

ZenGen: a tool to generate ordered configurations for systematic DFT calculations

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Abstract

”ZenGen” is a script-tool which helps to automatically generate first-principles input files of all the ordered configuration compounds of a given crystal structure. The heat of formation of every end-members can then be easily used in the thermodynamic modelling of the considered phase. ”ZenGen” is a free and open source code, which can be download at <http://zengen.cnrs.fr>.

1 Introduction

The field of thermodynamic modeling has been recently stimulated by the progress of techniques allowing the calculation of thermodynamic quantities from first-principles calculations, such as Density Functional Theory (DFT). These methods allow the estimation of formation enthalpies of fully ordered compounds, taking into account their crystal structures. These calculations can be done not only for stable compounds, but also for metastable ones which play an important role in the description of these phases within the Compound Energy Formalism (CEF). They can also be done not only for the stoichiometric composition corresponding to the normal arrangement of the atoms over the sites, but also for any other ordered distribution of atoms. By using CEF, any intermetallic phase could be described by a sublattice model for which every ordered configuration heat of formation has to be calculated using one sublattice per crystal site. As an example, a binary phase with five crystal sites, described in a five sublattice model generates $2^5 = 32$ different ordered configurations, a ternary phase $3^5 = 243$... a huge number, but which can be calculated with today’s super-computers.

Technically, performing calculation on a large number of end-members may cause two types of problems: (i) a mistake in the distribution of atoms among all different sites; (ii) a too fast relaxation of crystal structure, thus losing the initial symmetry.

To avoid these kinds of errors, the free and open source ”ZenGen” code was born. This code can be installed on Unix-Linux machines and uses Bash, Perl and Python languages. It requires as input the name of the n different elements and name of the phase φ under consideration which crystal structure is constituted by m different sites, then, ZenGen decomposes the process into three steps:

1. Automatic generation of all the n^m ordered configurations input files;
2. Setup of the convergence criteria and relaxation steps of the φ phase;
3. Job execution under the same conditions;
4. Collection of output results (total energy, crystallographic parameters) and generation of TDB file.

ZenGen has been designed for VASP program¹, but can be easily adapted to other first-principles codes. It has been tested on several phases, such as Laves phases ($C14$, $C15$...), or other topologically close packed phases ($A12$, $A13$, $D8_b$, P , δ , ...). It could also be used for managing SQS calculations.

2 The ZenGen work flow details

The work flow of ZenGen is shown schematically in the following diagram:

1 - generate ordered configurations

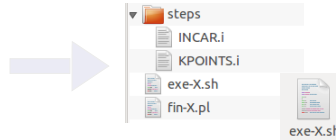
```
$ zengen.pl
```

phase?
elements?



2 - set-up calculations

relaxation steps?
configurations?



3 - execute DFT calculations

```
$ ./exe-X.sh
```

```
FOR i = relaxation steps
  FOR j = configurations
    DO VASP
```

4 - post-treatment

```
$ ./fin-X.pl
```



As shown in the schematic algorithm, the ZenGen is described using the 4 following steps:

1. Generate ordered configurations

By the command:

```
$ zengen.pl
```

the user should inform the structure ($X = C14$, chi -phase, SQS type...), and the system nature (name of the elements). The `zengen.pl` script will create a folder containing all the ordered configurations labeled into subfolders, including all the files needed to perform DFT calculations.

¹G. Kresse and J. Hafner. Ab initio molecular dynamics for liquid metals. Phys. Rev. B, 47:558, 1993. G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B, 54:11169, 1996.

2. **Set-up calculations** The calculations is built into 2 interlinked loops: one about the configurations to be calculated, one about the relaxation step. The `exe-X.sh` file have to be set-up regarding the particular demand. At least, give the minimum and maximum numbers of the configurations, and the minimum and maximum numbers of the relaxation step. See 5.1 for more details.
3. **Execute DFT calculations** after the set-up of the `exe-X.sh` file, its execution can be done in blind process mode by:

```
$ nohup ./exe-X.sh &
```

4. **Post-treatment** after the calculation, the post-treatment is made by the command:

```
$ ./fin-X.pl
```

This script generates several files: a temporary file `pos.out`, a summary file `sum.out`, and a database file `file.TDB`. The `sum.out` file contains the total energy, cell parameters, internal positions and magnetic moment of every configuration calculated by `exe-X.sh`. The `file.TDB` file can be used with a thermodynamic modelling software, such as Thermo-Calc.

3 Installation

ZenGen has been written and tested with `bash` shell, and requires that `perl` and `python` are installed.

It is not necessary to have `VASP` installed on the local machine where ZenGen will be installed; however, it will be easier to have a copy of the potential files for the generation of `POTCAR` files.

