Example 10.1: AgSbS

Refinement of anharmonic ADPs in Jana2006.

Chemical formula: Ag_3SbS_3

Reference: F. Laufek, J. Sejkora & M. Dušek (2010). Journal of Geosciences, 55, 161–167

Single crystal data measured with Oxford Diffraction four-circle diffractometer
Input files: agsbs.hkl, agsbs.cif_od
Frame scaling, absorption correction: done with software of diffractometer

In this example we shall need installation of VESTA for visualization of electron density associated with anharmonic ADP. VESTA is supplied as a zip archive which can be unpacked to arbitrary location (with simple path – not to Desktop). Then the path to VESTA.exe must be defined in "Parameters → Programs".

1. ***Creating new jobname***
   Start Jana2006
   "File → Structure → New" opens a file manager
   Left pane: locate the directory with input files
   Right pane: double-click agsbs
   Right pane detects possible Jana files and shows one jobname for each group of files

2. ***Import Wizard***
   Select "Known diffractometer formats"; NEXT
   Select "Oxford Diffraction – CCD"; NEXT
   Select "Input from "cif_od" file"; OK
   The used diffractometer software splits reflection file and another information (cell parameters, wavelength …). There are several output formats for both cases.
   Leave all settings unchanged; NEXT
   Leave all settings unchanged; NEXT
   The program reads 11948 reflections from hkl file
   For absorption correction select "None or done before importing"; NEXT
   FINISH

3. ***Data Repository***
   Each line in data repository window corresponds to one data set converted to Jana format. In our case we use only one data set.
   OK; YES to accept the data set

4. ***Symmetry Wizard***
   [On the screen: "Tolerances for crystal system recognition".]
   Symmetry wizard can be started separately by "File → Reflection file → Make space group test.
   Leave all settings default; NEXT
   [On the screen: Select Laue symmetry]
   Select Trigonal -3m1 Laue symmetry; NEXT

Select R-obverse cell; NEXT
[On the screen: Select space group]
Select *R3c*; NEXT
Selecting the non-centrosymmetric space group is a shortcut. It will be explained at "Verification of structure solution".
Accept the space group transformed into the original cell; FINISH
Symmetry is saved in file agsbs.M50.

5. ***Creating refinement reflection file***
In this step program creates file agsbs.M90 containing the data set merged by symmetry and with discarded forbidden reflections. M90 will be used for refinement.
NEXT to confirm threshold 3sigma
[On the screen: settings for merging of reflections]
Leave all settings default; NEXT
The program reports Rint 1.88% for 430 observed reflections merged from 3577 observed reflections.
Accept the new data block and calculate coverage; FINISH

6. ***Structure Solution Wizard***
[On the screen: window of Structure solution].
In "Formula" textbox type list of chemical elements: Ag Sb S
Select "Use Superflip", "Peaks from Jana2006";
Select "Use a specific random seed" and use "222"
Fixing the random seed to 222 guarantees for most processors that the Superflip returns exactly the same results like described in this cookbook. Otherwise each run of Superflip may return different equivalent origin. For normal work random seed should be automatic because the convergence of charge flipping is not guaranteed for every value of random seed.
Leave other settings default; OK
[On the screen: window of Superflip replaced after reaching the convergence with listing of Superflip]
Superflip converges (after noise suppression) with R value (after noise suppression) 16%.
Press CLOSE to leave the listing
Press "Accept the result"

7. ***Verification of the structure solution***
Start EditM50, go to page Composition, enter 6 for "Formula units", press "Formula from M40"
It displays formula Ag3 Sb S3 (for Z=6). This is the same as expected composition.
[On the screen: Information about formula]
OK; YES for updating the formula.
In next steps we shall verify with Superflip that centre of symmetry is not present.
Start "File → Structure → Save As"
Save the structure with jobname "testspg"
YES to continue with the new structure
Start "Run → Solution"
Select "Use Superflip" and press button "Change the space group"
For the "Space group" type R-3c; OK; YES to rewrite M50

