

T U T O R I A L - 1

Introduction to aspherical-atom refinement using the XD2006 suite of programs and the WinXD GUI.

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

EMAIL : louis.farrugia@glasgow.ac.uk

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This tutorial is heavily based on a tutorial originally given by A. Volkov and L. J. Farrugia

Programs to be used in the tutorials:

WinXD/XD2006
MolIso <http://www.molecoolqt.de/>
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:

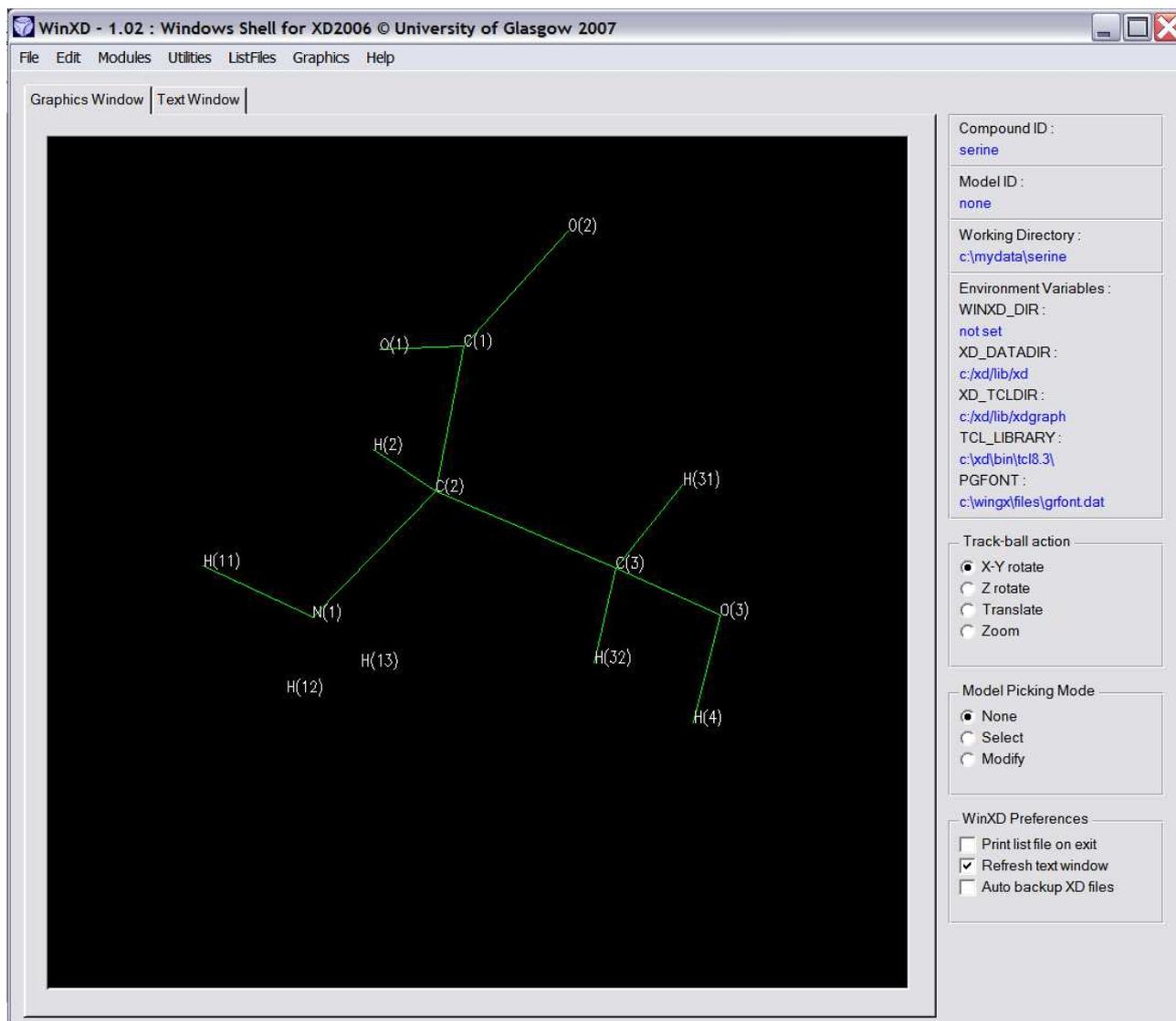
- xd.mas – XD master (instructions) file
- xd.inp and xd.res – XD parameter (atom data) file
- xd.hkl – XD reflection file

This is because the XD suite consists of several modules and each module requires its 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.



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

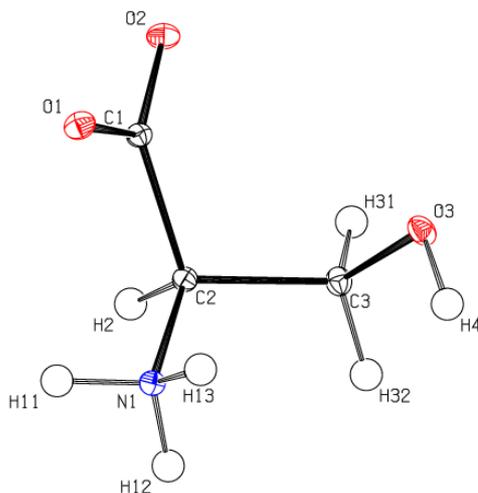
For this first tutorial on XD2006, a set of exercises based on the crystal structure of DL-serine from a recent low-temperature 20K study was chosen:

“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.

	298 K	100 K	20 K
Empirical formula	C ₃ H ₇ NO 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 θ/λ) _{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 > 2σ(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%

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

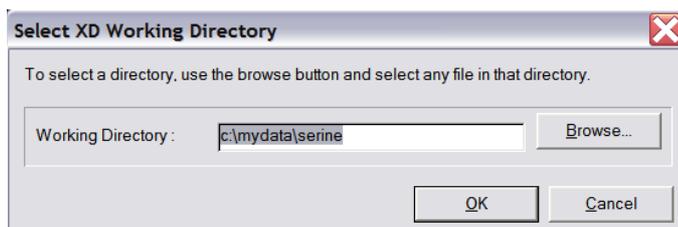
These data extend to $\sin\theta/\lambda \sim 1.18 \text{ \AA}^{-1}$ and have a fairly high completeness (~80%) and redundancy (~7). The molecular structure of DL-serine is



1.1. Importing data to XD from SHELX

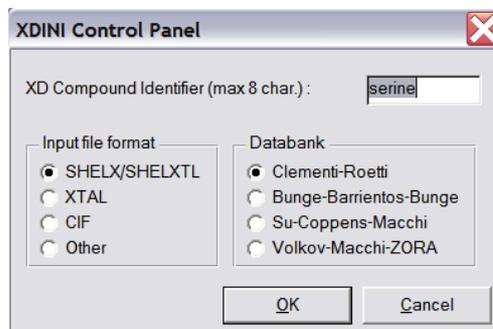
The folder serine contains the results of the spherical (or Independent-Atom Model, IAM) SHELX refinement of the DL-serine data (SER), the files shelx.ins and shelx.hkl

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



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-Roetti¹ scattering factor model that is the default in XD.



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) .

WinXD - 1.02 : Windows Shell for XD2006 © University of Glasgow 2007

File Edit Modules Utilities ListFiles Graphics Help

Graphics Window | Text Window

```

----- 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\igrfont.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

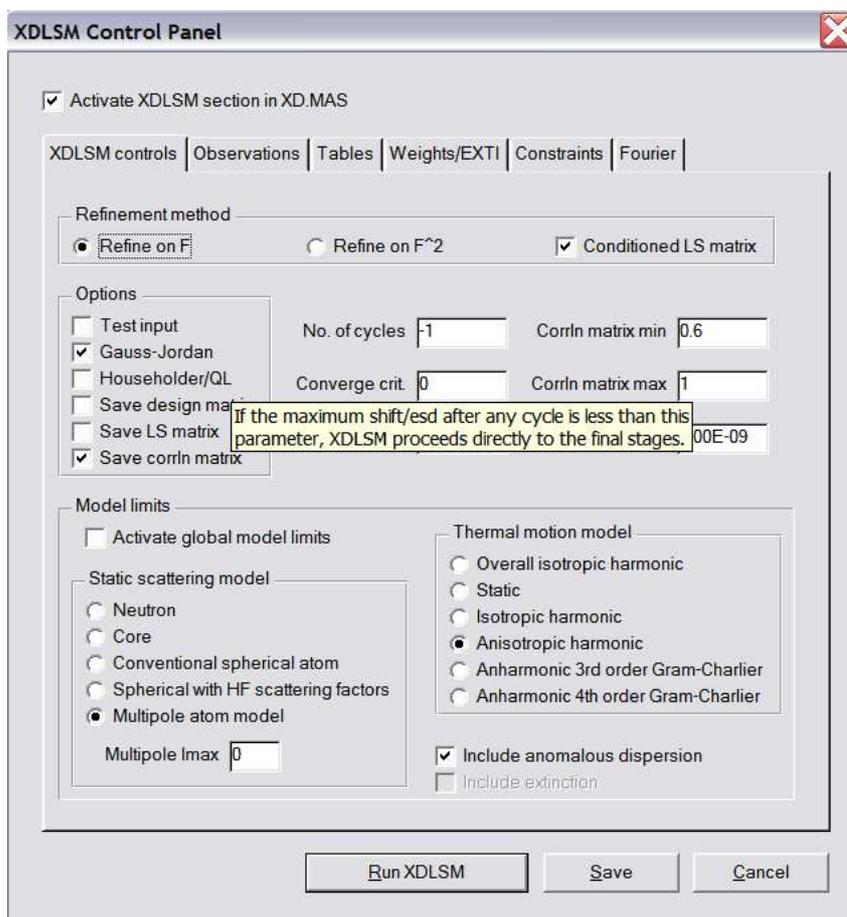
Note the messages that say that reading of `shelx.ins` and `shelx.hkl` file was successful. In the XD folder several new files have been created. These are the XDINI log file `xd_ini.out` and XD input/parameter/hkl files `xd.mas`, `xd.inp` and `xd.hkl`.

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)



It is **VERY IMPORTANT** that you save a copy of the original **xd.inp**, because the procedure described below will set all the atomic monopole populations back to zero, and you will need the correct default values for later refinements.

Now let's set the refinement options

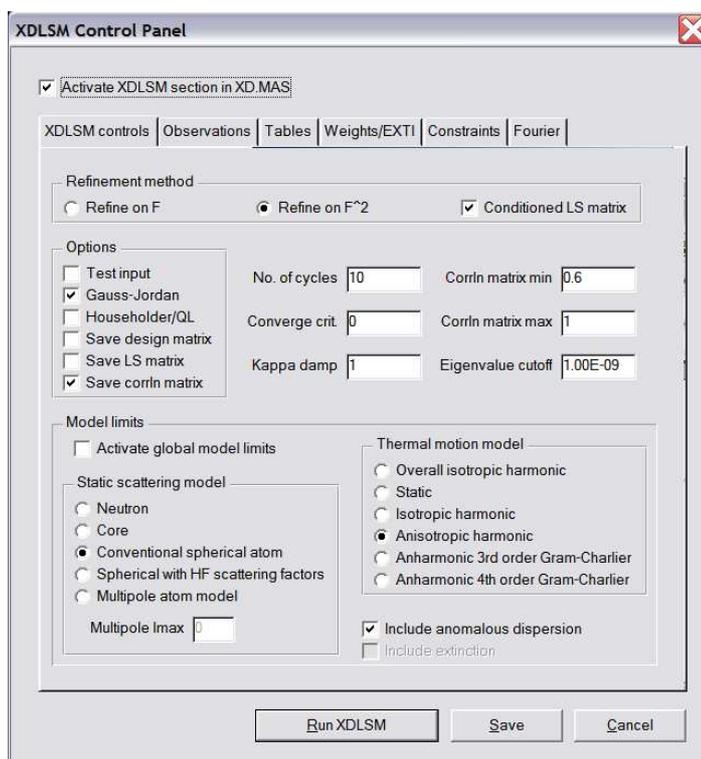
In **XDLSM controls** menu

select "Refine on F²"

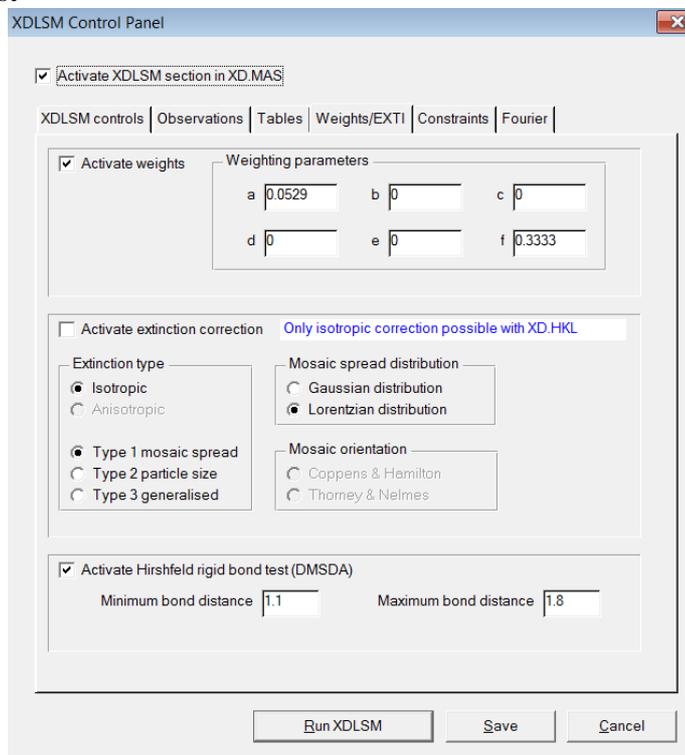
set number of cycles to 10

activate global model limits

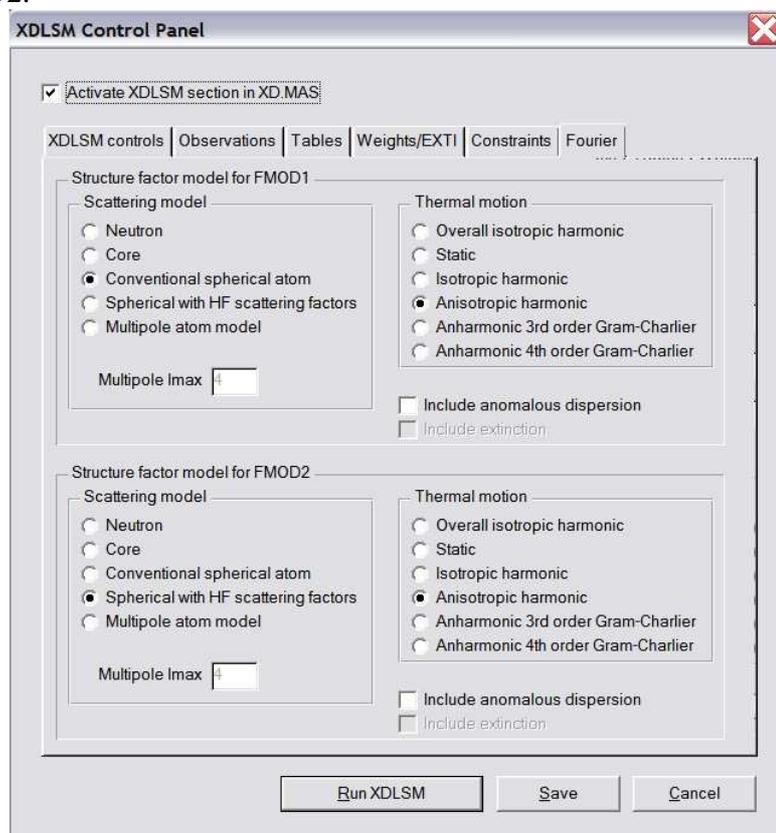
select "Conventional spherical atom" under "Static scattering model"



Under **Weights/EXTI** set the “a” parameter to the same value as in SHELX (0.0529) and activate Hirshfeld’s rigid-bond test²



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



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 F_{calc} 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 using the menu item File-Open XD Masterfile 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	0000000000000000	00	000	00000	0000000	000000000
O(2)	111	111111	0000000000	0000000000000000	00	000	00000	0000000	000000000
O(3)	111	111111	0000000000	0000000000000000	00	000	00000	0000000	000000000
N(1)	111	111111	0000000000	0000000000000000	00	000	00000	0000000	000000000
C(1)	111	111111	0000000000	0000000000000000	00	000	00000	0000000	000000000
C(2)	111	111111	0000000000	0000000000000000	00	000	00000	0000000	000000000
C(3)	111	111111	0000000000	0000000000000000	00	000	00000	0000000	000000000
H(2)	111	100000	0000000000	0000000000000000	00	000	00000	0000000	000000000
H(4)	111	100000	0000000000	0000000000000000	00	000	00000	0000000	000000000
H(11)	111	100000	0000000000	0000000000000000	00	000	00000	0000000	000000000
H(12)	111	100000	0000000000	0000000000000000	00	000	00000	0000000	000000000
H(13)	111	100000	0000000000	0000000000000000	00	000	00000	0000000	000000000
H(31)	111	100000	0000000000	0000000000000000	00	000	00000	0000000	000000000