To proceed to the installation, open and go into the installation package:

```
$ tar -xzf zengen-install.tar.gz
$ cd zengen-install
```

Set-up is needed. Open and modify the three lines of the `install.sh` file:

```
dir=/home/user/zengen
potdir=/home/user/POT/potpaw_PBE
profile=/home/user/.bashrc
```

The `dir` and `potdir` directories correspond to the target folder that you wish to use as the installation folder, and to the folder where the `VASP` pseudopotentials files are present, respectively. The set-up file path should be also indicated with the `profile` variable.

The installation will be done by using the command:

```
$ ./install.sh
```

All the necessary files and 4 directories will be copied into the `dir` folder:

- ZEN: folder of intermetallic structure files
- SQS: folder of quasi-random solution files
- pure: folder with reference energies (pure elements calculated in 5 sets of cut-off energy in different structures)
- tools: folder with several useful scripts

4 Tutorial: ZenGen use with an example

Open a new terminal, and type:

```
$ zengen.pl
```

As an input, give the code of the **first column** of the studied phase. For example, if the α -Mn (A12) is chosen, type `c` or `chi`.

```
#####  
## 1) choice of the studied phase;  
#####  
code    # phase  # prototype # Space Group # Pearson # Nb # comment  
#####  
c (chi) # A12   # alpha-Mn # I-43m   (217) # cI58   # 4 # chi phase  
b (betMn) # A13   # beta-Mn  # P4_132  (213) # cP20   # 2 # beta-Mn  
C14      # C14   # MgZn2    # P6_3/mmc (194) # hP12   # 3 # Laves AB2  
C15      # C15   # Cu2Mg    # Fd-3m   (227) # cF24   # 2 # Laves AB2  
C36      # C36   # MgNi2    # P6_3/mmc (194) # hP24   # 5 # Laves AB2  
C36-3s   # C36-3ss # MgNi2    # P6_3/mmc (194) # hP24   # 3 # 3 sublattices  
  
... (list of all phases available) ...  
  
# # # # # #  
#####  
Phase?  
chi
```

Then, the name of the elements have to be given, separated by a space. For our example, you could try a binary system ($n = 2$), as Mo-Re, but there is no limitation of the number of elements.

```
#####
## 2) choice of the element(s)?
#####
Ac Be Ce Cu F_h H Ho_3 Li N Ni P Pr Rh_pv Sm Te U Y_sv
Ac_s B_h Ce_3 Cu_pv F_s I Li_sv Na Ni_pv Pa Pr_3 Ru Sm_3 Th
Ag Bi C_h Dy_3 Ga In Lu Na_pv Np Pa_s Pt Ru_pv Sn Th_s V

... (list of all potentials available) ...

#####
Elements separated by a space? [A B ...]

Mo Re
```

We advise you to give elements in a systematic order, *e.g.* an alphabetical order. Then a summary table is printed out:

```
#####
Studied phase = chi
nb of inequivalent sites = 4
table of multiplicity = 1 4 12 12
table of element = Mo Re
nb of element = 2
nb of ordered configurations = 16
#####
Is it alright? [y/n]

y
```

In this example, the phase is composed of $m = 4$ inequivalent sites of multiplicity 1, 4, 12, 12 corresponding to the $2a$, $8c$, $24g_1$, $24g_2$ sites of the χ -phase ($I\bar{4}3m$ space group), respectively². The study of a binary system ($n = 2$) leads to $2^4 = 16$ ordered configurations. Please press y if it is fine for you.

Then the ZenGen code starts its generation procedure, depending of the size of the system it could take several seconds (several minutes if more than 4000 different configurations). Configurations are (i) sorted with, first, the unary compositions, then the binaries, ternaries, quaternaries..., (ii) sorted by increasing the concentration of first element, then second element..., and for a degenerated composition compounds (iii) sorted by filling first element on later sites... A summary table of all the sorted ordered configurations, referred to the name of element on each site and concentration of elements, is printed as follows (a copy is done into a file called `conf.out`):

```
#####
1 Mo Mo Mo Mo 1.000 0.000
2 Re Re Re Re 0.000 1.000
3 Re Mo Mo Mo 0.966 0.034
```

²Since calculation is done in the irreducible primitive cell, in this case, the multiplicity of site is divided by 2 because of centered cubic character of this phase.

```

4   Mo Re Mo Mo 0.862 0.138
5   Re Re Mo Mo 0.828 0.172
6   Mo Mo Re Mo 0.586 0.414
7   Mo Mo Mo Re 0.586 0.414
8   Re Mo Re Mo 0.552 0.448
9   Re Mo Mo Re 0.552 0.448
10  Mo Re Re Mo 0.448 0.552
11  Mo Re Mo Re 0.448 0.552
12  Re Re Re Mo 0.414 0.586
13  Re Re Mo Re 0.414 0.586
14  Mo Mo Re Re 0.172 0.828
15  Re Mo Re Re 0.138 0.862
16  Mo Re Re Re 0.034 0.966
#####

