# A Practical Guide to Creating Rigid Bodies for GSAS.

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The following gives a practical description of how to calculate coordinates and input rigid bodies in GSAS. [1]

Rigid bodies are useful when working with structures that contain molecules or "rigid" units. Especially when solving a structure from powder data or in the beginning of the refinement of a structure. Calculating rigid body input for GSAS, especially for large three dimensional molecules, may be time consuming. Here a detailed procedure for generating Cartesian coordinates suitable for input to GSAS is given. The description may be used together with available literature on using rigid bodies in GSAS, e.g. the article by Robert Dinnebier [2] giving a thorough and mathematical explanation of the use of rigid bodies in GSAS or the presentation by Ian Swainson [3] giving a quick introduction to rigid bodies in GSAS.

Rigid bodies add a lot of extra information to the calculation, helping to reveal the problems.

When using rigid bodies, meaningless changes within a molecule cannot occur, as the molecule is translated or rotated as one unit. Instead of calculating the positions of all atoms in a molecule, only 6 parameters are needed, the position of the center (x,y,z) and 3 rotation parameters. This saves computing time, and makes it possible to introduce and refine the positions of light atoms, even hydrogen, from the beginning, because their position is defined by the position of heavier atoms. All together this gives a more stable refinement with less probability of divergence and increase the chance of convergence to the correct structure. [4]

The atomic coordinates in a crystal structure are normally given as fractional coordinates, i.e. they are given relative to the axes of the unit cell. This means that as the unit cell changes, e.g. as a function of temperature, the distances between atoms and the angles between atoms may change, even when the atom coordinates are fixed.

The coordinates for the rigid bodies in GSAS are given as Cartesian coordinates. The Cartesian coordinates for an atom are calculated in a Cartesian coordinate system. The angles between the axes are always 90°, and the length of all axes is unity, i.e. 1 Å. The rigid body in the Cartesian system never changes, and it overrides everything else in GSAS. [3]

Calculating the rigid bodies for "smaller molecules", as shown by e.g. Robert Dinnebier [2] and Ian Swainson [3], can be done by calculating the atomic positions in Cartesian coordinates by knowing the bond length and angles.

Bigger and especially 3-dimensional molecules are more difficult, but there is a shortcut – if the molecule can be found in an already existing structure where the atomic coordinates are known. Alternatively an optimized model from energy minimization may be used.

1,3-adamantanedicarboxylic acid is chosen as an example. Though it may appear so, there are no symmetry elements within the molecule.

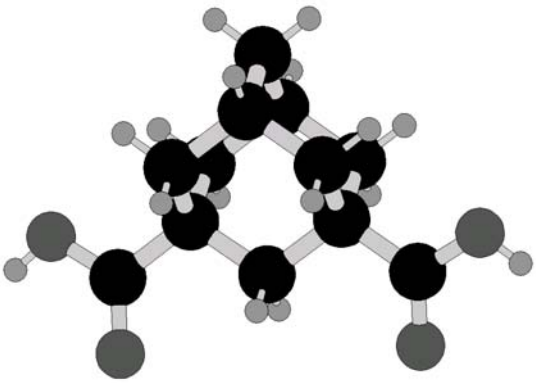

Figure 1

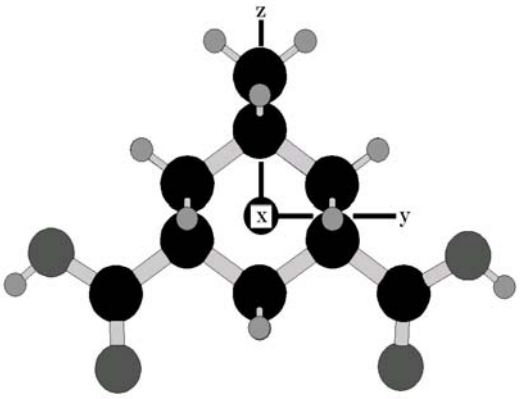


Figure 2

The molecule is 3D (see Figure 1), the formula is $C_{12}H_{16}O_4$ - all in all 32 atoms. This is not a very big molecule, but to calculate the positions of every atom would take a long time.

The crystal structure for the pure compound has been solved [5] and the atomic coordinates are deposited with the IUCr (Reference: CF1046).