```

H(32) 111 100000 0000000000 0000000000000000 00 000 00000 0000000 0000000000
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}	U11, U22, U33, U12, U13, U23	4-9
3rd order C^{ijk}	C111, C222, C333, C112, C122, C113, C133, C223, C233, C123	10-19
4th order D^{ijkl}	D1111, D2222, D3333, D1112, D1222, D1113, D1333, D2223, D2333, D1122, D1133, D2233, D1123, D1223, D1233	19-34
Multipole Populations		
Monopoles	M1, M2	35-36
Dipoles	D1+, D1-, D0	37-39
Quadrupoles	Q0, Q1+, Q1-, Q2+, Q2-	40-44
Octupoles	O0, O1+, O1-, O2+, O2-, O3+, O3-	45-51
Hexadecapoles	H0, H1+, H1-, H2+, H2-, H3+, H3-, H4+, H4-	52-60
Radial Screening		
$\kappa, \kappa'(l)$	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	OVTHP	74
Scale Factor	SCALE	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 U_{ij} 's) are to be refined, while for H-atom only one isotropic U_{iso} parameter will be refined. The order in which parameters are listed in KEY table is given in Table 1 above.

Now save the current MAS file by clicking on the "Save" button, close down the XDLSM Control Panel by clicking "Cancel" and then run XDLSM by clicking the "Modules - XDLSM" menu item.

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

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**

It is **VERY IMPORTANT** that you save a copy of **xd.inp** before you copy **xd.res** to **xd.inp**, because the procedure described above will set all the atomic monopole populations back to zero, and you will need the correct default values for later refinements.

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

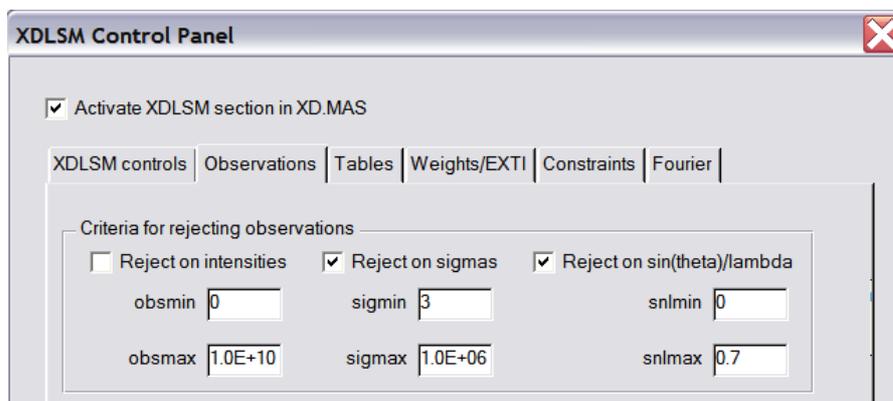
Note the results of the Hirshfeld's rigid-bond test:

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 $\leq 1 \times 10^{-3} \text{ \AA}^2$. 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 \AA^{-1}



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 multipole 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:

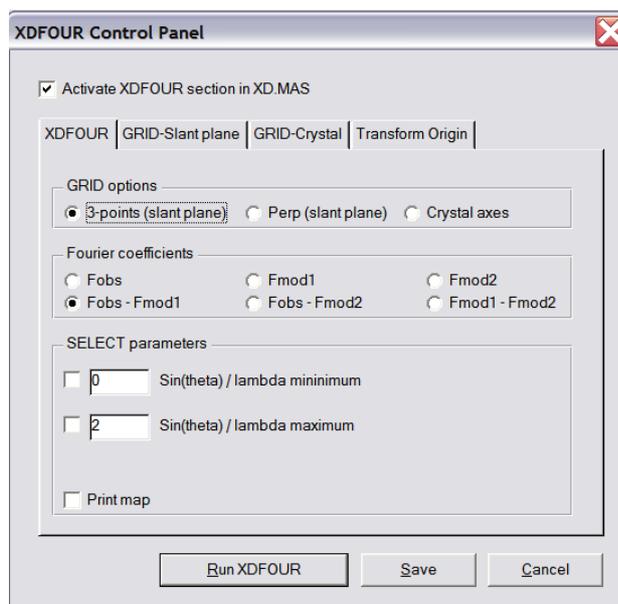
```

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

```

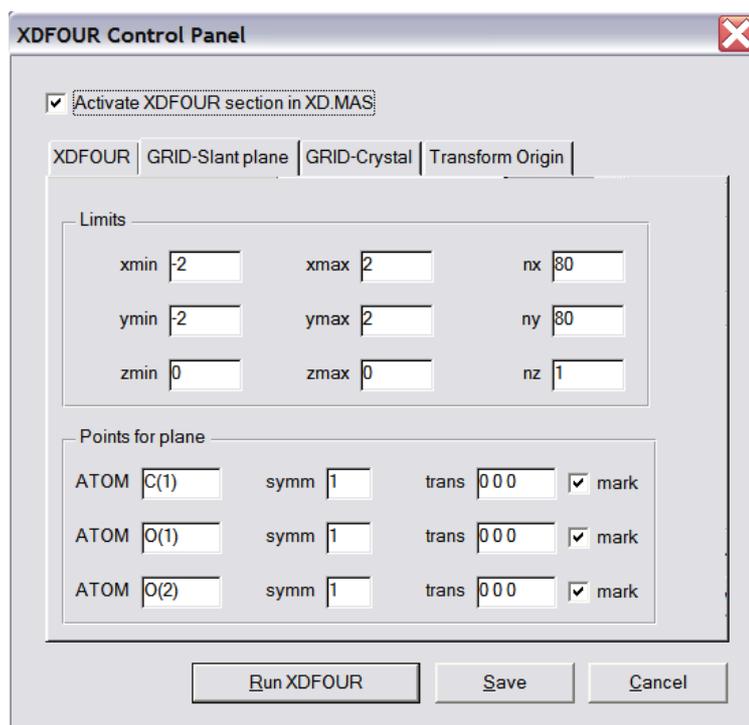
XDFOUR module uses the xd.fou file created by XDLSM for calculating Fourier maps.

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

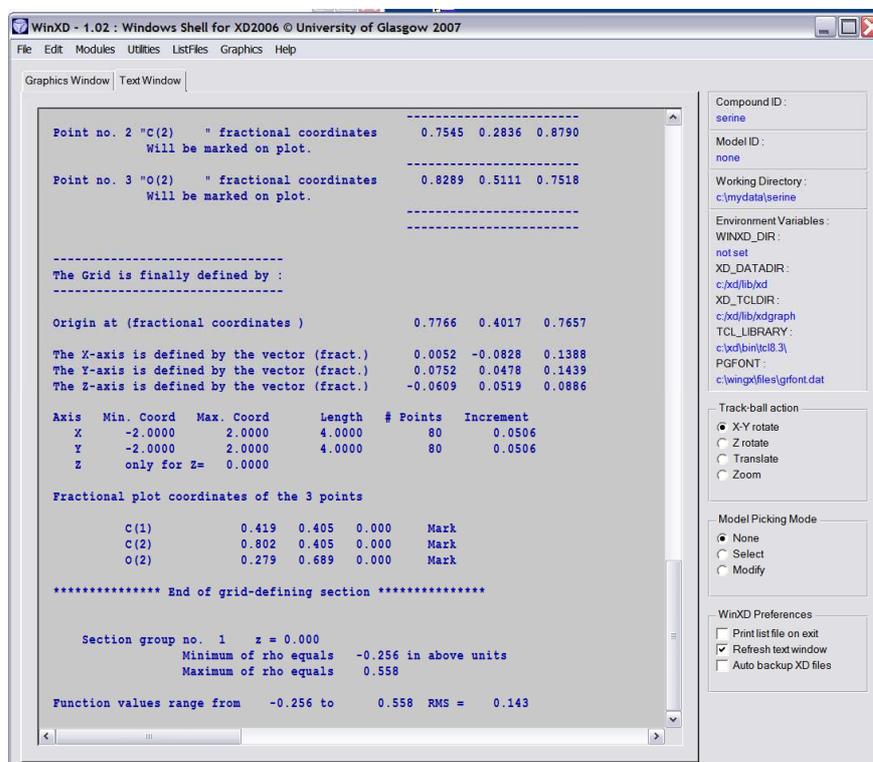


Note that XDFOUR allows various types of Fourier maps to be calculated from the three types of Fourier coefficients written to xd.fou file, *i.e.* Fobs, Fmod1 and Fmod2. Thus the choice of Fobs-Fmod1 will produce the difference map between Fobs and Fcalc produced by model selected under FMOD1 in XDLSM 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.*



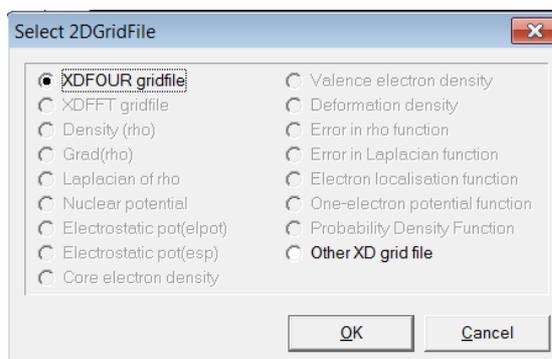
Now click the “Run XDFOUR” button (this has the effect of saving the current instructions in the MAS file and then running the XDFOUR module). Note the listing of the XDFOUR output file `xd_fou.out` appearing in the Text Window (using Listfile – XDFOUR menu item):