```

A new folder will be created, named after the phase name and the elements separated by an hyphen symbol, *i.e.* `chi-Mo-Re` in our case. This folder contains numbered folders of every ordered configuration, with initial input files corresponding to the labelled compound. In our example, the folder 10 presents 2 files: the POTCAR corresponding to the concatenation of Mo and Re POTCAR files³; and the POSCAR.ini file corresponding to the {Mo Re Re Mo} configuration in the χ -phase⁴:

```

chi-10- Mo Re Re Mo
1.0
-4.792345 4.792345 4.792345
4.792345 -4.792345 4.792345
4.792345 4.792345 -4.792345
13 16
Selective dynamics
Direct
0.000000 0.000000 0.000000 F F F ! A01 (2a) - Mo
0.3754030 0.3754030 0.1824065 T T T ! D01 (24g2) - Mo
0.1929965 0.1929965 0.8175935 T T T ! D02
0.8070035 0.6245970 0.000000 T T F ! D03
0.6245970 0.8070035 0.000000 T T F ! D04
0.1824065 0.3754030 0.3754030 T T T ! D05
0.8175935 0.1929965 0.1929965 T T T ! D06
0.000000 0.8070035 0.6245970 F T T ! D07
0.000000 0.6245970 0.8070035 F T T ! D08
0.3754030 0.1824065 0.3754030 T T T ! D09
0.1929965 0.8175935 0.1929965 T T T ! D10
0.6245970 0.000000 0.8070035 T F T ! D11
0.8070035 0.000000 0.6245970 T F T ! D12
0.6468555 0.6468555 0.6468555 T T T ! B01 (8c) - Re
0.000000 0.000000 0.3531445 F F T ! B02
0.000000 0.3531445 0.000000 F T F ! B03
0.3531445 0.000000 0.000000 T F F ! B04
0.3962520 0.3962520 0.7121445 T T T ! C01 (24g1) - Re
0.6841075 0.6841075 0.2878555 T T T ! C02
0.3158925 0.6037480 0.000000 T T F ! C03
0.6037480 0.3158925 0.000000 T T F ! C04
0.7121445 0.3962520 0.3962520 T T T ! C05
0.2878555 0.6841075 0.6841075 T T T ! C07
0.000000 0.3158925 0.6037480 F T T ! C06
0.000000 0.6037480 0.3158925 F T T ! C08
0.3962520 0.7121445 0.3962520 T T T ! C09
0.6841075 0.2878555 0.6841075 T T T ! C10
0.6037480 0.000000 0.3158925 T F T ! C11
0.3158925 0.000000 0.6037480 T F T ! C12

```

³order of concatenation of multi-elements compounds is the same as the order of input elements

⁴literature average crystal parameters of the phase are taken as the initial values

The `chi-Mo-Re` folder contains also a `steps` folder which contains all the `INCAR.n` and `KPOINTS.n` files, with n the step number. In fact, in order to control the relaxation scheme, each implemented phases has been tested to be relaxed in a specific way. In our example of χ -cubic phase, **we propose** a 5-step procedure: first a volume relaxation is done, then the internal parameters are relaxed, then the meshing of k -points increases, and finally a static calculation using the tetrahedron method with Blöchl corrections. Naturally, **everyone can modify the input files of the steps folder with his own preference**. Most important is that calculation will be done using the same convergence criteria for every configuration. As an example, the default cut-off energy is set at 400 eV, but can be manually changed in all the necessary input files.

The `chi-Mo-Re` folder also contains two executable scripts: `exe-X.sh` and `fin-X.pl`. The first one is the executable `exe-X.sh` file which allows to perform the VASP calculations by 2 interlinked loops: one variable is the configuration and the other the step. A detailed explanation of the set-up of this file is done on section 5.1. At least, some parameters have to be set up like the variable range of configurations and the steps. In the following example, calculation will only be run on the binaries configuration (compounds number 3 to 16), from step 0 to step 5:

```
# Which compound?
CMIN=3 # Minimal Compound number
CMAX=16 # Maximal Compound number
# Which STEP?
SMIN=0 # Minimal relaxation step
SMAX=5 # Maximal relaxation step
```

Then, comes the most time consuming part: the DFT calculation of every compound by each relaxation step. Depending of the phase nature, number of elements, and ... your computer facilities, it takes more or less time. Written in the `exe-X.sh` file, the syntax depends on your VASP execution procedure, see section 5.1 for details.

