TUTORIAL-3

Aspherical-atom refinement using the XD2006 suite of programs and the WinXD GUI.

L. J. FARRUGIA
DEPARTMENT CHEMISTRY
UNIVERSITY GLASGOW
GLSAGOW G12 8QQ
SCOTLAND

EMAIL : louis@chem.gla.ac.uk

Table of Contents

These tutorials are heavily based on an XD tutorial given by A. Volkov and L. J. Farrugia

Programs to be used in the tutorials:

WinXD/XD2006	
MolIso	http://userpage.chemie.fu-berlin.de/~chuebsch/moliso/
Ghostscript	http://www.cs.wisc.edu/~ghost/
GSview	http://www.cs.wisc.edu/~ghost/

Main examples used in the tutorials:

Coordinate and reflection data files have been taken from recent articles in *Acta Crystallogr* with kind permission of the authors and the IUCr.

Example #1	*Acta Cryst.* (2005). **A61,** 314-320 http://dx.doi.org/10.1107/S0108767305005039
Example #2	*Acta Cryst.* (1995). **B51**, 559-570 http://dx.doi.org/10.1107/S0108768195005088
Example #3	*Acta Cryst.* (2005). **B61,** 443-448 http://dx.doi.org/10.1107/S010876810501637X
Example #4	*Acta Cryst.* (2002). **B58,** 690-700 http://dx.doi.org/10.1107/S0108768102006109
Example #4	*Acta Cryst.* (2003). **B59,** 234-246 http://dx.doi.org/10.1107/S0108768103000892

Introduction to the XD2006 and WinXD programs

The XD2006 package consists of several main programs, called modules, and utility programs. Each module performs a specific task. The main modules are:

module	task
XDINI	importing data to XD
XDLSM	least-squares refinement
XDGEOM	calculation of tables of geometries, ADPs, multipolar parameters and errors
XFOUR	calculation of Fourier maps
XDFFT	fast Fourier transform program
XDPROP	calculation of one-electron properties
XDGRAPH	visualization
TOPXD	full topological analysis of crystal structures

Unlike SHELX, XD uses three input files:

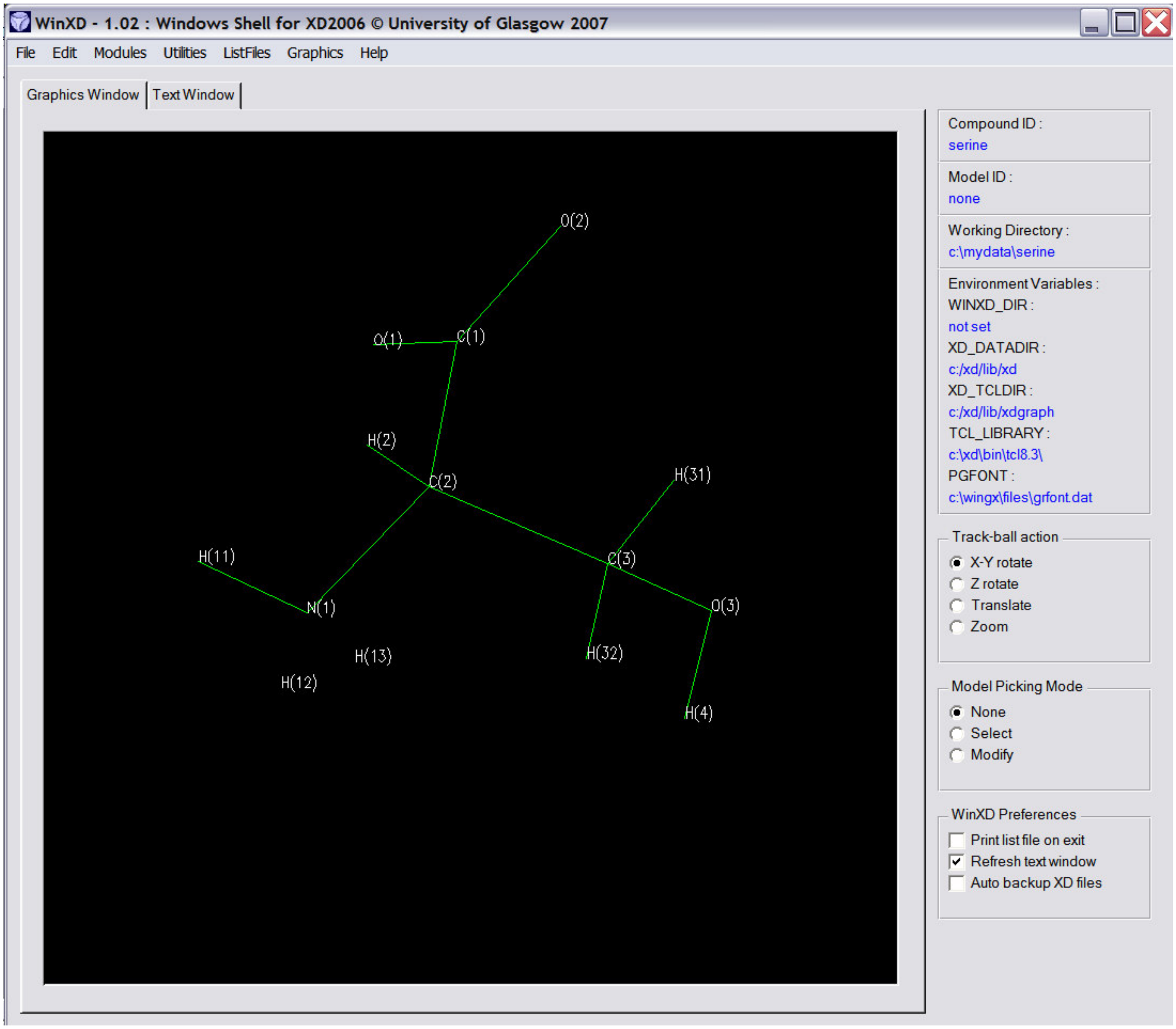
xd.mas – XD master (instructions) file
xd.inp and xd.res – XD parameter (atom data) file
xd.hkl – XD reflection file

This is because the XD suite consists of several modules and each module requires it own set of instructions. Merging instructions and parameter files would greatly complicate the task of working with XD.

Each of these files can be edited in any text editor or using the graphical user interface called WinXD. WinXD is a shell program for the Windows version of XD2006. It allows the user to modify the main instruction file xd.mas through a GUI interface, as well as execute all XD modules. Some graphical displays are also available in addition to the graphics in XDGRAPH.

To start WinXD, click the WinXD icon on the desktop or under **Start → Programs → WinXD menu.**

The WinXD main Window is as shown below. It has two panes, one allocated to graphical output, the other to textual output. The program automatically switches between these panes according to the menu items selected. The status panel to the right displays the current compound and model ID's, the current working directory and various user preferences regarding the operation of these two panes.



Compound ID :
serine

Model ID :
none

Working Directory :
c:\mydata\serine

Environment Variables :
WINXD_DIR :
not set
XD_DATADIR :
c:/xd/lib/xd
XD_TCLDIR :
c:/xd/lib/xdgraph
TCL_LIBRARY :
c:\xd\bin\tcl8.3\
PGFONT :
c:\wingx\files\grfont.dat

Track-ball action
- ● X-Y rotate
- ○ Z rotate
- ○ Translate
- ○ Zoom

Model Picking Mode
- ● None
- ○ Select
- ○ Modify

WinXD Preferences
- ☐ Print list file on exit
- ☑ Refresh text window
- ☐ Auto backup XD files

The Track-ball Action and Model Picking Modes are only operative when the graphics display is in Model or Bond Path mode.

1. Example # 1 Serine

For this first tutorial on XD2006, a set of exercises based on the crystal structure of DL-serine from a recent low-temperature 20K study was chosen:
“The invariom model and its application: refinement of D,L-serine at different temperatures and resolution” B. Dittrich, C. B. Hübschle, M. Messerschmidt, R. Kalinowski, D. Girnt and P. Luger *Acta Cryst.* (2005). **A61**, 314-320.

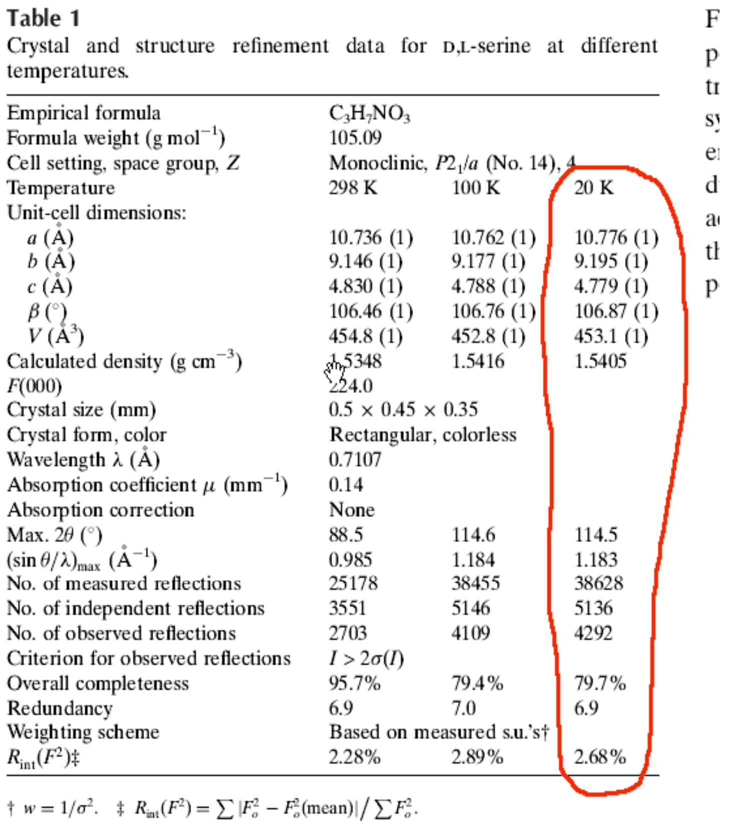
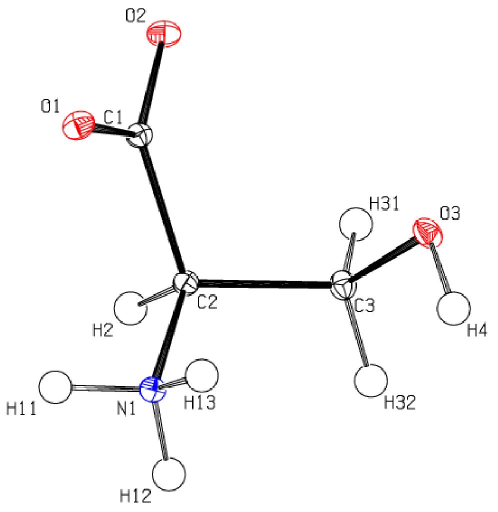


Table 1
Crystal and structure refinement data for D,L-serine at different temperatures.

Empirical formula	$C_3H_7NO_3$		
Formula weight (g mol^{-1})	105.09		
Cell setting, space group, Z	Monoclinic, $P2_1/a$ (No. 14), 4		
Temperature	298 K	100 K	20 K
Unit-cell dimensions:			
a (Å)	10.736 (1)	10.762 (1)	10.776 (1)
b (Å)	9.146 (1)	9.177 (1)	9.195 (1)
c (Å)	4.830 (1)	4.788 (1)	4.779 (1)
β (°)	106.46 (1)	106.76 (1)	106.87 (1)
V (Å^3)	454.8 (1)	452.8 (1)	453.1 (1)
Calculated density (g cm^{-3})	1.5348	1.5416	1.5405
F(000)	224.0		
Crystal size (mm)	0.5 × 0.45 × 0.35		
Crystal form, color	Rectangular, colorless		
Wavelength λ (Å)	0.7107		
Absorption coefficient μ (mm^{-1})	0.14		
Absorption correction	None		
Max. 2θ (°)	88.5	114.6	114.5
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.985	1.184	1.183
No. of measured reflections	25178	38455	38628
No. of independent reflections	3551	5146	5136
No. of observed reflections	2703	4109	4292
Criterion for observed reflections	$I > 2\sigma(I)$		
Overall completeness	95.7%	79.4%	79.7%
Redundancy	6.9	7.0	6.9
Weighting scheme	Based on measured s.u.'s†		
$R_{int}(F^2)$‡	2.28%	2.89%	2.68%

† $w = 1/\sigma^2$. ‡ $R_{int}(F^2) = \sum |F_o^2 - F_o^2(\text{mean})| / \sum F_o^2$.

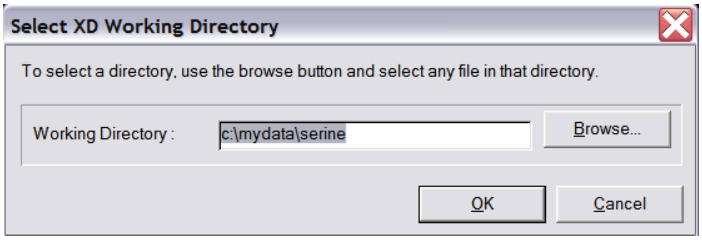
These data extend to sinθ/λ ~ 1.18 Å^{-1} and have a fairly high completeness (~80%) and redundancy (~7). The molecular structure of DL-serine is



1.1. Importing data to XD from SHELX

The folder serine contains the results of the spherical (or Independent-Atom Model, IAM) SHELX refinement of the DL-serine data (SER), the files shelx.ins and shelx.hkl

Now start WinXD. Under **File** menu go to **Select Work Directory** and point browser to "XD" folder, i.e. :



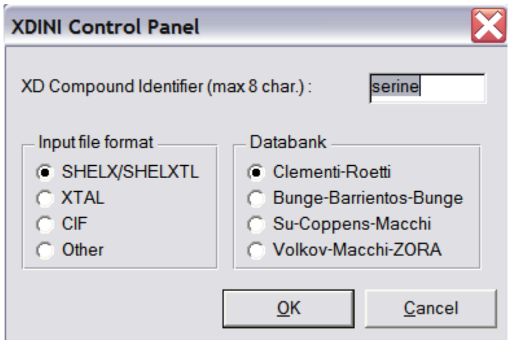
Select XD Working Directory

To select a directory, use the browse button and select any file in that directory.

Working Directory : c:\mydata\serine

and click OK.

Under **Modules** menu select **XDINI** – this is an interface for importing data to XD from programs like SHELX, XTAL, MOLLY or any other program *via* a special instructions file called xd_ini.inp. Here we import data from SHELX, so select SHELX in XDINI control panel. Also one must choose an "XD compound identifier" (CID) – this can be any name – it is used in XD input files to separate data block for different systems (XD files can, at the same time, contain data for several systems or datasets, but it is not recommended). Also choose the Clementi-Roetti[1] scattering factor model that is the default in XD.



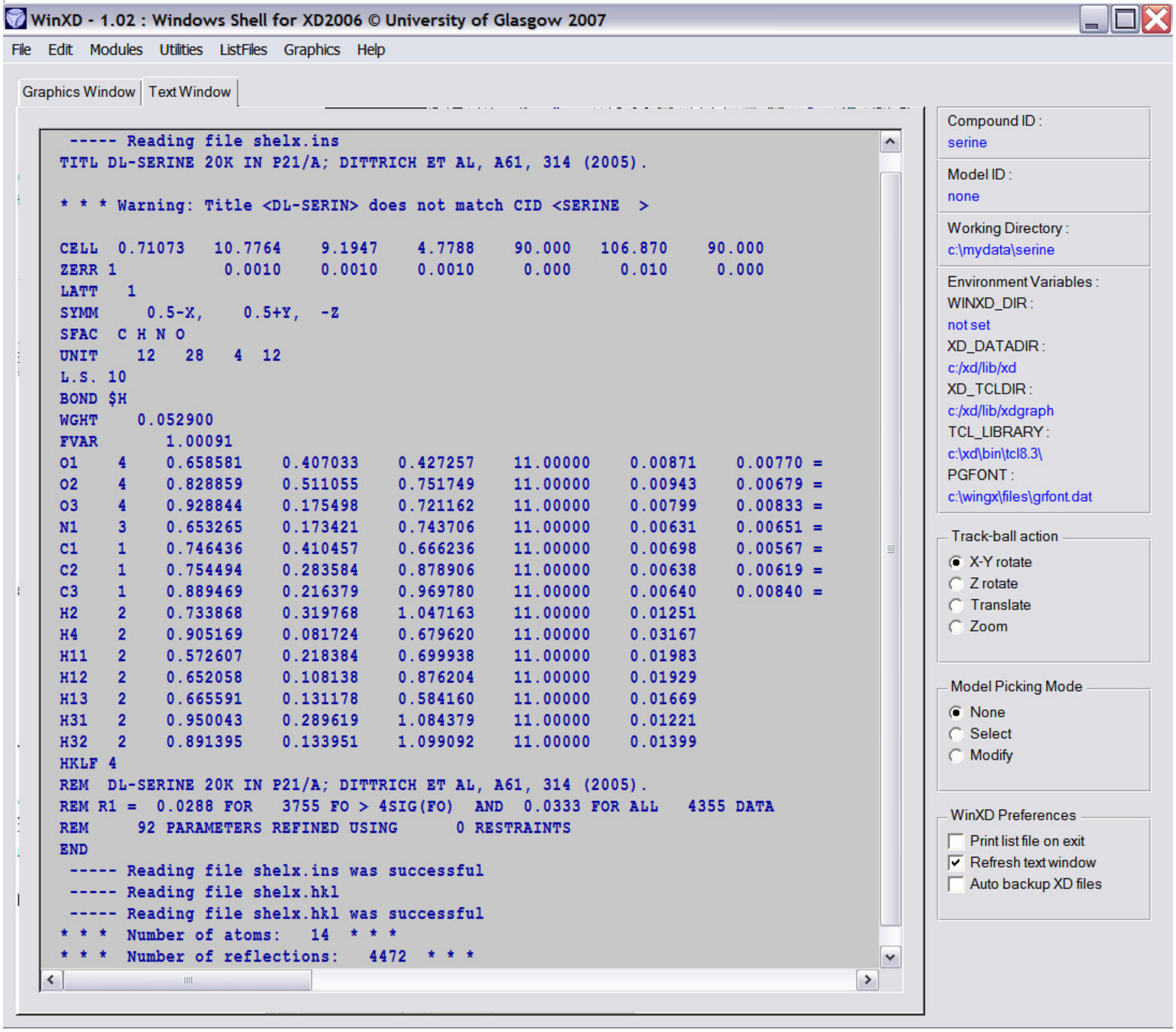
XDINI Control Panel

XD Compound Identifier (max 8 char.) : serine

Input file format
● SHELX/SHELXTL
○ XTAL
○ CIF
○ Other

Databank
● Clementi-Roetti
○ Bunge-Barrientos-Bunge
○ Su-Coppens-Macchi
○ Volkov-Macchi-ZORA

Now click OK. XDINI will run and if "Print list file on exit" is selected, some output will be printed out in the new Text Window (the list file can also be printed from the **ListFiles** menu item) .



```
 ----- Reading file shelx.ins
TITL DL-SERINE 20K IN P21/A; DITTRICH ET AL, A61, 314 (2005).

* * * Warning: Title <DL-SERIN> does not match CID <SERINE   >

CELL  0.71073   10.7764    9.1947    4.7788     90.000   106.870    90.000
ZERR 1           0.0010    0.0010    0.0010      0.000     0.010     0.000
LATT   1
SYMM     0.5-X,    0.5+Y,  -Z
SFAC  C H N O
UNIT    12   28   4  12
L.S. 10
BOND $H
WGHT    0.052900
FVAR       1.00091
O1    4    0.658581    0.407033    0.427257    11.00000    0.00871    0.00770 =
O2    4    0.828859    0.511055    0.751749    11.00000    0.00943    0.00679 =
O3    4    0.928844    0.175498    0.721162    11.00000    0.00799    0.00833 =
N1    3    0.653265    0.173421    0.743706    11.00000    0.00631    0.00651 =
C1    1    0.746436    0.410457    0.666236    11.00000    0.00698    0.00567 =
C2    1    0.754494    0.283584    0.878906    11.00000    0.00638    0.00619 =
C3    1    0.889469    0.216379    0.969780    11.00000    0.00640    0.00840 =
H2    2    0.733868    0.319768    1.047163    11.00000    0.01251
H4    2    0.905169    0.081724    0.679620    11.00000    0.03167
H11   2    0.572607    0.218384    0.699938    11.00000    0.01983
H12   2    0.652058    0.108138    0.876204    11.00000    0.01929
H13   2    0.665591    0.131178    0.584160    11.00000    0.01669
H31   2    0.950043    0.289619    1.084379    11.00000    0.01221
H32   2    0.891395    0.133951    1.099092    11.00000    0.01399
HKLF 4
REM  DL-SERINE 20K IN P21/A; DITTRICH ET AL, A61, 314 (2005).
REM R1 =  0.0288 FOR   3755 FO > 4SIG(FO)  AND  0.0333 FOR ALL   4355 DATA
REM     92 PARAMETERS REFINED USING      0 RESTRAINTS
END
 ----- Reading file shelx.ins was successful
 ----- Reading file shelx.hkl
 ----- Reading file shelx.hkl was successful
* * *  Number of atoms:    14  * * *
* * *  Number of reflections:    4472  * * *
```

Compound ID :
serine

Model ID :
none

Working Directory :
c:\mydata\serine

Environment Variables :
WINXD_DIR :
not set
XD_DATADIR :
c:/xd/lib/xd
XD_TCLDIR :
c:/xd/lib/xdgraph
TCL_LIBRARY :
c:\xd\bin\tcl8.3\
PGFONT :
c:\wingx\files\grfont.dat

Track-ball action
● X-Y rotate
○ Z rotate
○ Translate
○ Zoom

Model Picking Mode
● None
○ Select
○ Modify

WinXD Preferences
☐ Print list file on exit
☑ Refresh text window
☐ Auto backup XD files

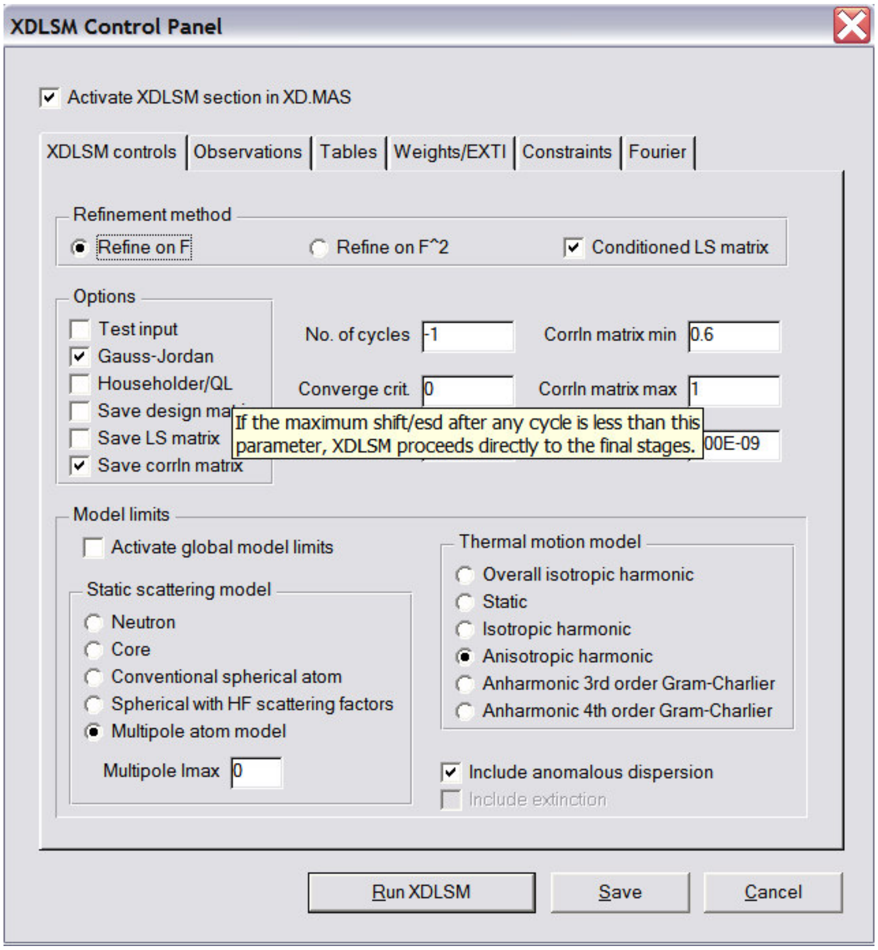
Note the messages that say that reading of shelx.ins and shelx.hkl file was successful. In the XD folder several new files have been created. These are the XDINI log file xd_ini.out and XD input/parameter/hkl files xd.mas, xd.inp and xd.hkl.

1.2. Repeating free spherical-atom (SHELX) refinement in XD.

Now that the starting XD files have been created we would like to repeat the spherical SHELX-type refinement in XD in order to make sure that all the data were imported correctly. The least-squares structure refinement program in XD2006 is called XDLSM.

In the **Edit** menu go to **Commands** and choose **XDLSM**:

We now have to edit instructions for the XDLSM. Most options are self-explanatory and for the more complicated options a balloon help is enabled (move cursor over an option to get help)



XDLSM Control Panel

☑ Activate XDLSM section in XD.MAS

Refinement method
● Refine on F ○ Refine on F^2 ☑ Conditioned LS matrix

Options
☐ Test input
☑ Gauss-Jordan
☐ Householder/QL
☐ Save design mat
☐ Save LS matrix
☑ Save corrln matrix

No. of cycles: -1
Corrln matrix min: 0.6
Converge crit: 0
Corrln matrix max: 1
00E-09

If the maximum shift/esd after any cycle is less than this parameter, XDLSM proceeds directly to the final stages.

Model limits
☐ Activate global model limits

Static scattering model
○ Neutron
○ Core
○ Conventional spherical atom
○ Spherical with HF scattering factors
● Multipole atom model

Multipole lmax: 0

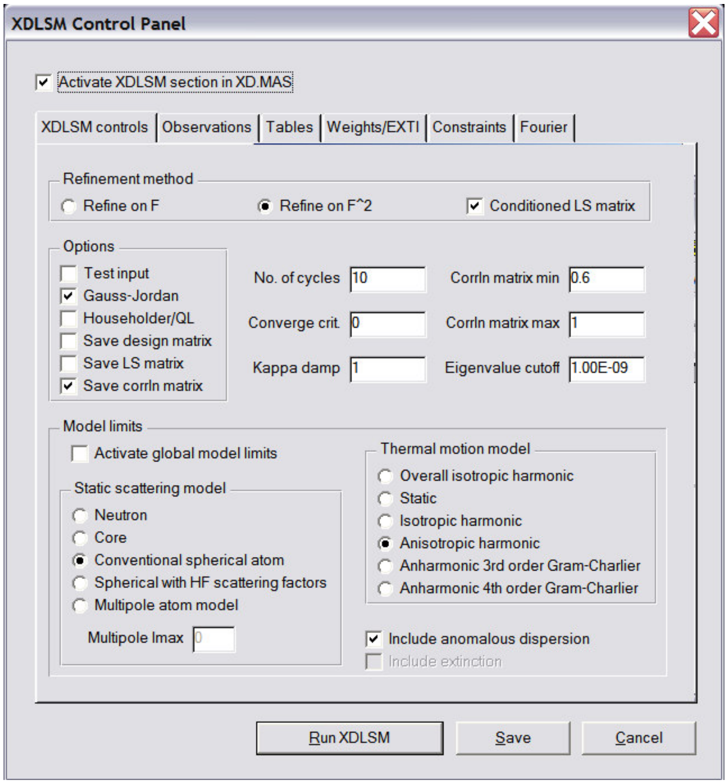
Thermal motion model
○ Overall isotropic harmonic
○ Static
○ Isotropic harmonic
● Anisotropic harmonic
○ Anharmonic 3rd order Gram-Charlier
○ Anharmonic 4th order Gram-Charlier

☑ Include anomalous dispersion
☐ Include extinction

Now let's set the refinement options

In **XDLSM controls** menu

select "Refine on F^2"
set number of cycles to 10
activate global model limits
select "Conventional spherical atom" under "Static scattering model"



☑ Activate XDLSM section in XD.MAS

Refinement method
○ Refine on F ● Refine on F^2 ☑ Conditioned LS matrix

Options
☐ Test input
☑ Gauss-Jordan
☐ Householder/QL
☐ Save design matrix
☐ Save LS matrix
☑ Save corrln matrix

No. of cycles 10
Converge crit 0
Kappa damp 1
Corrln matrix min 0.6
Corrln matrix max 1
Eigenvalue cutoff 1.00E-09

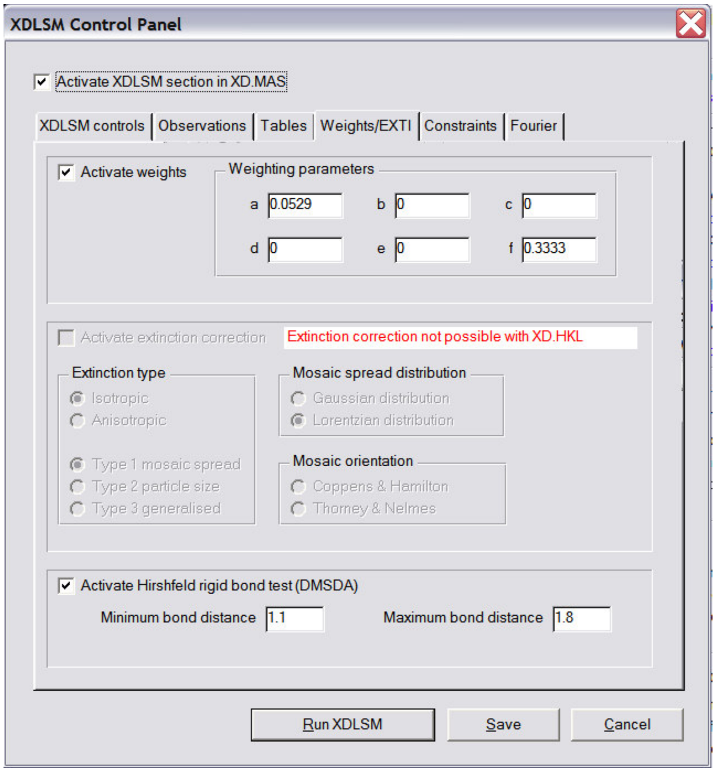
Model limits
☐ Activate global model limits

Static scattering model
○ Neutron
○ Core
● Conventional spherical atom
○ Spherical with HF scattering factors
○ Multipole atom model
Multipole lmax 0

Thermal motion model
○ Overall isotropic harmonic
○ Static
○ Isotropic harmonic
● Anisotropic harmonic
○ Anharmonic 3rd order Gram-Charlier
○ Anharmonic 4th order Gram-Charlier

☑ Include anomalous dispersion
☐ Include extinction

Under **Weights/EXTI** set the “a” parameter to the same value as in SHELX (0.0529) and activate Hirshfeld’s rigid-bond test[2]



☑ Activate XDLSM section in XD.MAS

☑ Activate weights

Weighting parameters
a 0.0529 b 0 c 0
d 0 e 0 f 0.3333

☐ Activate extinction correction Extinction correction not possible with XD.HKL

Extinction type
● Isotropic
○ Anisotropic
● Type 1 mosaic spread
○ Type 2 particle size
○ Type 3 generalised

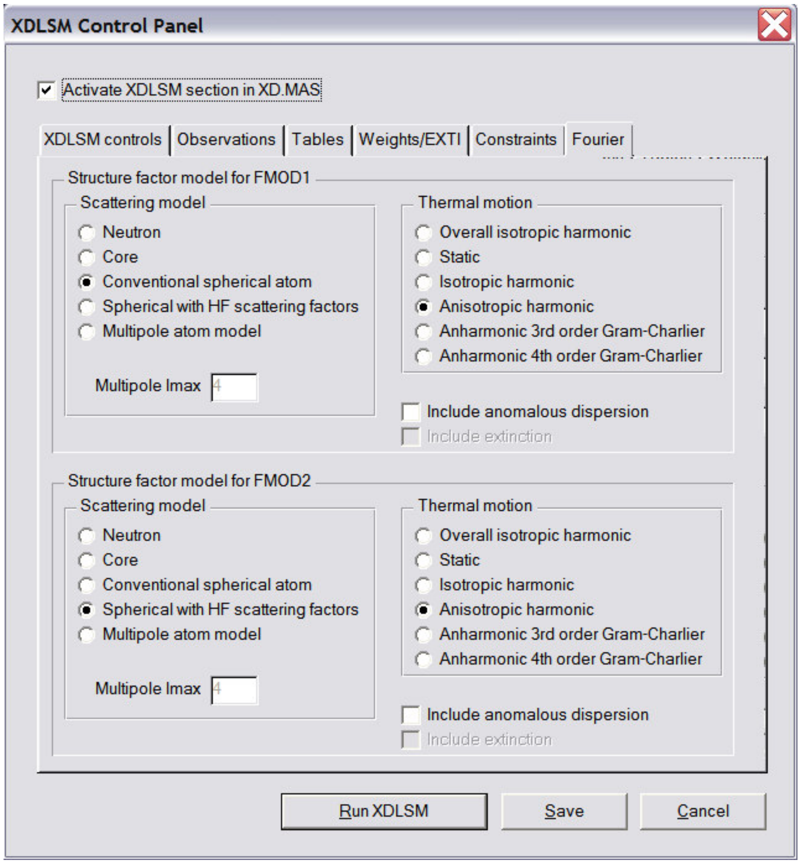
Mosaic spread distribution
○ Gaussian distribution
● Lorentzian distribution

Mosaic orientation
○ Coppens & Hamilton
○ Thorney & Nelmes

☑ Activate Hirshfeld rigid bond test (DMSDA)
Minimum bond distance 1.1 Maximum bond distance 1.8

Note that refinement of extinction is grayed out because our reflection file does not contain *tbar* (path length through the crystal) and directional cosines values. Correctly determined *tbar* values allow for an isotropic extinction refinement, while the presence of directional cosines allows for an anisotropic extinction model to be refined.