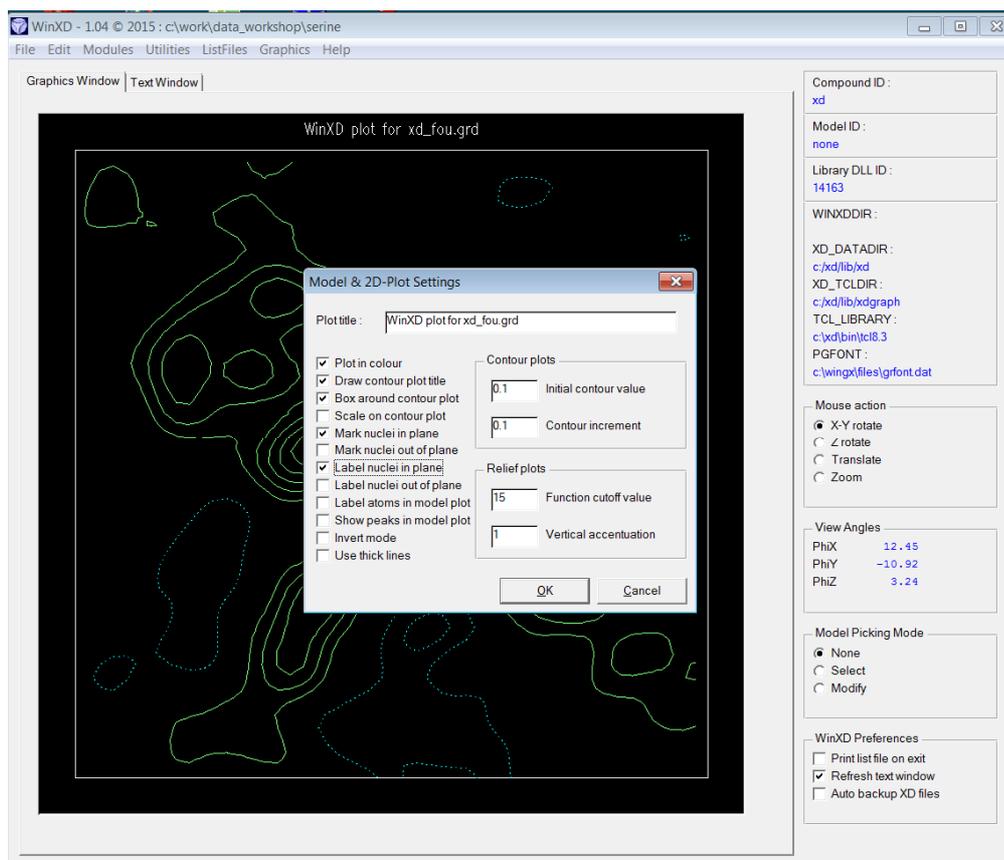
A grid file `xd_fou.grd` has now been created, which can be viewed in XDGRAPH.

1.4 Visualization of Fourier maps

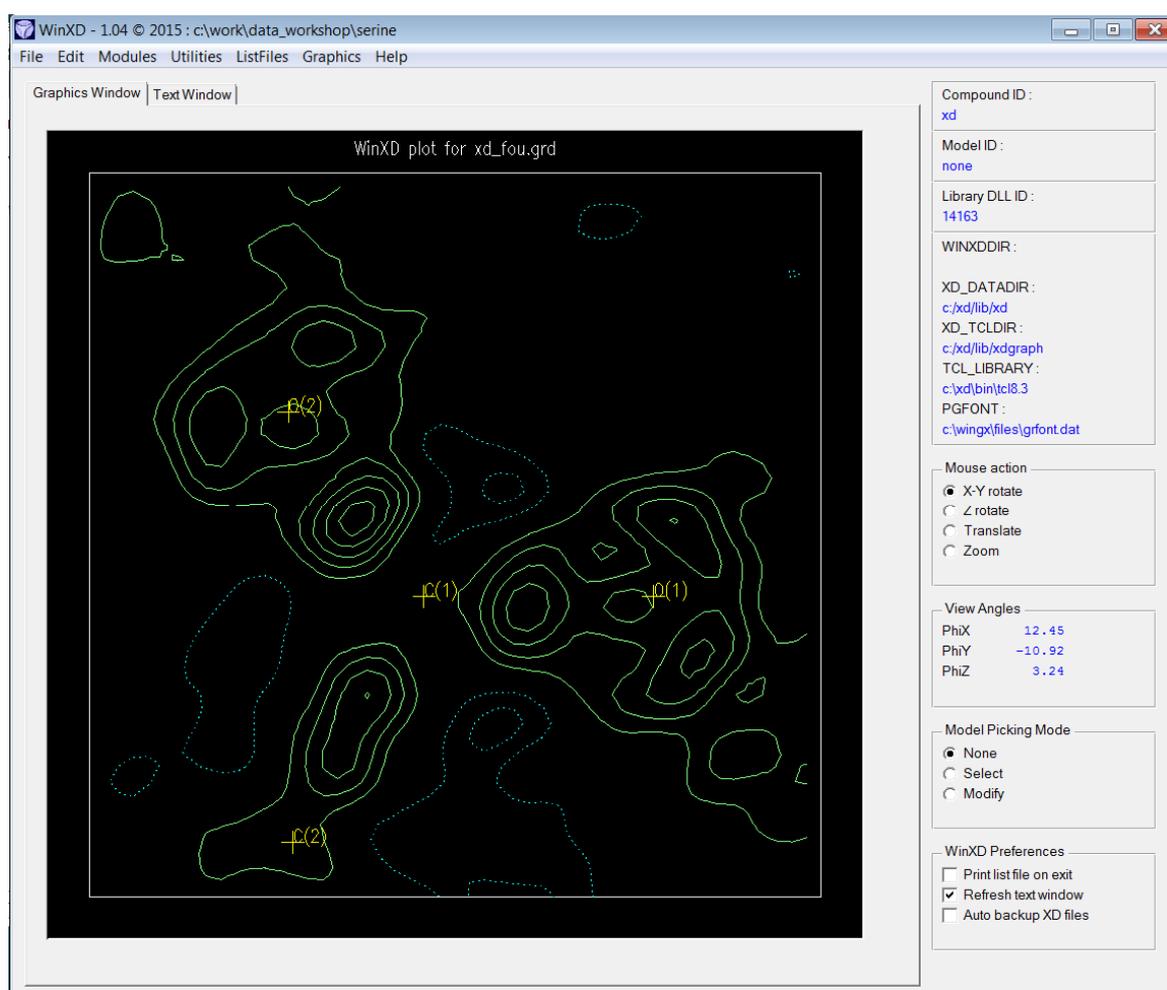
The grid files created by XDFOUR (and also by XDPROP) can then be visualized in the WinXD GUI. First of all we use the somewhat basic “Graphics – 2D Contour Plot” menu option.



Select the XDFOUR gridfile (in this case there is no choice, but often several grid files will be present). A right click with the mouse will give the Plot Setting Window. Select “Mark Nuclei in Plane” and “Label Nuclei in Plane”



This creates a set of positive of contours, starting from $0.1 \text{ e}/\text{\AA}^3$ with an increment of $0.1 \text{ e}/\text{\AA}^3$ (linear set).

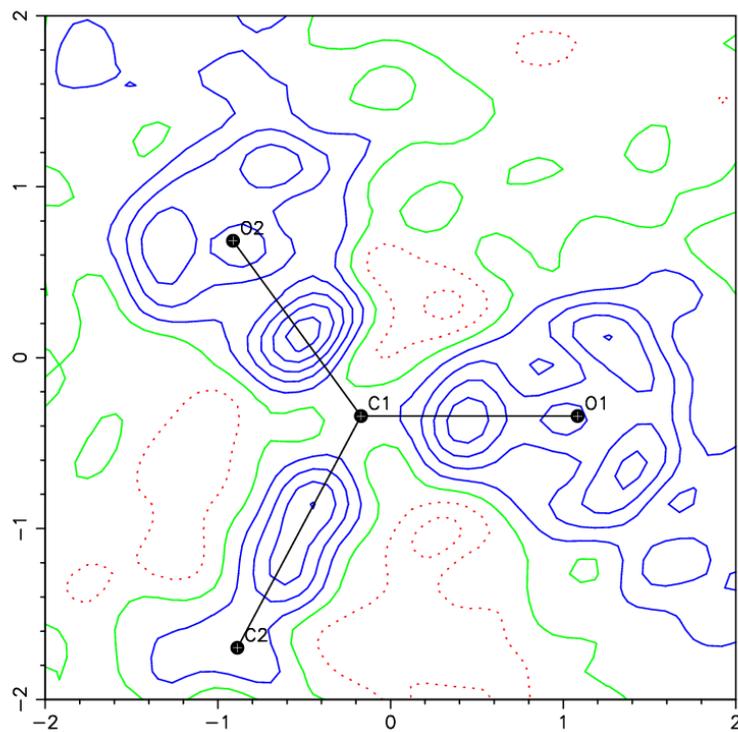
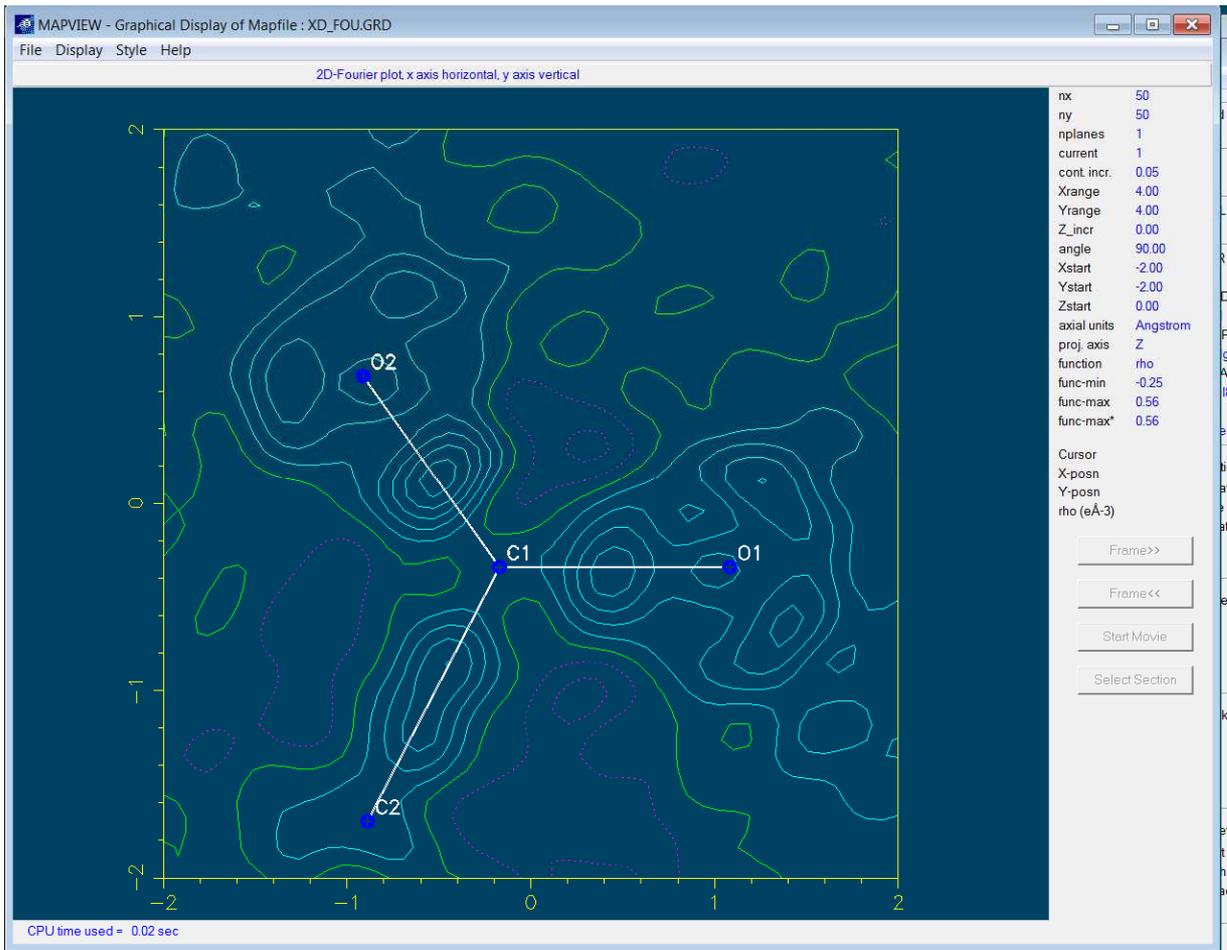


A more sophisticated map drawing routine is the option “Graphics – 2D Mapview” using the Mapview program from WinGX (MapView is now fully incorporated into the WinXD GUI). Again a right click gives the Options menu. Select “Draw Atoms” “Draw Bonds” “Label Atoms”.