The coordinates are stored in a cif file. By importing the cif file in a crystal structure visualization program, e.g. Atoms or Diamond, the molecule can be plotted. To simplify the later calculations, preferably only the molecule that is going to give the Cartesian coordinates should be seen.

A center must be chosen. The point of gravity is a good choice, especially if it lies on a symmetry element, like a rotation axis and/or mirror planes or if it lies close to an “apparent symmetry element”. The most important thing is to choose a logical center i.e. to make sure that the rotation axes are in logic directions within the molecule. If you e.g. have a long linear molecule, make sure that one of the rotation axis are along this line. If there is no atom at the center position, an extra atom must be added.

In this case I wanted to be able to rotate the molecule. I believe the position of the adamantane cage is true, but I am not sure about carboxylic acid groups, so I chose the center of the adamantane cage as my center and added an extra atom there.

The Cartesian coordinate system is always defined from the viewer’s point of view. This means that the molecule should be seen as symmetric as possible (see Figure 2). It also means that if the molecule is oriented in another way, the Cartesian coordinates will change!

Make sure the atoms are named, and let the program make a list of the Cartesian coordinates for all the viewed atoms (including the extra “center atom”.) Preferably the Cartesian coordinates should be given with 6 decimals, because that is what GSAS uses in the calculations.

The list of coordinates must then be written to a file and imported into a spreadsheet, e.g. Excel or a plotting program like SigmaPlot. Remember that Cartesian coordinates can have negative values. I have called these coordinates “found” in Table 1

The molecule is now placed in the Cartesian coordinate system, but the center point is not yet the zero point. In order to displace the molecule in the Cartesian coordinate system, so that the chosen center becomes the real center, the value of the zero point must be subtracted from all the other atoms. This means that the value of the x-coordinate from the found zero point must be subtracted from all x-coordinates, the found y-coordinate from all found y-coordinates and the found z-coordinate from all found z-coordinates.

For the 1,3-adamantanedicarboxylic acid the coordinates will be calculated like this:

Table 1

| Atom | X(found) | Y(found) | Z(found) | | X(calc) | Y(calc) | Z(calc) |
|---|---|---|---|---|---|---|---|
| C1 | 0.125215 | 3.559011 | -3.003911 | | 0.008983 | 1.235495 | -0.388175 |
| C2 | 0.124769 | 2.294231 | -3.873656 | | 0.008537 | -0.029285 | -1.257920 |
| H2A | -0.656665 | 2.297354 | -4.448191 | | -0.772897 | -0.026162 | -1.832455 |
| H2B | 0.912632 | 2.290523 | -4.438775 | | 0.796400 | -0.032993 | -1.823039 |
| C3 | 0.114191 | 1.035055 | -3.004124 | | -0.002041 | -1.288461 | -0.388388 |
| C4 | 1.378799 | 1.042553 | -2.108877 | | 1.262567 | -1.280963 | 0.506859 |
| H4A | 1.391860 | 0.249259 | -1.551107 | | 1.275628 | -2.074257 | 1.064629 |
| H4B | 2.174729 | 1.037293 | -2.663473 | | 2.058497 | -1.286223 | -0.047737 |
| C5 | 1.366578 | 2.297192 | -1.228355 | | 1.250346 | -0.026324 | 1.387381 |
| H5 | 2.162947 | 2.297318 | -0.657143 | | 2.046715 | -0.026198 | 1.958593 |
| C6 | 1.377851 | 3.550827 | -2.111537 | | 1.261619 | 1.227311 | 0.504199 |
| H6A | 2.174817 | 3.556426 | -2.664173 | | 2.058585 | 1.232910 | -0.048437 |
| H6B | 1.388942 | 4.344851 | -1.554300 | | 1.272710 | 2.021335 | 1.061436 |
| C7 | -1.139448 | 3.546896 | -2.109761 | | -1.255680 | 1.223380 | 0.505975 |
| H7A | -1.154700 | 4.340116 | -1.551167 | | -1.270932 | 2.016600 | 1.064569 |
| H7B | -1.934352 | 3.551142 | -2.665089 | | -2.050584 | 1.227626 | -0.049353 |
| C8 | -1.139274 | 1.040096 | -2.108452 | | -1.255506 | -1.283420 | 0.507284 |
| H8A | -1.937039 | 1.032251 | -2.659246 | | -2.053271 | -1.291265 | -0.043510 |
| H8B | -1.147307 | 0.247137 | -1.549726 | | -1.263539 | -2.076379 | 1.066010 |
| C9 | 0.120313 | 2.298935 | -0.351994 | | 0.004081 | -0.024581 | 2.263742 |
| H9A | 0.118834 | 3.086939 | 0.213382 | | 0.002602 | 0.763423 | 2.829118 |
| H9B | 0.121441 | 1.515294 | 0.220001 | | 0.005209 | -0.808222 | 2.835737 |
| C10 | -1.126243 | 2.292852 | -1.230955 | | -1.242475 | -0.030664 | 1.384781 |
| H10 | -1.922200 | 2.293153 | -0.659448 | | -2.038432 | -0.030363 | 1.956288 |
| C11 | 0.056822 | 4.792070 | -3.875989 | | -0.059410 | 2.468554 | -1.260253 |
| C12 | 0.106256 | -0.196955 | -3.881681 | | -0.009976 | -2.520471 | -1.265945 |
| O1 | -0.249491 | 4.740186 | -5.066205 | | -0.365723 | 2.416670 | -2.450469 |
| O2 | 0.336217 | 5.909286 | -3.263214 | | 0.219985 | 3.585770 | -0.647478 |
| H2 | 0.194978 | 6.540434 | -3.767945 | | 0.078746 | 4.216918 | -1.152209 |
| O3 | 0.210543 | -0.160567 | -5.101968 | | 0.094311 | -2.484083 | -2.486232 |
| O4 | -0.004839 | -1.318637 | -3.210086 | | -0.121071 | -3.642153 | -0.594350 |
| H4 | -0.080487 | -1.945052 | -3.734294 | | -0.196719 | -4.268568 | -1.118558 |
| center | 0.116232 | 2.323516 | -2.615736 | | 0.000000 | 0.000000 | 0.000000 |