Under **Fourier** choose “Conventional spherical atom” for FMOD1 and “Spherical with HF scattering factors” under FMOD2.



☑ Activate XDLSM section in XD.MAS

Structure factor model for FMOD1

Scattering model
○ Neutron
○ Core
● Conventional spherical atom
○ Spherical with HF scattering factors
○ Multipole atom model
Multipole lmax 4

Thermal motion
○ Overall isotropic harmonic
○ Static
○ Isotropic harmonic
● Anisotropic harmonic
○ Anharmonic 3rd order Gram-Charlier
○ Anharmonic 4th order Gram-Charlier

☐ Include anomalous dispersion
☐ Include extinction

Structure factor model for FMOD2

Scattering model
○ Neutron
○ Core
○ Conventional spherical atom
● Spherical with HF scattering factors
○ Multipole atom model
Multipole lmax 4

Thermal motion
○ Overall isotropic harmonic
○ Static
○ Isotropic harmonic
● Anisotropic harmonic
○ Anharmonic 3rd order Gram-Charlier
○ Anharmonic 4th order Gram-Charlier

☐ Include anomalous dispersion
☐ Include extinction

Note that XDLSM allows two types of model scattering factors to be written to the Fourier file xd.fou (called FMOD1 and FMOD2*, i.e.* F model 1 and F model 2). This is convenient for aspherical refinements when Fcalc from both multipole and spherical models can be written (together with a set of Fobs).

All parameter changes made in the GUI windows are written to the XD instruction file xd.mas. One can also open this file in any text editor and modify these parameters there, bypassing the GUI.

Note the “Atom Key” table in the xd.mas file. This table indicates which parameters are to be refined by setting a key to “1”. If a certain parameter needs to be fixed, its key value should be set to “0”.

```
KEY     XYZ --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
O(2)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
O(3)    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
C(2)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
C(3)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
H(2)    111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(4)    111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(11)   111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
```

```
H(12)   111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(13)   111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(31)   111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(32)   111 100000 0000000000 000000000000000 00 000 00000 0000000 000000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
KAPPA   000000
EXTCN   0000000
OVTHP   0
SCALE   1
END KEY
```

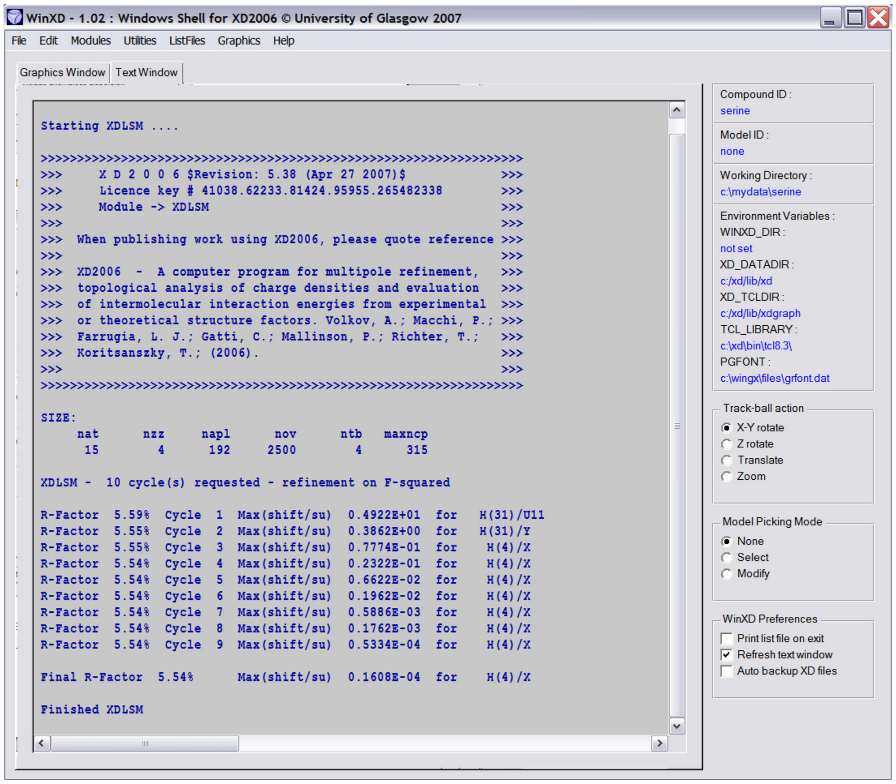
Table 1. Variable names and order numbers

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

In the example Key table shown above, all positional (*xyz*) parameters of all atoms (including hydrogens) are to be refined. For C, N and O-atoms, all anisotropic harmonic displacement parameters (ADPs or Uij's) are to be refined, while for H-atom only one isotropic Uiso parameter will be refined. The order in which parameters are listed in KEY table is given in Table 1 above.

Now run XDLSM by clicking the "Run XDLSM" button

In the **Text Window** a summary of the refinement progress is given, and clicking the menu item ListFile-XDLSM gives a fll listing of xd_lsm.out (XDLSM output file).



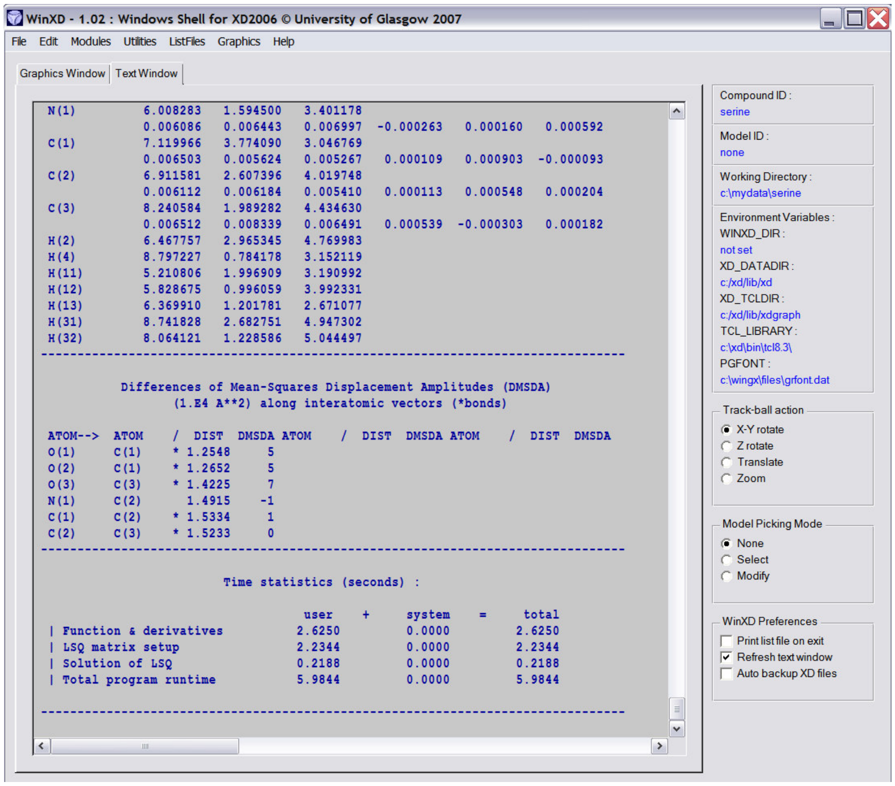
```
Starting XDLSM ....

>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
>>>     X D 2 0 0 6 $Revision: 5.38 (Apr 27 2007)$           >>>
>>>     Licence key # 41038.62233.81424.95955.265482338      >>>
>>>     Module -> XDLSM                                      >>>
>>>                                                          >>>
>>>  When publishing work using XD2006, please quote reference >>>
>>>                                                          >>>
>>>  XD2006  -  A computer program for multipole refinement,   >>>
>>>  topological analysis of charge densities and evaluation   >>>
>>>  of intermolecular interaction energies from experimental  >>>
>>>  or theoretical structure factors. Volkov, A.; Macchi, P.; >>>
>>>  Farrugia, L. J.; Gatti, C.; Mallinson, P.; Richter, T.;   >>>
>>>  Koritsanszky, T.; (2006).                                 >>>
>>>                                                          >>>
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>

SIZE:
     nat      nzz     napl      nov      ntb   maxncp
      15        4      192     2500        4      315

XDLSM -  10 cycle(s) requested - refinement on F-squared

R-Factor  5.59%  Cycle  1  Max(shift/su)  0.4922E+01  for   H(31)/U11
R-Factor  5.55%  Cycle  2  Max(shift/su)  0.3862E+00  for   H(31)/Y
R-Factor  5.55%  Cycle  3  Max(shift/su)  0.7774E-01  for    H(4)/X
R-Factor  5.54%  Cycle  4  Max(shift/su)  0.2322E-01  for    H(4)/X
R-Factor  5.54%  Cycle  5  Max(shift/su)  0.6622E-02  for    H(4)/X
R-Factor  5.54%  Cycle  6  Max(shift/su)  0.1962E-02  for    H(4)/X
R-Factor  5.54%  Cycle  7  Max(shift/su)  0.5886E-03  for    H(4)/X
R-Factor  5.54%  Cycle  8  Max(shift/su)  0.1762E-03  for    H(4)/X
R-Factor  5.54%  Cycle  9  Max(shift/su)  0.5334E-04  for    H(4)/X

Final R-Factor  5.54%      Max(shift/su)  0.1608E-04  for    H(4)/X

Finished XDLSM
```

Compound ID : serine
Model ID : none
Working Directory : c:\mydata\serine
Environment Variables :
WINXD_DIR : not set
XD_DATADIR : c:/xd/lib/xd
XD_TCLDIR : c:/xd/lib/xdgraph
TCL_LIBRARY : c:\xd\bin\tcl8.3\
PGFONT : c:\wingx\files\grfont.dat

Track-ball action
● X-Y rotate
○ Z rotate
○ Translate
○ Zoom

Model Picking Mode
● None
○ Select
○ Modify

WinXD Preferences
☐ Print list file on exit
☑ Refresh text window
☐ Auto backup XD files



```
 N(1)        6.008283  1.594500  3.401178
             0.006086  0.006443  0.006997 -0.000263  0.000160  0.000592
 C(1)        7.119966  3.774090  3.046769
             0.006503  0.005624  0.005267  0.000109  0.000903 -0.000093
 C(2)        6.911581  2.607396  4.019748
             0.006112  0.006184  0.005410  0.000113  0.000548  0.000204
 C(3)        8.240584  1.989282  4.434630
             0.006512  0.008339  0.006491  0.000539 -0.000303  0.000182
 H(2)        6.467757  2.965345  4.769983
 H(4)        8.797227  0.784178  3.152119
 H(11)       5.210806  1.996909  3.190992
 H(12)       5.828675  0.996059  3.992331
 H(13)       6.369910  1.201781  2.671077
 H(31)       8.741828  2.682751  4.947302
 H(32)       8.064121  1.228586  5.044497
------------------------------------------------------------------------

          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)    * 1.2548     5
 O(2)    C(1)    * 1.2652     5
 O(3)    C(3)    * 1.4225     7
 N(1)    C(2)      1.4915    -1
 C(1)    C(2)    * 1.5334     1
 C(2)    C(3)    * 1.5233     0
------------------------------------------------------------------------

                         Time statistics (seconds) :

                                user    +    system    =    total
 | Function & derivatives      2.6250        0.0000         2.6250
 | LSQ matrix setup            2.2344        0.0000         2.2344
 | Solution of LSQ             0.2188        0.0000         0.2188
 | Total program runtime       5.9844        0.0000         5.9844

------------------------------------------------------------------------
```

Compound ID : serine
Model ID : none
Working Directory : c:\mydata\serine
Environment Variables :
WINXD_DIR : not set
XD_DATADIR : c:/xd/lib/xd
XD_TCLDIR : c:/xd/lib/xdgraph
TCL_LIBRARY : c:\xd\bin\tcl8.3\
PGFONT : c:\wingx\files\grfont.dat

Track-ball action
● X-Y rotate
○ Z rotate
○ Translate
○ Zoom

Model Picking Mode
● None
○ Select
○ Modify

WinXD Preferences
☐ Print list file on exit
☑ Refresh text window
☐ Auto backup XD files

There are now several new files in the XD folder:

xd_lsm.out – XDLSM output
xd.res – XD parameter file with refined parameters
xd.fou – binary file with Fourier data

xd.fco and xd_lsm.cif – CIF-style files

As in SHELX, in order to use refined parameters as the input for another refinement, copy xd.res to xd.inp file or use GUI option **Utilities → RES-> INP**

XDLSM output file xd_lsm.out can be opened in any text editor and should be carefully examined…

Scroll down to the end of the file where the final statistics are printed:

```
 Number of data              =   4472
 Rejected based on OBS       =     82
 Rejected based on SIGOBS    =    896
 Rejected based on SINTHL    =      0
 Total number of rejections  =    896
 Included in the refinement  =   3576

                    Residuals after final cycle

 R{ F } =      0.0277     Rall{ F } =      0.0359     Rw{ F } =      0.0399
 R{F^2} =      0.0558     Rall{F^2} =      0.0565     Rw{F^2} =      0.0784
  GOFw  =      1.0648           GOF =      2.0823     Nref/Nv =     38.8696
```

These are close enough to those produced by SHELX:

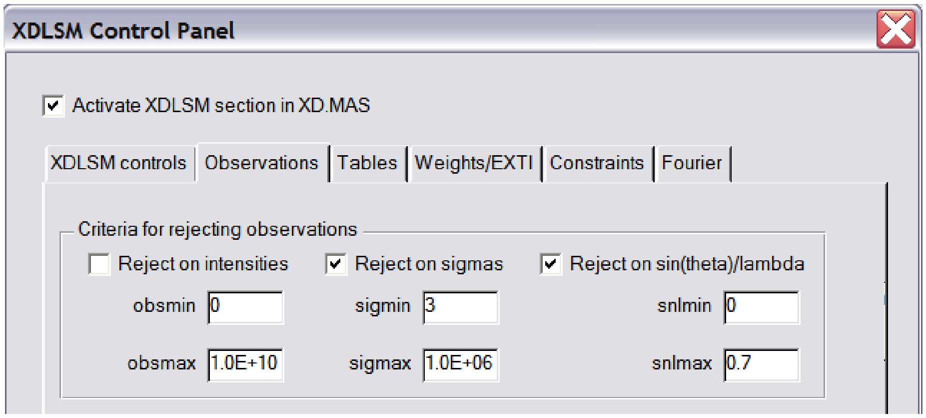
```
Final Structure Factor Calculation for  DL-serine 20K in P21/a; Dittrich et al, A61, 314 (2005).

 Total number of l.s. parameters =    92    Maximum vector length =  511      Memory required =   1034 /   22995

 wR2 =  0.0837 before cycle  11 for   4355 data and     0 /    92 parameters

 GooF = S =     1.029;     Restrained GooF =      1.029  for      0 restraints

 Weight = 1 / [ sigma^2(Fo^2) + ( 0.0529 * P )^2 +   0.00 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3

 R1 =  0.0288 for   3755 Fo > 4sig(Fo)  and  0.0333 for all   4355 data
 wR2 =  0.0837,  GooF = S =   1.029,  Restrained GooF =    1.029  for all data

 Occupancy sum of asymmetric unit =    7.00 for non-hydrogen and    7.00 for hydrogen atoms
```

Note the results of the Hirshfeld's rigid-bond test:

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

 ATOM-->  ATOM    /  DIST  DMSDA ATOM
 O(1)     C(1)    * 1.2548     5
 O(2)     C(1)    * 1.2652     6
 O(3)     C(3)    * 1.4225     7
 N(1)     C(2)      1.4915    -1
 C(1)     C(2)    * 1.5333     1
 C(2)     C(3)    * 1.5233     0
```

According to the rigid-bond test, refined ADPs are deemed to be physically meaningful if differences of mean-squared displacement amplitudes (DMSDA) along interatomic vectors are $\leq 1\times10^{-3}$ Å^{2}. Because of the presence of the high-order data the results of the rigid-bond test are very good.

If, for example, we truncate our data at 0.7 Å^{-1}



☑ Activate XDLSM section in XD.MAS

Criteria for rejecting observations

☐ Reject on intensities ☑ Reject on sigmas ☑ Reject on sin(theta)/lambda

obsmin 0 sigmin 3 snlmin 0

obsmax 1.0E+10 sigmax 1.0E+06 snlmax 0.7

and re-run the XDLSM, then the results get much worse

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

 ATOM-->  ATOM     /  DIST  DMSDA ATOM
 O(1)     C(1)     * 1.2560    13
 O(2)     C(1)     * 1.2664    16
 O(3)     C(3)     * 1.4243     7
 N(1)     C(2)       1.4931    -9
 C(1)     C(2)     * 1.5333     1
 C(2)     C(3)     * 1.5228    -4
```

NOTE. The rejection on sigma works in much the same way as in other refinement programs, such as SHELXL, except that it is applied to the data directly in the XD.HKL file. The header of this file shows the type of data present

```
SERINE       F^2        NDAT    6
```

This indicates that the data are present as F^2, so that the sigma cutoff (and intensity cutoffs) are applied to these data. In XD (unlike SHELXL !) the user has the option of refining on either F or F^2, since by default the quality of experimental structure factors will be high for any data which is to be refined by the miltipole method. If you are refining on F in XD (which would be normal), then if you wished to apply a cutoff of $3\sigma(F)$, then you would have to enter a value of 1.5 for sigmin.

1.3 Calculation of Fourier maps

Ok, let’s go back to the refinement of the complete data set. We’ve run XDLSM and examined the output file. Now we can create and visualize Fourier difference maps. This is done in the XDFOUR and XDFFT modules of XD2006. XDFOUR allows the user to choose sections of the map, and this is the option we will use.

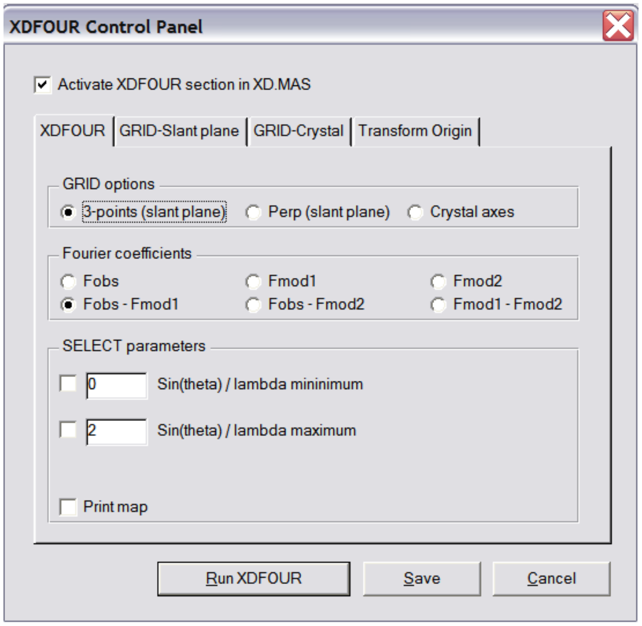
Note the comments in `xd_lsm.out` file almost at the very end:

```
          FCO file xd.fco is created.
  Content :  H K L F^2(CALC) F^2(OBS) SIG[F^2(OBS)] SIN(THETA)/LAMBDA
          Fourier file xd.fou is created.
  Content :  H K L FOBS SIGFOBS PHASE AMOD1 BMOD1 AMOD2 BMOD2
```

```
        FMOD1( -2  2  0  0)
-2 - Spherical, neutral atom model (RHF)
 2 - Anisotropic displacement parameters
 0 - Anomalous dispersion excluded
 0 - No extinction model
        FMOD2( -2  2  0  0)
-2 - Spherical, neutral atom model (RHF)
 2 - Anisotropic displacement parameters
 0 - Anomalous dispersion excluded
 0 - No extinction model
```

XDFOUR module uses the xd.fou file created by XDLSM for calculating Fourier maps.

Let's edit the commands of the XDFOUR module: In the **XDFOUR Control Panel** window choose the following options:



XDFOUR Control Panel

☑ Activate XDFOUR section in XD.MAS

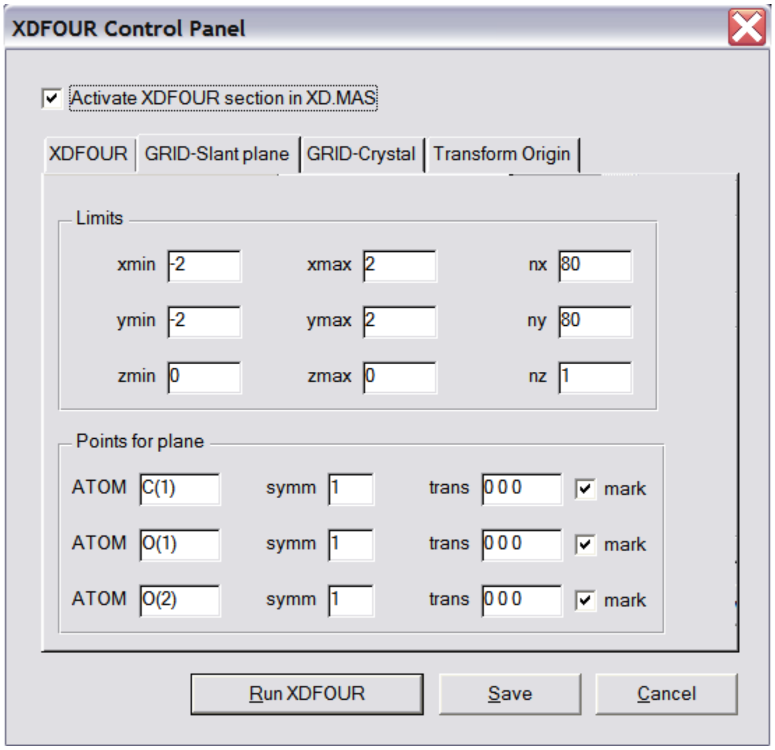
GRID options: ● 3-points (slant plane) ○ Perp (slant plane) ○ Crystal axes

Fourier coefficients:
○ Fobs ○ Fmod1 ○ Fmod2
● Fobs - Fmod1 ○ Fobs - Fmod2 ○ Fmod1 - Fmod2

SELECT parameters:
☐ 0 Sin(theta) / lambda mininimum
☐ 2 Sin(theta) / lambda maximum
☐ Print map

Note that XDFOUR allows various types of Fourier maps to be calculated from the three types of Fourier coefficients written to xd.fou file, *i.e.* Fobs, Fmod1 and Fmod2. Thus the choice of Fobs-Fmod1 will produce the difference map between Fobs and Fcalc produced by model selected under FMOD1 in XDLSM part of xd.mas file (i.e. Conventional spherical atom). While Fobs-Fmod2 would produce the difference between Fobs and model selected under FMOD2 (i.e. Spherical with HF scattering factors). Since we are right now interested in residual Fourier maps, let's choose Fobs-Fmod1.

Under **GRID-Slant plane** we must define the grid limits and the plane. Plane is defined by the three atoms with x-axis of the plane to be defined by a vector from atom 1 to atom 2 with the third atoms point being in the half-plane y>0. For example, if we want to look at the plane of the COO^- group, we can choose C(1) at atom 1, O(1) as atom 2 and O(2) as atom 3, *i.e.*



☑ Activate XDFOUR section in XD.MAS

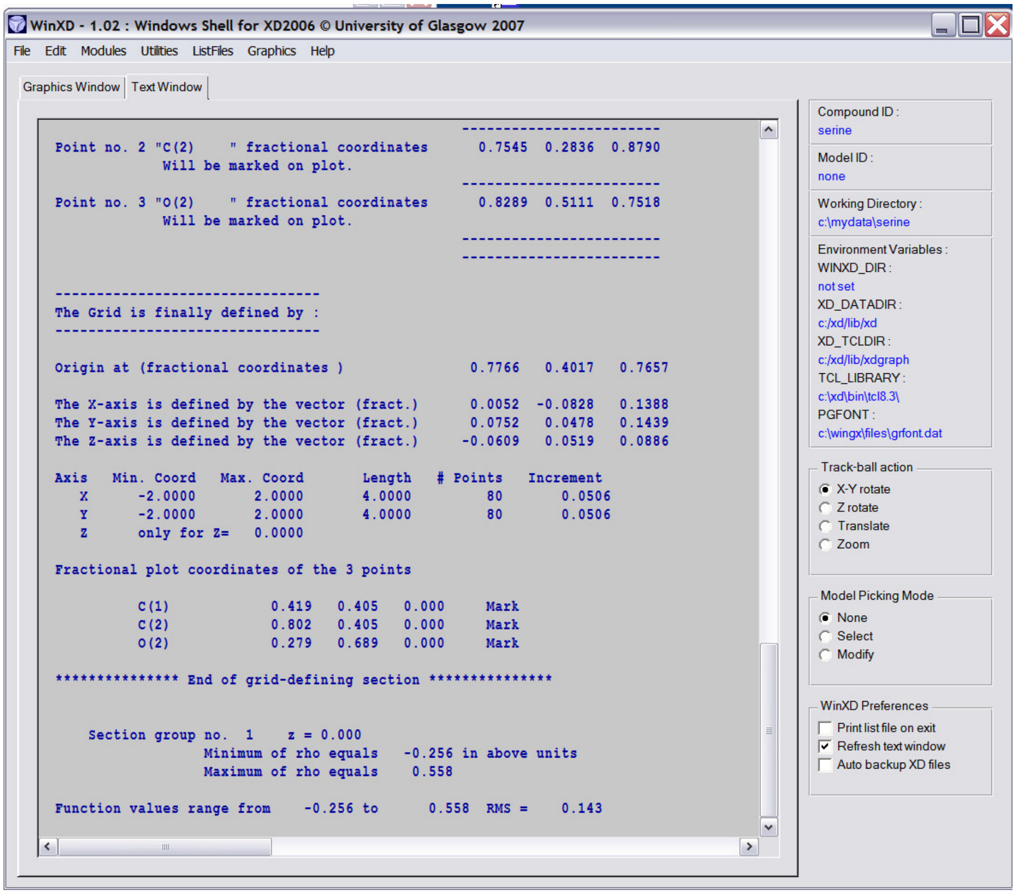
Limits

xmin	-2	xmax	2	nx	80
ymin	-2	ymax	2	ny	80
zmin	0	zmax	0	nz	1

Points for plane

ATOM	C(1)	symm	1	trans	0 0 0	☑ mark
ATOM	O(1)	symm	1	trans	0 0 0	☑ mark
ATOM	O(2)	symm	1	trans	0 0 0	☑ mark

Now run XDFOUR. Note the listing of the XDFOUR output file xd_fou.out appearing in the Text Window (xd_fou.out file can also be opened in your favorite text editor):



```
                                                    ------------------------
Point no. 2 "C(2)    " fractional coordinates      0.7545  0.2836  0.8790
             Will be marked on plot.
                                                    ------------------------
Point no. 3 "O(2)    " fractional coordinates      0.8289  0.5111  0.7518
             Will be marked on plot.
                                                    ------------------------
                                                    ------------------------


--------------------------------
The Grid is finally defined by :
--------------------------------

Origin at (fractional coordinates )                0.7766   0.4017   0.7657

The X-axis is defined by the vector (fract.)       0.0052  -0.0828   0.1388
The Y-axis is defined by the vector (fract.)       0.0752   0.0478   0.1439
The Z-axis is defined by the vector (fract.)      -0.0609   0.0519   0.0886

Axis   Min. Coord   Max. Coord       Length   # Points   Increment
   X      -2.0000       2.0000       4.0000         80      0.0506
   Y      -2.0000       2.0000       4.0000         80      0.0506
   Z      only for Z=   0.0000

Fractional plot coordinates of the 3 points

          C(1)            0.419   0.405   0.000     Mark
          C(2)            0.802   0.405   0.000     Mark
          O(2)            0.279   0.689   0.000     Mark

*************** End of grid-defining section ***************


    Section group no.  1    z = 0.000
                  Minimum of rho equals   -0.256 in above units
                  Maximum of rho equals    0.558

Function values range from    -0.256 to      0.558  RMS =    0.143
```

Compound ID :
serine

Model ID :
none

Working Directory :
c:\mydata\serine

Environment Variables :
WINXD_DIR :
not set
XD_DATADIR :
c:/xd/lib/xd
XD_TCLDIR :
c:/xd/lib/xdgraph
TCL_LIBRARY :
c:\xd\bin\tcl8.3\
PGFONT :
c:\wingx\files\grfont.dat

Track-ball action
● X-Y rotate
○ Z rotate
○ Translate
○ Zoom

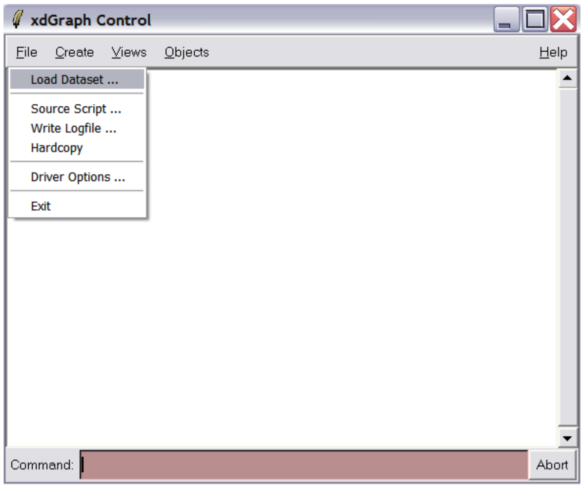
Model Picking Mode
● None
○ Select
○ Modify

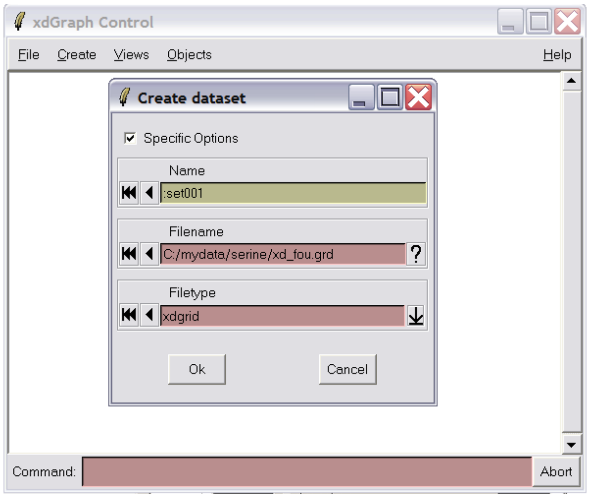
WinXD Preferences
☐ Print list file on exit
☑ Refresh text window
☐ Auto backup XD files

A grid file xd_fou.grd has now been created, which can be viewed in XDGRAPH.

