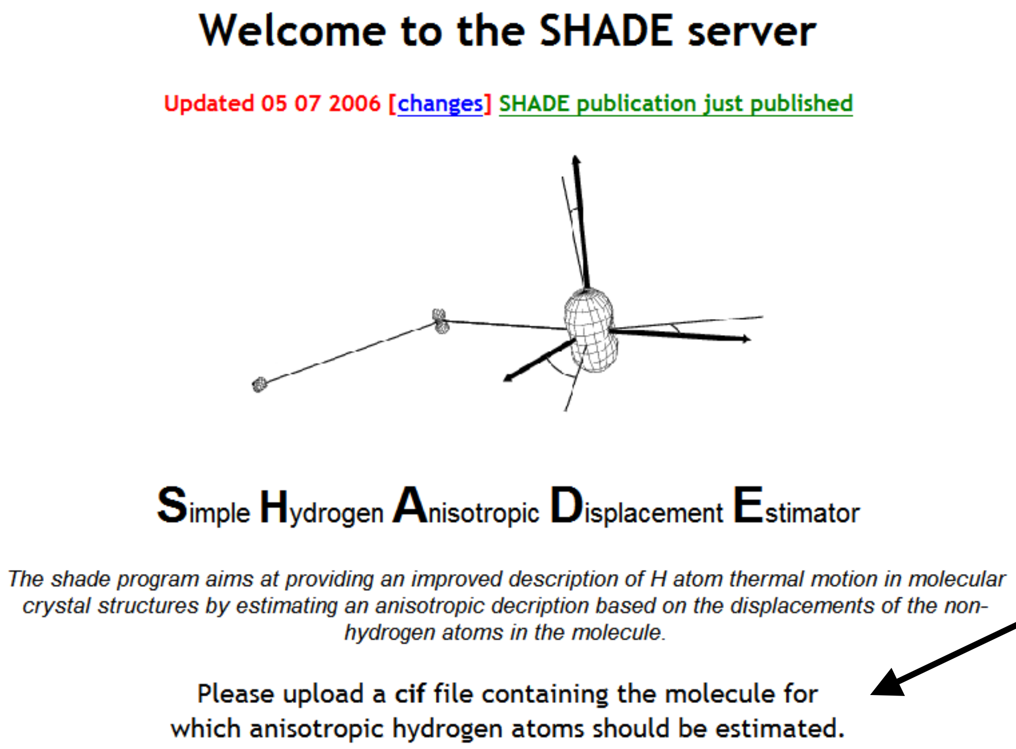
```
H(1)      1 2    2   4   3 1  4  4 1  1   0  0.211760  0.258310  0.138580 1.0000
  0.040036  0.000000  0.000000  0.000000  0.000000  0.000000
  0.7956  0.0000  0.1828  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
```

Replace these with the *scaled* neutron parameters

R. H. Blessing (1995). *Acta Cryst*, **B51**, 816.

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 mutipole 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 **H**ydrogen **A**nisotropic **D**isplacement **E**stimator