After the full DFT calculation, the execution of the finalization script, `fin-X.pl`, provides a summary `sum.out` file, which indicates total energies, relaxed parameters... as follows:

```
#PBE 2a 8c 24g1 24g2 : energy | cubic cell par. | Volume X_8c X_24g1 Z_24g1 X_24g2 Z_24g2
chi-3- Re Mo Mo Mo : -621.992644 eV 9.742636932 924.76 0.31863219 0.36199639 0.04734459 0.09364659 0.28324695
chi-4- Mo Re Mo Mo : -630.436204 eV 9.722293058 918.98 0.31867283 0.36197108 0.04848883 0.09322655 0.28305483
chi-5- Re Re Mo Mo : -632.902352 eV 9.713127816 916.38 0.31948973 0.36196150 0.04878494 0.09334232 0.28252237
chi-6- Mo Mo Re Mo : -662.013824 eV 9.67359412 905.24 0.31653559 0.36086130 0.04705841 0.09199084 0.28359886
chi-7- Mo Mo Mo Re : -667.057600 eV 9.692783528 910.64 0.32242985 0.35993103 0.04526083 0.09228353 0.28396337
chi-8- Re Mo Re Mo : -664.700708 eV 9.664209766 902.6 0.31715434 0.36078070 0.04711553 0.09206885 0.28322124
chi-9- Re Mo Mo Re : -669.426922 eV 9.685025184 908.46 0.32355064 0.35978510 0.04510775 0.09232368 0.28384192
chi-10- Mo Re Re Mo : -672.07236 eV 9.64744123 897.92 0.31545394 0.36099135 0.04815535 0.09115571 0.28285386
chi-11- Mo Re Mo Re : -676.652914 eV 9.667679268 903.58 0.32350280 0.35965679 0.04506474 0.09174621 0.28351883
chi-12- Re Re Re Mo : -674.442674 eV 9.638774308 895.5 0.31595589 0.36098859 0.04797859 0.09120674 0.28234812
chi-13- Re Re Mo Re : -678.636738 eV 9.661460366 901.84 0.32417359 0.35956838 0.04499195 0.09175311 0.28331232
chi-14- Mo Mo Re Re : -706.531290 eV 9.616519848 889.32 0.32036751 0.35883481 0.04332944 0.09105890 0.28395510
chi-15- Re Mo Re Re : -708.864342 eV 9.608878078 887.2 0.32144193 0.35868390 0.04313154 0.09105332 0.28379972
chi-16- Mo Re Re Re : -715.476010 eV 9.592525606 882.68 0.32183843 0.35865434 0.04329651 0.09078853 0.28362074
```

The `fin-X.pl` script generates also a `X.TDB` database file, in the usual and familiar TDB file format readable in all classical thermodynamic modelling software. The corresponding formation energy of a configuration C in a phase φ , called $\Delta_f H^\varphi(C)$ is given in Joule per formula unit, and is obtained by the

total energy differences of $E^\varphi(C)$ related to the weighted composition of DFT pure i elements in their stable state, E_i^{SER} :

$$\Delta_f H^\varphi(C) = E^\varphi(C) - \sum_i x_i \cdot E_i^{\text{SER}}$$

For several cut-off energies, E_i^{SER} has been already calculated with values located in files included in the pure folder of ZEN path (See choice of elements given in Appendices C). In our example, this file is called chi-MoRe.TDB, and the description of the χ -phase is given for the 58 atoms, extracted as follows:

```

...
$*****
PHASE chi % 4 2 8 24 24 !
CONSTITUENT chi : MO,RE : MO,RE : MO,RE : MO,RE : !
$*****
PARA G(chi,MO:MO:MO:MO:0) 298.15 1515293.33; 6000 N ZenGen !
PARA G(chi,MO:RE:RE:MO:0) 298.15 977644.4; 6000 N ZenGen !
PARA G(chi,MO:RE:RE:RE:0) 298.15 535685.06; 6000 N ZenGen !
PARA G(chi,RE:RE:RE:MO:0) 298.15 1033201.61; 6000 N ZenGen !
PARA G(chi,RE:RE:MO:RE:0) 298.15 628533.15; 6000 N ZenGen !
PARA G(chi,MO:MO:RE:RE:0) 298.15 -73085.25; 6000 N ZenGen !
PARA G(chi,RE:MO:RE:RE:0) 298.15 -13932.77; 6000 N ZenGen !
PARA G(chi,MO:RE:RE:RE:0) 298.15 200911.83; 6000 N ZenGen !
PARA G(chi,RE:RE:RE:RE:0) 298.15 284370.68; 6000 N ZenGen !
PARA G(chi,RE:MO:MO:MO:0) 298.15 1545745.86; 6000 N ZenGen !
PARA G(chi,MO:RE:MO:MO:0) 298.15 1583838.53; 6000 N ZenGen !
PARA G(chi,RE:RE:MO:MO:0) 298.15 1630149.11; 6000 N ZenGen !
PARA G(chi,MO:MO:RE:MO:0) 298.15 811114.96; 6000 N ZenGen !
PARA G(chi,MO:MO:MO:RE:0) 298.15 324461.19; 6000 N ZenGen !
PARA G(chi,RE:MO:RE:MO:0) 298.15 836127.61; 6000 N ZenGen !
PARA G(chi,RE:MO:MO:RE:0) 298.15 380114.12; 6000 N ZenGen !
$*****
...