1.4 Visualization of Fourier maps

The grid files created by XDFOUR (and also by XDPROP) can then be visualized in XDGRAPH module: In the opened **XDGRAPH Control** window choose the grid file





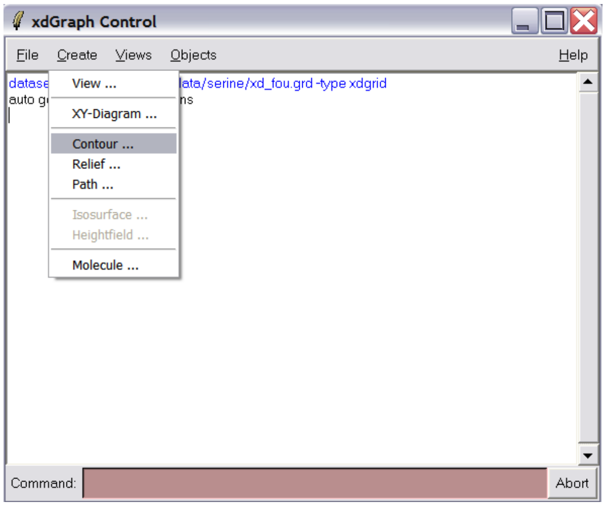
☑ Specific Options

Name: :set001

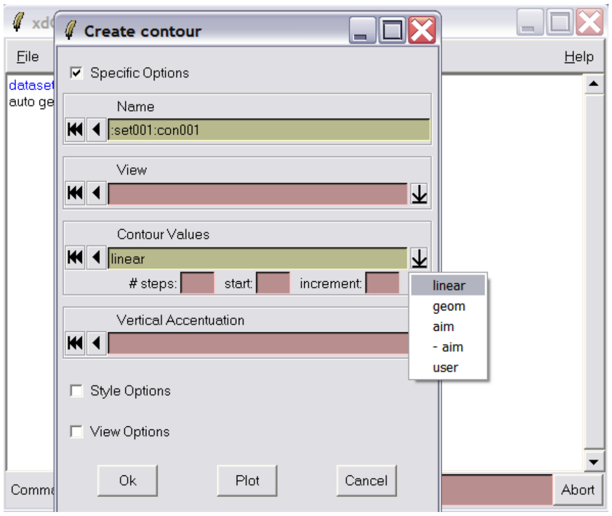
Filename: C:/mydata/serine/xd_fou.grd

Filetype: xdgrid

Then create a set of positive of contours, starting from 0.1 e/Å^3 with an increment of 0.1 e/Å^3 (linear set).



datase ata/serine/xd_fou.grd -type xdgrid
auto g ns



☑ Specific Options

Name: :set001:con001

View:

Contour Values: linear

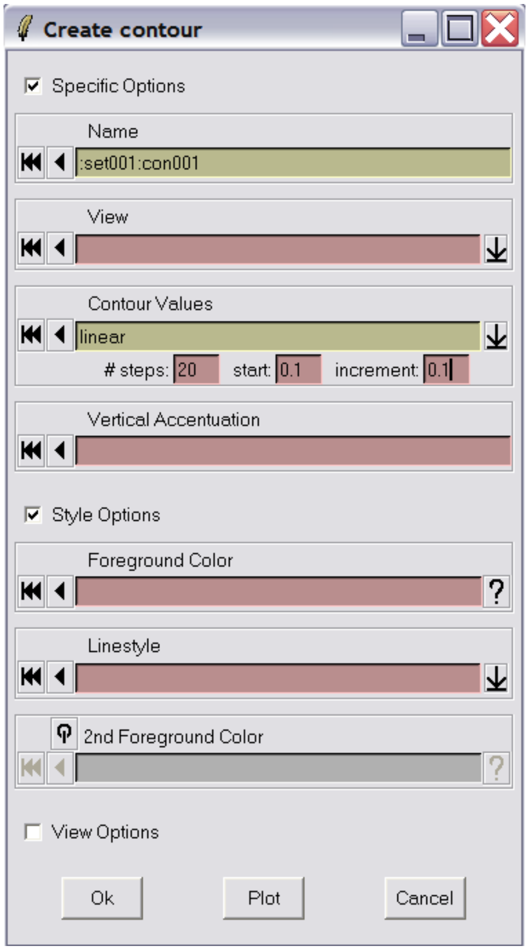
steps: start: increment:

Vertical Accentuation:

☐ Style Options

☐ View Options

Checking **Style Options** allow customize the color and the line style of the given set of contours



☑ Specific Options

Name: :set001:con001

View:

Contour Values: linear

steps: 20 start: 0.1 increment: 0.1

☑ Style Options

☐ View Options

For example, let’s select red color for positive contours by dragging color selection bars in **Foreground color** option

● rgb ○ hsv ○ yuv

red 253

green 0

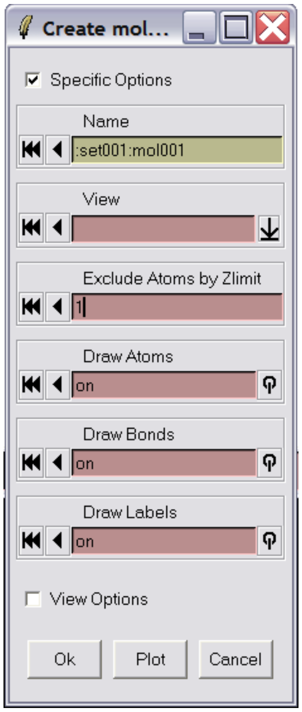
blue 0

Also select “solid” under **Linestyle**

Finally, click the **Plot** button: A new window is now opened with plotted positive contours:

Now repeat the same procedure for negative contours starting at -0.1 e/Å^3 with an increment of -0.1 e/Å^3, blue color and dashed line. Go back to **xdGraph Control** window and make the following input: Steps 20 start -0.1 increment -0.1. Also select a different colour like blue and a different linestyle like dash. In the **Contour** window a new set of contours is plotted:

Now add the molecule to the plot, i.e. atoms, bonds and labels: Use **Create → Molecule**



☑ Specific Options

Name: :set001:mol001

View:

Exclude Atoms by Zlimit: 1

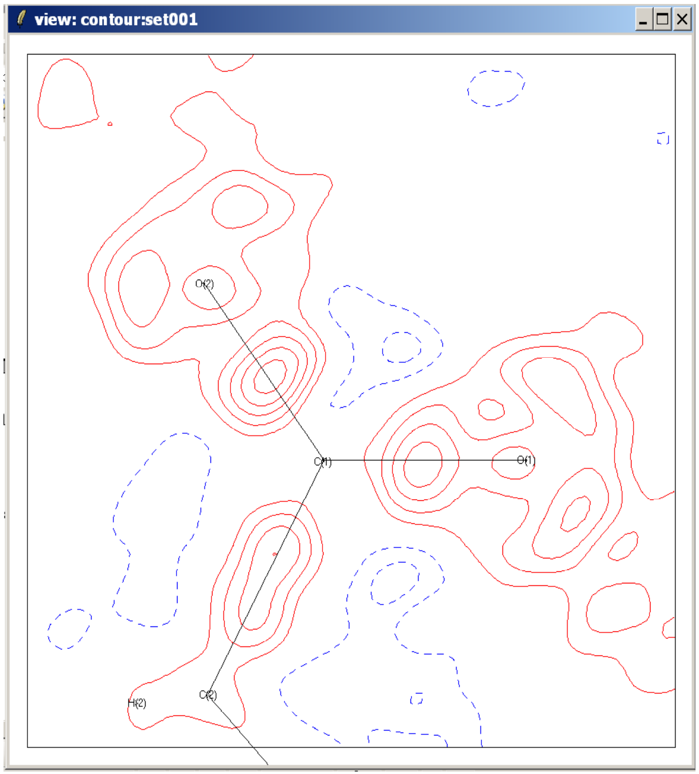
Draw Atoms: on

Draw Bonds: on

Draw Labels: on

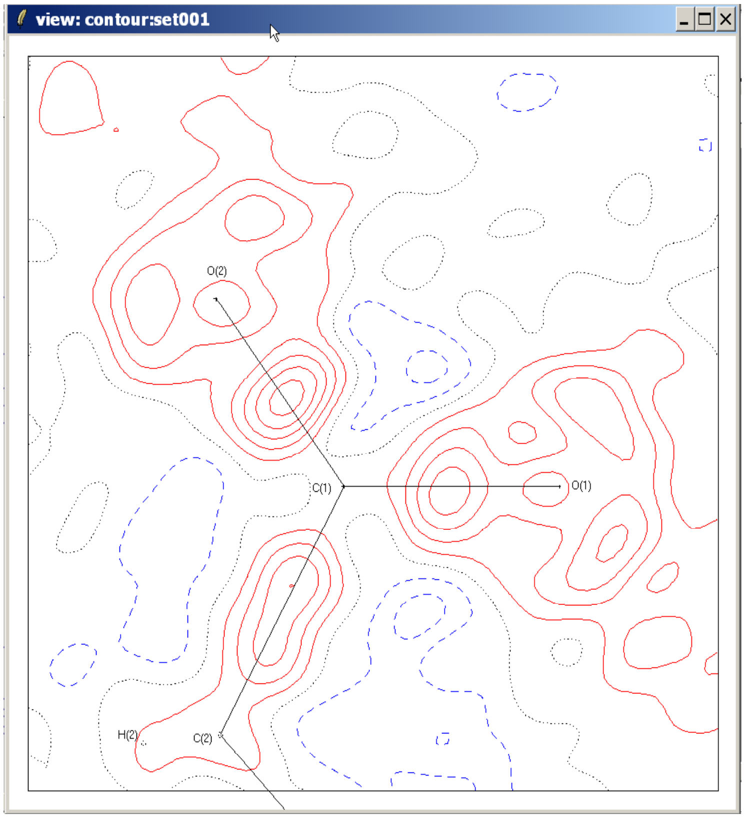
☐ View Options

The molecule is now plotted on top of the contours:



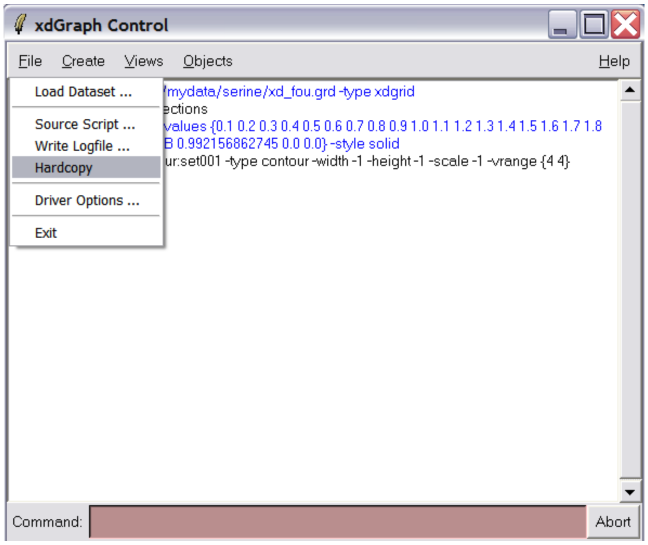
Note: Get the mouse cursor over one of the atoms labels – the color of the label changes from black to light blue, now click the left button of the mouse and, with left button pressed, drag the label to an empty space:

Now the contour map is complete!



To make a hard copy of this map, go back to **xdGraph Control** window and under **File** select **Hardcopy** option: Note that file xdgraph.ps has appeared in XD folder. Since the saved files are always called xdgraph.ps, in order to save the map, rename it to something like c1o1o2_fou.ps

When plotting another map, one, of course, can follow this procedure from the beginning to the end. But this is very inconvenient. There is a better way! Go to **xdGraph Control** window and select **Write logfile** option:



```
/mydata/serine/xd_fou.grd -type xdgrid
ections
values {0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8
B 0.992156862745 0.0 0.0} -style solid
ur:set001 -type contour -width -1 -height -1 -scale -1 -vrange {4 4}
```

In the **Save as** window change the filename from default xdgraph.log to something like fou.log and save it: Now open this file in your favorite text editor. As you can see, it contains the same set of instructions as was entered before. You can edit this file to plot other maps…

```
dataset :set001 -load C:/mydata/serine/xd_fou.grd -type xdgrid
auto generated 13 connections
contour :set001:con001 -values {0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0} -foreground {RGB
0.992156862745 0.0 0.0} -style solid
auto creating view contour:set001 -type contour -width -1 -height -1 -scale -1 -vrange {4 4}
:set001:con001 plot
:set001:con001 remove
```

For the future, the most important things to change are

- Name and location of the dataset
- Contour values and corresponding line colors and styles

Note that there is an easier way to modify the contour level in the log file. Instead of listing the contour values one by one, i.e. 0.1, 0.2, 0.3 ..., one can just use the following command (note the use of square instead of curly brackets):

```
-values [generate linear 20 0.1 0.1]
```

Let’s try to change the contour level from 0.1 to 0.05 using this option.

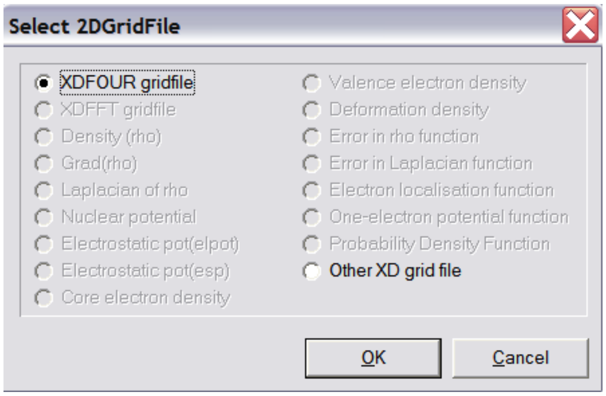
- Replace -values {0.1 0.2 0.3 0.4 0.5 0.6 …} with -values [generate linear 20 0.05 0.05]
- Replace -values {-0.1 -0.2 -0.3 -0.4 -0.5 -0.6 …} with -values [generate linear 20 -0.05 -0.05]

Save fou.log file. Close and re-start XDGRAPH. Under **File** menu choose **Source script.** Then choose fou.log file and click **Open**

If everything was done correctly, a new map with a new contour level of ±0.05 e/Å^3 will be plotted. Save a hardcopy of this map and rename it to something like c1o1o2_fou1.ps

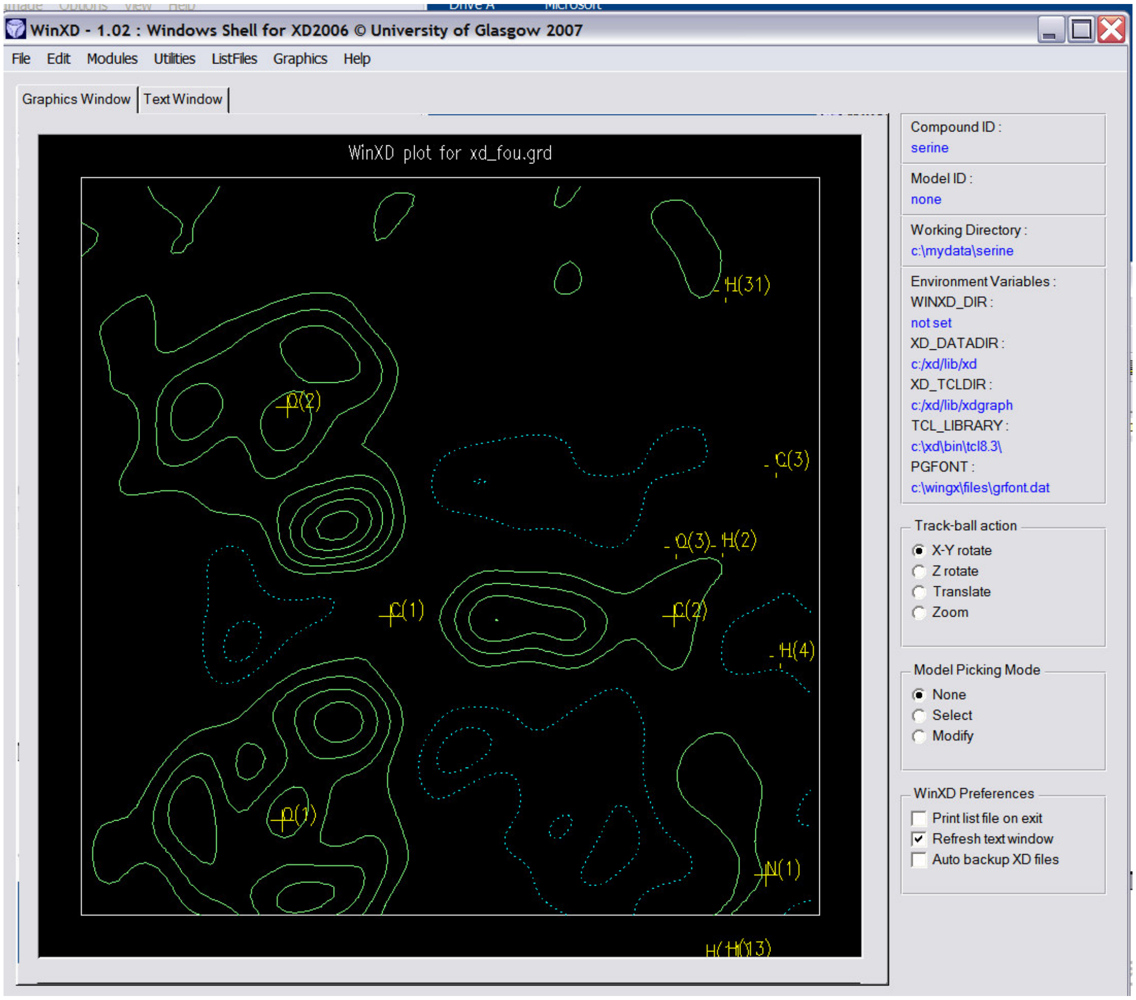
Analysis of these maps shows a clear residual density in the bonding regions as well as the lone pairs on the oxygen atoms. Thus this confirms the good quality of the data as all the bonding features are clearly seen in the residual maps after the spherical refinement.

Another (actually quicker) way of visualizing 2D - maps is by using the WinXD GUI. From the Graphics menu, select "2D Contour Plot", and then the type of file you wish to plot



Select 2DGridFile

● XDFOUR gridfile
○ XDFFT gridfile
○ Density (rho)
○ Grad(rho)
○ Laplacian of rho
○ Nuclear potential
○ Electrostatic pot(elpot)
○ Electrostatic pot(esp)
○ Core electron density
○ Valence electron density
○ Deformation density
○ Error in rho function
○ Error in Laplacian function
○ Electron localisation function
○ One-electron potential function
○ Probability Density Function
○ Other XD grid file



Compound ID : serine

Model ID : none

Working Directory : c:\mydata\serine

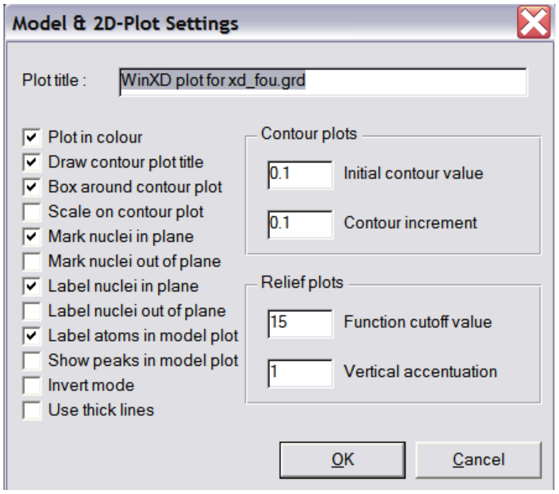
Environment Variables :
WINXD_DIR : not set
XD_DATADIR : c:/xd/lib/xd
XD_TCLDIR : c:/xd/lib/xdgraph
TCL_LIBRARY : c:\xd\bin\tcl8.3\
PGFONT : c:\wingx\files\grfont.dat

Track-ball action
● X-Y rotate
○ Z rotate
○ Translate
○ Zoom

Model Picking Mode
● None
○ Select
○ Modify

WinXD Preferences
☐ Print list file on exit
☑ Refresh text window
☐ Auto backup XD files

There is much less flexibility with this program, but it requires less effort and gives an immediate result. A right mouse click gives the Plot settings dialog box, which allows you at adjust some of the plotting parameters.



Plot title : WinXD plot for xd_fou.grd

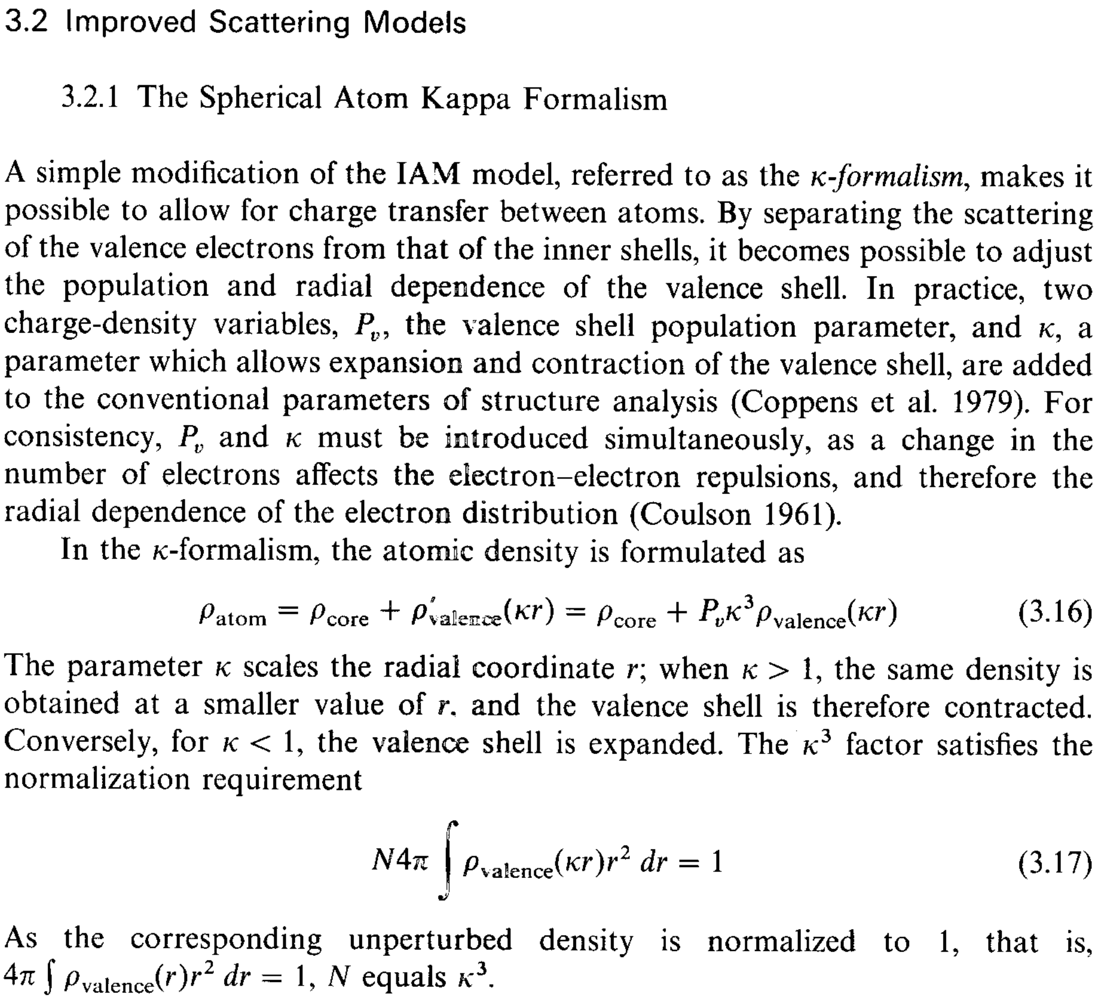
☑ Plot in colour
☑ Draw contour plot title
☑ Box around contour plot
☐ Scale on contour plot
☑ Mark nuclei in plane
☐ Mark nuclei out of plane
☑ Label nuclei in plane
☐ Label nuclei out of plane
☑ Label atoms in model plot
☐ Show peaks in model plot
☐ Invert mode
☐ Use thick lines

Contour plots
0.1 Initial contour value
0.1 Contour increment

Relief plots
15 Function cutoff value
1 Vertical accentuation

1.5 Refinement using kappa formalism.

Before refinement of the aspherical density it is usually a good idea to perform a spherical atom kappa refinement that, unlike the free spherical atom formalism used in programs like SHELX, allows for expansion-contraction of the atomic valence shells and the charge transfer between atoms. The following is the description of the kappa formalism taken from P. Coppens book:[3]



3.2 Improved Scattering Models

3.2.1 The Spherical Atom Kappa Formalism

A simple modification of the IAM model, referred to as the *κ-formalism*, makes it possible to allow for charge transfer between atoms. By separating the scattering of the valence electrons from that of the inner shells, it becomes possible to adjust the population and radial dependence of the valence shell. In practice, two charge-density variables, P_v, the valence shell population parameter, and κ, a parameter which allows expansion and contraction of the valence shell, are added to the conventional parameters of structure analysis (Coppens et al. 1979). For consistency, P_v and κ must be introduced simultaneously, as a change in the number of electrons affects the electron–electron repulsions, and therefore the radial dependence of the electron distribution (Coulson 1961).

In the κ-formalism, the atomic density is formulated as

$$\rho_{\text{atom}} = \rho_{\text{core}} + \rho'_{\text{valence}}(\kappa r) = \rho_{\text{core}} + P_v \kappa^3 \rho_{\text{valence}}(\kappa r) \tag{3.16}$$

The parameter κ scales the radial coordinate r; when $\kappa > 1$, the same density is obtained at a smaller value of r, and the valence shell is therefore contracted. Conversely, for $\kappa < 1$, the valence shell is expanded. The κ^3 factor satisfies the normalization requirement

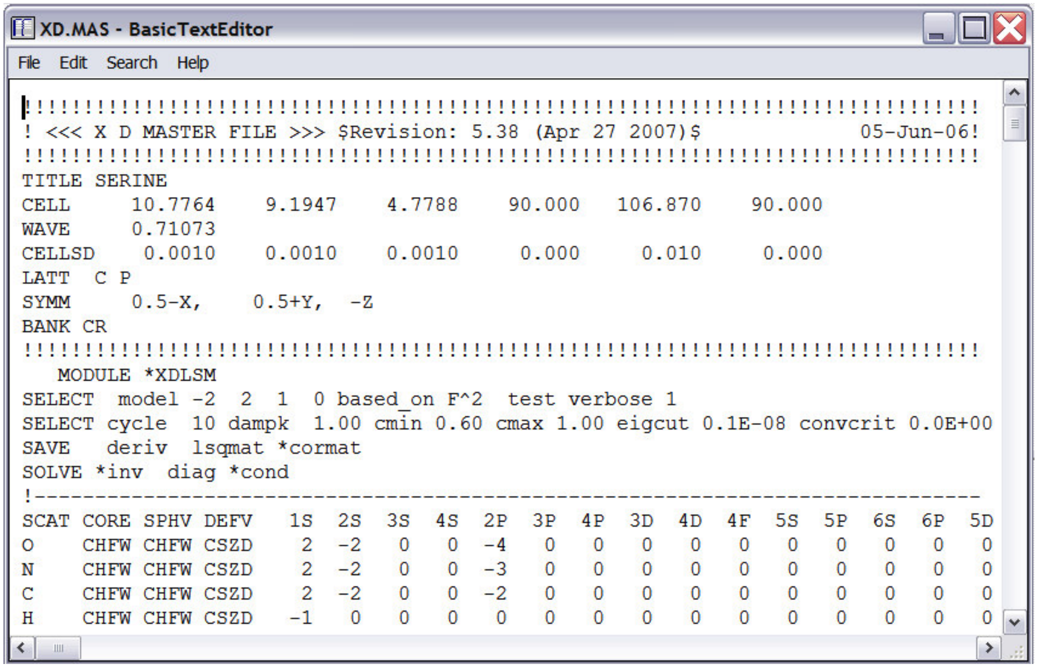
$$N 4\pi \int \rho_{\text{valence}}(\kappa r) r^2 \, dr = 1 \tag{3.17}$$

As the corresponding unperturbed density is normalized to 1, that is, $4\pi \int \rho_{\text{valence}}(r) r^2 \, dr = 1$, N equals κ^3.

In order to perform a kappa refinement, one must set the keys for atomic valence populations *Pv* and κ parameters to “1” in the KEY table in the XDLSM part of xd.mas file (see Table 1). Parameters *Pv* and κ are referred to in the Table 1 as M1 (i.e. first monopole population) and KS, respectively. This can be done either by using WinXD GUI or just modifying the xd.mas file in the text editor.

To use GUI, select **Edit → Commands → XDLSM → Tables → Edit atom parameters**.

However, in this particular case it is recommended to modify xd.mas file by hand.
Go to **File → Open XD Master File**



```
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! <<< X D MASTER FILE >>> $Revision: 5.38 (Apr 27 2007)$             05-Jun-06!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
TITLE SERINE
CELL     10.7764    9.1947    4.7788    90.000   106.870    90.000
WAVE     0.71073
CELLSD    0.0010    0.0010    0.0010     0.000     0.010     0.000
LATT  C P
SYMM     0.5-X,    0.5+Y,  -Z
BANK CR
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
   MODULE *XDLSM
SELECT  model -2  2  1  0 based_on F^2  test verbose 1
SELECT cycle  10 dampk  1.00 cmin 0.60 cmax 1.00 eigcut 0.1E-08 convcrit 0.0E+00
SAVE   deriv  lsqmat *cormat
SOLVE *inv  diag *cond
!------------------------------------------------------------------------------
SCAT CORE SPHV DEFV   1S  2S  3S  4S  2P  3P  4P  3D  4D  4F  5S  5P  6S  6P  5D
O    CHFW CHFW CSZD    2  -2   0   0  -4   0   0   0   0   0   0   0   0   0   0
N    CHFW CHFW CSZD    2  -2   0   0  -3   0   0   0   0   0   0   0   0   0   0
C    CHFW CHFW CSZD    2  -2   0   0  -2   0   0   0   0   0   0   0   0   0   0
H    CHFW CHFW CSZD   -1   0   0   0   0   0   0   0   0   0   0   0   0   0   0
```

At this time an idea of chemical equivalency should be introduced, because it determines the number of refined κ parameters. Atoms are defined to be chemically equivalent if their chemical bonding environment is similar enough. This also suggests that only single κ parameters could be refined for this group of atoms. For example, the two oxygen atoms of the carboxylate group COO^- can be initially considered to be chemically equivalent. Later one, once the approximate model of the aspherical density is constructed this chemical constraint can be released. It is especially important in the studies of intermolecular bonding when the two atoms differ significantly in the hydrogen bonds formed.

A slightly different situation is observed for H-atoms. Because an H-atom has only 1 electron in its valence shell the precise determination of κ from X-ray data is not possible unless accurate neutron data are available (this way the positional and ADP parameters of H-atoms are determined much more reliably than from X-ray data). Therefore, it is usual to constrain the κ-parameters for all H-atom to a fixed value of 1.2 or 1.4. In our studies using theoretical data,[4] we found the κ parameter for H-atoms to be about 1.13(2), which is in very good agreement with previously reported κ_H values of 1.166[5] and 1.126[6]. While only one κ parameter is assigned to all H-atoms and is fixed, the populations of valence shells of H-atoms can be refined separately using the same kind of chemical constraints as used for heavier atoms, *i.e.* all 3 H-atoms of the amino NH_3^+ group should be treated as chemically equivalent, as well as the two H-atoms of the CH_2 group.