With this program, it is possible to save the plot as a PostScript file. For the best results select “Display – Default Scheme 2” and then “File – Save as Postscript-Colour”. This will write a copy of the displayed screen as a PostScript file “mapv001.ps” (If the Postscript viewer program GhostView is installed and Mapview is set up properly, then GhostView will open up this file automatically).

A screen shot of the MapView plot and the PostScript plot are shown below.

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.



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

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

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

$$N4\pi \int \rho_{\text{valence}}(\kappa r) r^2 dr = 1 \quad (3.17)$$

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 P_v and κ parameters to “1” in the KEY table in the XDLSM part of `xd.mas` file (see Table 1). Parameters P_v 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. For this part of the exercise, we will need to use the original saved version of `xd.inp`, which has the correct starting atomic monopole populations, so copy this saved file to `xd.inp`.

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**

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(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

```

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. $P_{v_{O(1)}}=P_{v_{O(2)}}$, $P_{v_{H(11)}}=P_{v_{H(12)}}=P_{v_{H(13)}}$ and $P_{v_{H(31)}}=P_{v_{H(32)}}$. Refinement keys for P_v '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 P_v parameters for all atoms. At the same time it is 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 0000000000000000 10 000 00000 0000000 000000000
O(2)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
O(3)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
N(1)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
C(1)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
C(2)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
C(3)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(2)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(4)    000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(11)   000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(12)   000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(13)   000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(31)   000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
H(32)   000 000000 0000000000 0000000000000000 10 000 00000 0000000 000000000
KAPPA   100000
KAPPA   000000
EXTCN   0000000
OVTHP   0
SCALE   1
END KEY

```

With yellow we highlight the fixed positional and ADP parameters, with green the refined P_v 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. Since we have added an extra three ‘KAPPA’ types, we now need to have 7 ‘KAPPA’ entries in the master file. We also need to modify the “KEEP KAPPA” instruction (this is not strictly needed for what we are doing right now, but will be necessary later on)

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

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 (i.e. does NOT have a “!” as the first character):

```
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

<i>m1</i> 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 <i>lmax</i> in the expansion over spherical harmonics [1]
<i>m2</i> thermal motion models	
-1	overall-isotropic-harmonic
0	static
1	isotropic – harmonic
2	anisotropic – harmonic
tmax	anharmonic model: Gram-Charlier expansion up to 4 th order [24]
<i>m3</i> anomalous dispersion	
0	excluded
1	included
<i>m4</i> 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 (remember to save it right now!!) , 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`. Below is an example of `xd.inp` file:

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 first change we need to make is to the circled fourth parameter (number of kappa sets), which should be changed from 4 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 P_v . These parameters usually need not be modified by hand

```

xd.inp
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
! <<< 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  1.000000  5
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

```

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 $l = 1, \dots, 4$. 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 must be changed to 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.

So in summary, the two changes to the `xd.inp` file that must be made are:

- change the total number of kappa parameters in the header from 4 to 7
- change the number and starting values of the kappa parameters as given just above

Save the `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 P_V (Pval), κ -parameters (Kappa) and net atomic charges derived from P_V (Net charge).

Table 1. Monopole Populations, Radial Parameters and Net Atomic Charges.

Atom	Pval	Kappa	P00	Kappa'	Atomic charge
O(1)	6.403(24)	0.980(2)	0.000	1.000	-0.403(24)
O(2)	6.403	0.980(2)	0.000	1.000	-0.40330
O(3)	6.338(38)	0.983(3)	0.000	1.000	-0.337(38)
N(1)	4.742(47)	1.028(5)	0.000	1.000	+0.257(47)
C(1)	3.537(48)	1.052(8)	0.000	1.000	+0.462(48)
C(2)	3.953(57)	1.038(7)	0.000	1.000	+0.047(57)
C(3)	3.659(53)	1.045(8)	0.000	1.000	+0.340(53)

H(2)	0.991(23)	1.130	0.000	1.200	+0.008(23)
H(4)	0.866(24)	1.130	0.000	1.200	+0.134(24)
H(11)	0.954(15)	1.130	0.000	1.200	+0.045(15)
H(12)	0.954	1.130	0.000	1.200	+0.04590
H(13)	0.954	1.130	0.000	1.200	+0.04590
H(31)	1.123(17)	1.130	0.000	1.200	-0.122(17)
H(32)	1.123	1.130	0.000	1.200	-0.12250

 Total charge in the ASU : +0.0001
 Sum of monopoles in ASU : 41.9999

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:

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

Each pseudoatom is modeled using the modified Laplace series:

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

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

$$d_{lm\pm}(\Omega) = D_{lm} y_{lm\pm}(\Omega) \quad (3)$$

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

$$\begin{aligned} y_{00} &= Y_{00} \\ y_{lm+} &= (-1)^m (Y_{lm} + Y_{l,-m}) / \sqrt{2} & m > 0 \\ y_{lm-} &= (-1)^m (Y_{lm} - Y_{l,-m}) / \sqrt{-2} & m > 0 \end{aligned} \quad (4)$$

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

62 X-ray Charge Densities and Chemical Bonding

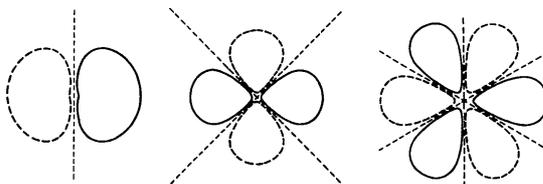


FIG. 3.3 Graphic representation of some multipolar functions: (from left to right) a dipole ($l = 1$), a quadrupole ($l = 2$), and an octupole ($l = 3$) function. Functions are negative with the dotted areas. If the x axis is horizontal and the y axis is vertical, the functions are x , $x^2 - y^2$, and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

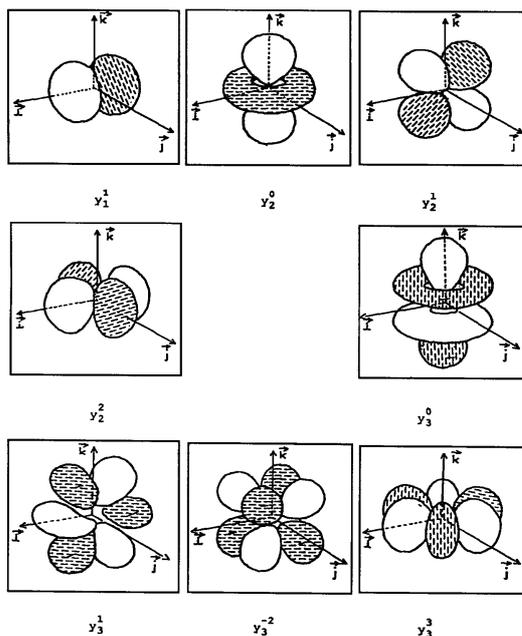


FIG. 3.4 Drawing of some dipolar, quadrupolar, and octupolar functions. Source: Hansen (1978).

Thus, the refinement of the aspherical density introduces parameters $P_{lm\pm}$ of the deformation 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	<i>Valence-shell parameters</i>
Positional parameters x_i, y_i, z_i	Population parameters $P_{i, \text{val}}$
Thermal parameters	Expansion–contraction parameters κ_i
harmonic β_i, β_{ijk}	
higher-order quasimoments $c_i^{jkl\dots}$	<i>Deformation parameters</i>
or	Population parameters $P_{i, \text{tmp}}$
higher-order cumulants $\kappa_i^{jkl\dots}$	Expansion–contraction parameters κ_i'
Extinction parameters	
isotropic or anisotropic	
Occupancy parameters	

1.8 Introduction to the local coordinate system

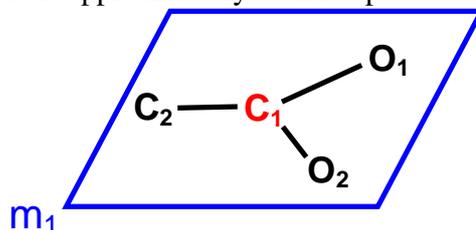
Atoms in molecules and crystals often have a local symmetry. In general it has nothing to do with the crystallographic symmetry of the crystal structure, unless an atom lies on a crystallographic symmetry element. This case is not going to be discussed here.

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.

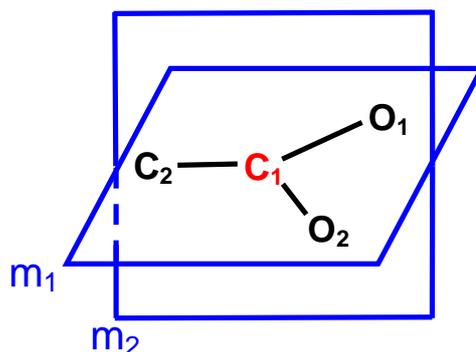
We will determine the local symmetry and corresponding local axes of the carbon atom (shown in red) in carboxylate anion and the carboxylic acid group:



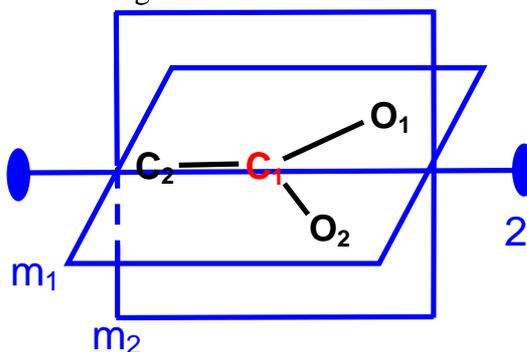
For simplicity we assume that both groups are planar. First consider the carboxylate anion. Because the group is planar we can say that there is approximately a mirror plane in the plane of the group, i.e.



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 $mm2$. 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

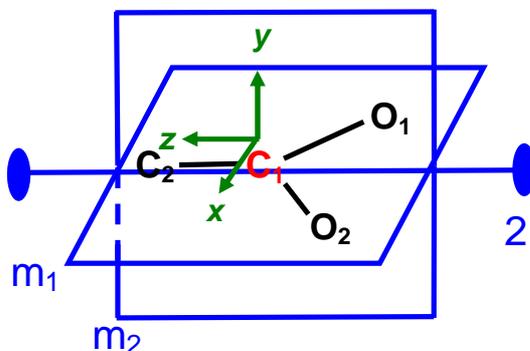
Table 3. Index Picking Rules of Site-Symmetric Spherical Harmonics.

Symmetry	Choice of coordinate axes	Indices of symmetric y_{lmp} (λ, μ are integers)
1	any	all (l, m, \pm)
$\bar{1}$	any	($2\lambda, m, \pm$)
2	$2 \parallel z$	($l, 2\mu, \pm$)
m	$m \perp z$	($l, l-2\mu, \pm$)
2/m	$2 \parallel z, m \perp z$	($2\lambda, 2\mu, \pm$)
222	$2 \parallel z, 2 \parallel y, (2 \parallel x)$	($2\lambda, 2\mu, +$), ($2\lambda+1, 2\mu, -$)
mm2	$2 \parallel z, m \perp y, (m \perp x)$	($l, 2\mu, +$)
mmm	$m \perp z, m \perp y, m \perp x$	($2\lambda, 2\mu, +$)
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	$4 \parallel z, m \perp y, (m \perp x)$	($l, 4\mu, +$)
$\bar{4}2m$	$\bar{4} \parallel z, 2 \parallel x, (m \hat{=} xy \rightarrow yx)$ $m \perp y, (2 \hat{=} xyz \rightarrow yx\bar{z})$	($2\lambda, 4\mu, +$), ($2\lambda+1, 4\mu+2, -$) ($2\lambda, 4\mu, +$), ($2\lambda+1, 4\mu+2, +$)
4/mmm	$4 \parallel z, m \perp z, (m \perp x), (m \hat{=} xy \rightarrow yx)$	($2\lambda, 4\mu, +$)

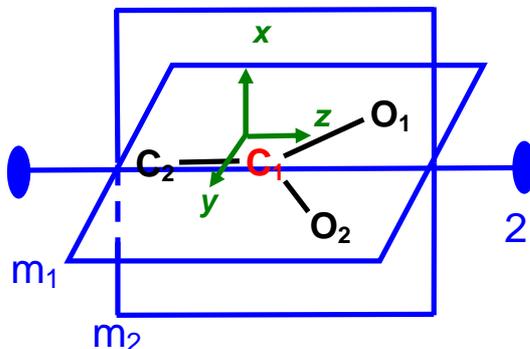
3	3 z	(l,3μ,±)
$\bar{3}$	$\bar{3}$ z	(2λ,3μ,±)
32	3 z, 2 y, 2 x	(2λ,3μ,+),(2λ+1,3μ,-) (3μ+2j,3μ,+),(3μ+2j+1,3μ,-)
3m	3 z, m ⊥ y m ⊥ x	(l,3μ,+) (l,6μ,+),(l,6μ+3,-)
$\bar{3}m$	$\bar{3}$ z, m ⊥ y m ⊥ x	(2λ,3μ,+) (2λ,6μ,+),(2λ,6μ+3,-)
6	6 z	(l,6μ,±)
$\bar{6}$	$\bar{6}$ z = (3 z, m ⊥ z)	(2λ,6μ,±),(2λ+1,6μ+3,±)
6/m	6 z, m ⊥ y 2 y, (2 x)	(2λ,6μ,±)
622	6 z, 2 y, (2 x)	(2λ,6μ,+),(2λ+1,6μ,-)
6mm	6 z, m ⊥ y, (m ⊥ x)	(l,6μ,+)
$\bar{6}m2$	$\bar{6}$ z, m ⊥ y, (2 x) m ⊥ x, (2 y)	(2λ,6μ,+),(2λ+1,6μ+3,+) (2λ,6μ,+),(2λ+1,6μ+3,-)
6/mmm	6 z, m ⊥ z, m ⊥ y, (m ⊥ x)	(2λ,6μ,+)

We see that for $mm2$ 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.

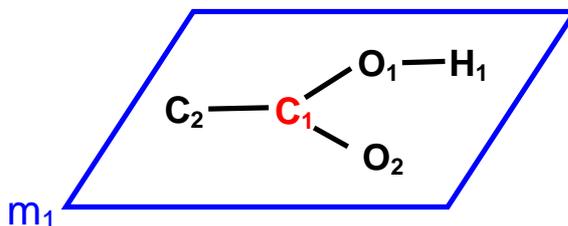
The following arrangement satisfies these rules:



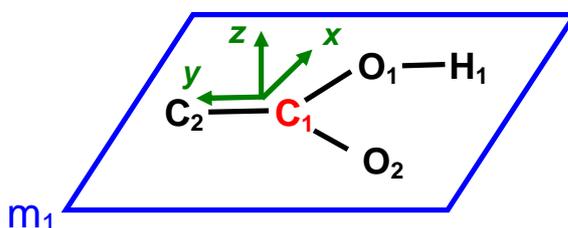
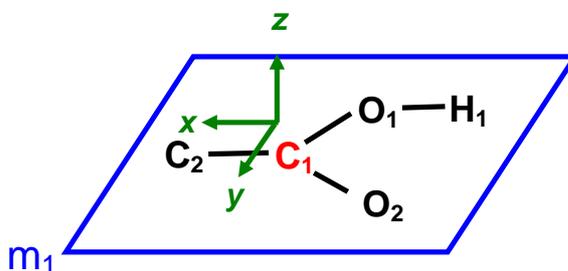
which is identical to the another definition:



How does the symmetry of C_1 atom in the carboxylic group differ from that in carboxylate ? Mirror plane m_1 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.

$$\mathbf{v}_1 = (\mathbf{r}_0 - \mathbf{r})$$

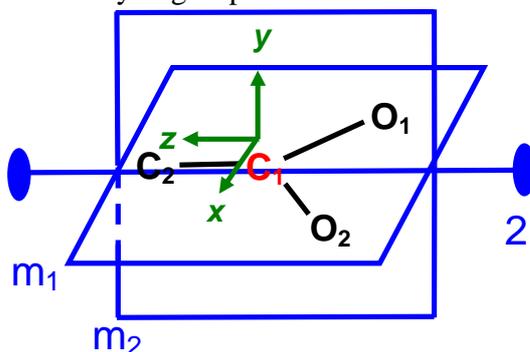
$$\mathbf{v}_2' = (\mathbf{r}_2 - \mathbf{r}_1)$$

$$\mathbf{v}_3 = \mathbf{v}_1 \times \mathbf{v}_2'$$

$$\mathbf{v}_2 = \mathbf{v}_1 \times \mathbf{v}_3$$

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 $C_1 \rightarrow O_2$

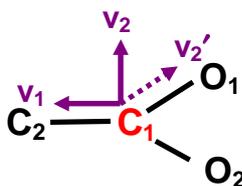
vector \mathbf{v}_3 (y-axis) is defined to be perpendicular to the plane of vectors \mathbf{v}_1 and \mathbf{v}_2'

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

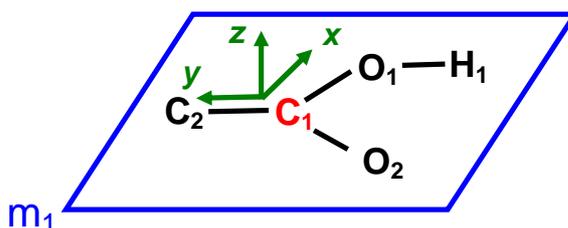
In the plane of COO^- group it will look like that (with vector \mathbf{v}_3 being perpendicular to the plane of the group)



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 $C_1 \rightarrow C_2$

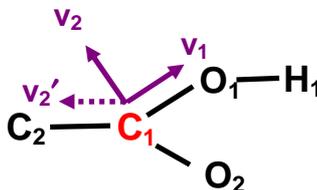
vector \mathbf{v}_3 (z-axis) is defined to be perpendicular to the plane of vectors \mathbf{v}_1 and \mathbf{v}_2'

(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 $m=0\dots l$. 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 $mm2$ 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 $mm2$ symmetry we get the following rule: $(l, 2\mu, +)$

where $\mu=0,1,2,3,\dots$ 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:

l	μ	$m=2\mu$	spherical harmonics function ($lm+$)	Note
DIPOLES				
1	0	0	10	OK
	1	2	12+	NOT allowed: $m > l$
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!				
QUADRUPOLES				
2	0	0	20	OK
	1	2	22+	OK
	2	4	24+	NOT allowed: $m > l$
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!				

OCTUPOLES				
3	0	0	30	OK
	1	2	32+	OK
	2	4	34+	NOT allowed: $m > l$
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!				
HEXADECAPLES				
4	0	0	40	OK
	1	2	42+	OK
	2	4	44+	OK
	3	6	46+	NOT allowed: $m > l$
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!				

Thus only 10, 20, 22+, 30, 32+, 40, 42+ and 44+ functions should be refined for an atom with $mm2$ 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 $(l, l-2\mu, \pm)$

l	j	$m=l-2\mu$	spherical harmonics function ($lm\pm$)	Note
DIPOLES				
1	0	1	11 \pm	OK
	1	-1	1(-1) 11 \pm	Not allowed: $m < 0$
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!				
QUADRUPOLES				
2	0	2	22 \pm	OK
	1	0	20	OK
	2	-2	2(-2) \pm	NOT allowed: $m < 0$
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!				
OCTUPOLES				
3	0	3	33 \pm	OK
	1	1	31 \pm	OK
	2	-1	3(-1) \pm	NOT allowed: $m < 0$
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!				
HEXADECAPLES				
4	0	4	44 \pm	OK

1	2	42±	OK
2	0	40	OK
3	-2	4(-2)±	NOT allowed: $m < 0$

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!

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 $(l, 3\mu, \pm)$], 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 :

- Basic program control section
- the SCAT table - the scattering factor tables (like SFAC entries in SHELX)
- the ATOM table - where the local coordinate system and some refinement limits are defined
- section with refinement options
- 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.

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

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

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