Follow steps for creating the refinement reflection file
Merging the data yields Rint 2.11% and the program returns to the structure solution wizard
[On the screen: Structure solution wizard]
OK to start structure solution
[On the screen: listing of Superflip]
At the end of the listing we can see unsatisfactory agreement factor for the symmetry operator "2". This indicates the space group is probably wrong.
Press "Accept the result"
Start EditM50, go to page Composition, enter 6 for "Formula units", press "Formula from M40"
It displays formula Ag0 Sb S6 (for Z=6) which is also wrong
Return to the basic window of Jana2006
Start "File → Structure → History" and open the previous structure (with space group R3c)

8. ***Refinement***

[On the screen: basic window of Jana]
Right-click the icon of Refine.
[On the screen: refinement options]
Define 100 of cycles, damping factor 0.5; OK
Choose "YES+START"
Refinement converges with R value about 12%
Start "Edit atoms"
[On the screen: list of atoms]
Press "Select all" and "Action → Edit/define"
Choose "harmonic" for ADP parameters. *This defines anisotropic temperature parameters for all atoms.* OK, OK, Yes to save changes
Double-click the icon Refine.
Refinement converges with R value about 4%.

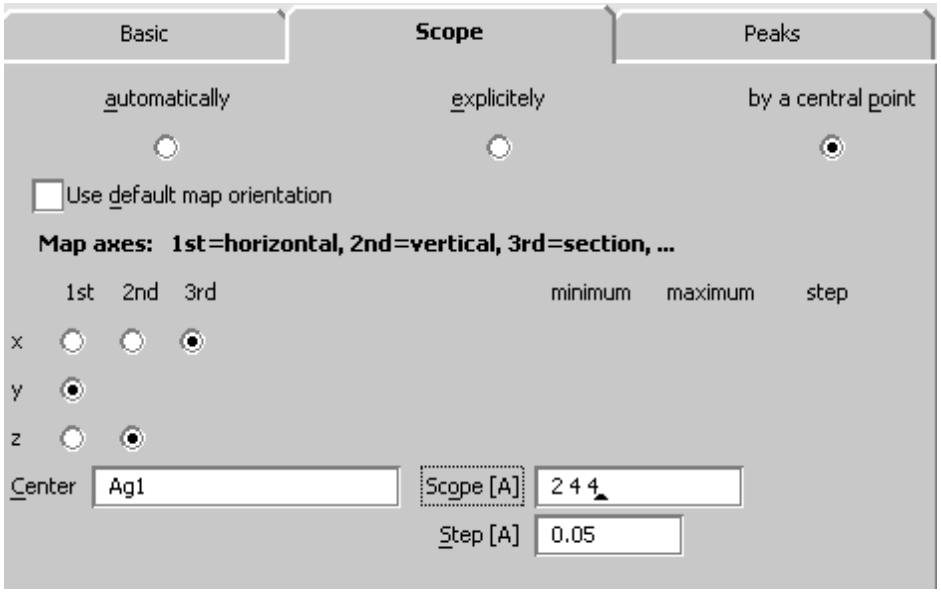
9. ***Extinction correction***

The results seem to be OK, but:
[On the screen: basic window of Jana2006]
Open listing of Refine (by "Edit/View → View of Refine")
Press "Go to" and select "Statistics Fo, sin(th)/lambda after refinement"
R value should decrease with increasing intensity or with lowering the diffraction angle. Here the R value for the strongest reflections as well as for the low angle reflections is higher than in the previous shell. This suggests that extinction correction is required.
Close the refinement listing
"Parameters → Extinction"
Select "Isotropic"; OK
Refinement of extinction coefficient is enabled by default
Double-click Refine and refine the final structure
Refinement converges with R factor 3.67 %.
Check the extinction coefficient through "Parameters → Extinction"
View listing of Refine; Go to "Statistics"; check improved R value for strongest reflections.