Now we can calculate how many κ parameters should be refined in SER:

1 for O(1) and O(2) atoms
1 for O(3) atom
1 for C(1) atom
1 for C(2) atom
1 for C(3) atom
1 for N(1) atom

+1 for all H-atoms will be fixed

So there are a total of 7 κ parameters. Let's put them in xd.mas file and also modify the KEY table to set which parameters are to be refined.

Note that by default, XDINI creates only one κ parameter per atom type, i.e. one κ parameter for all oxygens, one κ for all carbons etc.. This is written in ATOM table of xd.mas file (see highlighted values in the table below)

```
ATOM     ATOM0    AX1 ATOM1    ATOM2   AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(1)      Z  O(1)     O(2)     Y   R   2  1   1   4  NO
O(2)     C(1)      Z  O(2)     O(1)     Y   R   2  1   1   4  NO
O(3)     H(4)      Z  O(3)     C(3)     Y   R   2  1   1   4  NO
N(1)     H(12)     Z  N(1)     H(13)    Y   R   2  2   2   4  NO
C(1)     O(1)      Z  C(1)     O(2)     Y   R   2  3   3   4  NO
C(2)     H(2)      Z  C(2)     N(1)     Y   R   2  3   3   4  NO
C(3)     H(32)     Z  C(3)     H(31)    Y   R   2  3   3   4  NO
H(2)     C(2)      Z  H(2)     N(1)     Y   R   1  4   4   2  NO
H(4)     O(3)      Z  H(4)     C(3)     Y   R   1  4   4   2  NO
H(11)    N(1)      Z  H(11)    H(12)    Y   R   1  4   4   2  NO
H(12)    N(1)      Z  H(12)    H(11)    Y   R   1  4   4   2  NO
H(13)    N(1)      Z  H(13)    H(12)    Y   R   1  4   4   2  NO
H(31)    C(3)      Z  H(31)    H(32)    Y   R   1  4   4   2  NO
H(32)    C(3)      Z  H(32)    H(31)    Y   R   1  4   4   2  NO
DUM0      0.0000  0.0000  0.0000
END ATOM
```

This means that the κ parameter No. 1 is assigned to the oxygen atoms, κ number 2 is assigned to the nitrogen atom, κ No. 3 to the carbon atoms and No. 4 to the hydrogens. But we already decided that we want to separate oxygen atoms into two groups: O(1) and O(2) in one group and O(3) in another, and assign different κ parameters to these groups. The same goes for C-atoms. Thus, we have to modify the values in the KAP column in the ATOM table above. It should now look like this

```
ATOM     ATOM0    AX1 ATOM1    ATOM2   AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(1)      Z  O(1)     O(2)     Y   R   2  1   1   4  NO
O(2)     C(1)      Z  O(2)     O(1)     Y   R   2  1   1   4  NO
O(3)     H(4)      Z  O(3)     C(3)     Y   R   2  1   2   4  NO
N(1)     H(12)     Z  N(1)     H(13)    Y   R   2  2   3   4  NO
C(1)     O(1)      Z  C(1)     O(2)     Y   R   2  3   4   4  NO
C(2)     H(2)      Z  C(2)     N(1)     Y   R   2  3   5   4  NO
C(3)     H(32)     Z  C(3)     H(31)    Y   R   2  3   6   4  NO
H(2)     C(2)      Z  H(2)     N(1)     Y   R   1  4   7   2  NO
H(4)     O(3)      Z  H(4)     C(3)     Y   R   1  4   7   2  NO
H(11)    N(1)      Z  H(11)    H(12)    Y   R   1  4   7   2  NO
H(12)    N(1)      Z  H(12)    H(11)    Y   R   1  4   7   2  NO
H(13)    N(1)      Z  H(13)    H(12)    Y   R   1  4   7   2  NO
H(31)    C(3)      Z  H(31)    H(32)    Y   R   1  4   7   2  NO
H(32)    C(3)      Z  H(32)    H(31)    Y   R   1  4   7   2  NO
DUM0      0.0000  0.0000  0.0000
END ATOM
```

Because we decided that some atoms are chemically equivalent we also have to set CHEMCON parameters in the ATOM table. This is done as follows. If, say, atom O(2) is chemically equivalent to atom O(1), in the CHEMCON part of ATOM table for atom O(2) we put a label of atom O(1), so the final ATOM table will look like this:

```
ATOM     ATOM0    AX1 ATOM1    ATOM2    AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(1)      Z  O(1)     O(2)      Y   R   2  1   1   4  NO
O(2)     C(1)      Z  O(2)     O(1)      Y   R   2  1   1   4  NO        O(1)
O(3)     H(4)      Z  O(3)     C(3)      Y   R   2  1   2   4  NO
N(1)     H(12)     Z  N(1)     H(13)     Y   R   2  2   3   4  NO
C(1)     O(1)      Z  C(1)     O(2)      Y   R   2  3   4   4  NO
C(2)     H(2)      Z  C(2)     N(1)      Y   R   2  3   5   4  NO
C(3)     H(32)     Z  C(3)     H(31)     Y   R   2  3   6   4  NO
H(2)     C(2)      Z  H(2)     N(1)      Y   R   1  4   7   2  NO
H(4)     O(3)      Z  H(4)     C(3)      Y   R   1  4   7   2  NO
H(11)    N(1)      Z  H(11)    H(12)     Y   R   1  4   7   2  NO
H(12)    N(1)      Z  H(12)    H(11)     Y   R   1  4   7   2  NO        H(11)
H(13)    N(1)      Z  H(13)    H(12)     Y   R   1  4   7   2  NO        H(11)
H(31)    C(3)      Z  H(31)    H(32)     Y   R   1  4   7   2  NO
H(32)    C(3)      Z  H(32)    H(31)     Y   R   1  4   7   2  NO        H(31)
DUM0      0.0000  0.0000  0.0000
END ATOM
```

So we set O(2) to be chemically equivalent to O(1), atoms H(11), H(12) and H(13) to all be chemically equivalent and the same for atoms H(31) and H(32). This will constrain the valence shell populations of the specified atom to be equivalent, i.e. $Pv_{O(1)}=Pv_{O(2)}$, $Pv_{H(11)}=Pv_{H(12)}=Pv_{H(13)}$ and $Pv_{H(31)}=Pv_{O(32)}$. Refinement keys for *Pv*'s should be set in the KEY table.

Ok, now we have to change the key settings in the KEY table for those parameters that we want to refine, i.e. κ parameters for non-H atoms and Pv parameters for all atoms. At the same time it advised to keep all positional and ADP parameters fixed, i.e. the KEY table should look like this

```
KEY     XYZ --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
O(2)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
O(3)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
N(1)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
C(1)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
C(2)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
C(3)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(2)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(4)    000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(11)   000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(12)   000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(13)   000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(31)   000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
H(32)   000 000000 0000000000 000000000000000 10 000 00000 0000000 000000000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   00000
EXTCN   0000000
OVTHP   0
SCALE   1
END KEY
```

With yellow we highlight the fixed positional and ADP parameters, with green the refined Pv parameters, with cyan the refined κ parameters for non-H atoms, and with magenta the fixed κ parameter for H-atoms.

Note that there must be as many ‘KAPPA’ entries in the KEY table as KAP parameters were defined in the ATOM table.

Because of the CHEMCON flags in the ATOM table, although we set the key for $Pv_{O(2)}$ to be refined, it will actually be constrained to be equivalent to $Pv_{O(1)}$. The same holds true for H(12), H(13) and H(32) atoms.

It is also very important to make sure that the following instruction is enabled:

```
KEEP     CHARGE GROUP1
```

This tells the program to keep electro neutrality for the asymmetric unit (*i.e.* the sum of all Pv's is constrained to the total number of valence electrons, and the overall charge is zero). GROUP1 is, by definition composed of all the atoms in the asymmetric unit.

Because now the conventional scattering factors cannot be used anymore, we have to change the static scattering model to that of the aspherical atom model with l_{max}=0 (monopole-only formalism). We should also include anomalous dispersion in the model. It is also advised to switch to refinement of F (rather than on F squared) and change the weighting scheme. This is done by modifying the following instructions (see highlighted parameters):

```
SELECT *model 0  2  1  0 based_on F  test verbose 1

WEIGHT    -2.  0.0000   0.0000   0.0000   0.0000   0.000
```

Table 2 : The model limits

m1 static scattering models	
-4	neutron
-3	core
-2	conventional, spherical-atom promolecule model with RHF scattering factors taken from the International Tables
-1	neutral, spherical-atom model with HF scattering factors generated from Slater-type wavefunctions [14]
lmax	aspherical-atom model: frozen-core, spherical valence, multipolar deformation density up to *lmax* in the expansion over spherical harmonics [1]
m2 thermal motion models	
-1	overall-isotropic-harmonic
0	static
1	isotropic – harmonic
2	anisotropic – harmonic
tmax	anharmonic model: Gram-Charlier expansion up to 4th order [24]
m3 anomalous dispersion	
0	excluded
1	included
m4 extinction	
0	excluded
1	included

`*model` command provides a global control over certain parameters which characterize the structure factor formalism applied in the refinement. These parameters are shown in Table 2 above. The value of lmax given in the static scattering model option is applied for all atoms only as an upper limit. The option has only limited applications but can provide an easy way to reduce the complexity of the scattering formalism without having to modify all necessary parameters one by one. Note that certain combinations of the control parameters are meaningless, which might not be recognized by the program.

If extra output from XDLSM is desired, the verbosity level can be increased by setting `verbose` to a higher number than 1, for example, 2 or 3.

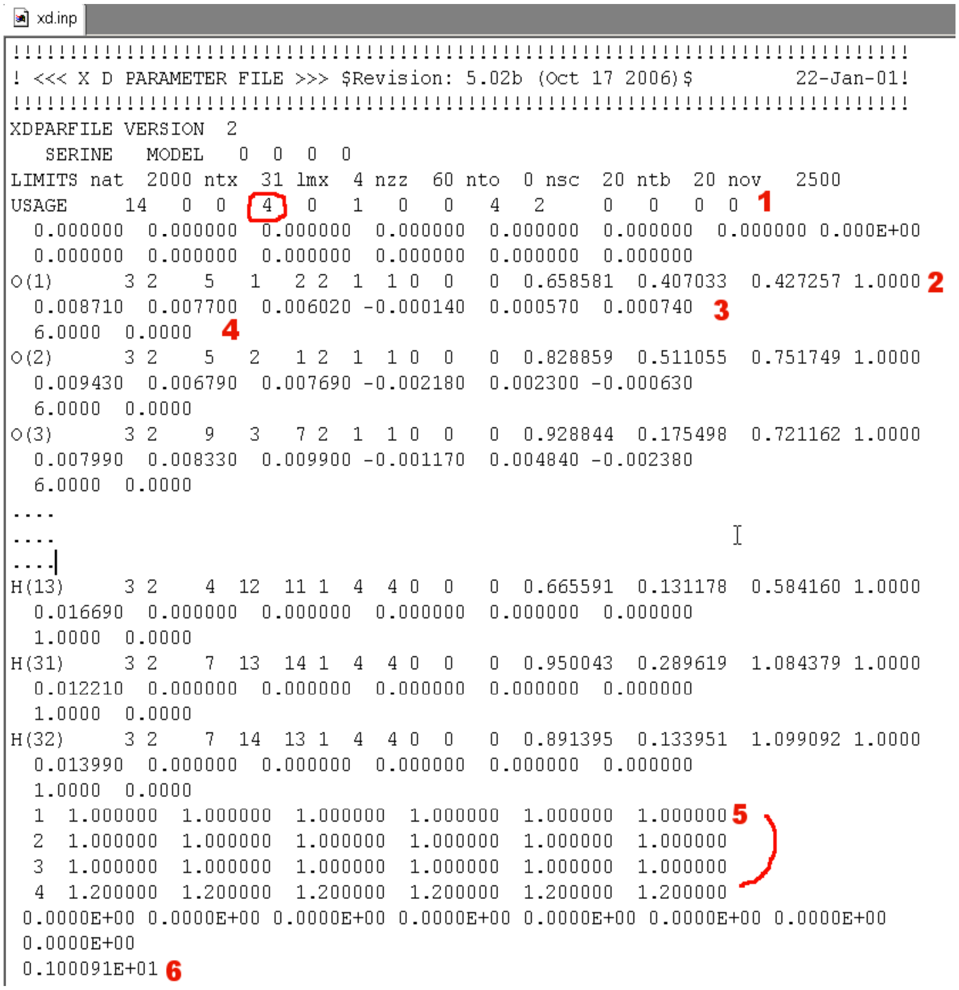
If one wants to create and examine the Fourier difference maps with the kappa model, the FOUR instructions should be also modified:

```
FOUR  fmod1 0  2  0  0   fmod2 -2  2  0  0
```

Fobs to be written to xd.fou file will have phases from kappa refinement, Fcalc1 will be those calculated from the kappa model while Fcalc2 will be those of free spherical atoms. Both sets will be free of anomalous dispersion and extinction

We are done with instructions in xd.mas file, but now we have to change some parameters in the XD parameter file – namely put in the values of 1.13 for κ parameters for H-atoms.

Many entries in the XD parameter file xd.inp are also present in the master file. Specifications given in the master file have the priority. It means that the xd.inp and xd.res may differ according to any changes made in xd.mas. Here is an example of xd.inp file:



```
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! <<< X D PARAMETER FILE >>> $Revision: 5.02b (Oct 17 2006)$        22-Jan-01!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
XDPARFILE VERSION  2
   SERINE   MODEL   0  0  0  0
LIMITS nat  2000 ntx  31 lmx  4 nzz  60 nto  0 nsc  20 ntb  20 nov   2500
USAGE     14   0   0   4   0   1   0   0   4   2     0   0   0   0  1
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000 0.000E+00
  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
O(1)      3 2   5   1   2 2  1  1 0  0   0  0.658581  0.407033  0.427257 1.0000 2
  0.008710  0.007700  0.006020 -0.000140  0.000570  0.000740  3
  6.0000  0.0000  4
O(2)      3 2   5   2   1 2  1  1 0  0   0  0.828859  0.511055  0.751749 1.0000
  0.009430  0.006790  0.007690 -0.002180  0.002300 -0.000630
  6.0000  0.0000
O(3)      3 2   9   3   7 2  1  1 0  0   0  0.928844  0.175498  0.721162 1.0000
  0.007990  0.008330  0.009900 -0.001170  0.004840 -0.002380
  6.0000  0.0000
....
....
....
H(13)     3 2   4  12  11 1  4  4 0  0   0  0.665591  0.131178  0.584160 1.0000
  0.016690  0.000000  0.000000  0.000000  0.000000  0.000000
  1.0000  0.0000
H(31)     3 2   7  13  14 1  4  4 0  0   0  0.950043  0.289619  1.084379 1.0000
  0.012210  0.000000  0.000000  0.000000  0.000000  0.000000
  1.0000  0.0000
H(32)     3 2   7  14  13 1  4  4 0  0   0  0.891395  0.133951  1.099092 1.0000
  0.013990  0.000000  0.000000  0.000000  0.000000  0.000000
  1.0000  0.0000
  1  1.000000  1.000000  1.000000  1.000000  1.000000  1.0000005
  2  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  3  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  4  1.200000  1.200000  1.200000  1.200000  1.200000  1.200000
 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00 0.0000E+00
 0.0000E+00
 0.100091E+01 6
```

The most important sections of the XD parameter file xd.inp are numbered **1** to **6**.

Number **1** shows the line which contains the following parameters: 1: number of atoms, 2: atomic displacement model (0: none, static; 1: isotropic; 2: anisotropic harmonic; 3: including third order, 4: including fourth order), 3: maximum level of multipole expansion, 4: number of kappa sets, 5: not used, 6: scale factors, 7: extinction model, 8: number of constraints, 9: number of scattering factor tables, 10: number of symmetry cards, 11: number of variables, 12: [not used], 13: number of cycles, 14: number of dummy atoms. The circled fourth parameter (number of kappa sets) should be changed to 7 (as we've already have done in xd.mas file).

Lines with numbers **2…4** denote the atomic parameters. Line **2** contains, among others, atomic coordinates and multiplicity. Line **3** contains isotropic or anisotropic ADPs. Line 4 contains the first (M1) and second m(M2) monopoles. First monopole M1 is equivalent to valence population Pv. These parameters usually need not be modified by hand

Lines denoted with number **5**,

```
  1  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  2  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  3  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  4  1.200000  1.200000  1.200000  1.200000  1.200000  1.200000
```

contain the κ parameters for the two monopoles and the multipoles with *l* = 1,…4. The first (integer) number refers to the entry in the SCAT table in the xd.mas file to which given kappa set is assigned.

```
SCAT CORE SPHV DEFV   1S  2S  3S  4S  2P  3P   ...    5F  DELF'   DELF''  NSCTL
O    CHFW CHFW CSZD    2  -2   0   0  -4   0   ...     0  0.0106  0.0060  0.580
N    CHFW CHFW CSZD    2  -2   0   0  -3   0   ...     0  0.0061  0.0033  0.936
C    CHFW CHFW CSZD    2  -2   0   0  -2   0   ...     0  0.0033  0.0016  0.665
H    CHFW CHFW CSZD   -1   0   0   0   0   0   ...     0  0.0000  0.0000 -0.374
END  SCAT
```

Thus, for the 1st kappa set refers to oxygen atom, second – to nitrogen etc. Note that XDINI automatically assigned a value of 1.2 to the κ set of an H-atom.

Because we need to assign a specific value to a given set, we have to modify the kappa sets. According to the ATOM table in xd.mas file

the first two kappa sets are assigned to oxygen atoms (1st atom type in SCAT table),
the third one describes the nitrogen atom (2nd atom type in SCAT table)
κ sets 4..6 belong to C-atoms (3rd atom type in SCAT table)
finally, the seventh κ set describes hydrogen atoms (4th atom type in SCAT table), which we want to constrain to be 1.13

Thus the kappa set section xd.inp file should look like this:

```
  1  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  1  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  2  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  3  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  3  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
```

```
  3  1.000000  1.000000  1.000000  1.000000  1.000000  1.000000
  4  1.130000  1.200000  1.200000  1.200000  1.200000  1.200000
```

Note that we have changed only the 1st κ (KS, or valence shell κ) of the H-atom kappa set (7th line) to 1.13 – other kappas are for aspherical (deformation) parameters which are not used in the kappa formalism.

Save xd.inp file and run XDLSM. In the created xd_lsm.out file, examine the section "Variables after final cycle". You can see that valence populations of the atoms (labeled as M1) and KS parameters have been refined.

1.6 Molecular geometry and population analysis with XDGEOM

At this stage, in order to get a better idea of the resulting atomic charges are, it is recommended to run the module XDGEOM.

First check XDGEOM input parameters: In the **XDGEOM Control Panel**, activate XDGEOM section in xd.mas file, and run XDGEOM. This module creates xd_geo.out output file which is also listed in the **Text Window**. Open xd_geo.out file in the text editor and scroll down to the "List of atomic parameters from XD.COV file", which lists the refined monopole population parameters Pv (Pval), κ-parameters (Kappa) and net atomic charges derived from Pv (Net charge).

```
  Atom             Pval            Kappa            P00            Kappa'    Net charge
------------------------------------------------------------------------------------
  O(1)          6.407           0.980           0.000           1.000          -0.407
  O(2)          6.407           0.980           0.000           1.000          -0.407
  O(3)          6.340           0.982           0.000           1.000          -0.339
  N(1)          4.752           1.028           0.000           1.000          +0.248
  C(1)          3.533           1.052           0.000           1.000          +0.467
  C(2)          3.950           1.038           0.000           1.000          +0.049
  C(3)          3.655           1.045           0.000           1.000          +0.344
  H(2)          0.996           1.130           0.000           1.200          +0.004
  H(4)          0.864           1.130           0.000           1.200          +0.135
  H(11)         0.950           1.130           0.000           1.200          +0.050
  H(12)         0.950           1.130           0.000           1.200          +0.050
  H(13)         0.950           1.130           0.000           1.200          +0.050
  H(31)         1.123           1.130           0.000           1.200          -0.123
  H(32)         1.123           1.130           0.000           1.200          -0.123
```

As expected, oxygen atoms are negative and most of H-atoms are positive. Note that atomic charges and refined κ parameters of atoms O(1) and O(2) are the same , as was intended when modifying instructions in xd.mas file. The same holds true for atoms H(11), H(12) and H(13), as well as for atoms H(31) and H(32). As we put in xd.inp file, the κ parameter for H-atoms is 1.13 (!).

1.7 Introduction to the aspherical model of the electron density

By far the most widely used aspherical pseudoatom formalism is based on the Hansen-Coppens multipolar model of ED.[3,7] In this formalism, the electron density at each point in space $\rho(\mathbf{r})$ is described by a superposition of atomic-like densities $\rho_{at}(\mathbf{r})$, called pseudoatoms:

$$\rho(\mathbf{r}) = \sum \rho_{at}(\mathbf{r}) \qquad (1)$$

Each pseudoatom is modeled using the modified Laplace series:

$$\rho_{at}(\mathbf{r}) = P_{core}\rho_{core}(r) + P_{val}\kappa^3\rho_{val}(\kappa r) + \sum_{l=0}^{l_{\max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\Omega) \qquad (2)$$

The first and second terms of expansion are equivalent to those in kappa model describe in Exercise 6. These are the spherically averaged Hartree-Fock core and valence densities.[1] The third term describes the aspherical deformation density. Coefficients $P_{lm\pm}$ are the population parameters and κ' are the dimensionless adjustment coefficients of the radial functions R_l. In equation (2) r is the distance from the pseudoatom center, $r=|\mathbf{r}-\mathbf{R}|$, and Ω are the corresponding angular coordinates. The angular factor $d_{lm\pm}$ is a real density-normalized spherical harmonic

$$d_{lm\pm}(\Omega) = \mathrm{D}_{lm}\, y_{lm\pm}(\Omega) \qquad (3)$$

where $m \geq 0$ and $y_{lm\pm}$ is the normalized linear combination of complex spherical harmonics:

$$y_{00}=Y_{00}$$

$$y_{lm+} = (-1)^m \left(Y_{lm} + Y_{l,-m}\right)/\sqrt{2} \qquad m > 0$$

$$y_{lm-} = (-1)^m \left(Y_{lm} - Y_{l,-m}\right)/\sqrt{-2} \qquad m > 0 \qquad (4)$$

Renormalization factors D_{lm} are given by Coppens *et al.*.[3,8]

62 X-ray Charge Densities and Chemical Bonding

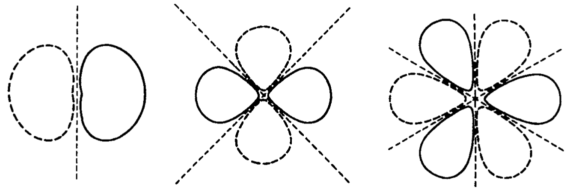


FIG. 3.3 Graphic representation of some multipolar functions: (from left to right) a dipole ($l = 1$), a quadrupole ($l = 2$), and an octupole ($l = 3$) function. Functions are negative with the dotted areas. If the x axis is horizontal and the y axis is vertical, the functions are x, $x^2 - y^2$, and $x^3 - 3xy^2$, respectively.

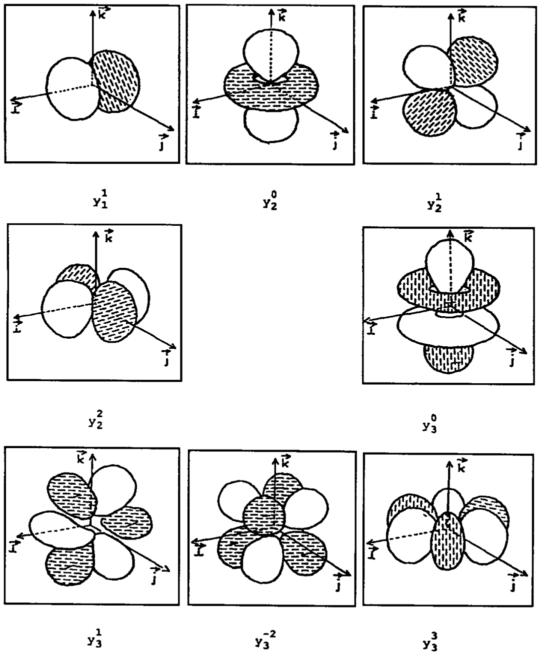


FIG. 3.4 Drawing of some dipolar, quadrupolar, and octupolar functions. *Source*: Hansen (1978).

Thus, the refinement of the aspherical density introduces parameters $P_{lm\pm}$ of the deformations functions and in some cases, the corresponding expansion-contraction coefficients κ′. Note the difference between parameters κ and κ′: the first one is applied to the spherical valence density, while the second one is applied to the aspherical deformation density. The charge density refinement parameters are conveniently summarized in the following table:[3]

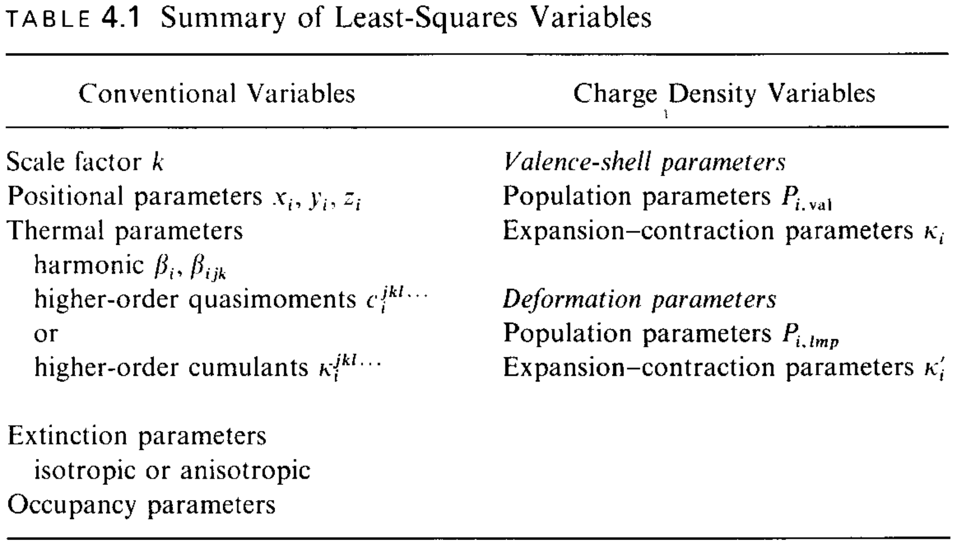


TABLE 4.1 Summary of Least-Squares Variables

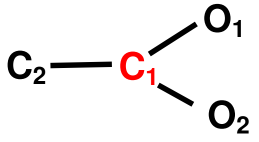
Conventional Variables	Charge Density Variables
Scale factor k	*Valence-shell parameters*
Positional parameters x_i, y_i, z_i	Population parameters $P_{i,\mathrm{val}}$
Thermal parameters	Expansion–contraction parameters κ_i
harmonic β_i, β_{ijk}	
higher-order quasimoments $c_i^{jkl\cdots}$	*Deformation parameters*
or	Population parameters $P_{i,lmp}$
higher-order cumulants $\kappa_i^{jkl\cdots}$	Expansion–contraction parameters κ_i'
Extinction parameters	
isotropic or anisotropic	
Occupancy parameters	

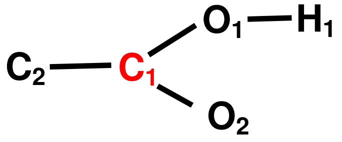
1.8 Introduction to the local coordinate system

Atoms in molecules and crystals often have a local symmetry. In general it has nothing to do with the crystallographic symmetry of the crystal structure, unless an atom lies on a crystallographic symmetry element. This case is not going to be discussed here.

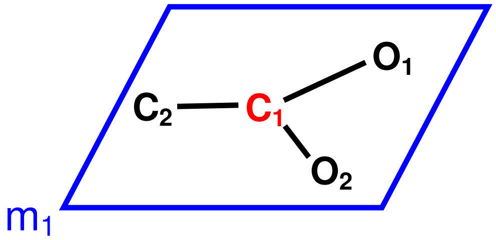
The local symmetry is determined by the chemical environment of an atom, i.e. the atom's bonding environment and in some case also the nature of the bonding of its neighbours.

We will determine the local symmetry and corresponding local axes of the carbon atom (shown in red) in carboxylate anion and the carboxylic acid group:

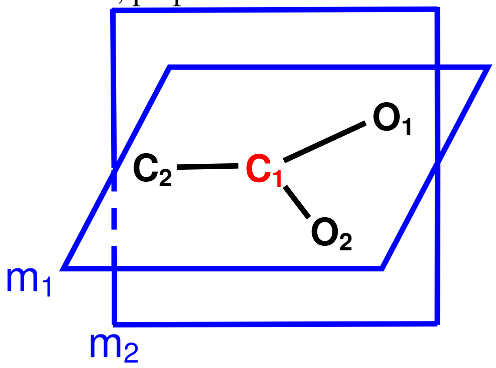




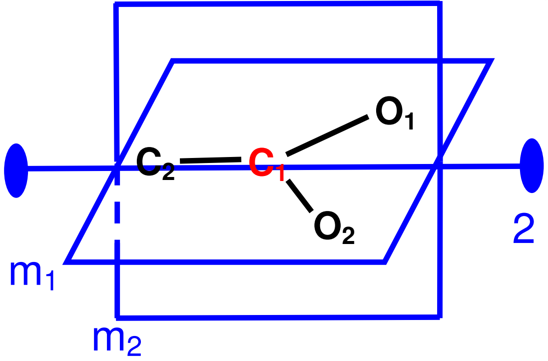
For simplicity we assume that both groups are planar. First consider the carboxylate anion. Because the group is planar we can say that there is approximately a mirror plane in the plane of the group, i.e.



Because the two oxygen atoms are also approximately equivalent and lie in the same plane as the carbon atom, the second mirror plane can be drawn, perpendicular to the first one:



Two mirror planes intersecting each other give rise to a two-fold axis along the intersection line



Thus the local symmetry of the carbon atom of the carboxylate group is approximately *mm*2. Now we have to choose the local axis layout and determined what multipolar functions are present and which vanish due to the local symmetry. The following table helps us:[9]

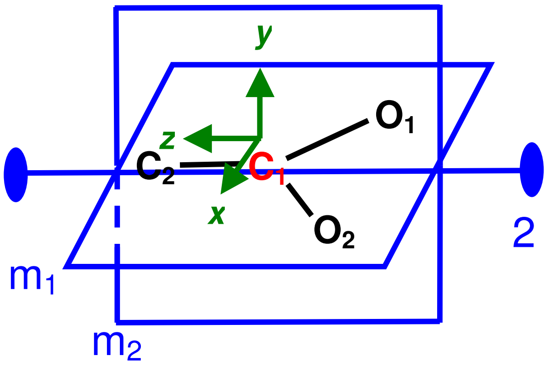
Table 3. Index Picking Rules of Site-Symmetric Spherical Harmonics.