```

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)          X   O(1)         O(2)        Y   R   2   1   1   4   m
O(2)      C(1)          X   O(2)         O(1)        Y   R   2   1   1   4   m          O(1)
O(3)      H(4)          X   O(3)         C(3)        Y   R   2   1   2   4   m
N(1)      C(2)          Z   N(1)         C(3)        X   R   2   2   3   4   3m
C(1)      C(2)          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)      C(2)          X   C(3)         O(3)        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  0000000000000000  00  000  00000  0000000  0000000000

```

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  00000000000  0000000000000000  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  00000000000  0000000000000000  10  110  10011  0110011  100110011
O(2)    000  000000  00000000000  0000000000000000  00  000  00000  0000000  000000000
O(3)    000  000000  00000000000  0000000000000000  10  110  10011  0110011  100110011
N(1)    000  000000  00000000000  0000000000000000  10  001  10000  1000010  100001000
C(1)    000  000000  00000000000  0000000000000000  10  001  10010  1001000  100100010
C(2)    000  000000  00000000000  0000000000000000  10  111  11111  1111111  111111111
C(3)    000  000000  00000000000  0000000000000000  10  110  10011  0110011  100110011
H(2)    000  000000  00000000000  0000000000000000  10  001  00000  0000000  000000000
H(4)    000  000000  00000000000  0000000000000000  10  001  00000  0000000  000000000
H(11)   000  000000  00000000000  0000000000000000  10  001  00000  0000000  000000000
H(12)   000  000000  00000000000  0000000000000000  00  000  00000  0000000  000000000
H(13)   000  000000  00000000000  0000000000000000  00  000  00000  0000000  000000000
H(31)   000  000000  00000000000  0000000000000000  10  001  00000  0000000  000000000
H(32)   000  000000  00000000000  0000000000000000  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 \pm 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    000000

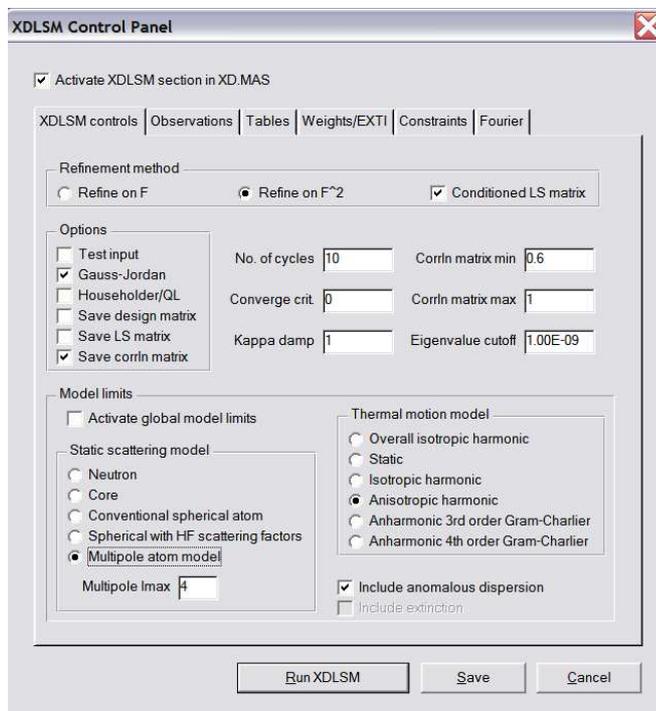
```

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 ($l=4$):



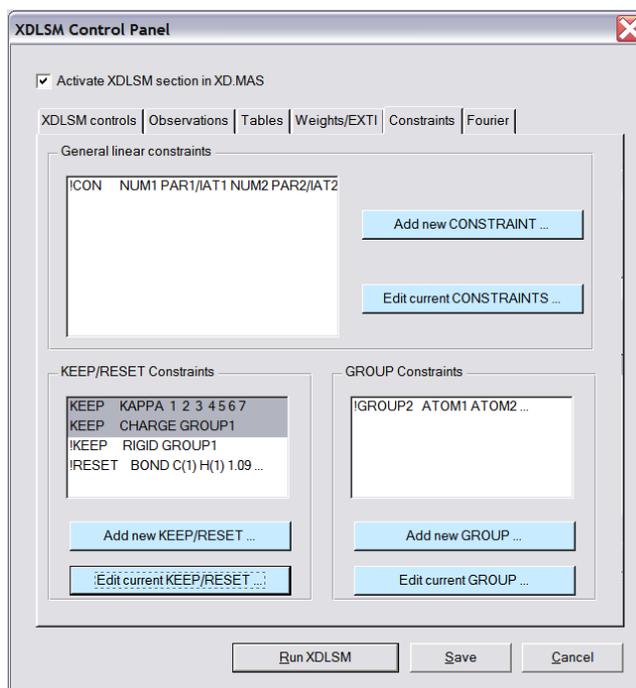
This change corresponds to the following line in `xd.mas`

```
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 multipole populations to the sum to the valence population.



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 F_{calc} (F_{mod1}) will be calculated from aspherical density while the second set of F_{calc} (F_{mod2}) will be calculated from spherical independent-atom model (as in SHELX). Phases of reflections for F_{obs} 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 0000000000000000 10 110 10011 0110011 100110011

```

Repeat this procedure for ALL non-H atoms. For 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:

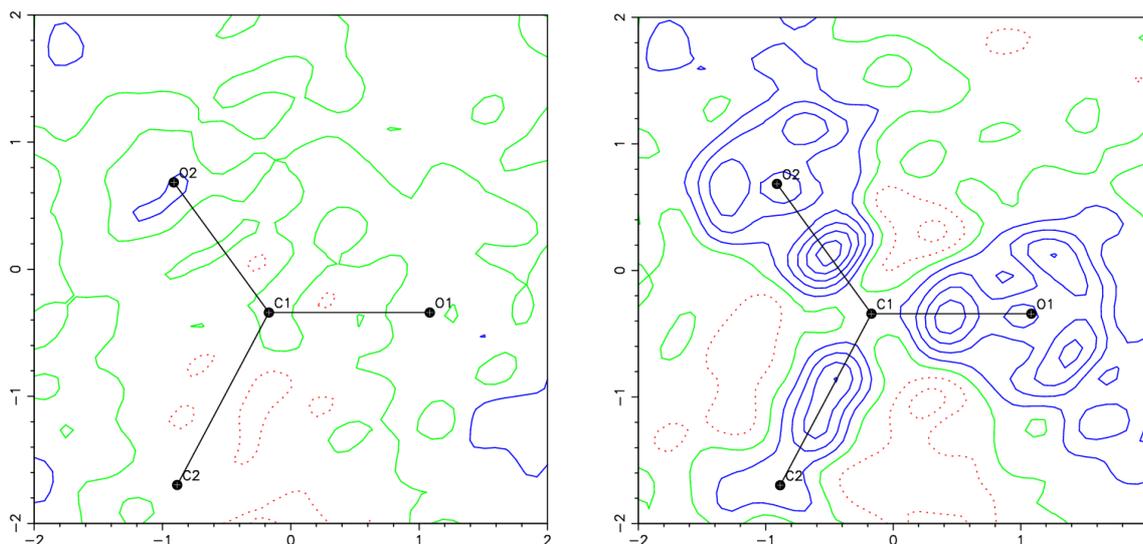
Differences of Mean-Squares Displacement Amplitudes (DMSDA)
(1.E4 A**2) along interatomic vectors (*bonds)

Multipole refinement					IAM refinement						
ATOM-->	ATOM	/	DIST	DMSDA	ATOM	ATOM-->	ATOM	/	DIST	DMSDA	ATOM
O(1)	C(1)	*	1.2538	1	O(1)	O(1)	C(1)	*	1.2548	5	
O(2)	C(1)	*	1.2642	1	O(2)	O(2)	C(1)	*	1.2652	5	
O(3)	C(3)	*	1.4221	3	O(3)	O(3)	C(3)	*	1.4225	7	
N(1)	C(2)		1.4905	-1	N(1)	C(2)		1.4915	-1		
C(1)	C(2)	*	1.5333	2	C(1)	C(2)	*	1.5334	1		
C(2)	C(3)	*	1.5231	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.