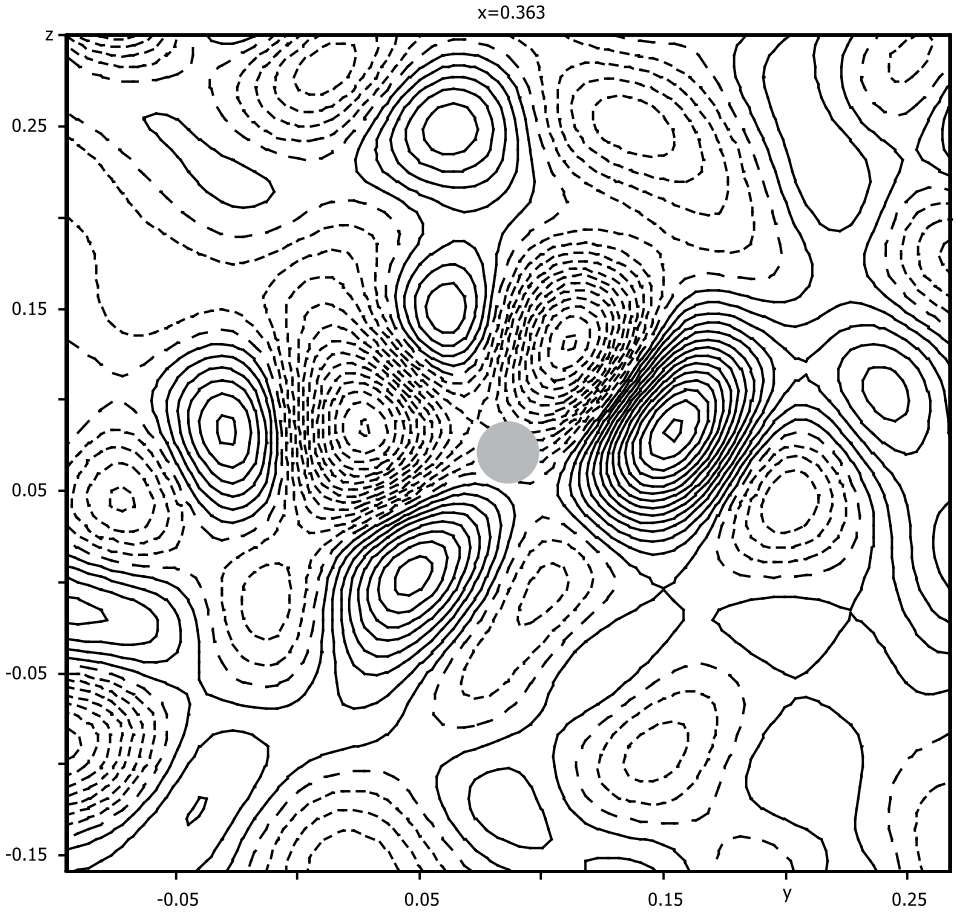
10. ***Anharmonic refinement***

Run Contour, start "New plot" – "Calculate new ones" +" Draw maps as calculated".

Here no previous map exists and therefore "Calculate new ones" will be disabled
[On the screen: Fourier commands]
In Basic thumbnail select "F(obs)-F(calc) – difference Fourier"; leave other settings default In Scope thumbnail define the vicinity of Ag1 according to the following screenshot; OK