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 ǁ z	(l,2μ, ±)
m	m ⊥ z	(l,$l-2\mu$, ±)
2/m	2 ǁ z, m ⊥ z	(2λ,2μ, ±)
222	2 ǁ z, 2 ǁ y, (2 ǁ x)	(2λ,2μ,+), ($2\lambda+1$,2μ,–)
mm2	2 ǁ z, m ⊥ y, (m ⊥ x)	(l,2μ,+)
mmm	m ⊥ z, m ⊥ y, m ⊥ x	(2λ,2μ, +)

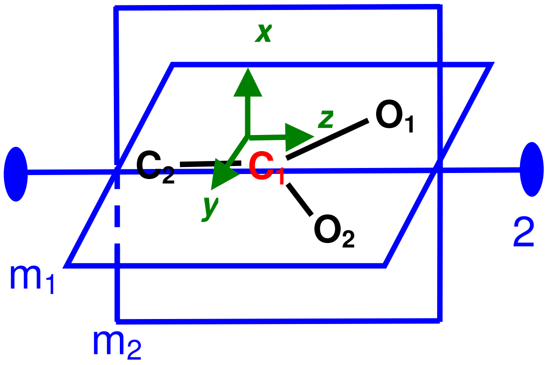
4	$4 \parallel z$	$(l,4\mu,\pm)$
$\bar{4}$	$\bar{4} \parallel z$	$(2\lambda,4\mu,\pm), (2\lambda+1,4\mu+2,\pm)$
$4/m$	$4 \parallel z, m \perp z$	$(2\lambda,4\mu,\pm)$
422	$4 \parallel z, 2 \parallel y, (2 \parallel x)$	$(2\lambda,4\mu,+), (2\lambda+1,4\mu,-)$
$4mm$	$4 \parallel z, m \perp y, (m \perp x)$	$(l,4\mu,+)$
$\bar{4}2m$	$\bar{4} \parallel z, 2 \parallel x, (m \triangleq xy \rightarrow yx)$ $m \perp y, (2 \triangleq xyz \rightarrow yx\bar{z})$	$(2\lambda,4\mu,+),(2\lambda+1,4\mu+2,-)$ $(2\lambda,4\mu,+),(2\lambda+1,4\mu+2,+)$
$4/mmm$	$4 \parallel z, m \perp z, (m \perp x), (m \triangleq xy \rightarrow yx)$	$(2\lambda,4\mu,+)$
3	$3 \parallel z$	$(l,3\mu,\pm)$
$\bar{3}$	$\bar{3} \parallel z$	$(2\lambda,3\mu,\pm)$
32	$3 \parallel z, 2 \parallel y,$ $2 \parallel x$	$(2\lambda,3\mu,+),(2\lambda+1,3\mu,-)$ $(3\mu+2j,3\mu,+),(3\mu+2j+1,3\mu,-)$
$3m$	$3 \parallel z, m \perp y$ $m \perp x$	$(l,3\mu,+)$ $(l,6\mu,+),(l,6\mu+3,-)$
$\bar{3}m$	$\bar{3} \parallel z, m \perp y$ $m \perp x$	$(2\lambda,3\mu,+)$ $(2\lambda,6\mu,+),(2\lambda,6\mu+3,-)$
6	$6 \parallel z$	$(l,6\mu,\pm)$
$\bar{6}$	$\bar{6} \parallel z = (3 \parallel z, m \perp z)$	$(2\lambda,6\mu,\pm),(2\lambda+1,6\mu+3,\pm)$
$6/m$	$6 \parallel z, m \perp y\ 2 \parallel y, (2 \parallel x)$	$(2\lambda,6\mu,\pm)$
622	$6 \parallel z, 2 \parallel y, (2 \parallel x)$	$(2\lambda,6\mu,+),(2\lambda+1,6\mu,-)$
$6mm$	$6 \parallel z, m \perp y, (m \perp x)$	$(l,6\mu,+)$
$\bar{6}m2$	$\bar{6} \parallel z, m \perp y, (2 \parallel x)$ $m \perp x, (2 \parallel y)$	$(2\lambda,6\mu,+),(2\lambda+1,6\mu+3,+)$ $(2\lambda,6\mu,+),(2\lambda+1,6\mu+3,-)$
$6/mmm$	$6 \parallel z, m \perp z, m \perp y, (m \perp x)$	$(2\lambda,6\mu,+)$

We see that for *mm*2 symmetry the z-axis must be directed along the 2-fold axis while the x and y-axes should be perpendicular to the mirror planes.

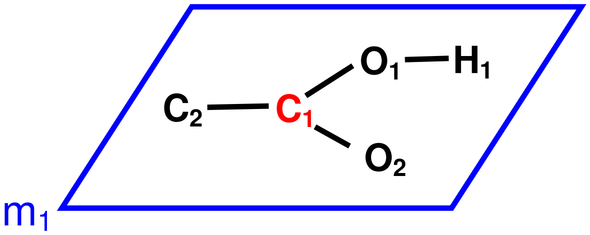
The following arrangement satisfies these rules:



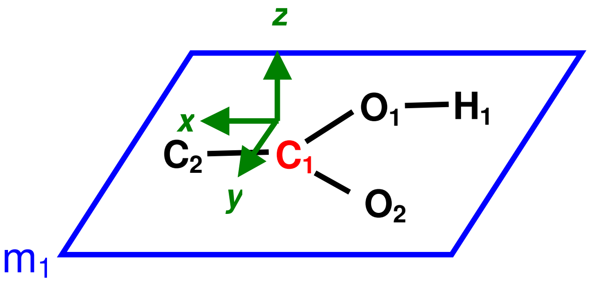
which is identical to the another definition:

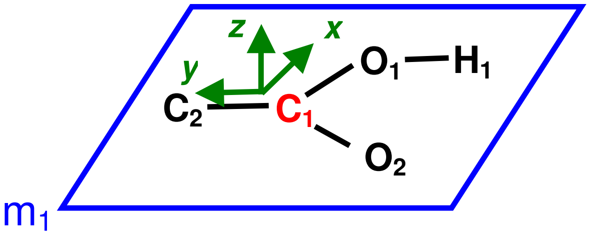


How does the symmetry of C_1 atom in the carboxylic group different from that in carboxylate ? Mirror plane m1 is still there:



But because O_1 and O_2 cannot be considered equivalent anymore, the mirror plane m_2 is not present. Thus the symmetry of the atom C_1 in carboxylic group is only *m* ! Looking in the Table 3 for rules for local symmetry axes one can see that the only condition is that the z-axis must be perpendicular to the mirror plane (m_1). Thus the following (and several others, not shown) arrangements are equally valid:





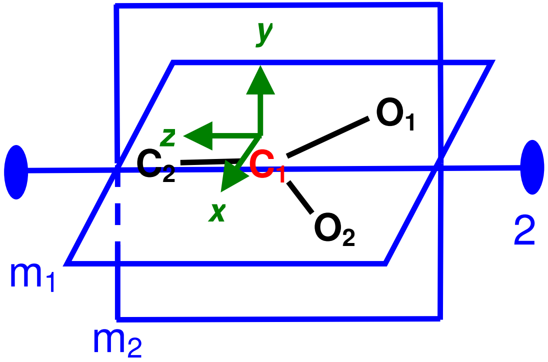
1.9 Definition of the local coordinate system in XD

Definition of the atomic local coordinate systems is done in the ATOM table of xd.mas file. The entries in the first seven columns define the local coordinate systems. *atom*, *atom0*, *atom1* and *atom2* are atom names from the **ATOM** table list. *ax1* and *ax2* stand for different axis assignments, each being either X or Y or Z. The first axis (*ax1*) is given by the internuclear vector from atom to atom0 ($\mathbf{v}_1$). This together with the second vector from *atom1* to *atom2* ($\mathbf{v}_2'$) define the (*ax1*,*ax2*) plane. The third vector ($\mathbf{v}_3$) is taken perpendicular to this plane.

$\mathbf{v}_1 = (\mathbf{r}_0 - \mathbf{r})$ $\mathbf{v}_2' = (\mathbf{r}_2 - \mathbf{r}_1)$ $\mathbf{v}_3 = \mathbf{v}_1 \times \mathbf{v}_2'$ $\mathbf{v}_2 = \mathbf{v}_1 \times \mathbf{v}_3$

where $\mathbf{r}$, $\mathbf{r}_0$, $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of atom, atom0, atom1 and atom2, respectively. Program will then internally normalize the lengths of vectors $\mathbf{v}_1$, $\mathbf{v}_2$ and $\mathbf{v}_3$ to unity.

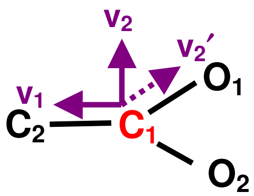
For the case of the C_1 atom of the carboxylic group



the definition of the local axes will be as follows:

vector $\mathbf{v}_1$ (z-axis) shall be vector $C_1 \rightarrow C_2$
vector $\mathbf{v}_2'$ shall be vector $C_1 \rightarrow O_2$
vector $\mathbf{v}_3$ (y-axis) is defined to be perpendicular to the plane of vectors $\mathbf{v}_1$ and $\mathbf{v}_2$
(i.e. $\mathbf{v}_3 = \mathbf{v}_1 \times \mathbf{v}_2'$)
finally, vector $\mathbf{v}_2$ (x-axis) is define to be perpendicular to the plane of vectors $\mathbf{v}_1$ and $\mathbf{v}_3$
(i.e. $\mathbf{v}_2 = \mathbf{v}_1 \times \mathbf{v}_3$)

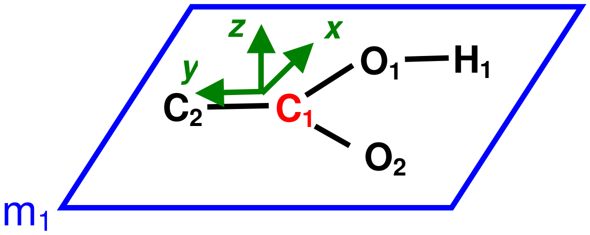
In the plane of COO^- group it will look like that (with vector $\mathbf{v}_3$ being perpendicular to the plane of the group)



The instruction for definition of the local coordinate system for atom C_1 in XD format will be:

```
ATOM  C1 C2 Z  C1 O1 X
```

For the C_1 atom in the carboxylic group,



the definition of the local axes will be as follows:

vector $\mathbf{v}_1$ (x-axis) shall be vector $C_1 \rightarrow O_1$

vector $\mathbf{v}_2'$ shall be vector $C_1 \rightarrow C_2$

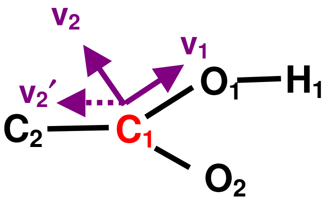
vector $\mathbf{v}_3$ (z-axis) is defined to be perpendicular to the plane of vectors $\mathbf{v}_1$ and $\mathbf{v}_2$

(i.e. $\mathbf{v}_3 = \mathbf{v}_1 \times \mathbf{v}_2'$)

finally, vector $\mathbf{v}_2$ (y-axis) is define to be perpendicular to the plane of vectors $\mathbf{v}_1$ and $\mathbf{v}_3$

(i.e. $\mathbf{v}_2 = \mathbf{v}_1 \times \mathbf{v}_3$)

In the plane of COOH group it will look like that (with vector $\mathbf{v}_3$ being perpendicular to the plane of the group)



The instruction for definition of the local coordinate system for atom C_1 in XD format will be:

```
ATOM  C1 O1 X  C1 C2 Y
```

Note that in the case of COO^- group vector $\mathbf{v}_1$ defines the z-axis, while in COOH group vector $\mathbf{v}_1$ defines the x-axis.

1.10 Local symmetry and multipolar functions

As mentioned above, because of the local symmetry some spherical harmonic functions vanish or have very small populations $P_{lm\pm}$. Thus in order to avoid instabilities in the refinement these 'vanishing' spherical harmonic functions should not be included in the refinement and kept fixed at zero. In order to understand which functions survive the symmetry a third column of Table 3 should be used. Note that spherical harmonic functions are defined as $lm\pm$ with $m=0\ldots l$. Thus, functions with values of m greater than l are not allowed. Consider the case of the C_1 atom in the carboxylate group discussed in the previous section. We've already determined that the local symmetry to be assigned to this atom is *mm*2 and we defined how the local axis should be directed. Now let's determine which multipole parameters will have to be refined. Looking in the third column of table 3 for *mm*2 symmetry we get the following rule: $(l,2\mu,+)$

where $\mu=0,1,2,3\ldots$ etc. We also note that only *lm*+ functions are allowed (*lm*- functions are ALL forbidden). In order to understand what particular *lm*+ functions should be refined the following table can be created:

<table>
<tr><th><i>l</i></th><th>μ</th><th><i>m</i>=2μ</th><th>spherical harmonics function (<i>lm</i>+)</th><th>Note</th></tr>
<tr><td colspan="5">DIPOLES</td></tr>
<tr><td>1</td><td>0</td><td>0</td><td>10</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>2</td><td>12+</td><td>NOT allowed: $m > l$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all result in $m>l$, thus only 10 function is allowed!</td></tr>
<tr><td colspan="5">QUADRUPOLES</td></tr>
<tr><td>2</td><td>0</td><td>0</td><td>20</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>2</td><td>22+</td><td>OK</td></tr>
<tr><td></td><td>2</td><td>4</td><td>24+</td><td>NOT allowed: $m > l$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all result in $m>l$, thus only 20 and 22+ functions are allowed!</td></tr>
<tr><td colspan="5">OCTUPOLES</td></tr>
<tr><td>3</td><td>0</td><td>0</td><td>30</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>2</td><td>32+</td><td>OK</td></tr>
<tr><td></td><td>2</td><td>4</td><td>34+</td><td>NOT allowed: $m > l$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all result in $m>l$, thus only 30 and 32+ functions are allowed!</td></tr>
<tr><td colspan="5">HEXADECAPOLES</td></tr>
<tr><td>4</td><td>0</td><td>0</td><td>40</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>2</td><td>42+</td><td>OK</td></tr>
<tr><td></td><td>2</td><td>4</td><td>44+</td><td>OK</td></tr>
<tr><td></td><td>3</td><td>6</td><td>46+</td><td>NOT allowed: $m > l$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all results in $m>l$, thus only 40, 42+ and 44+ functions are allowed!</td></tr>
</table>

Thus only 10, 20, 22+, 30, 32+, 40, 42+ and 44+ functions should be refined for an atom with *mm*2 symmetry.

For the C_1 atom in carboxylic group which has *m* symmetry there will be more functions to be refined. The rule from Table 3 is (l,l-2μ, ±)

<table>
<tr><th>l</th><th>j</th><th>m=l-2μ</th><th>spherical harmonics function (lm±)</th><th>Note</th></tr>
<tr><td colspan="5">DIPOLES</td></tr>
<tr><td>1</td><td>0</td><td>1</td><td>11±</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>-1</td><td>1(-1) 11±</td><td>Not allowed: $m < 0$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all results in m<0, thus only 11+ and 11- functions are allowed!</td></tr>
<tr><td colspan="5">QUADRUPOLES</td></tr>
<tr><td>2</td><td>0</td><td>2</td><td>22±</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>20</td><td>20</td><td>OK</td></tr>
<tr><td></td><td>2</td><td>-2</td><td>2(-2)±</td><td>NOT allowed: $m < 0$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all results in m>0, thus only 20, 22- and 22+ functions are allowed!</td></tr>
<tr><td colspan="5">OCTUPOLES</td></tr>
<tr><td>3</td><td>0</td><td>3</td><td>33±</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>1</td><td>31±</td><td>OK</td></tr>
<tr><td></td><td>2</td><td>-1</td><td>3(-1)±</td><td>NOT allowed: $m < 0$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all results in m<0, thus only 31+, 31-, 33+ and 33- functions are allowed!</td></tr>
<tr><td colspan="5">HEXADECAPOLES</td></tr>
<tr><td>4</td><td>0</td><td>4</td><td>44±</td><td>OK</td></tr>
<tr><td></td><td>1</td><td>2</td><td>42±</td><td>OK</td></tr>
<tr><td></td><td>2</td><td>0</td><td>40</td><td>OK</td></tr>
<tr><td></td><td>3</td><td>-2</td><td>4(-2)±</td><td>NOT allowed: $m < 0$</td></tr>
<tr><td colspan="5">At this stage there is no point to continue with larger values of μ because they will all results in m<0, thus only 40, 42+, 42-, 44+ and 44- functions are allowed!</td></tr>
</table>

As one can guess, the higher the symmetry the fewer symmetry-allowed multipolar functions need to be refined, thus for an atom with local symmetry of 3 (for example, N-atom of the NH_3^+ group) [rule (l,3μ,±)], only 10, 20, 30, 33±, 40 and 43± functions are allowed.

Now that we've covered the local symmetry we are ready to setup the atomic local coordinate systems and perform a multipole refinement.

1.11 Multipolar refinement in XD

The instructions for running all XD programs are in the xd.mas file. At this stage we are only concerned with the instructions which control the XDLSM program, and these are found in the section between the lines MODULE XDLSM and END XDLSM. The setup for refinement with XDLSM is quite a bit more complicated than for SHELXL. There are five sections to the instruction set for XDLSM :

(a) Basic program control section
(b) the SCAT table - the scattering factor tables (like SFAC entries in SHELX)
(c) the ATOM table - where the local coordinate system and some refinement limits are defined
(d) section with refinement options
(e) the KEY table - tells the program which parameters to refine

While section (a) and (d) can be conveniently modified using the WinXD GUI, it is more straight forward to make changes to sections (b), (c) and (e) directly by editing the xd.mas file.

1.11.1 The SCAT Table

The definition of the scattering model is of course very important for a successful multipole refinement. For this first example we shall stick with the default scattering model that has been created by the startup program XDINI, so it will not be necessary to edit this part. In this model we use core and spherical valence densities and radial functions derived from Clementi-Roetti's Hartree-Fock atomic wavefunctions, expanded in terms of Slater-type basis functions - for our examples these are adequate.

$$O_l = [(2n(l)!]^{-1/2}(2\zeta_l)^{n(l)+1/2, r^{n(l)}} \exp(-\zeta r)$$

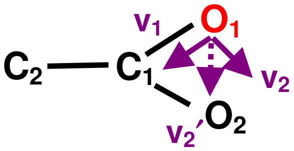
For the deformation valence, we will use radial functions of the single-zeta Slater type.

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

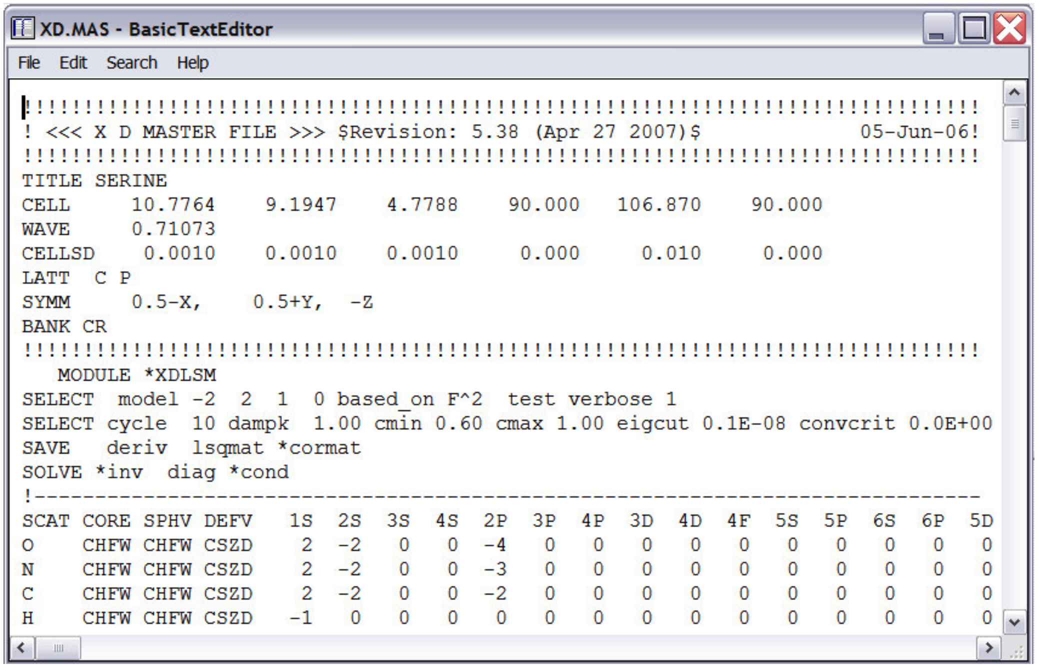
with $n(l) \geq l$ to obey Poisson’s equation and with values for a_l as deduced from the single-ζ wavefunctions. These a_l values are scaled by the refinable κ' parameters.

1.11.2. Setting up atomic local coordinate systems and refinement keys (ATOM and KEY tables)

As an example, we start by looking at the atomic local system for atom O(1). We note that it has local symmetry *m* with axes directed as follows:



Go to **File → Open XD Master File**



```
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! <<< X D MASTER FILE >>> $Revision: 5.38 (Apr 27 2007)$              05-Jun-06!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
TITLE SERINE
CELL     10.7764    9.1947    4.7788    90.000   106.870    90.000
WAVE     0.71073
CELLSD    0.0010    0.0010    0.0010     0.000     0.010     0.000
LATT  C P
SYMM     0.5-X,    0.5+Y,  -Z
BANK CR
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
   MODULE *XDLSM
SELECT  model -2  2  1  0 based_on F^2  test verbose 1
SELECT cycle  10 dampk  1.00 cmin 0.60 cmax 1.00 eigcut 0.1E-08 convcrit 0.0E+00
SAVE   deriv  lsqmat *cormat
SOLVE *inv  diag *cond
!-------------------------------------------------------------------------------
SCAT CORE SPHV DEFV   1S  2S  3S  4S  2P  3P  4P  3D  4D  4F  5S  5P  6S  6P  5D
O    CHFW CHFW CSZD    2  -2   0   0  -4   0   0   0   0   0   0   0   0   0   0
N    CHFW CHFW CSZD    2  -2   0   0  -3   0   0   0   0   0   0   0   0   0   0
C    CHFW CHFW CSZD    2  -2   0   0  -2   0   0   0   0   0   0   0   0   0   0
H    CHFW CHFW CSZD   -1   0   0   0   0   0   0   0   0   0   0   0   0   0   0
```

The default entry for atom O(1) in the ATOM table is shown below

```
ATOM     ATOM0    AX1 ATOM1    ATOM2   AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(1)      Z  O(1)     O(2)     Y   R   2  1   1   4  NO
```

This instruction specifies that the vector O(1)→C(1) comprises the local *z* axis and vector O(1)→O(2) defines the *yz* plane (vectors v_1 and v_2' in above diagram). HOWEVER, if we wish to impose local mirror symmetry on this atom, we can see from Table 3 that to do this we must have the local *z* axis perpendicular to the mirror plane. The easiest way to accomplish this is to set the O(1)→C(1) vector to comprise the local *x* axis and leave the other default entry. In this way, the local *z* axis must, by definition, be perpendicular to the *xy* plane we have just defined. The entry for atom O(1) must therefore be changed to

```
ATOM     ATOM0    AX1 ATOM1    ATOM2   AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(1)      X  O(1)     O(2)     Y   R   2  1   1   4  NO
```

Now we are specifying the correct local axial system ! The other parameters on this line tell us, respectively, that we have a right handed axial system (the "R" - good!), we restrict the thermal motion to harmonic anisotropic (the "2" - fine!), we indicate that this atom corresponds to the first entry in the SCAT table, i.e. an oxygen atom (the "1"), that it also corresponds to the first set of kappa parameters (the next "1") and that the maximum level of multipole expansion permissible for this atom is l=4, i.e. a hexadecapole (also fine!).

In the ATOM table, we must also specify which atoms will be treated as equivalent (CHEMCON indicator) . This aspect has been dealt with already in section 1.5.

This procedure above is repeated for all the atoms. Note that H-atoms are usually assigned so-called cylindrical symmetry with z-axis directed towards the bonding parent atom.

The final ATOM table should look like this :

```
ATOM     ATOM0    AX1 ATOM1    ATOM2    AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(1)      Z  O(1)     O(2)      Y   R   2  1   1   4   m
O(2)     C(1)      Z  O(2)     O(1)      Y   R   2  1   1   4   m        O(1)
O(3)     H(4)      Z  O(3)     C(3)      Y   R   2  1   2   4   m
N(1)     C(2)      Z  N(1)     H(13)     X   R   2  2   3   4   3m
C(1)     O(1)      Z  C(1)     O(2)      Y   R   2  3   4   4   mm2
C(2)     H(2)      Z  C(2)     N(1)      Y   R   2  3   5   4   NO
C(3)     H(32)     Z  C(3)     H(31)     Y   R   2  3   6   4   m
H(2)     C(2)      Z  H(2)     N(1)      Y   R   1  4   7   2   cyl
H(4)     O(3)      Z  H(4)     C(3)      Y   R   1  4   7   2   cyl
H(11)    N(1)      Z  H(11)    H(12)     Y   R   1  4   7   2   cyl
H(12)    N(1)      Z  H(12)    H(11)     Y   R   1  4   7   2   cyl   H(11)
H(13)    N(1)      Z  H(13)    H(12)     Y   R   1  4   7   2   cyl   H(11)
H(31)    C(3)      Z  H(31)    H(32)     Y   R   1  4   7   2   cyl
H(32)    C(3)      Z  H(32)    H(31)     Y   R   1  4   7   2   cyl   H(31)
DUM0      0.0000  0.0000  0.0000
END ATOM
```

At this early stage of multipole refinement, it is recommended to fix the atomic positional and ADP parameters, but we need to refine the multipole parameters. To tell the refinement program XDLSM which multipole parameters to refine requires us now to edit the entries in the KEY TABLE. The default entry for the O(1) atom in this table is :

```
KEY     XYZ --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    111 111111 0000000000 000000000000000 00 000 00000 0000000 000000000
```

Each refineable parameter has an associated refinement key, which is either given the value "0", meaning do NOT refine this parameter, or a value "1" meaning the opposite. The line above indicates that the positional and anisotropic thermal parameters will be refined, but all other parameters will be unrefined. We need to change this, to indicate that the positional and anisotropic thermal parameters will NOT be refined, but the allowed multipoles (for mirror symmetry) WILL be allowed to refine. The method for deciding which multipole parameters are allowed to refine for local *m* symmetry has been dealt with in the previous section 1.10 (by reference to Tables 1 and 3). The correct entry for the O(1) atom in this table should look like :

```
KEY     XYZ --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    000 000000 0000000000 000000000000000 10 110 10011 0110011 100110011
```

Note H-atoms are usually assigned so-called cylindrical symmetry with z-axis directed towards the bonding parent atom. Thus only bond directed functions 10 (and sometimes 20) should be refined.

The final modified KEY Table for the atoms should look like this :

```
KEY     XYZ --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    000 000000 0000000000 000000000000000 10 110 10011 0110011 100110011
O(2)    000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
O(3)    000 000000 0000000000 000000000000000 10 110 10011 0110011 100110011
N(1)    000 000000 0000000000 000000000000000 10 001 10000 1000010 100001000
C(1)    000 000000 0000000000 000000000000000 10 001 10010 1001000 100100010
C(2)    000 000000 0000000000 000000000000000 10 111 11111 1111111 111111111
C(3)    000 000000 0000000000 000000000000000 10 110 10011 0110011 100110011
H(2)    000 000000 0000000000 000000000000000 10 001 00000 0000000 000000000
H(4)    000 000000 0000000000 000000000000000 10 001 00000 0000000 000000000
H(11)   000 000000 0000000000 000000000000000 10 001 00000 0000000 000000000
H(12)   000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(13)   000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
H(31)   000 000000 0000000000 000000000000000 10 001 00000 0000000 000000000
H(32)   000 000000 0000000000 000000000000000 00 000 00000 0000000 000000000
```

Again, as in the case of Kappa refinement, we chose to apply chemical constrains for some atoms. Thus for atoms O(1) and O(2), only one set of Pv, κ, Plm± and κ′ will be refined. The same goes for H(11),H(12) and H(13), and H(31) and H(32) groups of atoms. *Note that for atoms which are tied to be chemically the same as other atoms, the refinement flags for all their multipoles should be set to zero.*

The local coordinate systems and refinement keys for all multipole population parameters have now been set up. Next, check if refinement keys for κ parameters have been set up. Scroll down to KEY table to the KAPPA command lines, which are in the following format:

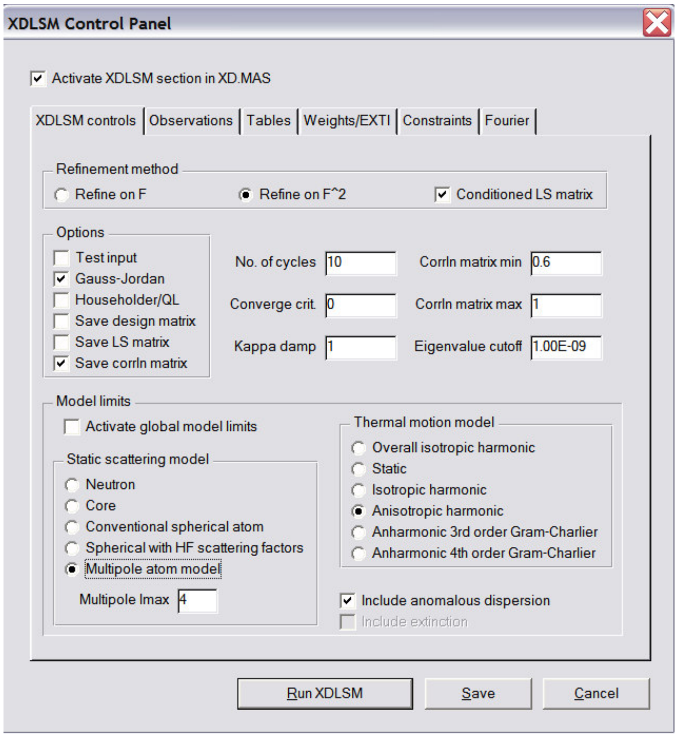
```
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   100000
KAPPA   00000
```

This tells to program to refine κ parameters of the spherical valence shell but to keep κ′ parameters of the deformation functions fixed at 1.0. Also note that the κ parameter for H-atoms is NOT refined, as in the case of Kappa refinement above. The modifications to the `xd.mas` file are now finished - it should now be saved !

1.11.2. Setting up general XDLSM instructions

After all the atomic local symmetries and refinement keys have been set up manually, we need to edit the following XDLSM instructions. This can be done by using the GUI

The maximum level of multipole expansion needs to be changed to 4 as our model will use functions up to hexadecapole level (l=4):



☑ Activate XDLSM section in XD.MAS

Refinement method
○ Refine on F ● Refine on F^2 ☑ Conditioned LS matrix

Options
☐ Test input
☑ Gauss-Jordan
☐ Householder/QL
☐ Save design matrix
☐ Save LS matrix
☑ Save corrln matrix

No. of cycles: 10
Converge crit.: 0
Kappa damp: 1
Corrln matrix min: 0.6
Corrln matrix max: 1
Eigenvalue cutoff: 1.00E-09

Model limits
☐ Activate global model limits

Static scattering model
○ Neutron
○ Core
○ Conventional spherical atom
○ Spherical with HF scattering factors
● Multipole atom model

Multipole lmax: 4

Thermal motion model
○ Overall isotropic harmonic
○ Static
○ Isotropic harmonic
● Anisotropic harmonic
○ Anharmonic 3rd order Gram-Charlier
○ Anharmonic 4th order Gram-Charlier

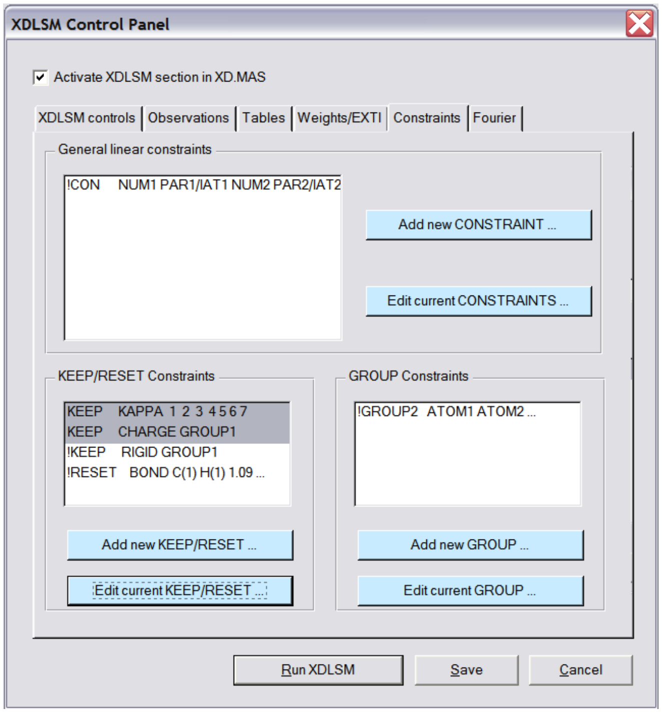
☑ Include anomalous dispersion
☐ Include extinction

This change corresponds to the following line in `xd.mas`

```
SELECT  *model 4  2  1  0 based_on F^2  test verbose 1
```

The global model limits are activated, and the maximum multipole level set to 4

Now change the instructions which says that the same κ parameter will be applied for all *l*'s, i.e. $\kappa_{l=1}=\kappa_{l=2}=\kappa_{l=3}=\kappa_{l=4}$ and which restricts the sum of all the monopole populations to the sum to the valence population.