On visualization of the map, it is obvious that the multipole refinement results in a much cleaner difference maps – below we see the map *after* and *before* the multipole 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 MoleCoolQT, 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.

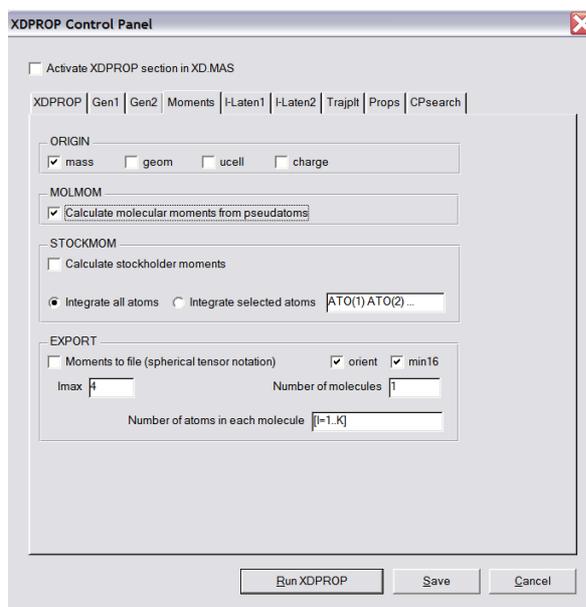
In this tutorial we will cover the main properties that are of general interest to show the abilities of XDPROP. XDPROP uses the `xd.mas` file with instructions which can also be input within the GUI and `xd.res` file which should contain the results of the latest refinement.

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:

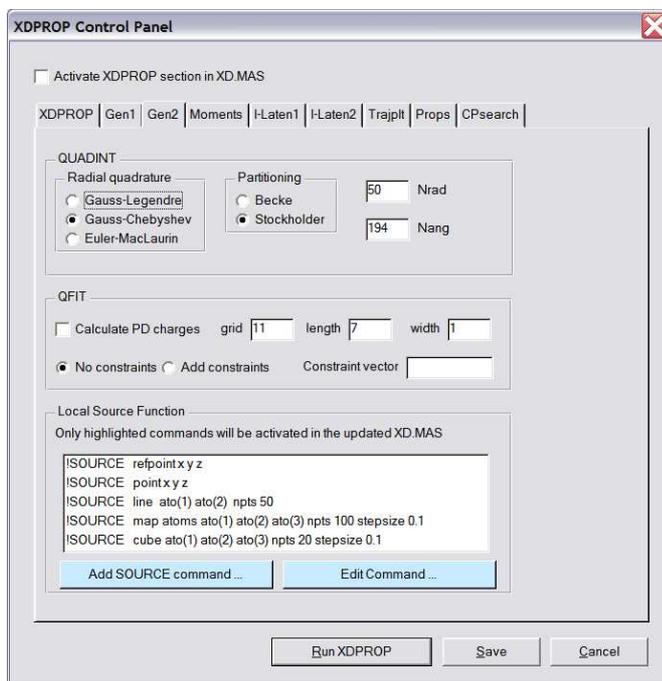
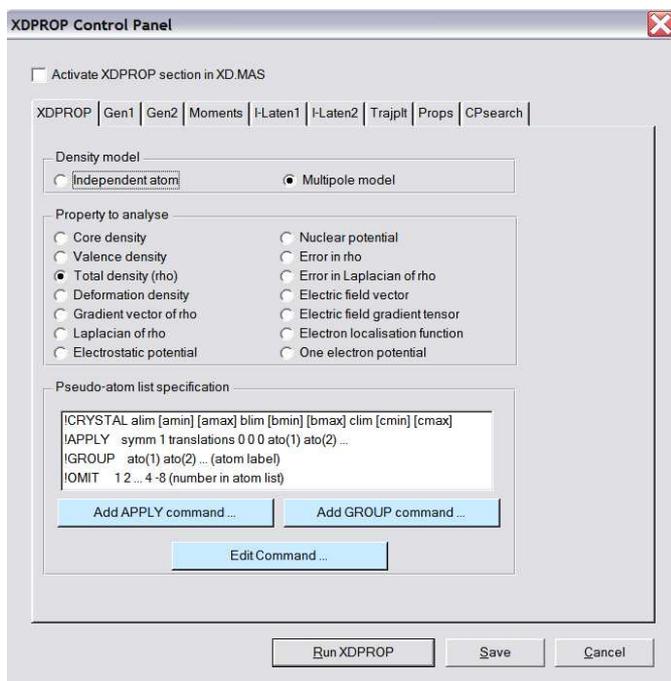
- directly from the refined valence populations of the atoms
- using Hirshfeld's stockholder's approach¹⁰
- using a fit to the electrostatic potential
- using Bader's Quantum Theory of Atoms in Molecules¹¹ (QTAIM)

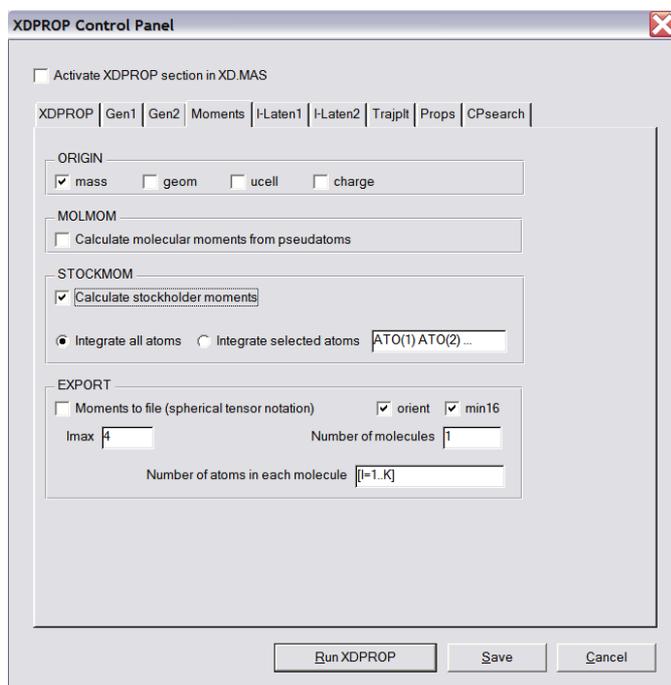
We've already shown how the net charges based on valence populations can be printed by XDGEOM to the `xd_geo.out` file. Printout of atomic charges and higher atomic moments based on multipole model is done in XDPROP using the following commands:



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)

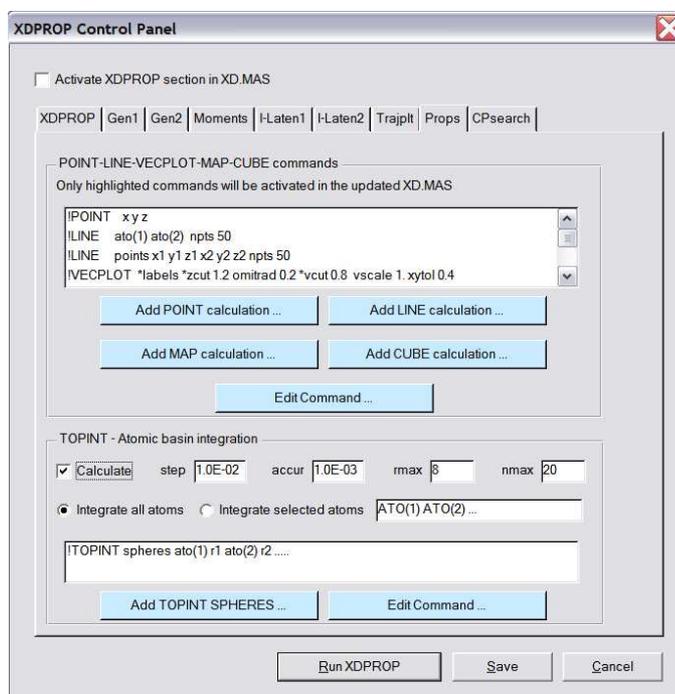
The calculation of Hirshfeld's charges in XDPROP is done via numerical (quadrature) integration:





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:



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 Spek¹² prints out the following information:

Analysis of Potential Hydrogen Bonds and Schemes

=====

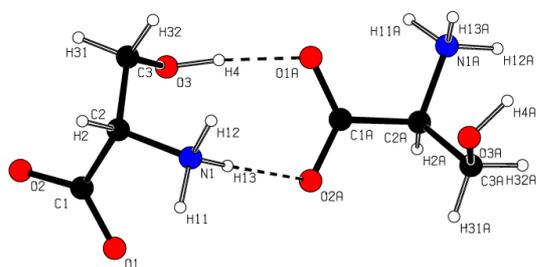
Nr	Res	Donor	---	H....	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
1	1	O(3)	--	H(4)	..O(1)	[2646.01]		0.97	1.70	2.6631	173
	1	N(1)	--	H(13)	..O(2)	[2646.01]		0.97	1.89	2.8535	170

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

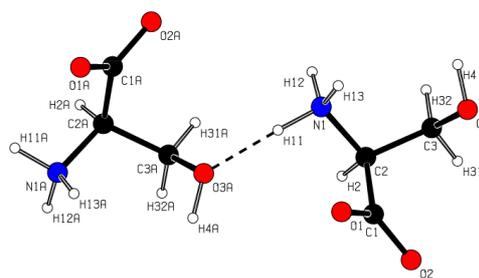
Translation of ARU-code to Equivalent Position Code

```
=====
[ 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
```

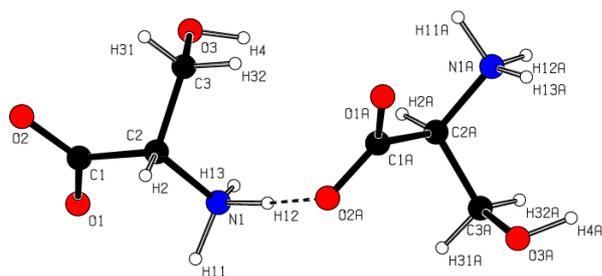
Note there are two H-bonds in the first dimer.



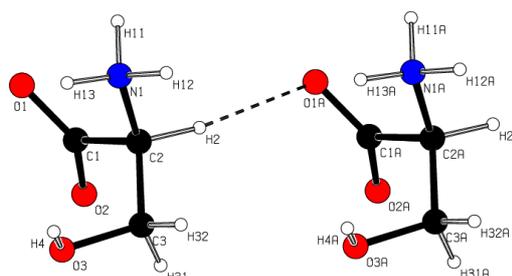
dimer 1



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 XDPROB can be specified as symmetry operation number 2 ($1/2 - x$, $1/2 + y$, $-z$) with added translations of $tx=1$, $ty = -1$, $tz = 1$.