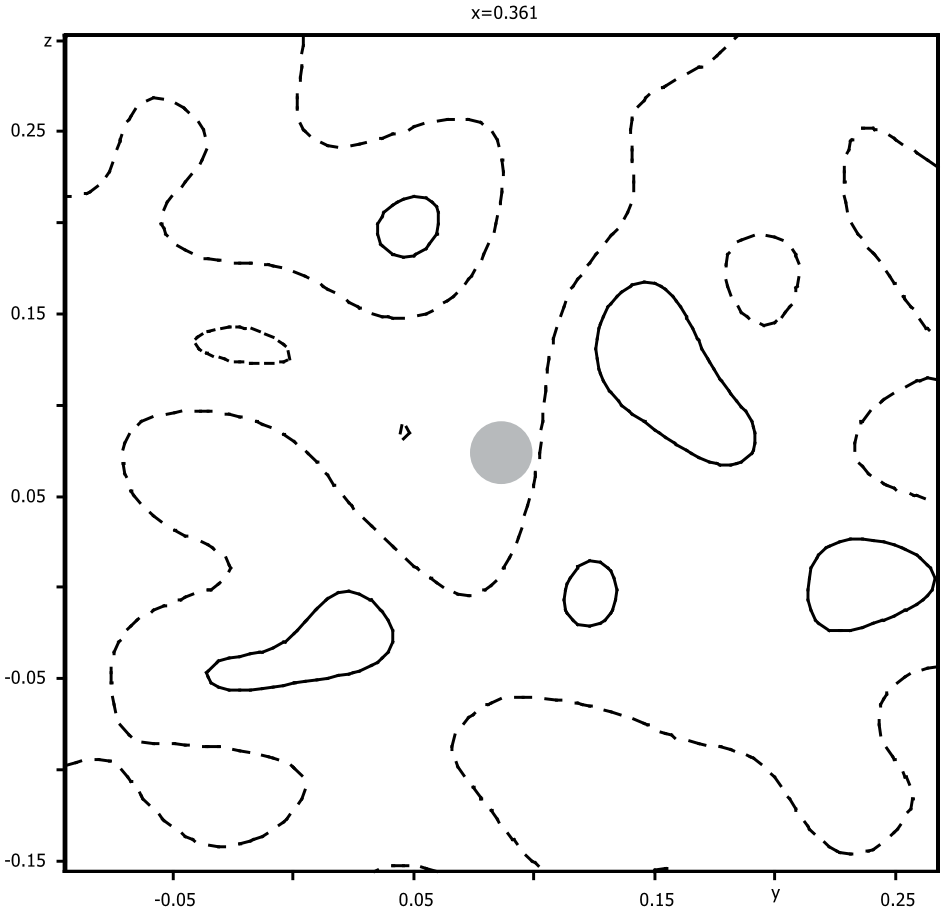
[On the screen: contour plot of the first section]
In "Contours" define both positive and negative contours to 0.1 $e^-/Å^3$;
In "Atoms edit" add Ag1;
Examine the sections using "M+" and "M-"



We can see residua of positive density in the vicinity of the Ag atom.

Quit Contour

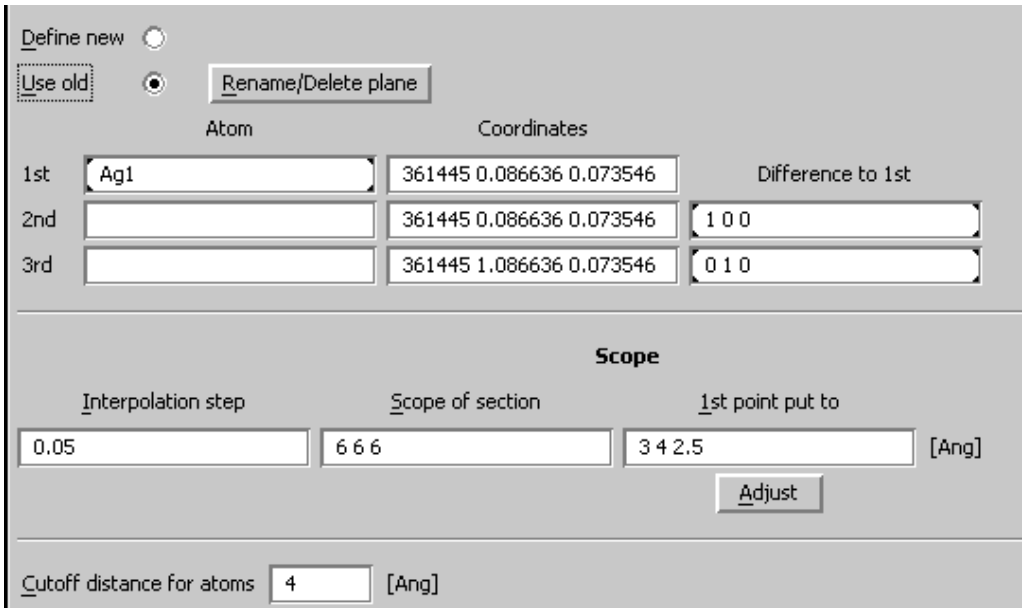
Run "Edit atoms" and select Ag1.
"Action → Edit/define atoms": check "Anharmonic ADP", third order;
Run Refine
Refinement converges with R factor 1.14 %.
In Contour draw the same difference Fourier section as previous (calculate new maps). Use the same limits for contours.