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

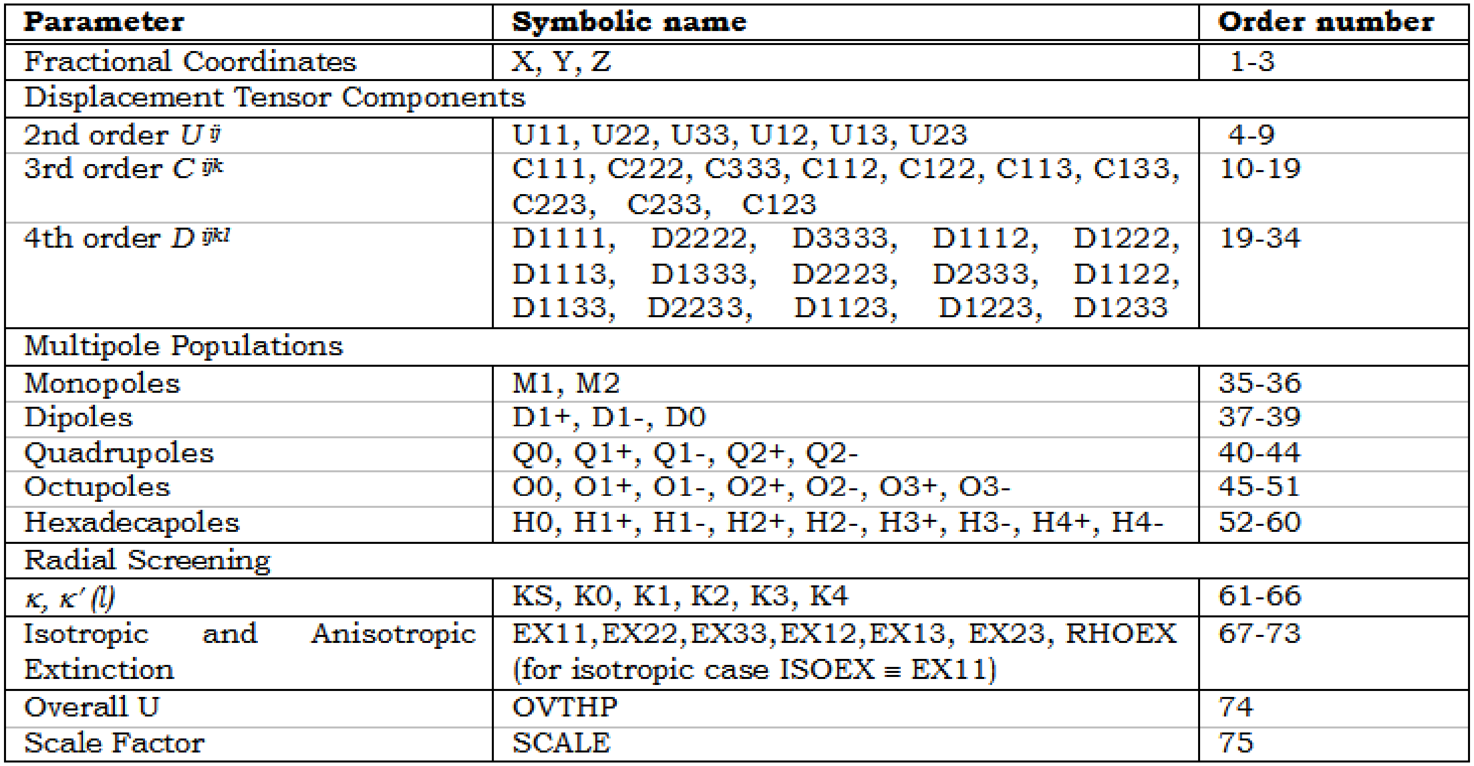
Please upload a cif file containing the molecule for which anisotropic hydrogen atoms should be estimated.

Only required data is a CIF file with the anisotropic thermal parameters of all the non-H atoms.

Method is only valid if there is no internal motion, *i.e.* need a rigid molecule.

F. Hirshfeld (1976) *Acta Cryst*, **32**, 239
A. Ø. Madsen (2006) *J. Appl. Cryst*. **39**, 757. – SHADE server http://shade.ki.ku.dk/
A. A. Whitten & M. A. Spackman (2006) *Acta Cryst*. **B62**, 875. –Uses ONIOM calculation – most rigourous