☑ Activate XDLSM section in XD.MAS

General linear constraints

```
!CON    NUM1 PAR1/IAT1 NUM2 PAR2/IAT2
```

KEEP/RESET Constraints

```
KEEP   KAPPA 1 2 3 4 5 6 7
KEEP   CHARGE GROUP1
!KEEP   RIGID GROUP1
!RESET   BOND C(1) H(1) 1.09 ...
```

GROUP Constraints

```
!GROUP2  ATOM1 ATOM2 ...
```

This edit corresponds to these instructions in xd.mas

```
KEEP     KAPPA  1  2  3  4  5 6 7
KEEP     CHARGE GROUP1
```

At the early stages of multipole refinement it is advisable to reset X-H distances to their standard (neutron) values after each cycle of refinement. At the last stage of multipole refinement it can be lifted and in ideal case the H-atom will keep their positions at almost neutron-like distances. Values for standard distances can be found in International Tables, Volume C.

Add the following RESET BOND instruction:

```
RESET BOND  C(2) H(2) 1.099  O(3) H(4) 0.965  N(1) H(11) 1.033  N(1) H(12) 1.033
```

Finally, modify the type of the Fourier coefficients to be written to xd.fou file:

```
FOUR  fmod1  4  2  0  0   fmod2 -1  2  0  0
```

The first set of Fcal (Fmod1) will be calculated from aspherical density while the second set of Fcalc (Fmod2) will be calculated from spherical independent-atom model (as in SHELX). Phases of reflections for Fobs will be taken from multipole model.

Now run XDLSM

The R-factor should drop down to about 1.9% (based on F). Then run XDGEOM and examine the table of multipole parameters

If everything looks good, copy file xd.res with refined parameters to xd.inp using **Utilities → RES → INP**

Modify XDLSM instructions to refine positional and ADP parameters together with multipole parameters for ALL atoms. For example, for atom O(1):

```
KEY     XYZ --U2-- ----U3---- ------U4------- M- -D- --Q-- ---O--- ----H----
O(1)    111 111111 0000000000 000000000000000 10 110 10011 0110011 100110011
```

Repeat this procedure for ALL non-H atoms (only set the FIRST U2 key to 1, so that the isotropic parameter is refined). The H-atom positional parameters should not be refined.

Run XDLSM – the R-factor should now drop down to about 1.68%. Open xd_lsm.out file in the text editor and scroll down to the results of Hirshfeld rigid-bond test and compare those to the results of IAM refinement:

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

Multipole refinement

```
ATOM-->  ATOM    /  DIST  DMSDA ATOM
 O(1)     C(1)    * 1.2537     1
 O(2)     C(1)    * 1.2644     1
 O(3)     C(3)    * 1.4220     1
 N(1)     C(2)      1.4908    -1
 C(1)     C(2)    * 1.5332     2
 C(2)     C(3)    * 1.5234     1
```

IAM refinement

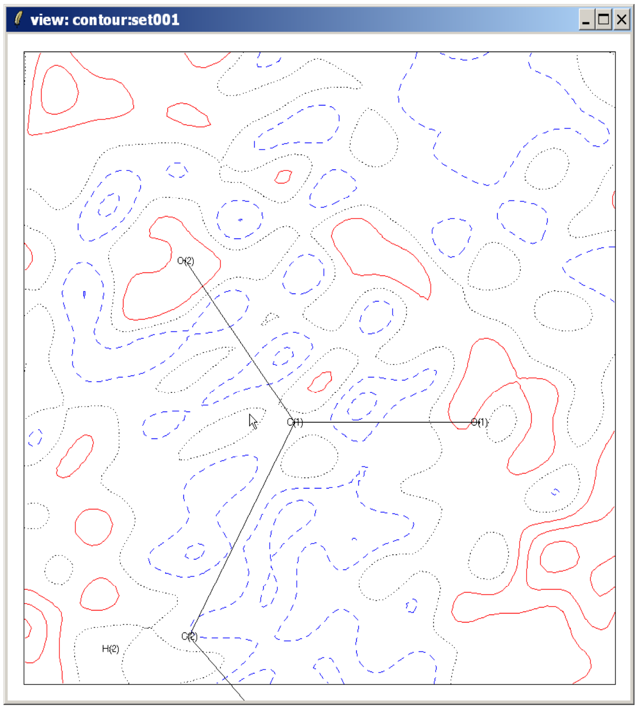
```
ATOM-->  ATOM    /  DIST  DMSDA ATOM
 O(1)     C(1)    * 1.2548     5
 O(2)     C(1)    * 1.2652     5
 O(3)     C(3)    * 1.4225     7
 N(1)     C(2)      1.4915    -1
 C(1)     C(2)    * 1.5334     1
 C(2)     C(3)    * 1.5233     0
```

Note how much the results are improved for O-C bonds (!)

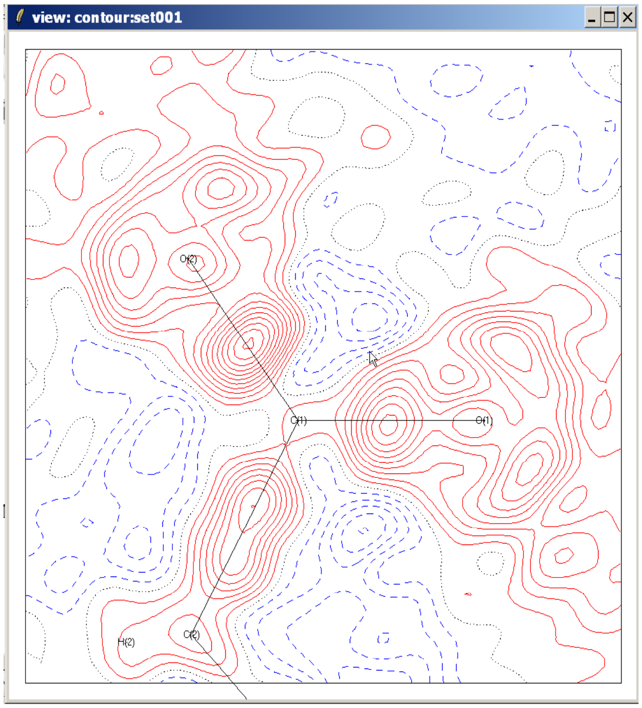
Re-run XDGEOM and examine the tables of multipole parameters again, to make sure there are no unphysical values. Run XDFOUR to calculate the residual density after multipole refinement, *i.e.* Fobs-Fmod1, in the plane of C(1)-O(1)-O(2), *i.e.* in the same plane and on the same grid as after SHELX refinement.

Now visualize it in XDGRAPH using previously created script `fou.log` with contour level of ±0.05 e/Å^3 and compared the plot with that after SHELX refinement:

Residual density after multipole refinement:



Residual density after IAM refinement:



Note that all aspherical density features are gone (!), which means our multipole model produces a very good fit to the observed structure factors.

Note that results of this quality are obtained without refinement of expansion-contraction coefficients κ′ for the deformation functions. In general, the refinement of κ′ coefficients should be attempted ONLY for exceptional quality data. In our own studies, we usually constrain these parameters at the values obtained from refinement of theoretical structure factors

1.12 Calculation of electrostatic properties

The module XDPROP in XD2006 is able to evaluate a wealth of electrostatic properties from the final static electron density model refined with XDLSM. In addition to using XD's own graphical program XDGRAPH, an interface is provided to several public-domain graphics programs, such as MOLDEN, MOLEKEL, PLOTMTV. XPROP is also capable of producing a number of vector and trajectory plots. Which properties are evaluated depends mainly on the requirements of the user.

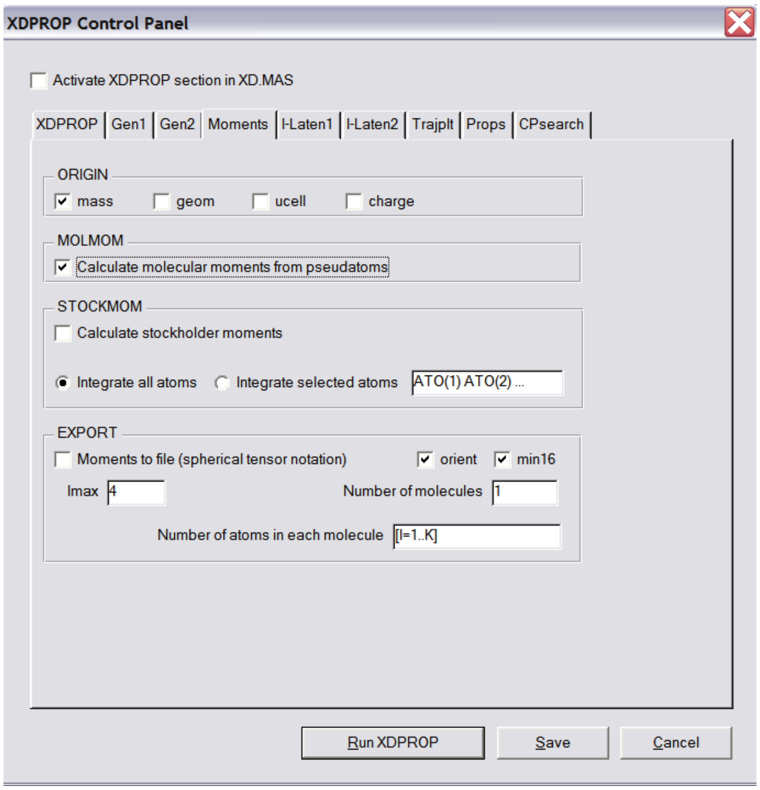
In this tutorial we will cover the main properties that are of general interest to show the abilities of XDPROP. XDPROP uses the xd.mas file with instructions which can also be input within the GUI and xd.res file which should contain the results of the latest refinement.

1.12.1. Net charges & higher moments

One of the main interests for a chemist are the net atomic charges. Unfortunately, the definition of a net charge is ambiguous, so XD2006 provides several ways to calculate net atomic charges:

directly from the refined valence populations of the atoms
using Hirshfeld's stockholder's approach[10]
using a fit to the electrostatic potential
using Bader's Quantum Theory of Atoms in Molecules[11] (QTAIM)

We've already shown how the net charges based on valence populations can be printed by XDGEOM to the xd_geo.out file. Printout of atomic charges and higher atomic moments based on multipole model is done in XDPROP using the following commands:



☐ Activate XDPROP section in XD.MAS

ORIGIN
☑ mass ☐ geom ☐ ucell ☐ charge

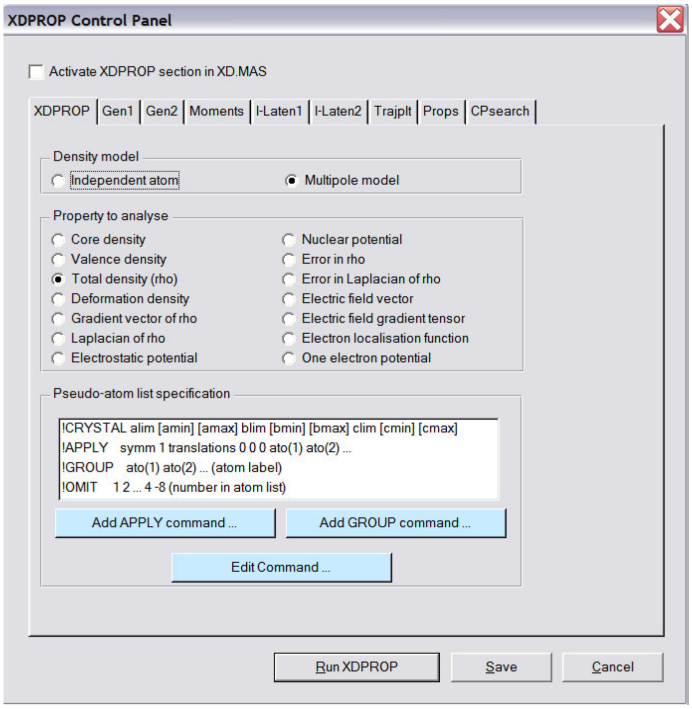
MOLMOM
☑ Calculate molecular moments from pseudatoms

STOCKMOM
☐ Calculate stockholder moments
● Integrate all atoms ○ Integrate selected atoms ATO(1) ATO(2) ...

EXPORT
☐ Moments to file (spherical tensor notation) ☑ orient ☑ min16
lmax 4
Number of molecules 1
Number of atoms in each molecule [I=1..K]

ORIGIN options sets up the origin of the coordinate system for calculation of the total MOLECULAR moments from ATOMIC moments (center of mass, center of charge, center of unit cell or geometrical center of the molecule)

The calculation of Hirshfeld's charges in XDPROP is done via numerical (quadrature) integration:



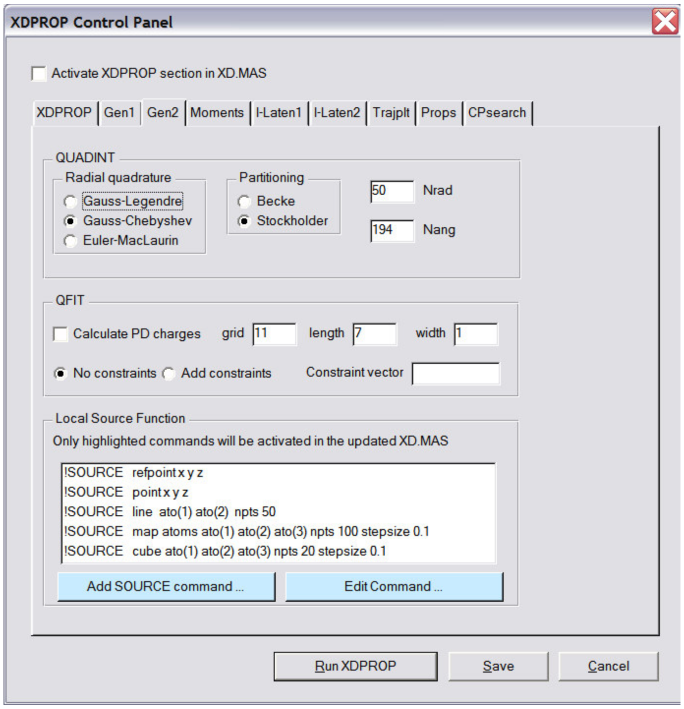
☐ Activate XDPROP section in XD.MAS

Density model
○ Independent atom ● Multipole model

Property to analyse
○ Core density
○ Valence density
● Total density (rho)
○ Deformation density
○ Gradient vector of rho
○ Laplacian of rho
○ Electrostatic potential
○ Nuclear potential
○ Error in rho
○ Error in Laplacian of rho
○ Electric field vector
○ Electric field gradient tensor
○ Electron localisation function
○ One electron potential

Pseudo-atom list specification

```
!CRYSTAL alim [amin] [amax] blim [bmin] [bmax] clim [cmin] [cmax]
!APPLY   symm 1 translations 0 0 0 ato(1) ato(2) ...
!GROUP   ato(1) ato(2) ... (atom label)
!OMIT    1 2 ... 4 -8 (number in atom list)
```



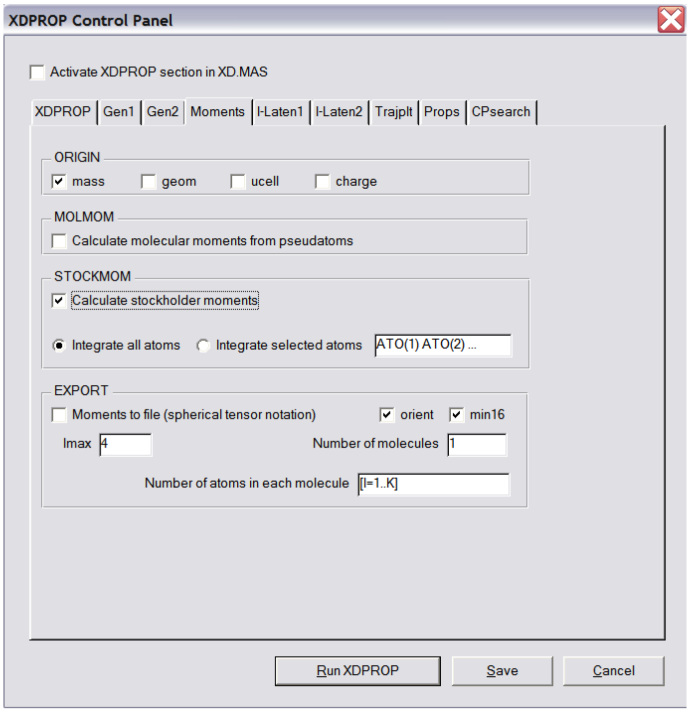
☐ Activate XDPROP section in XD.MAS

QUADINT
Radial quadrature: ○ Gauss-Legendre ● Gauss-Chebyshev ○ Euler-MacLaurin
Partitioning: ○ Becke ● Stockholder
Nrad 50
Nang 194

QFIT
☐ Calculate PD charges grid 11 length 7 width 1
● No constraints ○ Add constraints Constraint vector

Local Source Function
Only highlighted commands will be activated in the updated XD.MAS

```
!SOURCE   refpoint x y z
!SOURCE   point x y z
!SOURCE   line  ato(1) ato(2)  npts 50
!SOURCE   map atoms ato(1) ato(2) ato(3) npts 100 stepsize 0.1
!SOURCE   cube ato(1) ato(2) ato(3) npts 20 stepsize 0.1
```



☐ Activate XDPROP section in XD.MAS

ORIGIN
☑ mass ☐ geom ☐ ucell ☐ charge

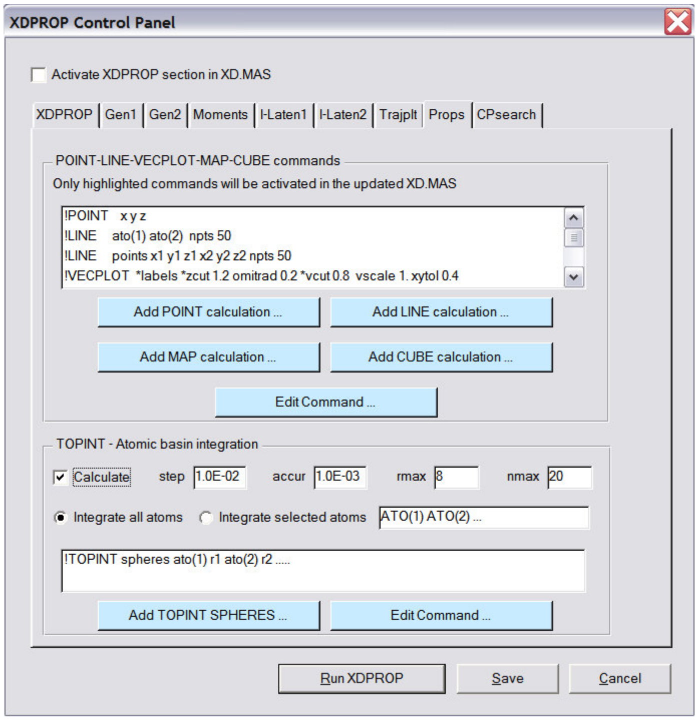
MOLMOM
☐ Calculate molecular moments from pseudatoms

STOCKMOM
☑ Calculate stockholder moments
● Integrate all atoms ○ Integrate selected atoms ATO(1) ATO(2) ...

EXPORT
☐ Moments to file (spherical tensor notation) ☑ orient ☑ min16
lmax 4 Number of molecules 1
Number of atoms in each molecule [I=1..K]

Note the ORIGIN option applies to both stockholder and multipole-based moments. Calculation of stockholder moments takes much longer because of the numerical integration.

The calculation of Bader's QTAIM charges takes even longer than stockholder's and, thus, is not covered in this tutorial. The relevant option in XDPROP is **TOPINT**, which can be invoked under **Props** menu:



☐ Activate XDPROP section in XD.MAS

POINT-LINE-VECPLOT-MAP-CUBE commands

Only highlighted commands will be activated in the updated XD.MAS

```
!POINT   x y z
!LINE    ato(1) ato(2)  npts 50
!LINE    points x1 y1 z1 x2 y2 z2 npts 50
!VECPLOT  *labels *zcut 1.2 omitrad 0.2 *vcut 0.8  vscale 1. xytol 0.4
```

TOPINT - Atomic basin integration

☑ Calculate step 1.0E-02 accur 1.0E-03 rmax 8 nmax 20

● Integrate all atoms ○ Integrate selected atoms ATO(1) ATO(2) ...

```
!TOPINT spheres ato(1) r1 ato(2) r2 .....
```

Nevertheless, the values of QTAIM charges based on the same static multipole model are listed in the following table:

Atom	Net atomic charges			
	Multipole	**Stockholder**	**Fitted to ESP**	**QTAIM**
O(1)	-0.373	-0.331	-0.561	-0.908
O(2)	-0.373	-0.345	-0.583	-0.893
O(3)	-0.252	-0.227	-0.366	-0.889
N(1)	+0.117	+0.090	+0.119	-0.818
C(1)	+0.288	+0.255	+0.742	+1.358
C(2)	+0.324	+0.117	+0.153	+0.345
C(3)	-0.227	+0.029	+0.156	+0.392
H(2)	-0.024	+0.049	+0.035	+0.049
H(4)	+0.106	+0.119	+0.239	+0.449
H(11)	+0.124	+0.141	+0.149	+0.378
H(12)	+0.124	+0.146	+0.147	+0.377
H(13)	+0.124	+0.143	+0.140	+0.409
H(31)	+0.021	-0.100	-0.216	-0.127
H(32)	+0.021	-0.086	-0.154	-0.118

As one can see, the multipole and stockholder charges, both being based on the so-called fuzzy-boundary electron density partitioning model, are in a very good agreement with each other. The ESP-based charges are slightly different and have higher absolute values. As is generally the case, the QTAIM charges, based on a discrete-boundary electron-density partitioning, differ significantly from the other methods. Nevertheless, each type of atomic charge provides valuable information about chemical bonding.

Note that during the multipole, stockholder and QTAIM analyses, the program calculates not only the atomic charges, but also the higher moments and automatically computes the total molecular moments. The XDPROP output file `xd_pro.out` provides exhaustive information.

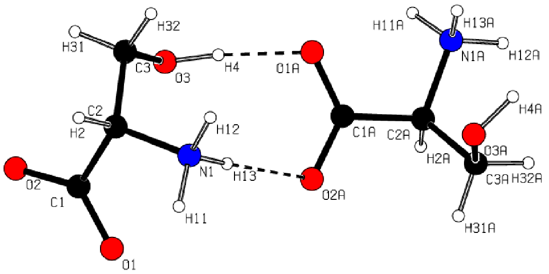
1.12.2. Calculations of electrostatic interaction energies between molecules

XDPROP provides a powerful and accurate set of algorithms for calculation of the electrostatic interaction energies in crystals.

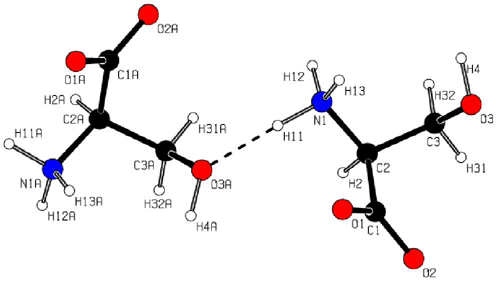
Before the actual calculation, a little bit of preliminary work needs to be done. Suppose, we would like to calculate the electrostatic interactions between hydrogen-bonded dimers of serine in the crystal structure. First we have to identify what symmetry operations we need to apply to the central molecule in order to generate the symmetry-equivalent hydrogen-bonded monomer. The program PLATON by Ton Spek[12] prints out the following information:

```
Analysis of Potential Hydrogen Bonds and Schemes
================================================

Nr Res Donor --- H....Acceptor [    ARU  ] D - H   H...A    D...A  D - H...A
-------------------------------------------------------------------------------
 1   1 O(3)  --H(4)    ..O(1)   [  2646.01]  0.97    1.70   2.6631        173
     1 N(1)  --H(13)   ..O(2)   [  2646.01]  0.97    1.89   2.8535        170
 2   1 N(1)  --H(11)   ..O(3)   [  4455.01]  1.03    1.77   2.7647        159
 3   1 N(1)  --H(12)   ..O(2)   [  2647.01]  1.03    1.80   2.7947        161
 4   1 C(2)  --H(2)    ..O(1)   [  1556.01]  1.10    2.19   3.2865        172

Translation of ARU-code to Equivalent Position Code
===================================================
   [  2646. ]  = 3/2-x,-1/2+y,1-z
   [  2647. ]  = 3/2-x,-1/2+y,2-z
   [  4455. ]  = -1/2+x,1/2-y,z
   [  1556. ]  = x,y,1+z
```

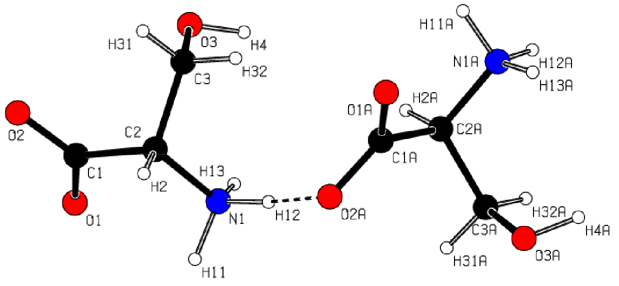
Note there are two H-bonds in the first dimer.



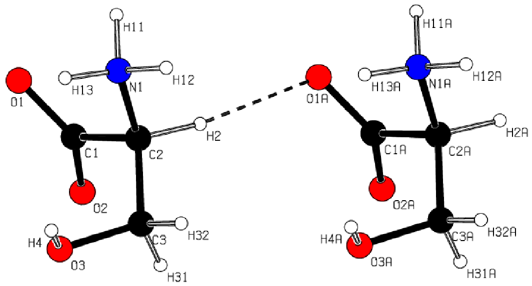
dimer 1



dimer 2



dimer 3



dimer 4

Now we have to apply given symmetry operations in XDPROP to generate a symmetry-equivalent monomer and then calculate the interaction between it and the original molecule. This is done in XDPROP using the **APPLY** instruction in the XDPROP section :

```
APPLY    symm 2 translations 0 0 0 ALL
```

XDPROP needs the number of the symmetry operations and the translations along the crystal x, y and z-axes. If we look in the xd_pro.out file from the previous runs of XDPROP, we find the printout of the symmetry operations in the following format:

```
Symmetry information
 The crystal is centrosymmetric, lattice type P( 1)

 SYMM  1      + X, + Y, + Z
 SYMM  2      1/2 - X, 1/2 + Y, - Z
 ----  symmetry generated from lattice type:
 SYMM  3      - X, - Y, - Z
 SYMM  4      1/2 + X, 1/2 - Y, + Z
```

Symmetry operations are numbered 1 through 4, and these are exactly the numbers that need to be specified as the symmetry operator in the APPLY command.

Consider the first dimer. The symmetry operation needed to generate it is

```
[  2646. ]  = 3/2-x,-1/2+y,1-z
```

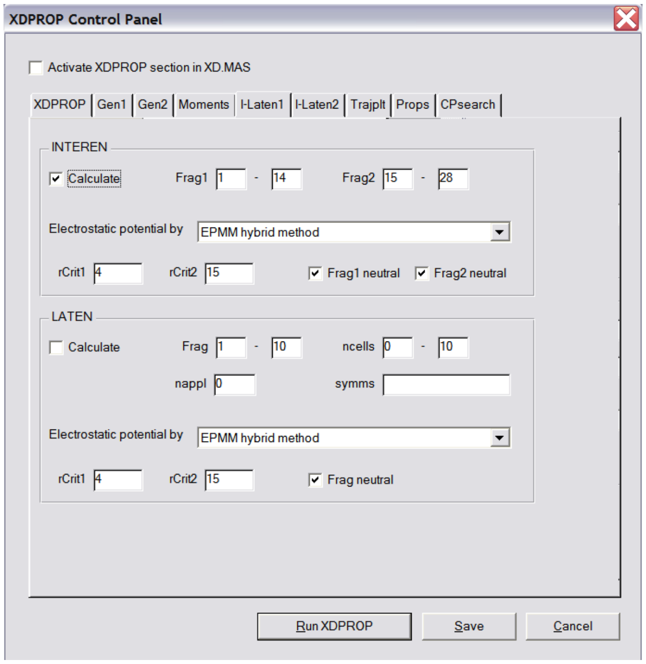
which in XDPROP can be specified as symmetry operation number 2 (`1/2 - X, 1/2 + Y, - Z`) with added translations of tx=1, ty = -1, tz = 1.

So we specify them in **APPLY** command:

```
APPLY    symm 2 translations 1 -1 1 ALL
```

Note that we want to apply these operations to ALL atoms of the serine molecule in order to get a correct dimer. To set up the LATEN commands, we can do this by the GUI, or by hand. Using the GUI,
Edit → Commands → XDPROP

Go to **I-Laten1** menu and enable **Calculate** under **INTEREN** menu:



☐ Activate XDPROP section in XD.MAS

INTEREN

☑ Calculate Frag1 1 - 14 Frag2 15 - 28

Electrostatic potential by EPMM hybrid method

rCrit1 4 rCrit2 15 ☑ Frag1 neutral ☑ Frag2 neutral

LATEN

☐ Calculate Frag 1 - 10 ncells 0 - 10

nappl 0 symms

Electrostatic potential by EPMM hybrid method

rCrit1 4 rCrit2 15 ☑ Frag neutral

Note how we specify the fragments between which we wish to compute the interaction energy. The original molecule consists of 14 atoms (i.e. atoms 1 through 14 in the list) – these are specified under Frag1. When we applied a symmetry element to all atoms we generated another 14 atoms (i.e. atoms 15 to 28) in the list – these are specified under Frag2. This kind of fragment specification allows considerable flexibility - for instance in some cases one may wish to calculate the interaction energy between certain parts of the molecules, not the whole molecule.

Under **I-Laten2** deselect **Atom-Atom potentials** because we are now interested only in electrostatic energy. These edits by the GUI corresponds to these commands in `xd.mas` :

```
!ATATPOT  *EXREP  spack *wilcox  lj
!ATATPOT  *DISPR  spack *wilcox  lj
INTEREN   frag 1   1 -14 *neutral
INTEREN   frag 2   15 -28 *neutral
INTEREN   EP  aMM  mMM *EPMM rcrit1   4.0 rcrit2  15.0
```

Now run XDPROP.

It takes some time to calculate the energy, because a very accurate Exact Potential and Multipole moments[13] (EPMM) algorithm has been chosen. In this method, the short-range interatomic interactions are evaluated via quadrature integration of the exact Coulomb potential (EP), while multipole expansion in atomic moments (aMM) is used for long-range interatomic interactions.

When the calculation is completed, the final value of -189.24 kJ/mol for the electrostatic interaction energy is printed out.

```
Electrostatic Interaction Energy between fragments :
                   -0.07207858 Hartree
                 -189.24230000 kJ/mol
                  -45.22999088 kcal/mol
                   -1.96135783 eV
               -22760.58695363 Kelvin
```

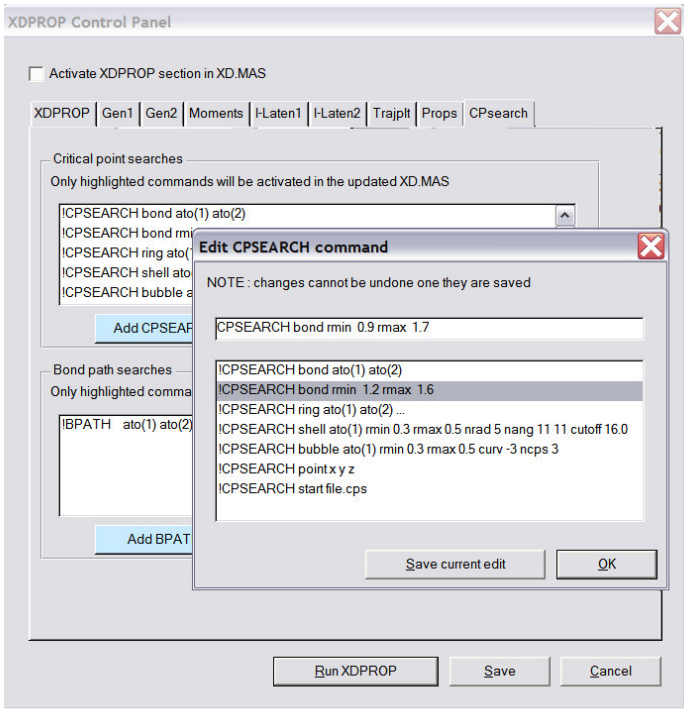
Open xd_pro.out file to see all the atom-atom contributions to the energy.