The residua have significantly decreased.

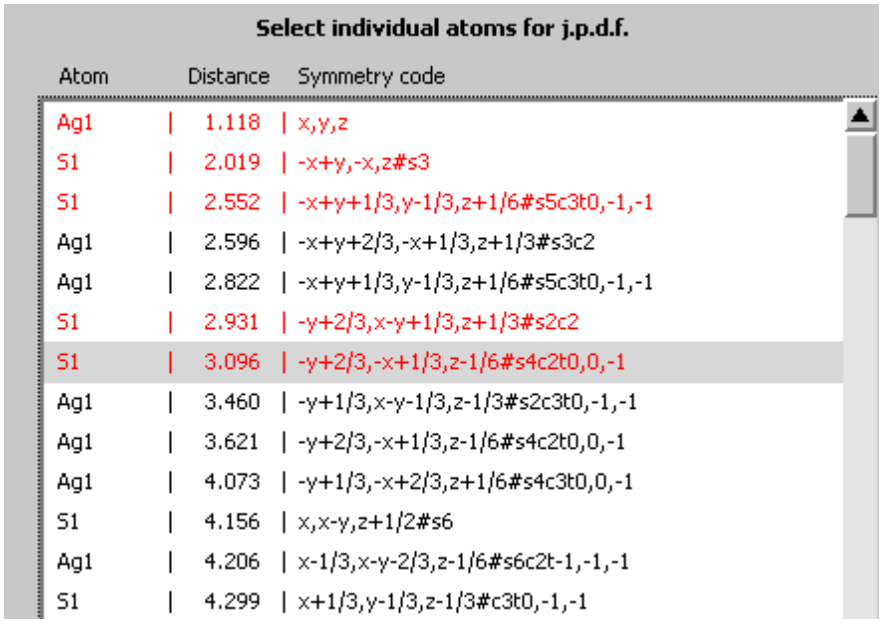
11. *Density modeling using the joint probability density function*

Run Contour, start "New plot" – select j.p.d.f.
[On the screen: Select atoms and basic parameters for j.p.d.f]
Select Ag1 and S1; Next
[On the screen: Plane/Volume]
For 1st atom use Ag1; for the 2nd and 3rd atom use difference to 1st 1 0 0 and 0 1 0, respectively;
Define scope of the section: 6 6 6 and "1st point to" 3 4 2.5;
Use cutoff distance for atoms 4 Å; NEXT



[On the screen: Select individual atoms for j.p.d.f]

Select Ag1, and all symmetry related sulphur atoms close to Ag1 and note their symmetry codes (i.g. S1#s5c3t0,-1,-1); NEXT



Select individual atoms for j.p.d.f.

Atom	Distance	Symmetry code
Ag1	1.118	x,y,z
S1	2.019	-x+y,-x,z#s3
S1	2.552	-x+y+1/3,y-1/3,z+1/6#s5c3t0,-1,-1
Ag1	2.596	-x+y+2/3,-x+1/3,z+1/3#s3c2
Ag1	2.822	-x+y+1/3,y-1/3,z+1/6#s5c3t0,-1,-1
S1	2.931	-y+2/3,x-y+1/3,z+1/3#s2c2
S1	3.096	-y+2/3,-x+1/3,z-1/6#s4c2t0,0,-1
Ag1	3.460	-y+1/3,x-y-1/3,z-1/3#s2c3t0,-1,-1
Ag1	3.621	-y+2/3,-x+1/3,z-1/6#s4c2t0,0,-1
Ag1	4.073	-y+1/3,-x+2/3,z+1/6#s4c3t0,0,-1
S1	4.156	x,x-y,z+1/2#s6
Ag1	4.206	x-1/3,x-y-2/3,z-1/6#s6c2t-1,-1,-1
S1	4.299	x+1/3,y-1/3,z-1/3#c3t0,-1,-1

In "Atoms Edit" of Contour define the Ag1 atom and all four S1 atoms using their symmetry codes.