The three columns to the right contain the three calculated Cartesian coordinates for each atom, and they are the ones to be put in GSAS.

The order of the atoms in the rigid body must be the same as the order of the atoms in the list of atoms in the file. The rigid body does not refer to any atom name, it simply takes the atoms in the order they are listed. This means, that if the atoms and the rigid body are not matched, the atoms will switch positions and be placed at the wrong coordinates.

Personally, I prefer to make sure that the rigid body looks as I expect it, and that the position and rotation is as I want it to be. In order to see this, I import the .EXP-file into the visualization program ATOMS. This gives me an opportunity to look at the structure I am working on to make sure that everything is as I expect. This is especially useful when linking several rigid bodies together. One must remember though, that the atoms are only moved by GSAS by a refinement or a listing of the rigid bodies in the rigid body menu. If the parameters for the rigid body are changed, this will be shown when the rigid bodies are listed. If one uses the ATOMS programme, the .EXP-file can be imported as soon as the rigid bodies have been listed – there is no need to exit EXPEDT.

If the rigid body does not have the correct conformation, e.g. if it contains a carboxylate group that have to be rotated, it is a good idea to keep it as simple as possible in the beginning of a refinement. The rigid body may not have the correct position or the correct orientation, and then it makes no sense initially to refine e.g. the size of the rigid body. The simplest possibility is to use only one “translation vector” fixed to 1.

When the correct position and orientation of the molecule has been found, and refinement is almost finished, then it is time to refine the rigid body too. For example several “translation vectors” can be introduced [2], or the rigid body can be split into smaller fractions held together by soft constrains. (See e.g. [6].)

If a symmetry operation is used within the rigid body, so that some of the atoms are generated from others, it gives a better refinement if only the asymmetric unit is used as a rigid body. To make sure that the molecule still looks as expected, fix the coordinates or rotation parameters that are connected to this symmetry element (e.g. y = 0.25) and do not refine them. The other coordinates and rotation parameters may of course be refined as usual.

When defining a rigid body in GSAS, the number of atoms must be given from the beginning. In this case there are 32 atoms. I choose to have only one translation vector, which I set to one. Then the calculated Cartesian coordinates for each atom are ready to be put in GSAS.

If the rigid body is defined from the program, all coordinates must be typed in. For more advanced users a smaller rigid body might be defined, and then enlarged by “copy and paste” directly into the .EXP-file. If this is done, remember to change the number of atoms.