Refinement strategy for Multipoles



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

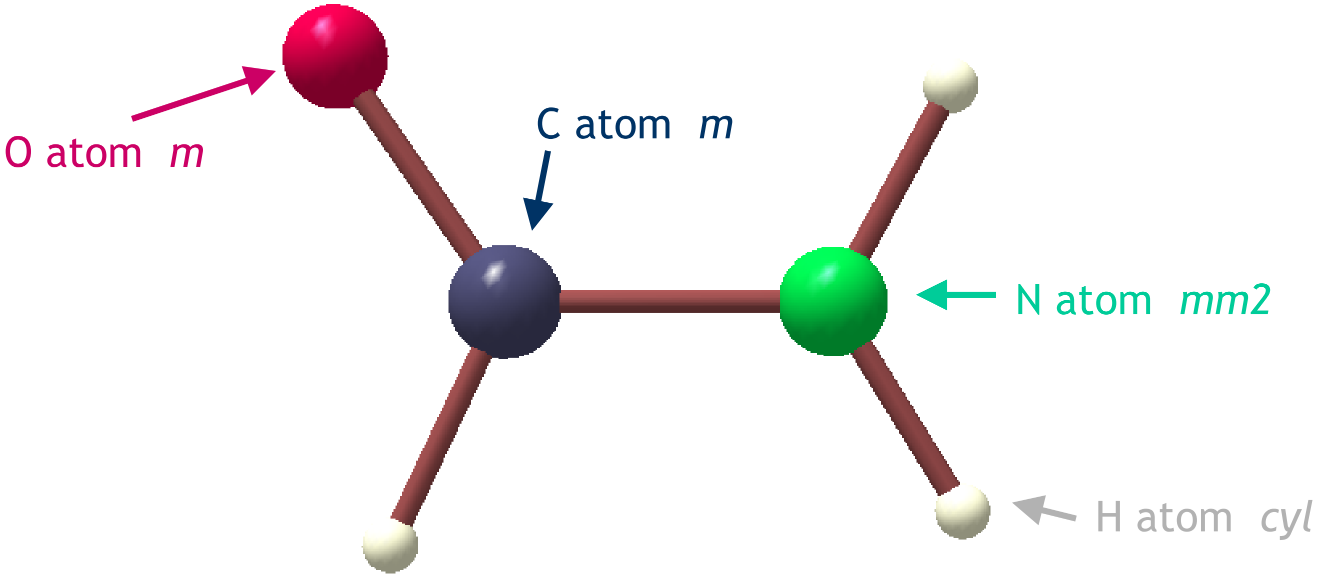
H atoms – monopoles, one bond directed dipole (D0) (up to quadrupoles)
Second period elements (Li – F) – up to octupoles
Third period elements (Na – Cl) – possibly up to hexadecapoles
Heavier elements – up to hexadecapoles

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).

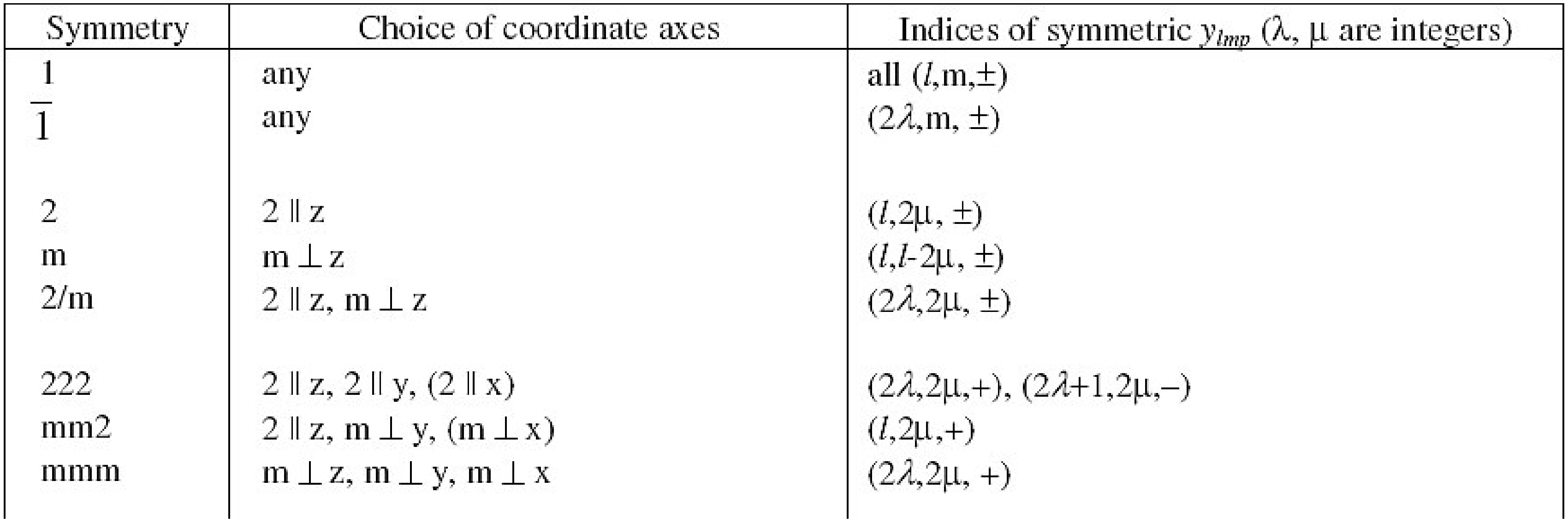
Think carefully about the *local coordinate system* which must be defined for all atoms.