```


5 Additional explanations

5.1 Set-up the exe-X.sh file

Depending of your demand, the number of configurations and the relaxation steps have to be set-up. Moreover, the execution of VASP command should be provided in the `exe-X.sh` file.

The execution manager is built by 2 interlinked loops, (*i*) one about the configurations to be calculated (corresponding to the `DIR` variable), (*ii*) one about the relaxation step (`STEP` variable).

The main bash procedure is the following:

```
#####
for STEP in `seq $SMIN $SMAX`; do
#####
for DIR in `seq $CMIN $CMAX`; do
#####
cd $DIR
  preparposcar # function: prepare POSCAR file
  cp ../steps/INCAR.$STEP INCAR
  cp ../steps/KPOINTS.$STEP KPOINTS
#####
  execution # function: execute VASP
#####
  savefiles # function: save output files
cd ..
#####
done
done
#####
```

The minimum and maximum numbers of configurations (`CMIN` and `CMAX`) and the minimum and maximum numbers of the relaxation step (`SMIN` and `SMAX`), have to be given at the beginning of the `exe-X.sh` file:

```
#####
### Parameters #
#####
# Which compound? (DIR)
CMIN=0 # Minimal Compound number
CMAX=3 # Maximal Compound number
# Which step? (STEP)
SMIN=0 # Minimal relaxation step
SMAX=0 # Maximal relaxation step
#
NbCPU=12 # Number of CPU allowed
```

The `NbCPU` variable corresponds to the number of CPUs used in case of a multi-processing execution. Put the value to 0 if the job will be monitored by a queuing task manager. The `execution` has to be configured according to the VASP execution method. The default configuration uses a local VASP execution by MPI:

```

execution()
{
echo "ready to run on "$NbCPU" core(s) ?..."
echo "*****"
echo $PWD
if [ $NbCPU -eq 0 ]      # if task-manager
then
    #qsub ../job.pbs
    sbatch ../job.slurm
elif [ $NbCPU -eq 1 ]   # if serial execution
then
    vasp5s
else                    # if multi-processing
    ulimit -s unlimited
    mpiexec -n $NbCPU ~/bin/vasp5m
fi
}

```

with `vasp5s` or `vasp5m`, your VASP exe-files in the `PATH`, for serial or multi-processing execution, respectively. If the VASP execution is monitored by a queuing task manager, then, (i) only one step should have been set-up (`SMAX=$SMIN`)⁵, and (ii) the `execution` function should be changed by the calling procedure depending of the system architecture (`l1submit`, `qsub`, `sbatch`...). See your administrator for more details about the execution of VASP in your institution.

5.2 Add your own phases

All the phases available in ZenGen are listed in the Table 2 of page 15. However, if a new phase has to be calculated, it is pretty easy to insert it in ZenGen. First of all, prepare the structure file of the new phase in a VASP format, named `POSCAR.ini`. There is several useful tools for helping you to prepare this file, starting from the Wyckoff positions. We recommend the free VESTA program⁶, able to convert many structure file formats. VESTA presents the regrettable fact that the `selective dynamics` line with the associated internal parameters flags are lacking, but it is easy to add manually.

As an example, we have chosen to add the well known σ -phase structure. Its prototype is σ -CrFe, $D8_b$, tetragonal symmetry with 30 atoms distributed in $m = 5$ sites in the unit cell. Details of the crystal structure are summarized in the Table 1, with its associated representation.

From the crystal structure information, the associated `POSCAR` file has to be built (with VESTA for example), as shown in the appendix, page 16. The original `POSCAR.ini` file should have to be cut manually into $1+m$ separated files: the header named `POS.0` with a first empty line and without the number of atoms (line 6), then, all the `POS.1`, ..., `POS.5` files, corresponding to the positions of each inequivalent m

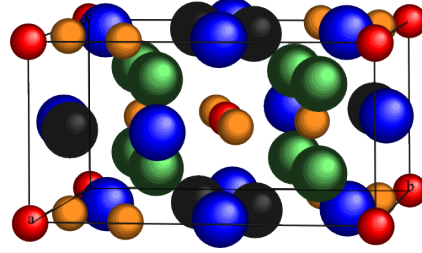
⁵ ... because the $i + 1$ step calculation job could not be sent since i step is not definitely finished.

⁶VESTA: <http://jp-minerals.org/vesta/en/>

sites. The first line of the POS.1, . . . , POS.5 files should finished by the string: - e1 as shown in page 16. This split is necessary to allow ZenGen to generate all the n^m ordered configurations, with n the number of different elements dealt into the m sites. For some reasons (model composition, computational time...), it could be interesting to merge some sites. This has been done for the P-phase, of original description with $m = 12$: a simplified model with $m = 3$ has been proposed by merging all the sites of similar CN.