The same procedure can be repeated for other 3 dimers. The relevant **APPLY** instructions to be used are:

Dimer	Symmetry operation	APPLY command	Electrostatic energy
1	`3/2-x,-1/2+y,1-z`	`APPLY symm 2 translations  1 -1  1 *all`	-189 kJ/mol
2	`-1/2+x,1/2-y,z`	`APPLY symm 4 translations -1  0  0 *all`	-108 kJ/mol
3	`3/2-x,-1/2+y,2-z`	`APPLY symm 2 translations  1 -1  2 *all`	-82 kJ/mol
4	`x,y,1+z`	`APPLY symm 1 translations  0  0  1 *all`	+19 kJ/mol

1.12.3. Critical point searches

Critical point (CP) searching in XDPROP is very easy. First, select the property in the scalar field of which the CP search it to be undertaken (sensible properties are the total density, Laplacian of the total density and electrostatic potential). Then how the CP search is to be done, *i.e.* between specific atom pairs, or all atoms pairs within the certain distance etc). Here we perform the CP search between all atoms pairs separated by the distance of 0.9 – 1.7 Å :



Only highlighted commands will be activated in the updated XD.MAS

```
!CPSEARCH bond ato(1) ato(2)
!CPSEARCH bond rmi
!CPSEARCH ring ato(
!CPSEARCH shell ato
!CPSEARCH bubble a
```

Only highlighted comma

```
!BPATH   ato(1) ato(2)
```

NOTE : changes cannot be undone one they are saved

```
CPSEARCH bond rmin  0.9 rmax  1.7
```

```
!CPSEARCH bond ato(1) ato(2)
!CPSEARCH bond rmin  1.2 rmax  1.6
!CPSEARCH ring ato(1) ato(2) ...
!CPSEARCH shell ato(1) rmin 0.3 rmax 0.5 nrad 5 nang 11 11 cutoff 16.0
!CPSEARCH bubble ato(1) rmin 0.3 rmax 0.5 curv -3 ncps 3
!CPSEARCH point x y z
!CPSEARCH start file.cps
```

A list of CPs is then printed in the **Text Window** and to the xd_pro.out file, e.g.

```
Searching internuclear distances between  0.900 and  1.700 Angstroms

       Bond               f            del2f        Rij     d1     d2
                                                    Hessian Eigenvalues   ellip
 O(1)    -C(1)           2.047           1.188      1.2548 0.8031 0.4517
                                                    -10.73 -10.48  22.40   0.02
```

1.12.4. Calculating and plotting 2D maps

There are various type of 2D maps can be created in XDPROP but we only choose to plot the deformation density map. The deformation density is obtained by subtracting the free spherical atom (promolecule) density from the total aspherical density. It shows the aspherical features of the ED which occur when atoms form molecules, and provides a picture of chemical bonding.

First, select the deformation density property in the xd.mas file.

```
PROPERTY core valence rho *defden gradrho d2rho esp nucpot sigrho siglap ef efg
```

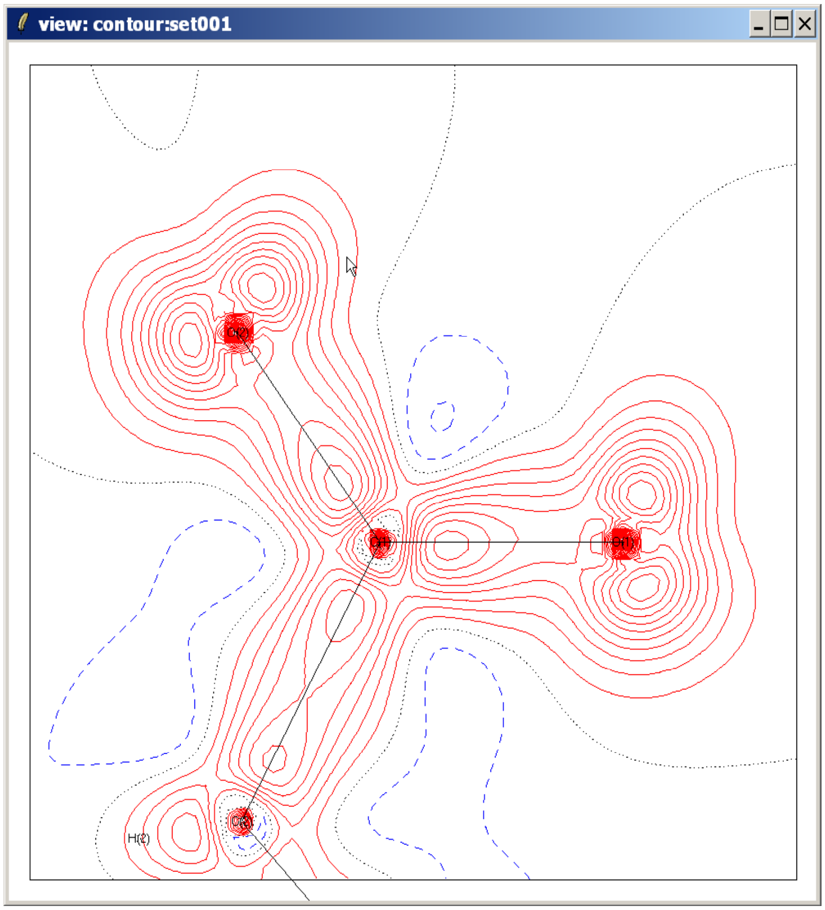
Then specify the names of three atoms in the plane of which the map will be plotted and dimensions of the maps (Å). For example, for the same plane of atoms C(1)-O(1)-O(2) as was used in XDFOUR tutorial make the following changes:

```
MAP    atoms C(1) O(1) O(2) npts 100 stepsize 0.1
```

Running XDPROP will create the xd_defden.grd file. It can be visualized the same way as the XDFOUR grid files. The easiest way to proceed it to copy fou.log file to prop.log, open it in the text editor, change the name of dataset from xd_fou.grd to xd_defden.grd and modify the contour levels to 0.1 e/Å^3 :

```
      -values [generate linear 40 0.1 0.1]
      -values [generate linear 40 -0.1 -0.1]
```

Then start XDGRAPH and under **Source Script** choose prop.log file. This will create a deformation density plot:



1.12.5. Visualization of gradient trajectories

Gradient trajectories can be visualized in a 2D plot for the scalar fields of density (gradient density) and electrostatic potential (negative of the electric field).

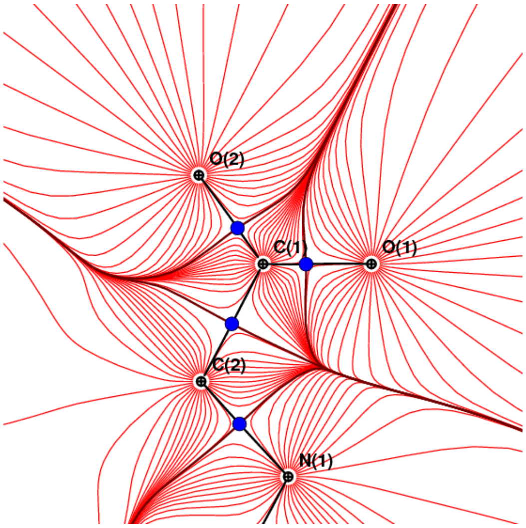
As in case of the other maps, first choose the property (in this case we choose the total density again)

```
PROPERTY core valence *rho defden gradrho d2rho esp nucpot sigrho siglap ef efg
```

Then, go to the TRAJPLT section (uncomment all the commands if necessary) and specify the 3 atoms or points which will define a plane of the plot. All other parameters should be left at default values in the first run:

```
TRAJPLT   origin atom  C(1)
TRAJPLT   xaxis atom   O(1) Xdim1 -3.00 Xdim2   3.00
TRAJPLT   yaxis  atom  O(2) Ydim1 -3.00 Ydim2   3.00
TRAJPLT   mark *atoms *labels *bonds *cps *basins *hbonds
TRAJPLT   params Circle  0.10 Atrad  0.05 CPrad  0.08 CPgrid  0.30 CPlim 0.100E-03
TRAJPLT   plot *plane  npath  36 *zcut  0.30 *xytol  0.50 *all  select ato(1)
```

Running XDPROP will create plots in the Postscript (rho_traj.ps) and CGM (rho_traj.cgm) formats:



Postscript files can be visualized with Ghostscript, GSview, Adobe Acrobat (using Adobe Distiller) or any other program capable of viewing these files

1.12.6. Mapping electrostatic potential on the density isosurface

In order to map the electrostatic potential (ESP) onto a density isosurface, two identically sized 3D grid files must be created: one with the density values and the other with the electrostatic potential.

First choose the property electron density rho

```
PROPERTY core valence *rho defden gradrho d2rho esp nucpot sigrho siglap ef efg
```

Then decide what the centre of your 3D grid, grid spacing and total grid size will be. For convenience, choose the center of grid to be the middle point of the C(2)-C(3) bond. The size of the grid box will be 8×8 Å with grid spacing of 0.1 Å. The CUBE command should be:

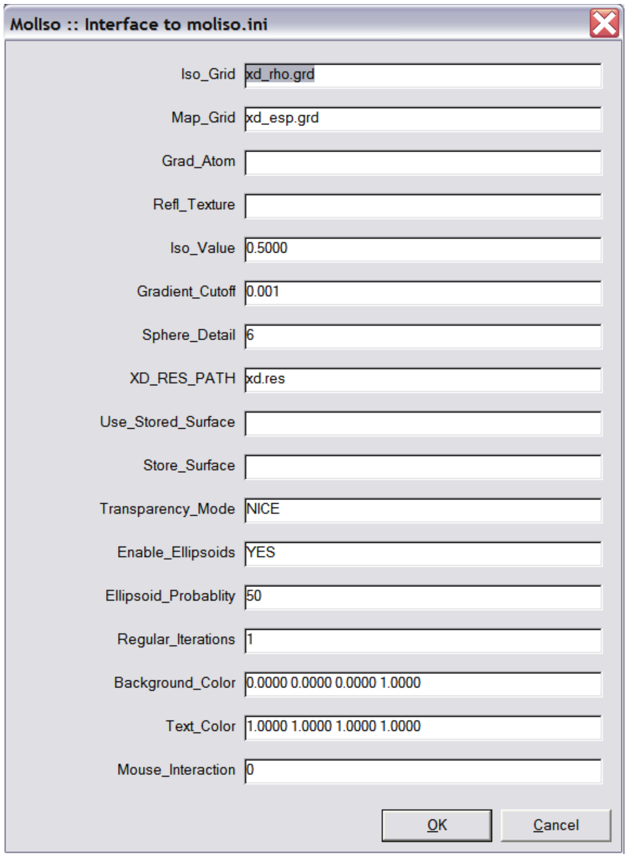
```
CUBE    C(3) C(2)  npts 80  stepsize 0.1
```

Then run XDPROP. When the calculation is finished, choose the electrostatic potential property

```
PROPERTY core valence rho defden gradrho d2rho *esp nucpot sigrho siglap ef efg
```

and run XDPROP again. This procedure will create two grid files for each property: xd_rho.grd and xd_rho.cube, and xd_esp.grd and xd_esp.cube, The first file contains grid in XDGRAPH format, unfortunately because of some missing 3D libraries, 3D grids cannot be visualized with the Windows version of XDGRAPH (there is no such problems under UNIX versions of XDGRAPH). However, XDPROP also creates the same grid in Gaussian9x/03-like CUBE format (xd_rho.cube) which can be visualized using any program that understands this format (MOLEKEL, MOLDEN etc).

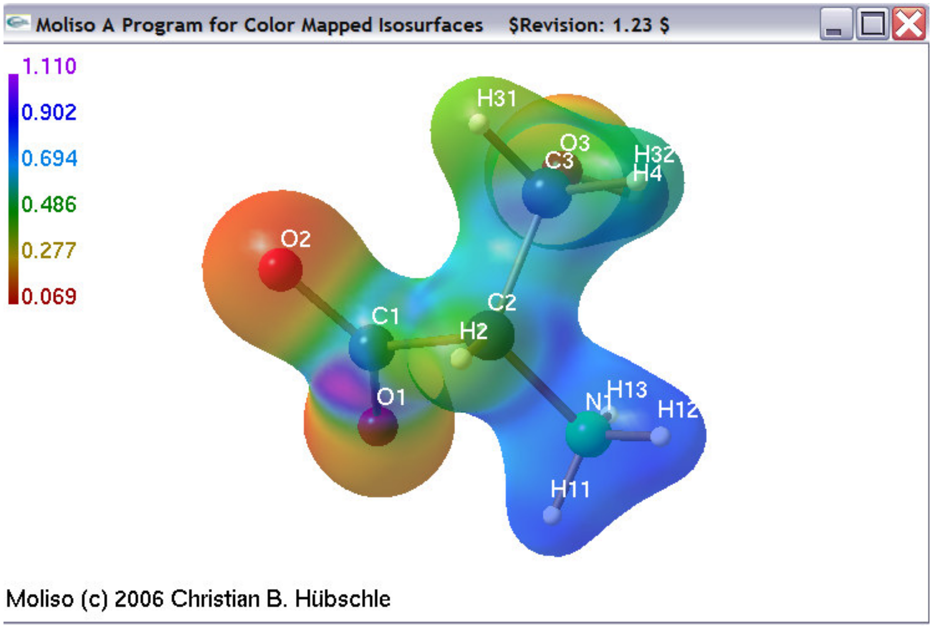
We will use the MolIso program of C. Hübschle to visualise the mapped isosurface. In the WinGX GUI, select **Graphics → 3D Iso-surface Plot**. This will give the GUI interface to MolIso.



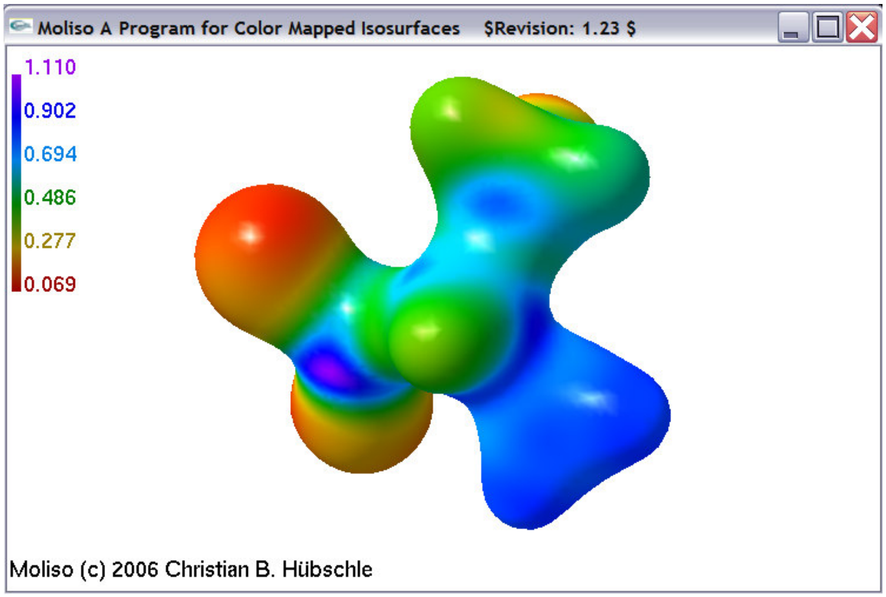
Iso_Grid	xd_rho.grd
Map_Grid	xd_esp.grd
Grad_Atom	
Refl_Texture	
Iso_Value	0.5000
Gradient_Cutoff	0.001
Sphere_Detail	6
XD_RES_PATH	xd.res
Use_Stored_Surface	
Store_Surface	
Transparency_Mode	NICE
Enable_Ellipsoids	YES
Ellipsoid_Probablity	50
Regular_Iterations	1
Background_Color	0.0000 0.0000 0.0000 1.0000
Text_Color	1.0000 1.0000 1.0000 1.0000
Mouse_Interaction	0

Select the Iso_grid to be xd_rho.grd and the map_grid to be xd_esp.grd. The other default parameters should be OK. The iso-surface plotted will be of the density at 0.5 eÅ^{-3}, with the value of the electrostatic potential at each point on the surface colour coded.

You should then see a plot like

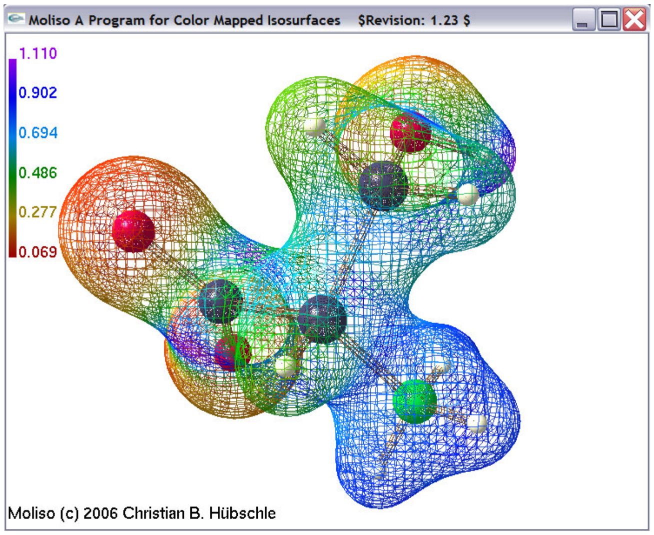


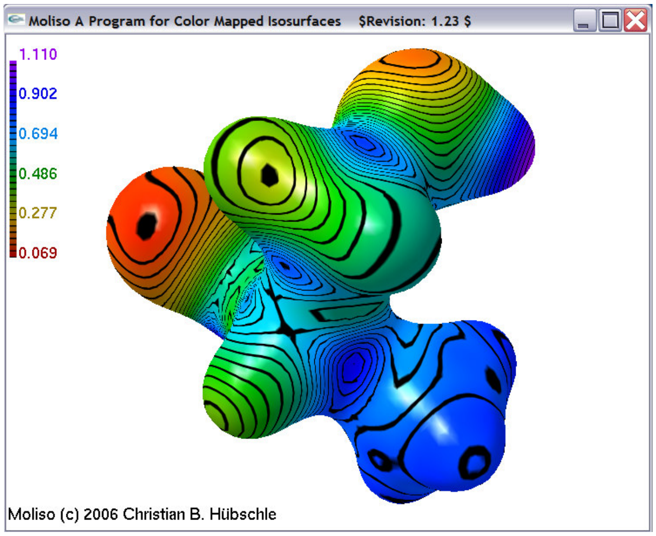
The default background colour (of black) has been changed to white by invoking the menu (right mouse click on the MolIso screen. On the left there is a scale which maps colors to values of ESP (in eÅ^{-1}). There are numerous program options to change the illustration - one is to deselect the atom labels and switch off the transparency, to give a picture like



The most negative (i.e. least positive) areas are associated with the most electronegative atoms, the O atoms, and suggest that these atoms are the most nucleophilic. They are also the atoms which bear the formal negative charge. Likewise, the part of the molecule with the largest positive esp is the NH_3^+ group which bears a formal positive charge.

The MolIso program is very versatile, you can rotate, zoom in & out, move the surface as well as change its properties:





This is a net or "chicken wire" representation of the surface (left), or a contoured representation (right) of the isosurface. To obtain a hard-copy of the picture, right click in the main window and choose **PDF Output**.

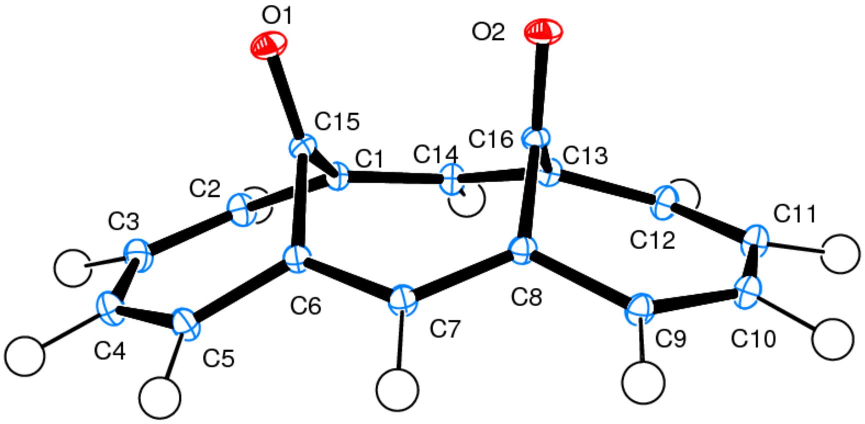
2 - Example # 2 Biscarbonyl-annulene

As a second example for this tutorial, we have chosen :

"Bond Lengths and Beyond" R. Destro and F. Merati *Acta Cryst*. (1995). **B51**, 559-570.

SOURCE DIRECTORY : BCA

This paper presents a charge density analysis on *syn*-1,6:8,13-biscarbonyl[14]annulene (BCA). The experimental data were obtained at 20K, and are of very high quality. They are available from the journal as Supplementary Materials.



The main point of interest about this study was that it was one of the first *experimental* charge density studies to show an unusual topology of the electron density, giving rise to a bond path and bond critical point between the formally non-bonded atoms C(15) and C(16). Such unusual bond paths had been previously observed in theoretical studies, and they "*challenge the traditional ideas of bonding in organic molecules*". They have been attributed to non-bonded steric repulsions, though this interpretation is controversial. The trans-annular distance C(15)..C(16) is actually ~ 0.1Å longer than the trans-annular distances C(1)..C(6) or C(8)..C(13), but no corresponding bond paths are found between these latter two pairs of atoms. It is interesting to note that BCA decomposes thermally to give in 70% yield the deoxygenated product dicyclohepta-pentalene, which itself is derived via the 1,2-dioxetane obtained by connecting with chemical bonds the atoms O(1)-O(2) and C(15)-C(16). The charge density study is thus clearly providing some information regarding the reactivity of BCA.

The procedure for carrying out the charge density analysis on BCA, and the treatment of the data is very similar to that described above for example #1 in Exercises 1-11, and we do not repeat these procedures in detail. The student is asked to carry out all these stages outlined in this previous example. Since the procedures are essentially identical, only salient points of difference will be mentioned.

2.1 Starting up

Once again, start up WinXD GUI and navigate to the BCA directory. Under "Modules" menu select "XDINI" – this is an interface for importing data to XD. Here we import data from the CIF format, so select SHELX in XDINI control panel. Choose an “XD compound identifier”, say "BCA" , and also choose Clementi-Roetti scattering factor model.

In contrast to the previous example, the two data files are in CIF format. This is a very common standard file format, and most crystallographic programs will recognize these files. In our case they are called xd.cif (containing the cell data, starting atomic coordinates and thermal parameters, etc) and xd.fcf (containing the reflection data). These names are mandatory as input files for "XDINI" . After running "XDINI", exactly the same set of files as before are produced, *i.e.* xd.mas, xd.inp, xd.hkl

2.2 Spherical Atom refinement

After creating the files, a spherical atom refinement may be carried out, in much the same way as above. Some points of difference regarding the setup for refinement with "XDLSM"

In “XDLSM controls”

- select “Refine on F”
- set number of cycles 10
- activate global model limits
- select “Conventional spherical atom” under “Static scattering model”
- select “anomalous dispersion”

As always, experimental data contains the effects of anomalous dispersion, but as this structure is centrosymmetric, and contains only C, O H atoms, the effects are virtually negligible.

For this example, use statistical weights based on $1/\sigma(F_{\mathrm{obs}})$ by setting the first parameter in the WEIGHT instruction to -2.0

Examination of output files and preparation of Fourier maps can be done in an identical fashion as described above. For the Kappa refinement in Exercise 5, it is obviously necessary to choose the chemical equivalences bearing in mind the almost exact C_{2v} symmetry of the BCA molecule.

The default ATOM TABLE is

```
ATOM     ATOM0    AX1 ATOM1    ATOM2   AX2 R/L TP TBL KAP LMX SITESYM  CHEMCON
O(1)     C(15)     Z  O(1)     C(1)     Y   R   2  1   1   4  NO
O(2)     C(16)     Z  O(2)     C(13)    Y   R   2  1   1   4  NO
C(1)     C(14)     Z  C(1)     C(2)     Y   R   2  2   2   4  NO
C(2)     H(2)      Z  C(2)     C(3)     Y   R   2  2   2   4  NO
C(3)     H(3)      Z  C(3)     C(2)     Y   R   2  2   2   4  NO
C(4)     H(4)      Z  C(4)     C(5)     Y   R   2  2   2   4  NO
C(5)     H(5)      Z  C(5)     C(4)     Y   R   2  2   2   4  NO
C(6)     C(7)      Z  C(6)     C(5)     Y   R   2  2   2   4  NO
C(7)     H(7)      Z  C(7)     C(6)     Y   R   2  2   2   4  NO
C(8)     C(7)      Z  C(8)     C(9)     Y   R   2  2   2   4  NO
C(9)     H(9)      Z  C(9)     C(10)    Y   R   2  2   2   4  NO
C(10)    H(10)     Z  C(10)    C(9)     Y   R   2  2   2   4  NO
C(11)    H(11)     Z  C(11)    C(12)    Y   R   2  2   2   4  NO
C(12)    H(12)     Z  C(12)    C(11)    Y   R   2  2   2   4  NO
C(13)    C(14)     Z  C(13)    C(12)    Y   R   2  2   2   4  NO
C(14)    H(14)     Z  C(14)    C(1)     Y   R   2  2   2   4  NO
C(15)    O(1)      Z  C(15)    C(6)     Y   R   2  2   2   4  NO
C(16)    O(2)      Z  C(16)    C(13)    Y   R   2  2   2   4  NO
H(2)     C(2)      Z  H(2)     C(1)     Y   R   1  3   3   1  NO
```

```
H(3)     C(3)     Z  H(3)     C(2)     Y   R   1  3   3   1  NO
H(4)     C(4)     Z  H(4)     C(5)     Y   R   1  3   3   1  NO
H(5)     C(5)     Z  H(5)     C(4)     Y   R   1  3   3   1  NO
H(7)     C(7)     Z  H(7)     C(8)     Y   R   1  3   3   1  NO
H(9)     C(9)     Z  H(9)     C(10)    Y   R   1  3   3   1  NO
H(10)    C(10)    Z  H(10)    C(9)     Y   R   1  3   3   1  NO
H(11)    C(11)    Z  H(11)    C(12)    Y   R   1  3   3   1  NO
H(12)    C(12)    Z  H(12)    C(13)    Y   R   1  3   3   1  NO
H(14)    C(14)    Z  H(14)    C(1)     Y   R   1  3   3   1  NO
DUM0      0.0000  0.0000  0.0000
```

However from the molecular structure, it is clear that atoms C(2), C(5), C(9), C(12) are chemically equivalent and so could share the same kappa parameter, as are the sets C(3), C(4) C(10), C(11) and C(1) C(6) C(8) C(13) and the pairs C(7),C(14) and C(15), C(16) and O(1),O(2). The H atoms could all be treated as equivalent.

3.3 Defining the Molecular Graph

The XDPROP program is used for the critical points and bond path searches. The graphical representation of the molecular graph (*i.e.* the union of the critical points and bond paths) is a feature of the WinXD GUI. It only makes sense to analyse the molecular graph once a full multipole refinement has been undertaken, so that the same calculations outlined in exercises 1 - 11 will need to have been carried out. To calculate the molecular graph, it is first necessary to determine all types of critical points in the multipolar derived density. The atomic nuclei comprise the (3,-3) critical points, *i.e.* the maxima in the density, but these are assumed and do not have to be sought explicitly. The (3,-1) or bond critical points are at a minimum along the direction of the bond path, but at a maximum in the directions orthogonal to the bond path. So first of all we search for these bond critical points using the CPSEARCH option in XDPROP. Although this can be done (in part) by manual editing of the instruction file xd.mas, it is easier using the WinXD GUI.

First make sure that the property selected is the density rho (so that we are searching in the right scalar field !!). In the xd.mas file the relevant line is

```
PROPERTY  *rho gradrho d2rho nucpot elpot core valence defden sigrho…
```

(in fact, in XDPROP, if the property is not specified it defaults to *rho). Then we just need to have an instruction to search for bond critical points. For an organic molecule, a normal such command might be

```
CPSEARCH  bond rmin 0.8 rmax 1.7
```

which ought to find the critical points associated with all the normal covalent bonds. Try running XDPROP with this command. In the resultant file xd_pro.out you should find 30 (3,-1) critical points, associated with "normal" C-C, C-H and C-O covalent bonds. Then add the following commands at the end of the XDPROP section in file xd.mas, and rerun XDPROP.

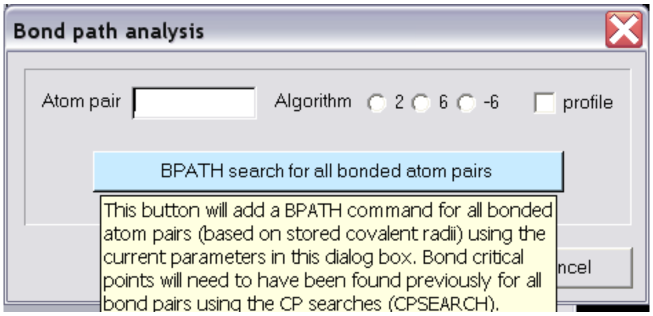
```
CPSEARCH  bond C(15) C(16)
CPSEARCH  bond C(1) C(6)
CPSEARCH  bond C(8) C(13)
CPSEARCH  ring C(1) C(2) C(3) C(4) C(5) C(6)
CPSEARCH  ring C(8) C(9) C(10) C(11) C(12) C(13)
CPSEARCH  ring C(1) C(15) C(16) C(13) C(14)
```

```
CPSEARCH  ring C(6) C(15) C(16) C(8) C(7)
```

You should now find an extra five critical points, one more (3,-1) cp between C(15)-C(16) and four extra (3,+1) ring critical points. To determine fully the molecular graph, we need to trace the bond paths associated with all these (3,-1) critical points. This is also done in XDPROP, using the BPATH command. You will need to have one BPATH command for each (3,-1) critical point found. For example, for the transannular C-C bcp, we would need

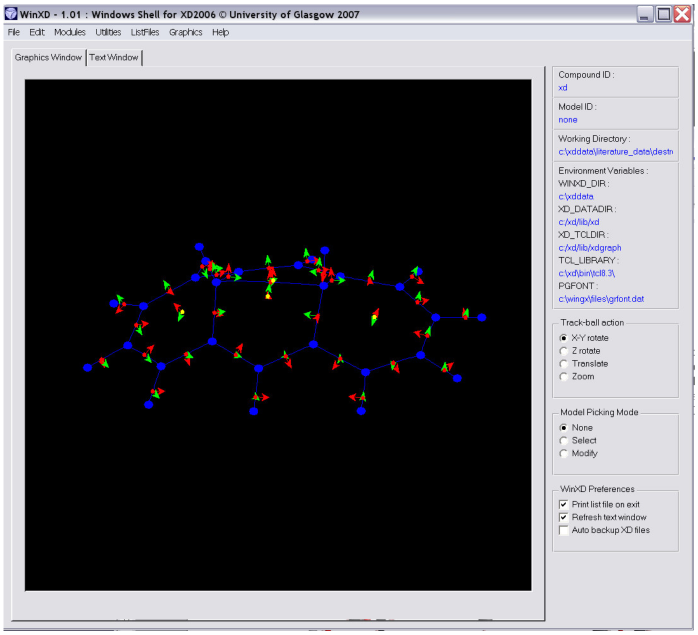
```
BPATH   C(15) C(16)  algrithm 2
```

This becomes a bit tedious, but the GUI provides an easier way of doing this. In the WinXD GUI select **Edit → Commands →XDPROP →CPSEARCH → Add Bpath Calculation**



This button will add a BPATH command for all bonded atom pairs (based on stored covalent radii) using the current parameters in this dialog box. Bond critical points will need to have been found previously for all bond pairs using the CP searches (CPSEARCH).