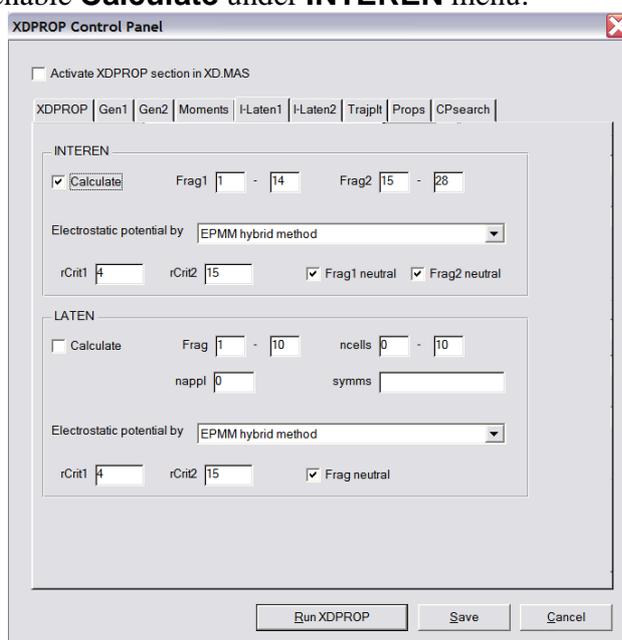
So we specify them in **APPLY** command:

```
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 → XDPROB

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



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 moments¹³ (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
```

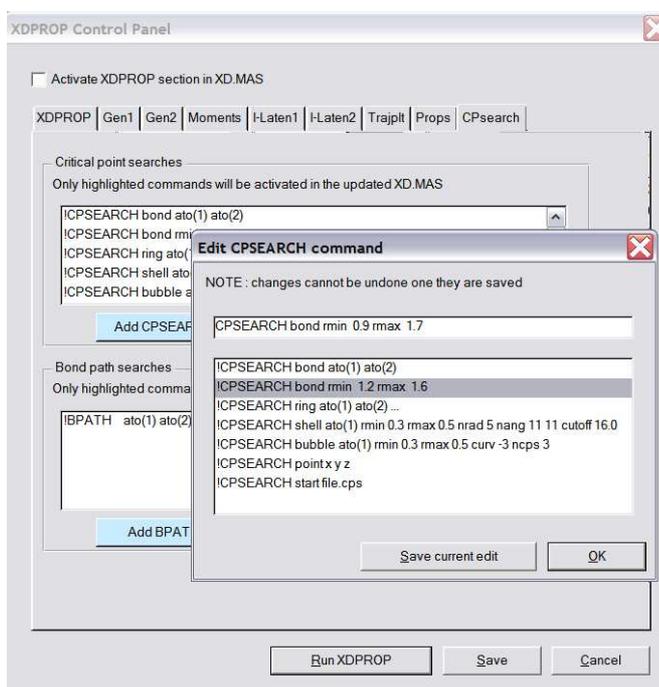
Open xd_pro.out file to see all the atom-atom contributions to the energy.

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 is 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 1.2 – 1.6 Å :



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	
O(1) -C(1)	2.047	1.188	1.2548	0.8031	0.4517	ellip
			-10.73	-10.48	22.40	0.02

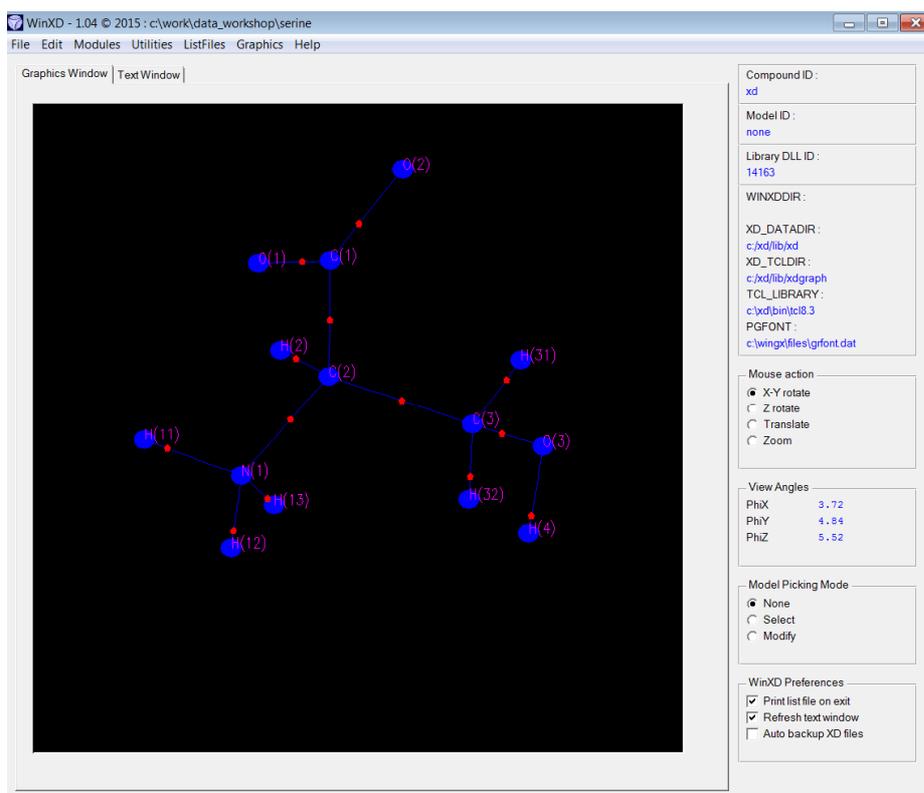
A new feature of XDPROP is the automatic calculation of the entire molecular graph. This can only be done by manual editing of the `xd.mas` file, using the `MOLGR` command

```
MOLGR *auto level 2 rmin 0.8 rmax 3.5 algorithm 2 profile
```

Generally the `auto` option should be selected (`*auto`) and the search level set to 2 to ensure a complete search for the molecular graph. For this option, it is only sensible to search the property `*rho`.

The result may be viewed in the graphic option of the GUI – Molecular graph. Bond critical points are displayed as small red spheres, ring critical points as yellow spheres and cage critical points as green spheres.

For a more detailed examination of the molecular graph, see the bis(carbonyl) annulene example given below.



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.

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).

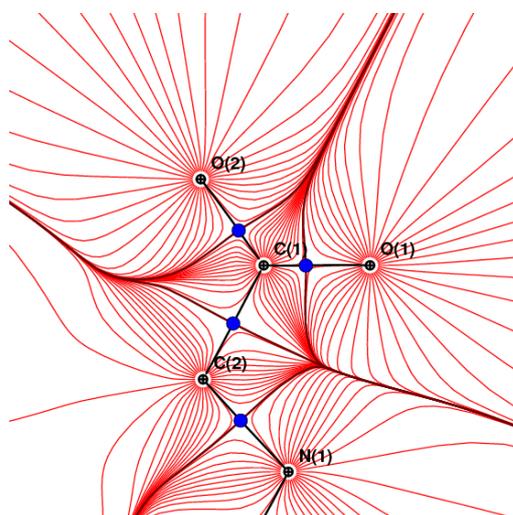
As in case of the other maps, first choose the property (in this case we choose the total density again)

```
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
```

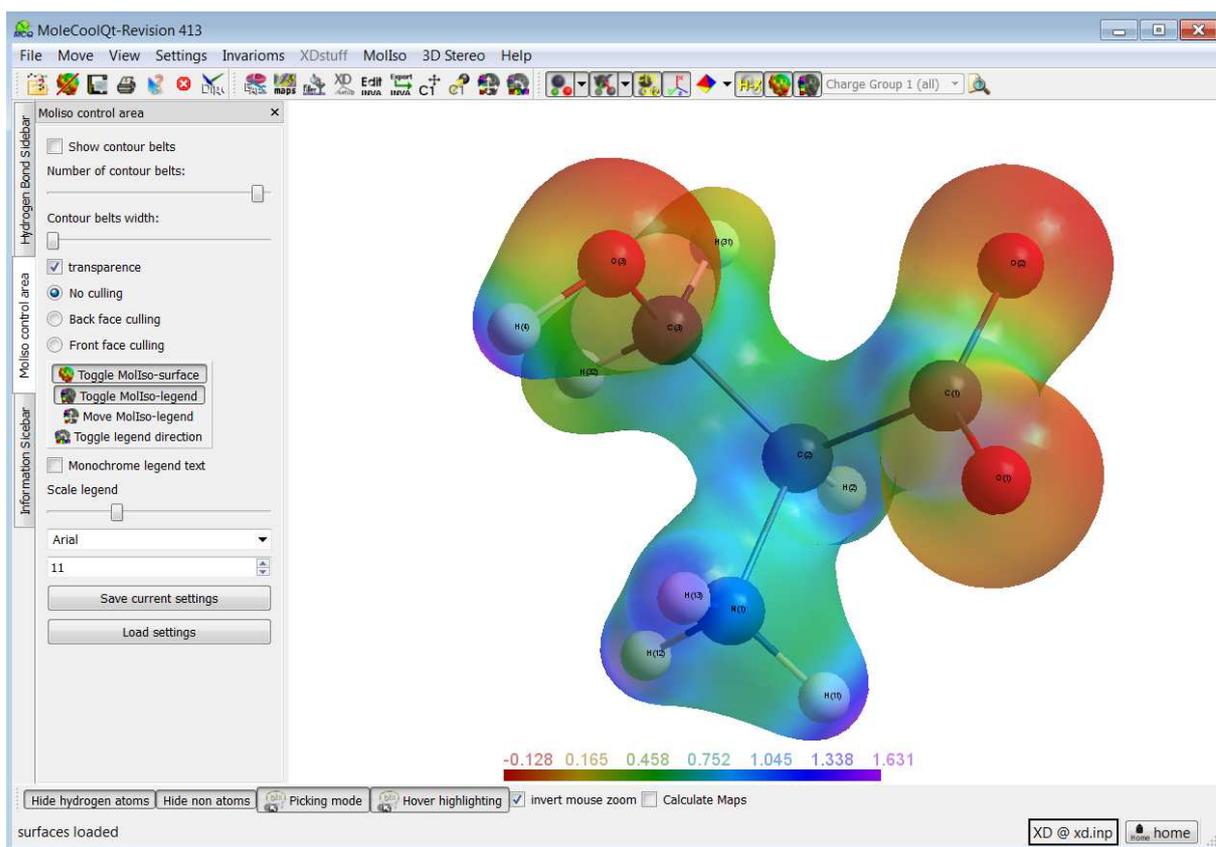
Then run XDPROP. When the calculation is finished, choose the electrostatic potential property

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

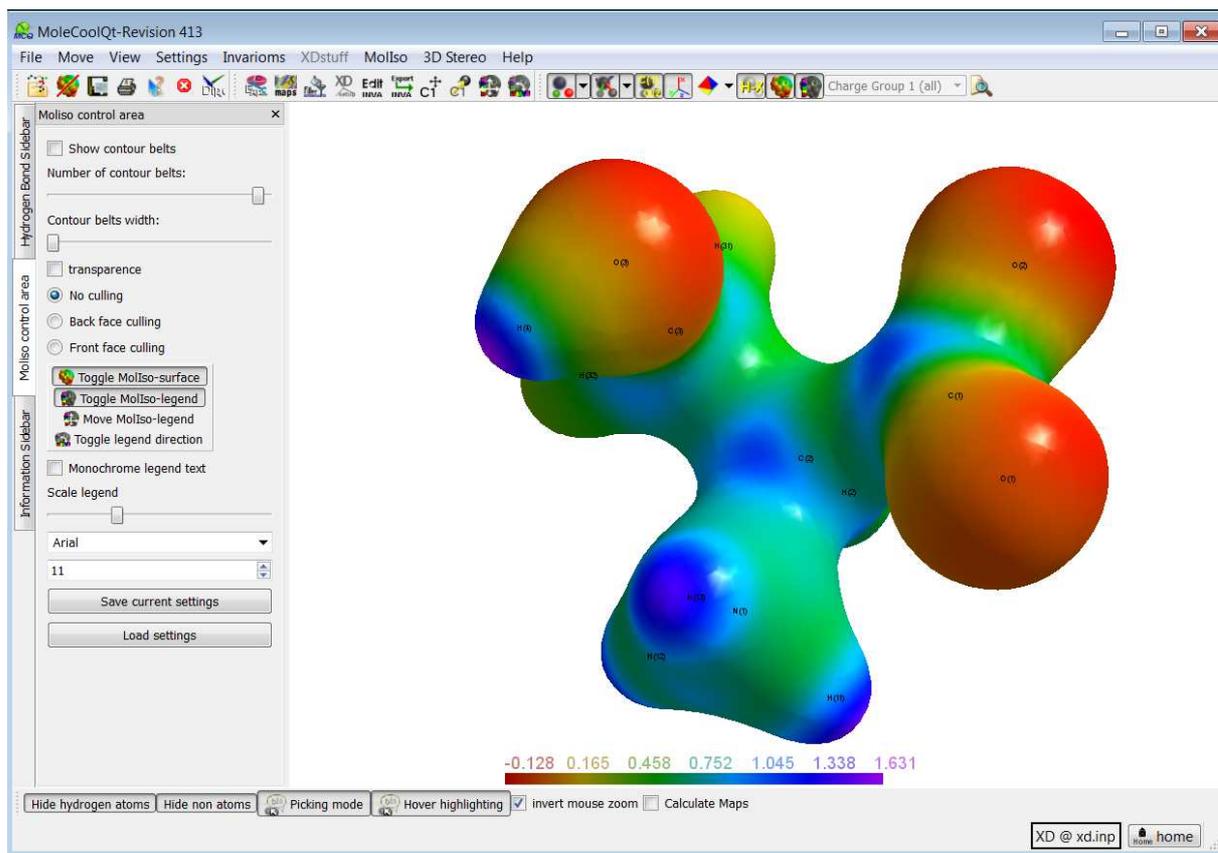
and run XDPROP again. This procedure will create two grid files for each property: `xd_rho.grd` and `xd_rho.cube`, and `xd_esp.grd` and `xd_esp.cube`. The first file contains grid in XDGRAPH format, unfortunately because of some missing 3D libraries, 3D grids cannot be visualized with the Windows version 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 MoleCoolQT program of C. Hübschle to visualise the mapped isosurface. In the WinGX GUI, select **Graphics** → **3D Iso-surface Plot (MoleCoolQT)**. This will give the GUI interface to MoleCoolQT. If properly set up (and program MoleCoolQT is installed – it is NOT a part of WinXD!), the MoleCoolQT program will start. Select Menu item “Moliso”. 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 $0.5 \text{ e}\text{\AA}^{-3}$, with the value of the electrostatic potential at each point on the surface colour coded.