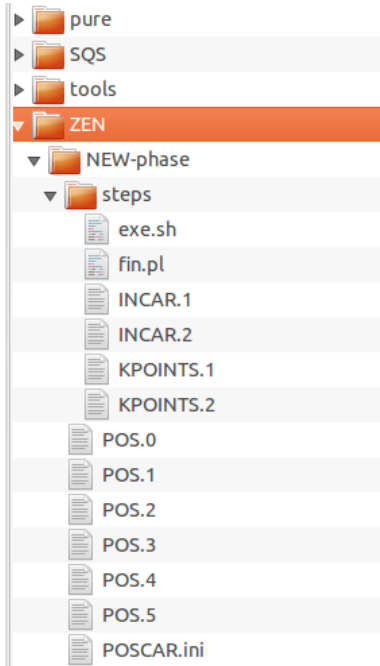
Table 1: Crystal structure of the σ -phase ($D8_b$): sites, Wyckoff positions, atomic positions (average values) in the $P4_2/mnm$ space group, and Coordination Number (CN).

Site	Wyc	x	y	z	CN
A	$2a$	0	0	0	12
B	$4f$	~ 0.39	x	0	15
C	$8i_1$	~ 0.46	~ 0.13	0	14
D	$8i_2$	~ 0.74	~ 0.07	0	12
E	$8j$	~ 0.18	x	~ 0.25	14



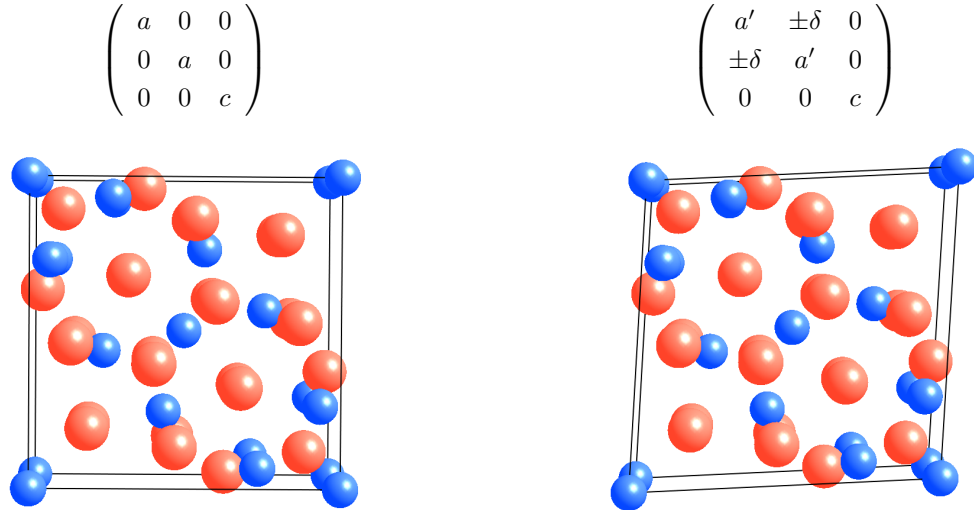
All the POS.X file of a new structure have to be pasted in a new folder of the ZEN folder of the dir path. A folder called NEW is present in the ZEN folder, and could be used as an example to prepare your new phase. In addition, the relaxation scheme of the new phase should have to be indicated by adding the INCAR.i and KPOINTS.i files of each i step into the steps folders as shown in the following screen view. We advise to start by a volume relaxation first, with a low k -points meshing, then adding more freedom of relaxation depending on your structure, then an increase of the k -points meshing , and finally a static calculation using the tetrahedron method with Blöchl corrections. Naturally, everyone is free and can modify the input files of the steps folder with his own preference. Moreover, the executable exe.sh and fin.pl should exist in the steps folder.

Finally, rename the new folder into the key-name you will input by calling ZenGen.



5.3 Distortion

In the previous section, we have drawn the reader's attention to the choice of relaxation scheme. Indeed, a premature relaxation with all degrees of freedom can lead to a distortion of the initial cell. Keeping our previous example of the σ -phase, the following representation compares the starting structure with one where a distortion occurs.