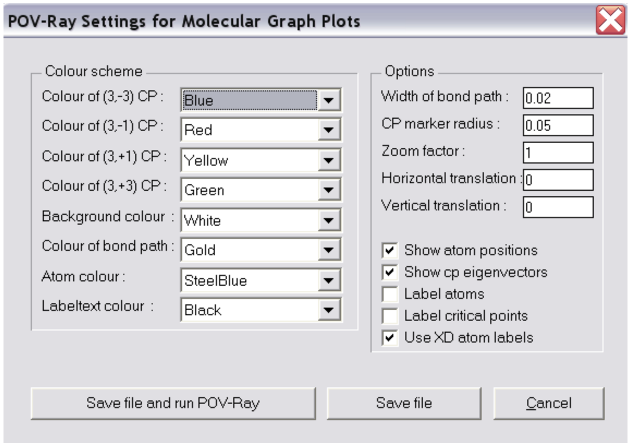
Click on the button "BPATH search for all bonded atoms". This adds one BPATH command for every covalent bond, and it is then only necessary to add the one given above manually. Once the xd.mas file has been set up with all the necessary CPSEARCH and BPATH commands, run XDPROP. This gives the files xd_pro.out with the results and also xd_rho.cps, which lists all the critical points and xd.pth, which has the coordinates of the path. It is possible to visualize the bond paths in XDGRAPH, but the WinXD GUI offers an easier solution. Just select **Graphics → Molecular Graph**, which gives the screen shown below



Compound ID : xd
Model ID : none
Working Directory : c:\xddata\literature_data\destr
Environment Variables :
WINXD_DIR : c:\xddata
XD_DATADIR : c:/xd/lib/xd
XD_TCLDIR : c:/xd/lib/xdgraph
TCL_LIBRARY : c:\xd\bin\tcl8.3\
PGFONT : c:\wingx\files\grfont.dat

Track-ball action: ● X-Y rotate ○ Z rotate ○ Translate ○ Zoom
Model Picking Mode: ● None ○ Select ○ Modify
WinXD Preferences: ☑ Print list file on exit ☑ Refresh text window ☐ Auto backup XD files

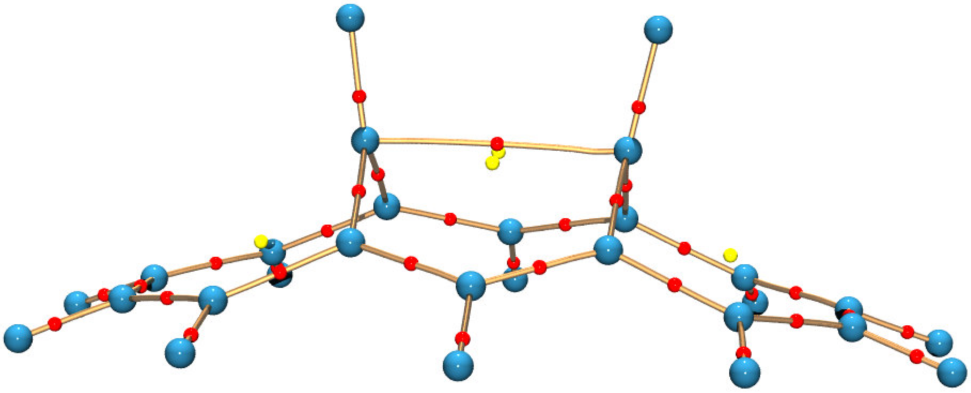
Each critical point (red sphere) is shown with two vectors, in red and green, which represent the major and minor directions respectively of the two negative eigenvectors of the Hessian (and hence the bond ellipticity). The bond path is traced in blue, and other critical points are shown in yellow - (3,+1) ring cp's, or in green - (3,+3) cage cp's. A right mouse click on the graphics window gives the dialog box shown below. This allows the user to switch on/off or choose the features of various graphical objects, and to use the POVray program to obtain a high-quality rendered picture.


POV-Ray Settings for Molecular Graph Plots

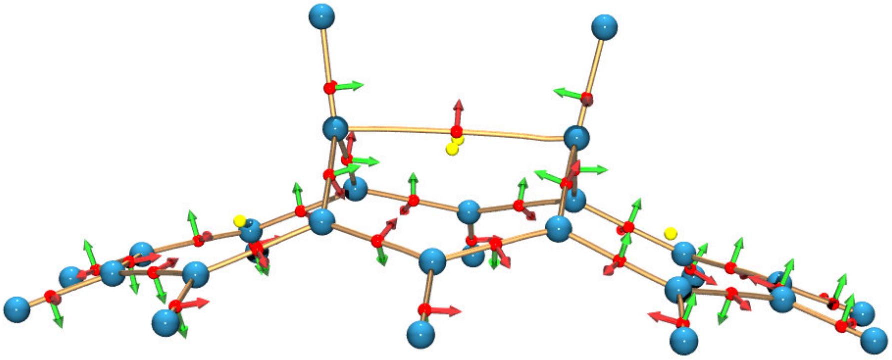
Colour scheme
Colour of (3,-3) CP : Blue
Colour of (3,-1) CP : Red
Colour of (3,+1) CP : Yellow
Colour of (3,+3) CP : Green
Background colour : White
Colour of bond path : Gold
Atom colour : SteelBlue
Labeltext colour : Black

Options
Width of bond path : 0.02
CP marker radius : 0.05
Zoom factor : 1
Horizontal translation : 0
Vertical translation : 0

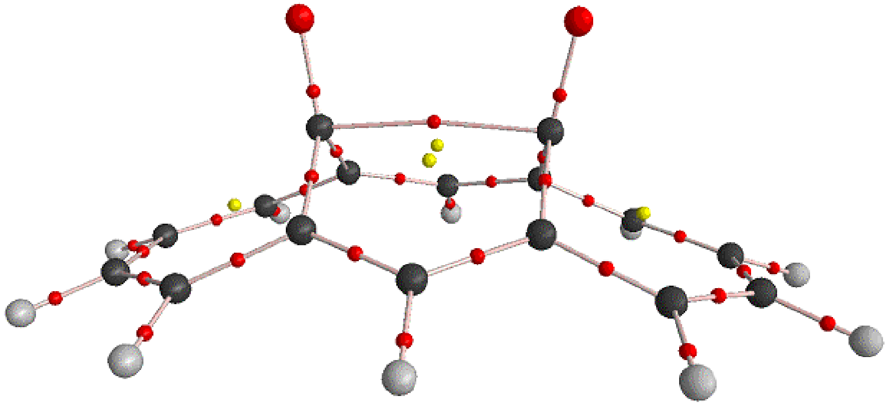
☑ Show atom positions
☑ Show cp eigenvectors
☐ Label atoms
☐ Label critical points
☑ Use XD atom labels



Above is a POV-Ray rendered plot of the molecular graph of the BCA molecule, from the experimental multipole refinement. The values of $\rho(\mathbf{r})$ and $\nabla^2 \rho(\mathbf{r})$ for the transannular C-C bond critical point are 0.016 and 0.060 au respectively. These compare very well with those obtained from a theoretical calculation (given below), and clearly demonstrate that, despite the relatively small value of $\rho(\mathbf{r})$, this is not an artefact. Below is a POV-Ray plot which includes the Hessian eigenvectors.



The theoretical molecular graph of BCA, obtained from a DFT-B3LYP calculation (6-311++G** basis) on the experimental geometry is shown below. (3,-1) bond critical points are shown as red spheres and (3,+1) ring critical points as yellow spheres. The values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ for the transannular C-C bond critical point are 0.0167 and 0.058 au respectively



3 - Example # 3 Morphine hydrate

Submolecular partitioning of morphine hydrate based on its experimental charge density at 25K
S. Scheins, M. Messerschmidt and P. Luger. *Acta Cryst*. (2005). **B61**, 443-448.

SOURCE DIRECTORY : morphine
This paper presents a charge density analysis on morphine hydrate and examines the submolecular transferability based on the experimental charge density. The experimental data were obtained at 25K, and are of very high quality. They are available from the journal as Supplementary Materials.

Charge density experiments are of great importance for bio-molecules and biologically active molecules. One of the main reasons for studying pharmacologically active molecules like morphine is to determine properties such as the electrostatic potential, which may be of great use in determining sites of chemical reactivity. See for example reference 15

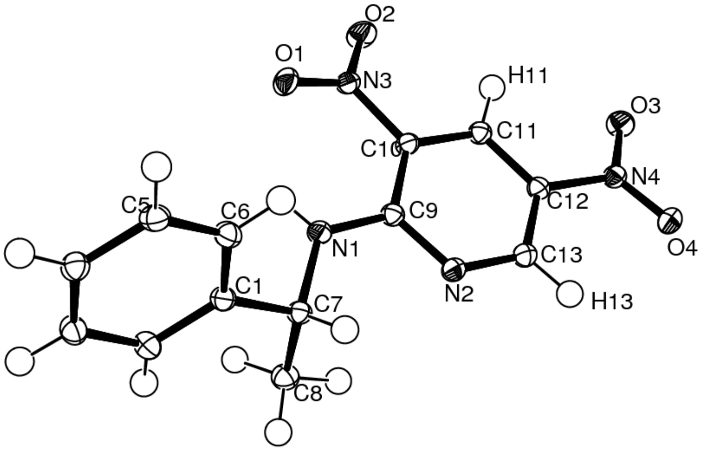
You will already have prepared the SHELX files which can act as a start into the XD refinement. This example presents a more realistic one for a charge density study, in terms of molecular size, than the serine example.

Follow in detail the steps outlined for example #1. Special points to note are :

- local *m* symmetry should be applied to the phenyl carbons C1, C2, C3 and to the sp^2 atoms C7 and C8.
- multipoles for all non-H atoms should be expanded to the octupole level, for H-atoms only a bond directed dipole should be used.
- The original paper reports using nine kappa sets, though no details are available as to which atoms were included in these sets. Finish the κ-refinement of the model by using a total of nine kappa sets, making a sensible choice as to which atoms to put into these groups.
- use RESET BOND to set the O-H and C-H distances to neutron obtained values. In the original paper the values used were O-H 0.97 Å, C-H 1.08 Å (apart from C10-H = 0.90, 0.93 Å, C14-H = 0.97 Å, which both seem too short and arbitary).
- compare the values for the topological properties at the bond and ring critical points (see example 2 for an explanation of how to calculate these) with those reported in Table 3 of the original article. You will need to add explicit searches for all normal covalent bonds, and also for the H-bonds.

4 - Example # 4 MBADNP 3,5-dinitro-2-{[1-phenyl ethyl]amino}-pyridine

X-ray and neutron diffraction studies of the non-linear optical compounds MBANP MBADNP at 20K : charge-density and hydrogen-bonding analyses J. M. Cole, A. E. Goeta, J. A. K. Howard and G. J. McIntyre *Acta Cryst.* (2002). **B58,** 690.



SOURCE DIRECTORY : MBADNP

This paper reports a combined X-ray and neutron charge density study at 20 K on the non-linear optical compound MBADNP. Both data sets are provided (SHELX.INS/HKL & NEUTRON.INS/HKL) in SHELX format files. The major advantage of using neutron data is that hydrogen atoms may be observed with the same or similar accuracy as other atom types. In addition, the (usually large) thermal motion of H atoms can be accurately refined and anisotropic thermal parameters obtained (impossible with just X-ray data). The H-atom positions and thermal parameters can then be used for an X-ray charge density refinement. Using the general procedures outlined in example #1, please attempt the following steps

- Solve the structure in WinGX using the X-ray data set. Refine the structure to convergence, using anisotropic thermal parameters for all the non-H atoms. For the H atoms, place these in calculated positions using the SHELXL HFIX instructions, and refine with riding isotropic thermal parameters.
- Use these atomic parameters as the starting point for a neutron refinement. For the next stage, it is important that the atomic numbering scheme, and the order of atoms in the SHELX INS files are exactly the same for the neutron and X-ray refinements. It is best if the neutron refinement is carried out in a sub-directory.
- When both refinements are complete, run the program SCALE-XN (WinGX) which will analyse the adp's from both refinements for the non-H atoms. Despite the fact that that both data sets were nominally collected at 20K, it is clear that there is not a good agreement between them (despite what is stated in the article !!). In fact, it is not at all unusual for there to be a systematic difference between neutron and X-ray derived adp's, due to differing experimental factors, like extinction, thermal diffuse scattering and different (actual) experimental temperatures. The SCALE-XN program determines the best fit between the two data sets and gives a set of scaled adps for the H atoms which can be used in an X-ray refinement.

The output from SCALE-XN shows that the mean ratio of $U_{X\text{-ray}}/U_{neutron}$ is ~ 1.8 !! It is not clear why there should be such a large discrepancy - possibly the actual temperature for the X-ray data collection was much higher than 20K (though the reported cell volumes are virtually identical), or possibly the neutron data is badly affected by uncorrected systematic errors such as extinction. In any case we will persevere with the neutron adps for the H-atoms. The best fit (in terms of the rms deviation) is for method #3 - a sum of isotropic temperature correction and an anisotropic diffraction correction.

```
Mean ratio of Uii values, <Uii(X-ray)/Uii(neutron)> =      1.813
Esd from the mean                                   =      0.259

 ------------------------------------------------------------------------
 3.  Sum of isotropic temperature correction and anisotropic diffraction corrections
 -----------------------------------------------------------------------------------
 Ux(i,j) = factor*un(i,j) + delta(i,j)
 chisq = sum(w(a,i,j)*(ux(a,i,j) - factor*un(a,i,j) - delta(i,j))**2
       factor
        0.954
     sigma(f)
        0.032
   delta(1,1)  delta(2,2)  delta(3,3)  delta(1,2)  delta(1,3)  delta(2,3)
     0.004648    0.003841    0.004306    0.000040    0.000505   -0.000125
   sigma(1,1)  sigma(2,2)  sigma(3,3)  sigma(1,2)  sigma(1,3)  sigma(2,3)
     0.000185    0.000184    0.000216    0.000086    0.000091    0.000091
 z    =  0.1369E+01
 nobs =126
 npar =  7
 rmsd =  0.000414

 Scaled H atom Uij's

 H1N   0.017777  0.021481  0.032292  0.006581  0.006216  0.009724
 H2    0.023651  0.023550  0.023005 -0.006043  0.003594 -0.008621
 H3    0.018130  0.030167  0.029307 -0.008951  0.005091 -0.004531
 H4    0.020371  0.028670  0.024025 -0.000131  0.010135 -0.003882
 H5    0.029153  0.022015  0.023653 -0.003001  0.004157 -0.010786
 H6    0.019560  0.027469  0.028859 -0.010429  0.005005 -0.006228
 H7    0.016423  0.018544  0.021489  0.001995 -0.002241  0.001991
 H8A   0.034178  0.014969  0.030871 -0.002496  0.002774  0.002068
 H8B   0.026178  0.030597  0.024759 -0.000446  0.010908 -0.006886
 H8C   0.022163  0.029939  0.023462  0.003892 -0.005731 -0.003272
 H11   0.021868  0.016914  0.024712  0.000546  0.004176  0.007360
 H13   0.016347  0.020966  0.033093  0.006934  0.003556  0.006892
```

- Create a starting set of XD refinement files from the X-ray refined coordinates. In the XD.INP file, replace the positional parameters for all the H-atoms with those obtained from the neutron refinement. Replace the isotropic thermal parameters of the H-atoms with those printed in the output of SCALE-XN (see above).
- Edit the key table and make sure that the positional parameters and thermal parameters for the H atoms are not refined (the default type of thermal parameter for an H atom is isotopic (code 1), but you need to change this to 2).
- Following the general procedure given in example #1, refine the multipole model for MBADNP. Compare your values for the atomic charges and topological properties with those reported in the paper.

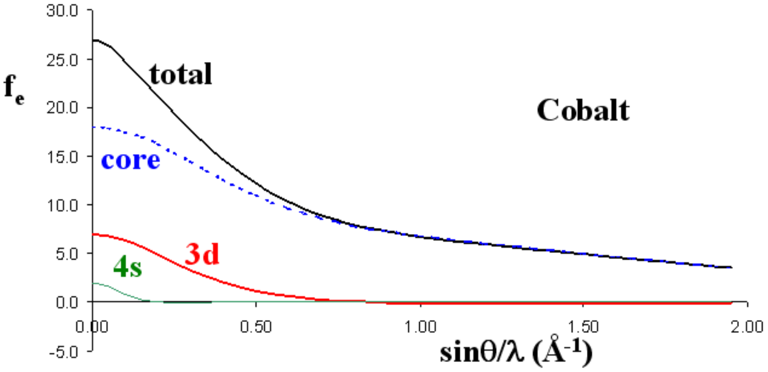
5 - Example # 5 Manganese decacarbonyl

Experimental charge density in the transition metal complex $Mn_2(CO)_{10}$: a comparative study L. J. Farrugia, P. R. Mallinson and B. Stewart *Acta Cryst.* (2003). **B59,** 234-246.

SOURCE DIRECTORY : mnco

This paper reports an experimental charge density study at 100 K of $Mn_2(CO)_{10}$. The nature of the metal-metal and metal-ligand interactions has been studied by topological analysis and the results compared with DFT calculations at the 6-311+G* B3LYP level.

This is the first example of a transition metal complex. These type of compounds present a different challenge than purely organic compounds in a charge density analysis. The most complex part if the correct modelling of the transition metal. Below is shown the atomic scattering factor for cobalt as a function of $\sin(\theta)/\lambda$, typical for first row transition metals. Though the core electrons and the 3*d* electron scatter to high angle, the scattering power of the 4*s* electrons falls off rapidly. As a result, information on the 4*s* electrons is only contained in the intense low angle data, which are often subject to high errors of absorption and extinction. In turn this means that it is very difficult to obtain accurate information about the 4*s* population



While in principle it is possible to refine separately the 3*d* and 4*s* valence populations for a transition metal, this is generally not practically possible, and the 4*s* population is often (usually) fixed (not an ideal situation!).
You can use this example data set to explore how a separate refinement can be made with the software. Firstly we will use the "normal" approach and keep the 4s in the "core".

- convert the supplied SHELX files to XD format using XDINI. This time select the Su-Coppens-Macchi databank (based on relativistic Dirac-Fock atomic wavefunctions), because this will give a better result for the Mn atoms. Below is shown the default generated SCAT entry for Mn

```
SCAT CORE SPHV DEFV   1S  2S  3S  4S  2P  3P  4P  3D  4D  4F  5S  5P  6S  6P  5D  7S  6D  5F
Mn   CHFW CHFW CSZD    2   2   2   2   6   6   0  -5   0   0   0   0   0   0   0   0   0   0
```

We will use the neutral atom scattering for Mn (since this atom is formally zero-valent in the compound). Note that only the 3*d* population is given as negative (*i.e.* is considered in the valence shell). The 4*s* population is given as +2, but is considered to be part of the core (which it patently is not of course !). The real point of this formalism is that the contribution from the 4*s* electrons are treated as fixed. One thing we will want to change is the type of radial functions used for the valence deformation. By default the core and spherical valence scattering is derived use radial functions derived from the HF wavefunctions taken from the databank, but the deformation valence uses simple Slater functions (code CSZD). Better radial functions for transition metals are those derived from the wavefunctions (code CHFW). For this type of radial function, we need to specify specifically the orbital products we use for each *l* value, as shown below (where we use the same 3d3d orbital product to construct the radial function).

```
SCAT CORE SPHV DEFV   1S   2S   3S   4S   2P   3P   4P   3D   4D   4F   5S   5P   6S   6P   5D   7S   6D   5F
Mn    CHFW CHFW CHFW    2    2    2    2    6    6    0   -5    0    0    0    0    0    0    0    0    0    0
0   chfw (3d3d)
1   chfw (3d3d)
2   chfw (3d3d)
3   chfw (3d3d)
4   chfw (3d3d)
```

This suitable as a starting point. You can refine the mutipole model for this compound, using the SHELX files in the kappa subdirectory as the starting point. The same process as decribed above can be followed, except that the multipole model for the Mn atom can be expanded up to the highest available level , the hexadecapole level. Some care is required in refining the κ and especially the κ' parameters, and these are best refined in separate blocks. To do this make two copies of the master file **xd.mas**, called **xd.mas.1** and **xd.mas.2**. In the first the positional and multipole parameters can be refined, and in the second one only the kappa's. Using the facility in WinXD **Utilities** → **XDBLOCK** these master files are used alternatively, and the strong correlations between parameters can be avoided.

- You can also try and investigate a second multipole model, one where a separate refinement of the 4s and 3d density will be attempted. First copy the final refined files **xd.mas, xd.inp, xd.hkl** to another subdirectory to avoid overwriting your previous work. The 4s population has to be removed from the "core"

```
SCAT CORE SPHV DEFV   1S   2S   3S   4S   2P   3P   4P   3D   4D   4F   5S   5P   6S   6P   5D   7S   6D   5F
Mn    CHFW CHFW CHFW    2    2    2    0    6    6    0   -5    0    0    0    0    0    0    0    0    0    0
0   chfw (3d3d)
1   chfw (3d3d)
2   chfw (3d3d)
3   chfw (3d3d)
4   chfw (3d3d)
```

and the extra two electrons are added manually into the parameter file **xd.inp** to the population for P_{00} because we will be trying to use the second monopole (the first multipole of the deformation valence) to model the 4s density.

```
Mn(1)     3 2    7   1   9 2  1  1 4  1   0  0.345602  0.236636  0.069066 1.0000
  0.011165  0.013092  0.013436 -0.000435  0.001761  0.002567
  3.9387  2.0000  0.0394  0.1019 -0.0425  0.2247 -0.0646  0.0348  0.0039  0.0085
  0.0127  0.0089 -0.0116 -0.0007  0.0034  0.0138 -0.0448 -0.2535  0.0180 -0.0265
 -0.0057  0.0140 -0.0089 -0.0398 -0.1997  0.0602
```

Finally we need to change the radial function for the second multipole, so that it is more appropriate for refinement of 4s density

```
SCAT CORE SPHV DEFV   1S   2S   3S   4S   2P   3P   4P   3D   4D   4F   5S   5P   6S   6P   5D   7S   6D   5F
Mn    CHFW CHFW CHFW    2    2    2    0    6    6    0   -5    0    0    0    0    0    0    0    0    0    0
0   chfw (4s4s)
1   chfw (3d3d)
2   chfw (3d3d)
3   chfw (3d3d)
4   chfw (3d3d)
```

You may well find that this refinement is not satisfactory (parameters adopt unrealistic values, such as negative populations !) and the program will probably complain that the molecule is charged.

- A third topic for investigation is the effect of using a different experimental data set, one obtained from a synchrotron source. This was the data used in Tutorial 2 on data reduction. You can use either the final merged reflection data you obtained in this tutorial (**xd.hkl**), or the prepared file in the synchrotron subdirectory. For this part, use again a separate subdirectory.

Copy the final refined model from the first refinement you tried (**xd.mas** and **xd.inp**) and use the new **xd.hkl** reflection file. Proceed exactly as before and then compare the results - look especially at the multipole populations and the derived charges. You should see that changing the data set makes a big difference !

6 - Example # 6 Potassium Sulfate

This tutorial illustrates a number of features

- refinement of a structure with site symmetry restrictions on atomic parameters
- model indeterminacy - two models give very similar fits
- effect of data quality on residuals in Fourier/FFT maps

SOURCE DIRECTORY : k2so4
Unit cell : 5.7463(1) 7.4365(1) 10.0202(2) 90.0000 90.0000 90.0000
Space group : *P*mnb (No 62, Hall symbol -P 2bc 2a, non-standard setting of *P*nma)
Centrosymmetric
Point group : mmm

```
SYMM  - X, 1/2 - Y, 1/2 + Z
SYMM  1/2 + X, - Y, - Z
SYMM  1/2 - X, 1/2 + Y, 1/2 - Z
```

Experimental data to $\sin(\theta)/\lambda = 1.11$ ($2\theta_{max} = 104.4^o$ with $\lambda = 0.71073$ collected at 100K). 2606 independent reflections obtained from 76236 measurements, *R*(int) = 0.0375, average redundancy of data points = 28.8. Unpublished data.

Part 1. File preparation and XLSLM refinement.

Supplied files are *shelx.ins, shelx.hkl* and *xd.hkl.ref* (XD reflection file with tbar entries)

Run XDINI to prepare starting XD files. Use the compid name "ks". Since an isotropic extinction refinement will be undertaken, it is necessary to copy the file *xd.hkl.ref* to *xd.hkl* after running XDINI.

Set the number of cycles of refinement in *xd.mas* to be 4 and run XDLSM. In this example, the refinement is stable if the correct constraints are not applied to the positional and U^{ij} parameters (default output of XDINI), but examination of the file *xd_lsm.out* will show that the least-squares matrix is ill-conditioned and the Gauss-Jordan inversion has failed.

From the SHELX files, determine the site symmetry of each of the atoms and apply the appropriate constraints in the *xd.mas* file to the positional and U^{ij} parameters.

With the correct constraints in place, there is no problem with matrix inversion

Now decide on a suitable local coordinate system for the multipoles on all the atoms (the z axis is normally chosen as the symmetry axis and the index picking rules given in the XD manual adhere to this convention). You may find it expedient to include dummy atoms to achieve this. An isotropic extinction correction should also be applied (type1 with a Gaussian distribution).

Now refine the multipole parameters in suitable stages, increasing the multipole expansion to hexadecapoles on all atoms. Keep κ' fixed at 1.0 for all atoms, and refine against F using the data with $F > 0.0$ and $F/\sigma(F) > 3.0$.

Explore TWO models, one where the only restriction on the monopole populations is that the cell has overall electroneutrality, the other where the ions are fixed at their "standard" charges (HINT - there are significant implications if the K atoms are treated as K^+ ions). You should not refine the κ' parameters of any atom, and you should find that the κ parameter on the K atoms does not refine sensibly (it gives large shifts and unreasonable values). Do you have a suggestion why this may be the case?

You should find that the second model gives virtually as good a fit (in terms of R values and difference density residuals) as the more extensive model with multipole expansion on the K atoms, but uses fewer parameters. Look critically at the standard deviations and magnitudes of the multipole populations of the K atoms for the first model.

Finally, in separate directories prepare refinements of both models, but with the κ' parameters for the S and O atoms refined to convergence.

Part 2. Use of properties to assess model and assessment of data quality

For all models you have prepared, run XPROP jobs to search for the critical points in ρ and the bond paths.
You should find that there are two types of bcp's - those between the S and O atoms and also some between the K and O atoms. These may not show up in all models. The absence of expected bond paths is an indicator of a problematical model.

Run XDFOUR and XDFFT jobs to ascertain the level and location of residual difference density. The relatively high level of residuals indicates some problem with data quality

Run XDWTAN and check the output file *xd_wta.out* to see if there are any systematic trends in $<w(F_o - F_c)>$ and whether there are any significant outliers

Calculate a Laplacian map 6x6Å in a O-S-O plane. Observe the large distortion from spherical symmetry for the S atom. You should also notice a visible difference in the maps between those calculated with and without κ' refinement. Calculate approximately where the Valence Shell Charge Concentration should lie (distance from S nucleus) and use the CPSEARCH BUBBLE command in XDPROP to search a suitable annulus of density for the charge concentrations, the (3,-3) critical points in the negative Laplacian.

7 - Other Examples

There are many other example data sets in this tutorial, all of them taken from the published literature. They have been selected to provide examples across a wide spectrum of modern chemistry, including (a) organic (b) organometallic (c) coordination and (d) non-molecular inorganic compounds You are encouraged to work at your own pace, select compounds you might find interesting and utilise what you have learnt in the examples above to undertake multipole refinements.

The original articles are in the "src" subfolder and should be read, at least briefly, to give you an idea why the study was undertaken, and the results the authors obtained. Only the briefest of details about each study are given here (in no special order).

1. **Alanyl-methionine** - a simple peptide molecule from the Lecomte group. Fairly straight-forward - compare deformation density maps maps reported with yours
2. **Cr2-hydride** - the organometallic salt [K(crypt-222)]$^+$ [$Cr_2(\mu\text{-}H)(CO)_{10}$]$^-$. The K^+ cation (as is normally found) can be treated effectively as a spherical ion, i.e. no multipole refinement. The Ct atom can be treated similarly to the manganese carbonyl example.
3. **Cu-imidazole** - centrosymmetric Cu(II) coordination complex - deformation and esp maps reported
4. **Diazapentalene** - a 90K study on an explosive organic molecule
5. **EDTTPC** - ethyl 4,6-dimethyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate - a combined experimental and theoretical study.
6. **KMNF3** - a perovskite structure. Non-molecular inorganic, and a bit of a challenge due to the high symmetry . Needs Kubic Harmonics - ask about this.
7. **KMNO4** - ionic inorganic compound, but in a relatively low symmetry.
8. **Mn-dimer** - a magnetic metal-organic material. A polymeric coordination complex of Mn(II) with a detailed description of the XD model used - see if you can reproduce this.
9. **NANO2** - simple ferroelectric inorganic compound - see if you can reproduce the charges.
10. **NICL2** - simple transition metal coordination complex - a good starting example
11. **nicotinamide** - an organic molecule - a straight forward example with esp maps.
12. **Ni-tacn**- a non-centrosymmetric Ni(II) coordination complex in a high symmetry space group. Try this example after you have attempted other simpler coordination complexes.
13. **oxalic acid** - a standard for charge density analysis. A straight forward example with a good data set.
14. **spodumene** - a non molecular inorganic silicate mineral $LiAl(SiO_3)_2$. Original paper compares data from different diffractometers.
15. **srtio3** - another perovskite structure in a high symmetry space group. An example for refinement using anharmonic thermal parameters, and needing the use of Kubic Harmonics.
16. **thiocoumarin** - relatively simple organic ring compound. See accompanying article on problems involving refinement of sulfur-containing compounds.
17. **thiouracil** - similar example to previous one
18. **urea** - standard experimental example for charge density - high quality data set with very small asymmetric unit !
19. **Zr-indenyl** - example of a charge density study on a second row transition metal, but with a flawed data set. Need to use the VM database for this example

References

1 Clementi, E. & Roetti, C. (1974). *At. Data and Nucl. Data Tables,* **14**, 177-478.

2 Hirshfeld, F. L. (1976). *Acta Cryst.* A**32**, 239-244.

3 Coppens, P. (1997). *X-ray Charge Densities and Chemical Bonding*. Oxford University Press, New York.

4 Volkov, A., Abramov, Y. A. & Coppens, P. (2001). *Acta Cryst.* A**57**, 272-282.

5 Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* 42, 3175-3187.

6 Chandler, G. S., Spackman, M. A. & Varghese, J. N. (1980). *Acta Cryst.* A36, 657-669.

7 Hansen, N. K. & Coppens, P. (1978). *Acta Cryst. A*(**34**, 909-921.

8 Paturle, A. & Coppens, P. (1988) *Acta Cryst. A*(**44**, 6-8.

9 Kara, M. & Kurki-Suonio, K. (1981) *Acta Cryst.* A**37**, 201.

10 Hirshfeld, F. L. (1977). *Theor. Chim. Acta*, **44**, 129-138.

11 Bader, R. F. W. (1990). *Atoms in Molecules: A Quantum Theor,* Oxford: Claredon Press.

12 Spek, A. L. (2003). *J. Appl. Cryst*. **36**, 7-13.

13 Volkov, A., Koritsanszky, T. S. & Coppens, P. (2004). *Chem. Phys. Lett.* **391**, 170-175.

14. Hübschle C. B. and Luger, P. (2006) *J. Appl. Crystallogr.* **39**, 901–904.

15. (a) Politzer, P., Murray, J. S., Peralta-Inga, Z. (2001) *Int J. Quantum Chem.* **85,** 676. (b) Politzer, P., Murray, J. S., (2002) *Theor. Chem. Acc.* **108**, 134.