If the rigid body of 1,3-adamantanedicarboxylic acid is defined in GSAS with one translation vector set to one and the above mentioned Cartesian coordinates, the end of the .EXP-file would look like this:

```
RGBD  NRBDS     1
RGBD 1 NATR    32
RGBD 1 NBDS     0
RGBD 1 NSMP     1
RGBD 11PARM    1.00000    0    0
RGBD 11SC  1  0.008983  1.235495 -0.388175
RGBD 11SC  2  0.008537 -0.029285 -1.257920
RGBD 11SC  3 -0.772897 -0.026162 -1.832455
RGBD 11SC  4  0.796400 -0.032993 -1.823039
RGBD 11SC  5 -0.002041 -1.288461 -0.388388
RGBD 11SC  6  1.262567 -1.280963  0.506859
RGBD 11SC  7  1.275628 -2.074257  1.064629
RGBD 11SC  8  2.058497 -1.286223 -0.047737
RGBD 11SC  9  1.250346 -0.026324  1.387381
RGBD 11SC 10  2.046715 -0.026198  1.958593
RGBD 11SC 11  1.261619  1.227311  0.504199
RGBD 11SC 12  2.058585  1.232910 -0.048437
RGBD 11SC 13  1.272710  2.021335  1.061436
RGBD 11SC 14 -1.255680  1.223380  0.505975
RGBD 11SC 15 -1.270932  2.016600  1.064569
RGBD 11SC 16 -2.050584  1.227626 -0.049353
RGBD 11SC 17 -1.255506 -1.283420  0.507284
RGBD 11SC 18 -2.053271 -1.291265 -0.043510
RGBD 11SC 19 -1.263539 -2.076379  1.066010
RGBD 11SC 20  0.004081 -0.024581  2.263742
RGBD 11SC 21  0.002602  0.763423  2.829118
RGBD 11SC 22  0.005209 -0.808222  2.835737
RGBD 11SC 23 -1.242475 -0.030664  1.384781
RGBD 11SC 24 -2.038432 -0.030363  1.956288
RGBD 11SC 25 -0.059410  2.468554 -1.260253
RGBD 11SC 26 -0.009976 -2.520471 -1.265945
RGBD 11SC 27 -0.365723  2.416670 -2.450469
RGBD 11SC 28  0.219985  3.585770 -0.647478
RGBD 11SC 29  0.219985  3.585770 -0.647478
RGBD 11SC 30  0.094311 -2.484083 -2.486232
RGBD 11SC 31 -0.121071 -3.642153 -0.594350
RGBD 11SC 32 -0.196719 -4.268568 -1.118558
ZZZZZZZZZZZZ  Last EXP file record
```

Stating that: There is one rigid body. It consists of 32 atoms. It is used 0 times in all phases. One translation vector is needed to build the rigid body. The translation vector has the value of 1, it has no damping and is not refined.

Now the rigid body is ready for use.

When inserting a rigid body in GSAS, one must know which number the first atom in the rigid body has. The position of the origin of the rigid body is given in fractional coordinates. There are six rotation parameters in a defined rigid body. Only three are needed for describing the orientation, but it is possible e.g. to use the first three to give a rotation and the last three to refine the rotation. Personally I only use the first three and fix the rest at zero.

When refining the parameters in the rigid body, they must be given a refinement number. If two parameters are given the same number, the value of these parameters will change equally, that makes it possible e.g. to keep the origin of the rigid body on a unit cell diagonal. If the number is 0, the parameter is not refined.

For further information about refinement of rigid bodies, see the GSAS manual.

References:


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[3] Swainson, Ian, The fireside Guide to Rigid Bodies in GSAS. *www.ccp14.ac.uk* (2001).

[4] Scheringer, C., Least-squares refinement with minimum number of parameters for structures containing rigid-body groups of atoms. *ACTA Crystallographica* **16** (6) (1963).

[5] Glidewell, Christopher; Ferguson, George, 1,3-Adamantanedicarboxylic Acid and 1,3-Adamantanediacetic Acid. *Acta Cryst.* **C** (52), 1466 (1996).

[6] Nielsen, Renie Birkedal, Kongshaug, K.O., and Fjellvåg, H., Delamination, synthesis, crystal structure and thermal properties of the layered metal-organic compound Zn(C12H14O4). *Journal of Materials Chemistry* **18** (9), 1002 (2008).