Formamide $HC(=O)NH_2$

Refinement strategy for Multipoles

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



Symmetry	Choice of coordinate axes	Indices of symmetric y_{lmp} (λ, μ are integers)
1	any	all (l,m,±)
$\bar{1}$	any	(2λ,m, ±)
2	2 ∥ z	(l,2μ, ±)
m	m ⊥ z	(l,l-2μ, ±)
2/m	2 ∥ z, m ⊥ z	(2λ,2μ, ±)
222	2 ∥ z, 2 ∥ y, (2 ∥ x)	(2λ,2μ,+), (2λ+1,2μ,–)
mm2	2 ∥ z, m ⊥ y, (m ⊥ x)	(l,2μ,+)
mmm	m ⊥ z, m ⊥ y, m ⊥ x	(2λ,2μ, +)

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)        Y    R    2    1    1    4   m
N(1)      C(1)        Z  N(1)       O(1)        Y    R    2    2    2    4   mm2
C(1)      N(1)        X  C(1)       O(1)        Y    R    2    3    3    4   m
H(1)      N(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(3)      C(1)        Z  H(3)       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 0000000 000000000
H(2)    000 000000 0000000000 000000000000000 10 001 10000 0000000 000000000
H(3)    000 000000 0000000000 000000000000000 10 001 10000 0000000 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 Δdmsa < 0.001 Å^2 for the covalently bonded pairs of atoms (except H atoms) – the DMSDA command in XDLSM.

```
 Differences of Mean-Squares Displacement Amplitudes (DMSDA)
                  (1.E4 A**2) along interatomic vectors (*bonds)

  ATOM-->   ATOM    /  DIST  DMSDA ATOM    /  DIST  DMSDA ATOM    /
 DIST  DMSDA
  O(1)      C(1)    * 1.2405     1
  N(1)      C(1)    * 1.3193    -4
```

F. L. Hirshfeld (1976). *Acta Cryst*, **A32**, 239

Deficiences 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).