Press "Run 3d maps"

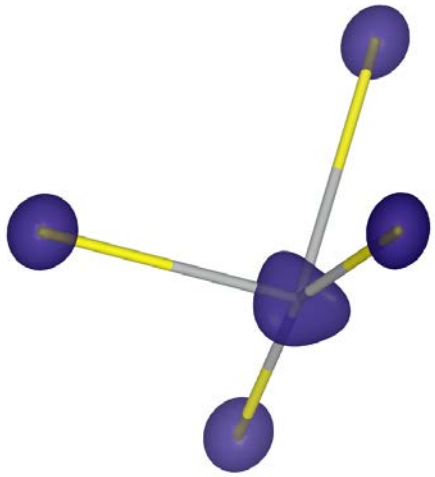
Jana2006 will call an external program for drawing isosurfaces, previously defined in "Tools → Programs", in our case VESTA

Setting drawing options:

In "Edit → Bonds" define bond between Ag and S; maximal distance 3.15 Å,

In "Objects → Structural model" select "Stick",

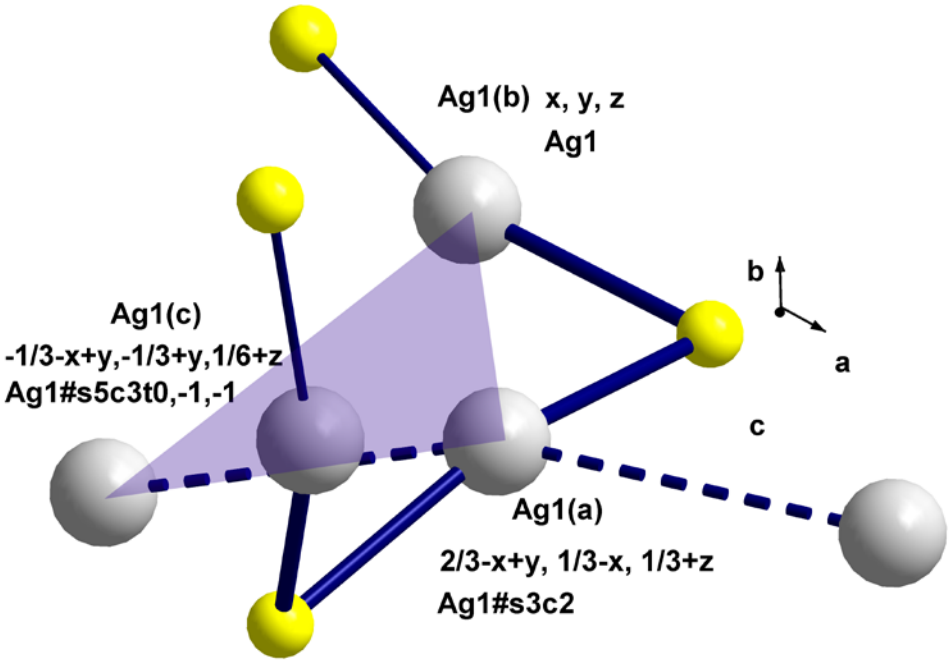
In "Properties" check "Do not show unit cell".