You should then see a plot like this



On the left there is a scale which maps colors to values of ESP (in $\text{e}\text{\AA}^{-1}$). 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 MoleCoolQt program is very versatile, you can rotate, zoom in & out, move the surface as well as change its properties:

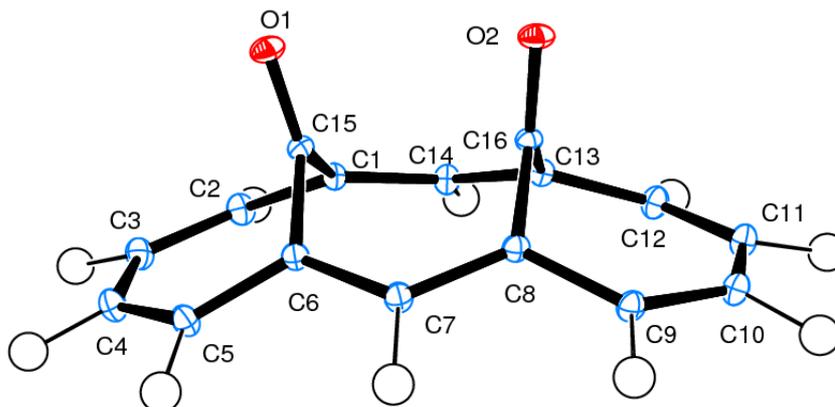
2 - Example # 2 Biscarbonyl-annulene

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 $\sim 0.1\text{\AA}$ 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 $1/\sigma(F_{\text{obs}})$ 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. The molecular graph can be calculated automatically (as described above), but it is also possible to do this by explicit and user defined searches. 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.

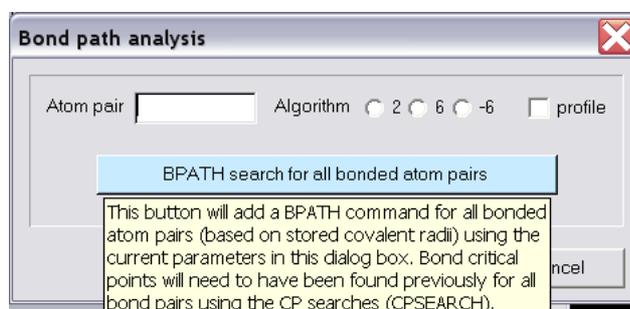
```
CPSEARCH bond C(15) C(16)
CPSEARCH bond C(1) C(6)
CPSEARCH bond C(8) C(13)
CPSEARCH ring C(1) C(2) C(3) C(4) C(5) C(6)
```

```
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)
```

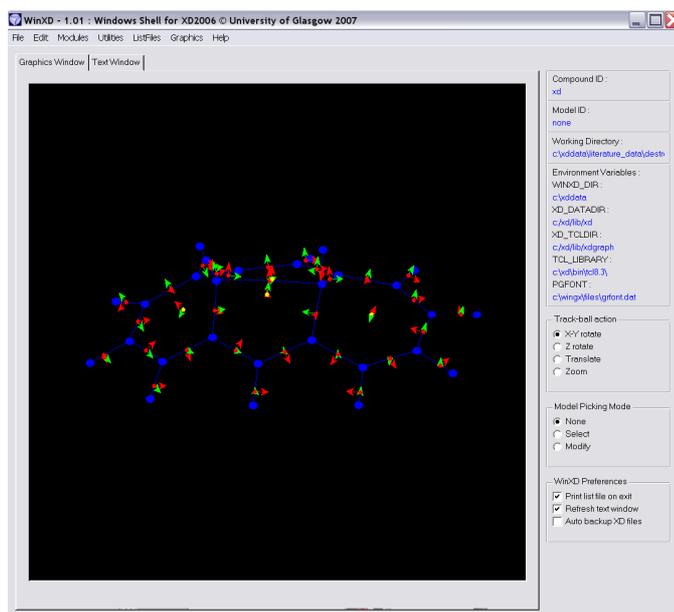
You should now find an extra five critical points, one more (3,-1) cp between C(15)-C(16) and four extra (3,+1) ring critical points. To determine fully the molecular graph, we need to trace the bond paths associated with all these (3,-1) critical points. This is also done in XDPROP, using the BPATH 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) algorithm 2
```

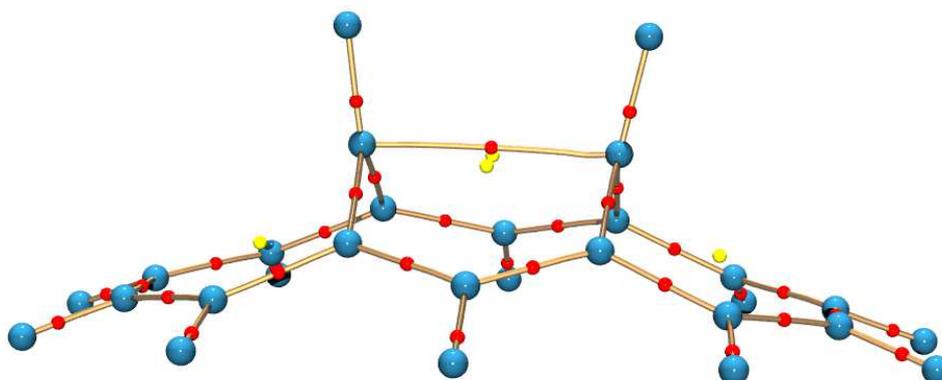
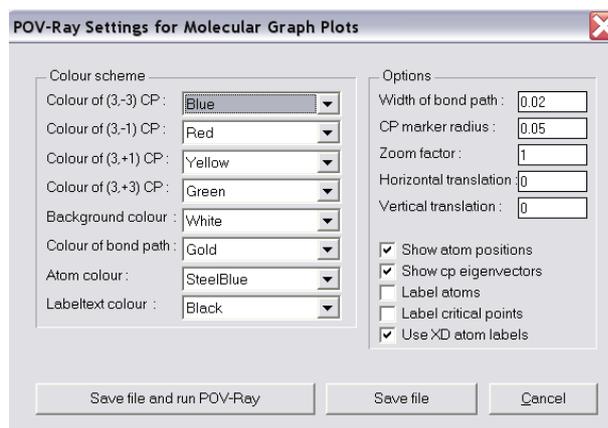
This becomes a bit tedious, but the GUI provides an easier way of doing this. In the WinXD GUI select **Edit → Commands → XDPROP → CPSEARCH → Add Bpath Calculation**



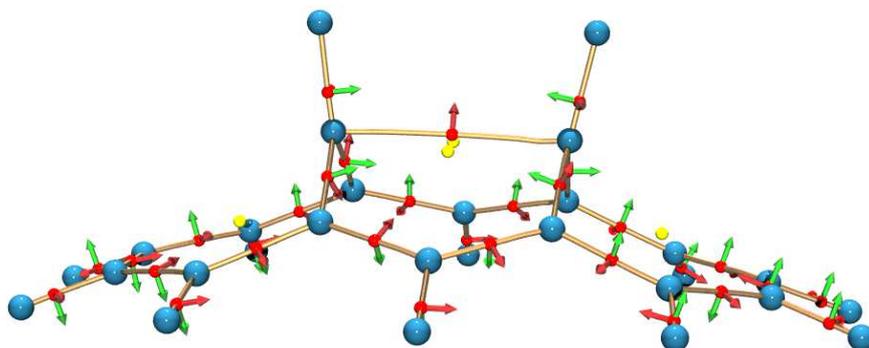
Click on the button "BPATH search for all bonded atoms". This adds one BPATH command for every covalent bond, and it is then only necessary to add the one given above manually. Once the xd.mas file has been set up with all the necessary CPSEARCH and BPATH commands, run XDPROP. This gives the files xd_pro.out 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



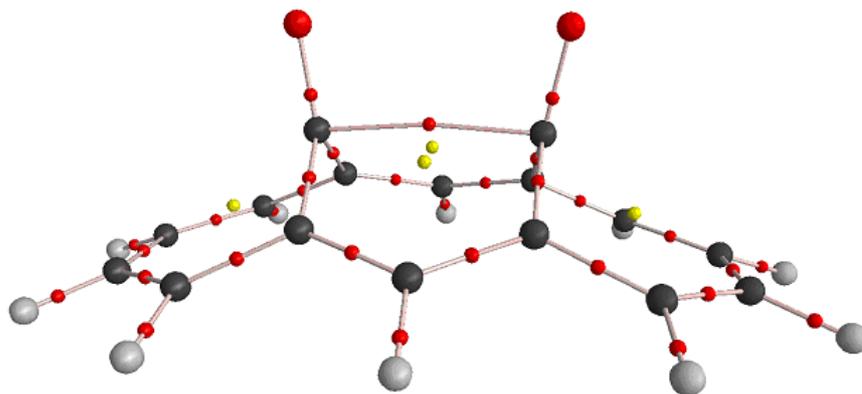
Each critical point (red sphere) is shown with two vectors, in red and green, which represent the major and minor directions respectively of the two negative eigenvectors of the Hessian (and hence the bond ellipticity). The bond path is traced in blue, and other critical points are shown in yellow - (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.



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

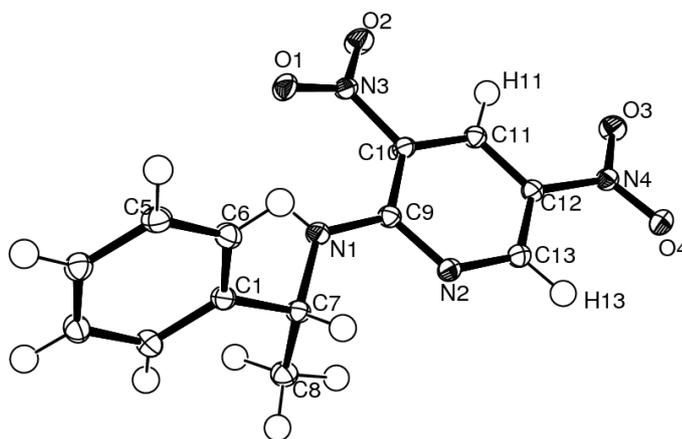
You will already have prepared the SHELX files which can act as a start into the XD refinement. This example presents a more realistic one for a charge density study, in terms of molecular size, than the serine example.

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 arbitrary).
- 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 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 $U_{X\text{-ray}}/U_{\text{neutron}}$ 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, $\langle U_{ii}(\text{X-ray})/U_{ii}(\text{neutron}) \rangle = 1.813$
 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 isotropic (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.

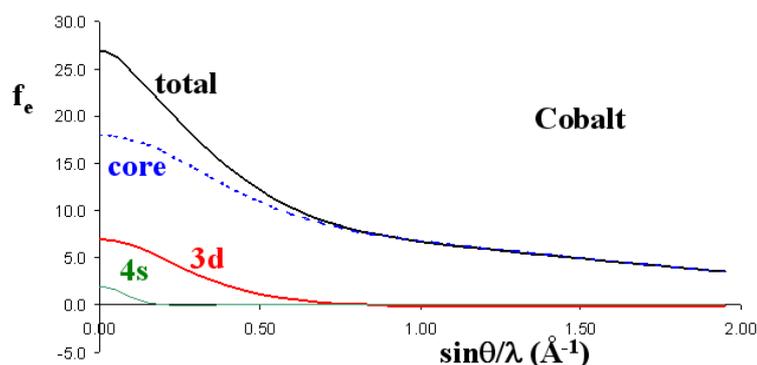
5 - Example # 5 Manganese decacarbonyl

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 is 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 3d electrons scatter to high angle, the scattering power of the 4s electrons falls off rapidly. As a result, information on the 4s 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 4s population



While in principle it is possible to refine separately the 3d and 4s valence populations for a transition metal, this is generally not practically possible, and the 4s 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   CHFV CHFV CSZD  2  2  2  2  6  6  0 -5  0  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 3d population is given as negative (*i.e.* is considered in the valence shell). The 4s 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 4s 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
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 multipole model for this compound, using the SHELX files in the kappa subdirectory as the starting point. The same process as described 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 - 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 reported with yours
2. **Cr₂-hydride** - the organometallic salt $[\text{K}(\text{crypt-222})]^+ [\text{Cr}_2(\mu\text{-H})(\text{CO})_{10}]^-$. The K^+ cation (as is normally found) can be treated effectively as a spherical ion, i.e. no multipole refinement. The Cr 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 $\text{LiAl}(\text{SiO}_3)_2$. 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

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