In order to avoid this kind of distortion, we suggested to realize the relaxation scheme split into several steps, as said previously. Moreover, between each step, forcing the symmetry to keep the tetragonal symmetry, by forcing the matrix to be diagonal, may be done when copying the CONTCAR of step i , into the POSCAR of step $i + 1$. This forcing procedure has been written in the `preparposcar()` function of `exe-X.sh` file, such as the `exe-sigma.sh` for the σ -phase:

```
preparposcar()
{
if [ $STEP -eq 0 ] ; then
# new POSCAR
cp POSCAR.ini POSCAR
else
# diagonalisation of CONTCAR
CHA=$IFS
cp CONTCAR TEST
head -n 5 TEST > tmp
head -n 2 tmp > tmp1
tail -n +3 tmp > tmp2
tail -n +6 TEST > tmp3
IFS=' '
ligne1=$(sed -ne '1p' tmp2)
ligne2=$(sed -ne '2p' tmp2)
ligne3=$(sed -ne '3p' tmp2)
echo "Before:"
echo ${ligne1[0]} ${ligne1[1]} ${ligne1[2]}
echo ${ligne2[0]} ${ligne2[1]} ${ligne2[2]}
echo ${ligne3[0]} ${ligne3[1]} ${ligne3[2]}
ligne1[0]=$(echo "scale=16; (${ligne1[0]}+${ligne2[1]})*0.5/1" | bc )
ligne1[1]=$(echo "scale=16; 0.0000000000000000" | bc )
ligne1[2]=$(echo "scale=16; 0.0000000000000000" | bc )
ligne2[0]=$(echo "scale=16; 0.0000000000000000" | bc )
ligne2[1]=$(echo "scale=16; ${ligne1[0]}" | bc )
ligne2[2]=$(echo "scale=16; 0.0000000000000000" | bc )
ligne3[0]=$(echo "scale=16; 0.0000000000000000" | bc )
ligne3[1]=$(echo "scale=16; 0.0000000000000000" | bc )
ligne3[2]=$(echo "scale=16; ${ligne3[2]}" | bc )
echo "After:"
echo ${ligne1[0]} ${ligne1[1]} ${ligne1[2]}
echo ${ligne2[0]} ${ligne2[1]} ${ligne2[2]}
echo ${ligne3[0]} ${ligne3[1]} ${ligne3[2]}
echo ${ligne1[0]} ${ligne1[1]} ${ligne1[2]} >tmp2
echo ${ligne2[0]} ${ligne2[1]} ${ligne2[2]} >>tmp2
echo ${ligne3[0]} ${ligne3[1]} ${ligne3[2]} >>tmp2
cat tmp1 tmp2 tmp3 > POSCAR
rm TEST tmp1 tmp2 tmp3
IFS=$CHA
fi
}
```

5.4 SQS

ZenGen is designed to generate all necessary files of ordered compounds calculation described in the CEF formalism. However, it could be used to prepare and execute Special Quasirandom Structures (SQS) calculation of a solid solution. At the moment, only the *fcc*, *bcc*, and *hcp* structures for **binary systems** are implemented. Generated structures have been taken from the literature.

In ZenGen, the procedure to generate SQS files is similar to that for the ordered compounds: After the execution of `zengen.pl`, at the first input, the user types `SQS`. Then, the user gives **two** element names, *e.g.* `Mo Re`. A new folder will be created, called `SQS-Mo-Re` in our example. It will contain:

- `A1-fcc` folder
- `A2-bcc` folder
- `A3-hcp` folder
- `go.sh` script, to run calculation on the 3 phases
- `mixing.pl` script, to extract the heat of mixing after DFT calculations

In each folder, all input files are generated for 16-atoms supercell structures of the corresponding phase (*A1 – fcc*, *A2 – bcc*...). It contains folders corresponding to each composition. The SQS investigated compositions are $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, with $\frac{1}{16}$ and $\frac{15}{16}$ to simulate dilute solutions. A relaxation scheme without and with magnetism is proposed, but could be easily adapted for the user need. Individual calculation should have to be managed using the `execute.sh` script as for the ordered compounds (See section 5.1). Additional scripts are available : the `check.sh` script to check if calculation of an individual step has been correctly finished, the `clean.sh` script to remove no necessary files before archive, and the `sum.pl` script to summarize the results of all composition into a `sum.out` file. We suggest to summarize the results after two relaxation schemes: first with a simple volume relaxation, second with an ionic relaxation, where `sum.out` file should have to being renamed `sum.vol.out` and `sum.full.out` respectively.

When DFT calculations are done, the `mixing.pl` script could be run. It works even if only 1 phase has been considered. this script read the only `sum*.out` files available in each sub-folders. For each phase, a easy reading of the mixing enthalpy is shown with an automatic `gnuplot` graphic. Moreover, a generated file lists the fitted coefficients for an upcoming assessment (Redlich-Kister polynomial type). The development of a better is under progress, and will come in a next release.

5.5 Additional tools

During the installation, a `pure` folder will be created which contains all reference states of pure element in their stable state (energy, cell parameters...). The results are also given for several host structures (*A1 – fcc*, *A2 – bcc*...). Calculations have been done with GGA-PBE functional with a 400 and 800 eV cutoff energy.