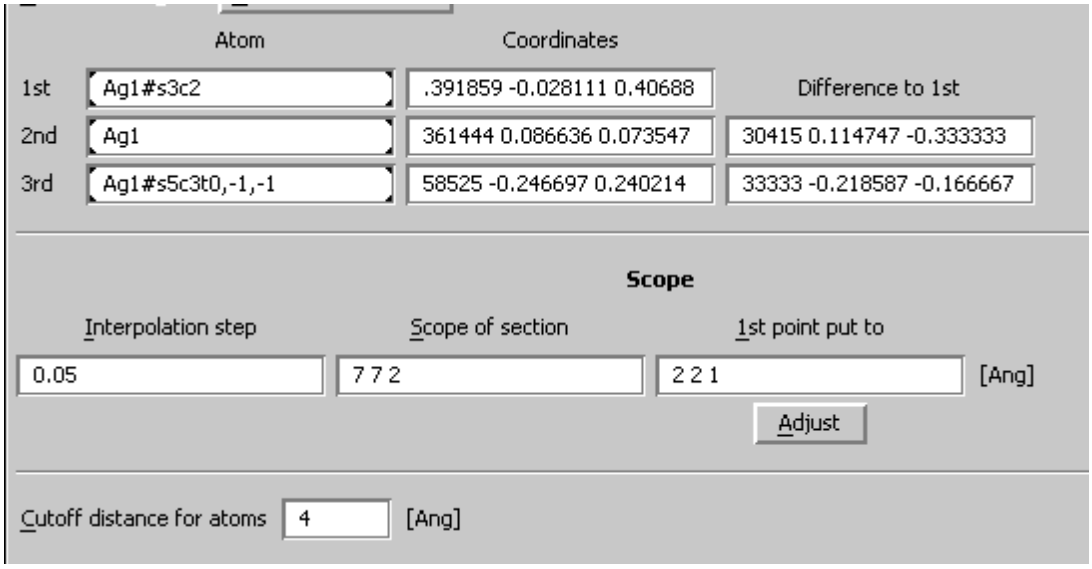
The application of non-harmonic parameters led to the triangular shape of the electron density centered in Ag1 position. The electron density is extended in directions between of Ag-S bonds.

12. **Drawing one particle potential curve**

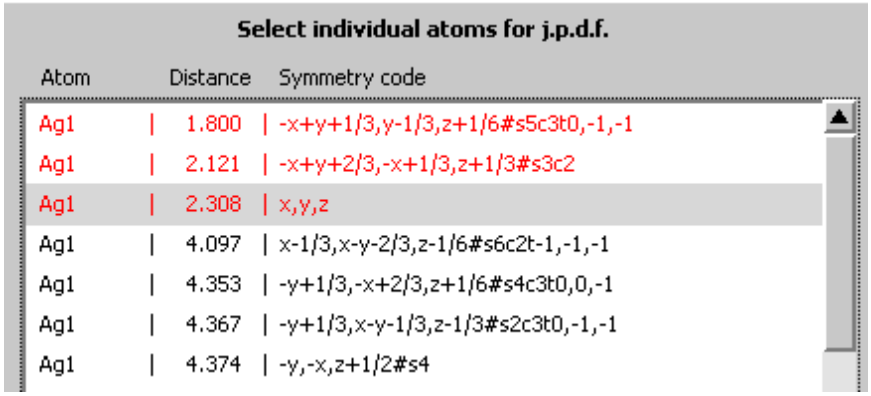
Sulphur and Silver form spirals defined by short Ag-S bonds. The possible exchange paths for silver atoms within and between the spirals can be tested with help of one particle potential along a proposed path. One of proposed paths is shown in the following figure where it goes along sides of the indicated triangle:



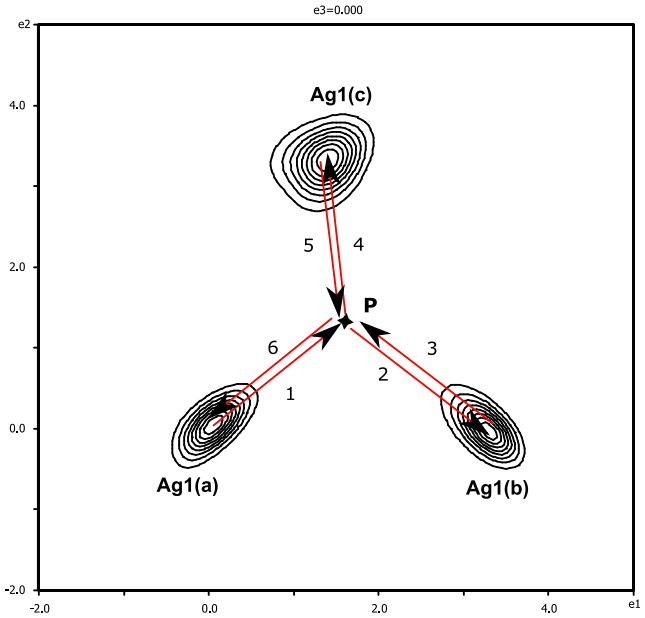
Run Contour, start “New plot” – select j.p.d.f.
[On the screen: Select atoms and basic parameters for j.p.d.f]
Select Ag1; Next
[On the screen: Plane/Volume]
Define the displayed volume according to the following screenshot; OK