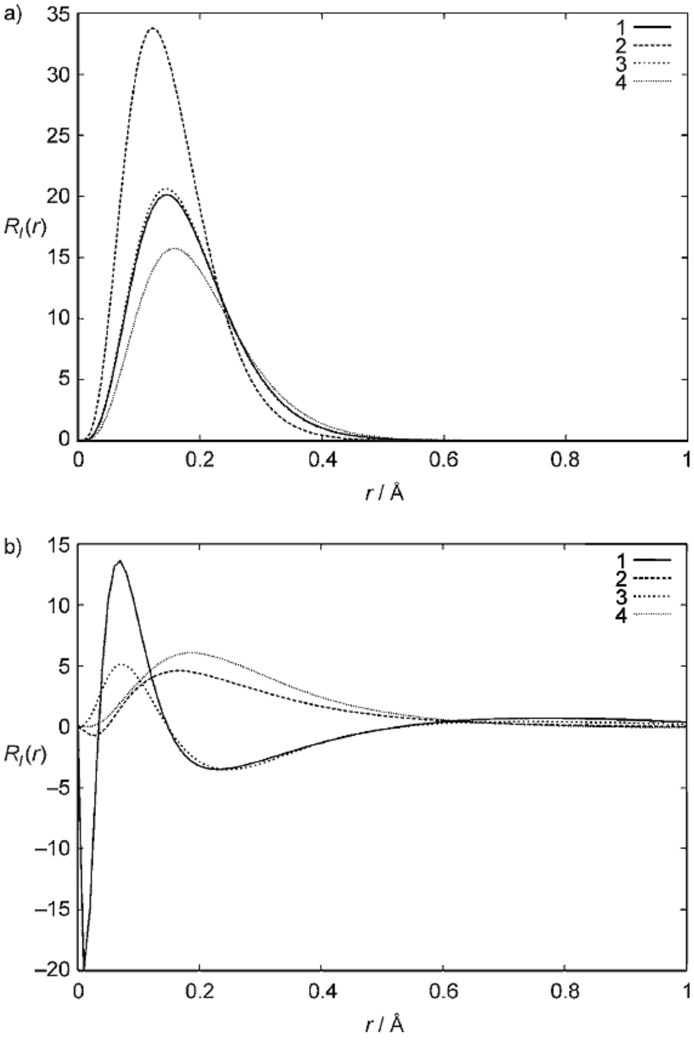
The KRMM was one proposed way of reducing the influence of kappa refinement.

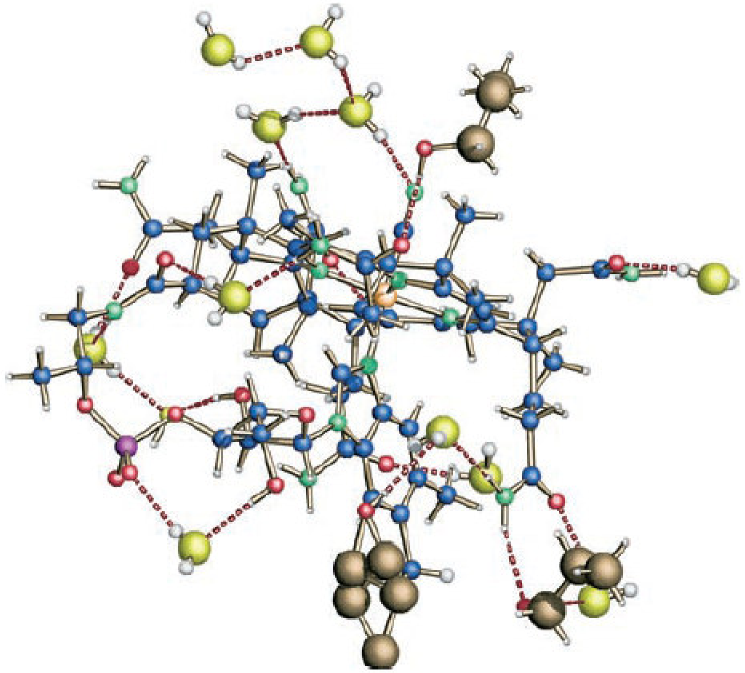
C. Gatti, R. Bianchi, R. Destro & F. Merati (1992) *J. Mol. Struct* **255** 409. (alanine)

A. Volkov, Y. Abramov, P. Coppens & C. Gatti (2000) *Acta Cryst.* ***A56***, 332. (*p*-nitro-aniline)

D. Stalke *et al* (2004) *J. Phys. Chem. A* **108** 9442. (S-N bonds)

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”

B. Dittrich, T. Koritsanszky, A. Volkov, S. Mebs, P. Luger (2007) *Angew Chemie*. ***46***, *2935*

T. Koritsanszky, A. Volkov (2004) *Chem Phys Lett*. **385**, 431