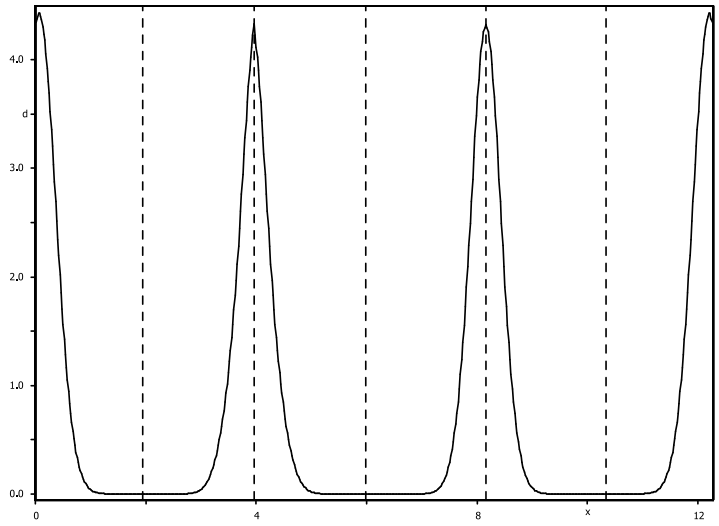
Select Ag1#s3c2, Ag1#s5c3t0,-1,0 and Ag1; NEXT



In “Curves” “Use mouse to define polyline” and draw the line Ag1(a)—P—Ag1(b)—P—Ag1(c)—P—Ag1(a) by mouse (2nd mouse button quits the selection). You can also fill in these points directly in the textboxes of the “Curves” dialogue. Fractional coordinates of the point P are approximately 0.267 -0.63 0.235. Ag atoms should be written with corresponding symmetry codes, i.e. Ag1#s3c2.

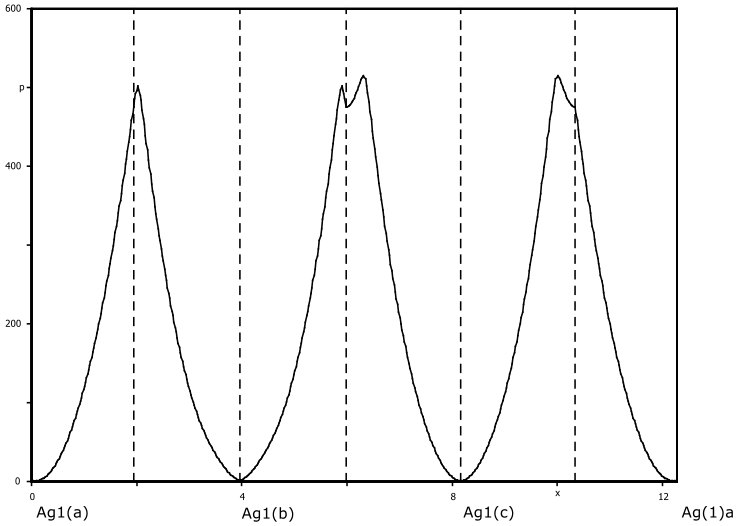


In the first plot we can see an electron density curve. The maximal electron density is located in Ag1 atoms.



Press “Continue”
Adjust “y-Scale”: Min and Max in meV: 0 600;

The resulting curve is one particle potential path. The peaks represent the potential barrier between Ag1 atoms when the exchange path runs through the point P. These values suggest that the silver transfer within and between neighboring Ag–S–Ag spirals is possible.


600
p
400
200
0
0
4
8
x
12
Ag1(a)
Ag1(b)
Ag1(c)
Ag(1)a