In addition, the ZenGen directory folder contains several scripts:

- `genpot.sh`, for copying the POTCAR file of an element
- `heat.sh`, for computing the heat of formation
- `kpt.sh`, `ecut.sh`, for optimizing the k-meshing and the cutoff energy
- `dila.sh`, for performing a dilatation

- `save.sh`, for saving a step of calculation (`OUTCAR.n...`)
- `clean.sh`, for removing no necessary backup files

Some tools for plotting DOS are also given (`split_dos.sh`, `sum_dos.sh`, `plot_dos.pl`).

6 Conclusion

Many thanks for using `ZenGen`. There are still many improvements that have to be done. All comments are welcome: new structures income, new relaxation steps procedure, additional scripts...it is a open code ;)

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A List of available phases

Table 2: Code for the choice of studied phases in ZenGen, name of the phase in Strukturbericht format, prototype compound, Space group, Pearson symbol, number of sublattices and additional comments.

Code	Phase	Prototype	Space Group	Pearson	Nb	comment
A15	A15	Cr ₃ Si	$Pm\bar{3}n$	(223)	cP8	2 sublattices (6c,2a)
c (chi)	A12	α -Mn	$I\bar{4}3m$	(217)	cI58	χ -phase
b (betaMn)	A13	β -Mn	$P4_132$	(213)	cP20	β -Mn
C14	C14	MgZn ₂	$P6_3/mmc$	(194)	hP12	Laves AB_2
C15	C15	Cu ₂ Mg	$Fd\bar{3}m$	(227)	cF24	Laves AB_2
C36	C36	MgNi ₂	$P6_3/mmc$	(194)	hP24	Laves AB_2
C36-3s	C36-3ss	MgNi ₂	$P6_3/mmc$	(194)	hP24	3 sublattices [A1, A2, B]
s (sigma)	$D8_6$	CrFe	$P4_2/mnm$	(136)	tP30	σ -phase
mu	$D8_5$	Fe ₇ W ₆	$R\bar{3}$	(166)	hR13	μ -phase
d (delta)		Mo ₇ Ni ₇	$P2_12_12_1$	(19)	oP56	δ -MoNi
delta-sim		Mo ₇ Ni ₇	$P2_12_12_1$	(19)	oP56	δ simplified [CN12,14,15+]
PP		Cr ₁₈ Mo ₄₂ Ni ₄₀	$Pnma$	(62)	oP56	P-CrMoNi
PPsim (Ps)		Cr ₁₈ Mo ₄₂ Ni ₄₀	$Pnma$	(62)	oP56	P simplified [CN12,14,15+]
Cu3Ti		Cu ₃ Ti, Ni ₃ Ta	$Pm\bar{m}n$	(59)	oP8	β -Cu ₃ Ti (LT)

B New phase: splitting the POSCAR.ini into POS.x

(see next page)

The POSCAR.ini file has to be cut into $1+m$ separated POS.x files :

```

Sigma phase - D8b
1.0
  9.624 0.000 0.000
  0.000 9.624 0.000
  0.000 0.000 5.088
30
Selective dynamics
Direct
-----
  0.0000  0.0000  0.0000  F  F  F
  0.5000  0.5000  0.5000  F  F  F
-----
  0.4000  0.4000  0.0000  T  T  F
  0.6000  0.6000  0.0000  T  T  F
  0.1000  0.9000  0.5000  T  T  F
  0.9000  0.1000  0.5000  T  T  F
-----
  0.4667  0.1333  0.0000  T  T  F
  0.5333  0.8667  0.0000  T  T  F
  0.3667  0.9667  0.5000  T  T  F
  0.6333  0.0333  0.5000  T  T  F
  0.0333  0.6333  0.5000  T  T  F
  0.9667  0.3667  0.5000  T  T  F
  0.1333  0.4667  0.0000  T  T  F
  0.8667  0.5333  0.0000  T  T  F
-----
  0.1833  0.1833  0.2498  T  T  T
  0.8167  0.8167  0.2498  T  T  T
  0.3167  0.6833  0.7498  T  T  T
  0.6833  0.3167  0.7498  T  T  T
  0.3167  0.6833  0.2502  T  T  T
  0.6833  0.3167  0.2502  T  T  T
  0.1833  0.1833  0.7502  T  T  T
  0.8167  0.8167  0.7502  T  T  T

```

POS.0:

```

1.0
  9.624 0.000 0.000
  0.000 9.624 0.000
  0.000 0.000 5.088

Selective dynamics
Direct

```

POS.1:

```

0.0000  0.0000  0.0000  F  F  F  - e1
0.5000  0.5000  0.5000  F  F  F

```

POS.2:

```

0.4000  0.4000  0.0000  T  T  F  - e1
0.6000  0.6000  0.0000  T  T  F
0.1000  0.9000  0.5000  T  T  F
0.9000  0.1000  0.5000  T  T  F

```

POS.3:

```

0.4667  0.1333  0.0000  T  T  F  - e1
0.5333  0.8667  0.0000  T  T  F
0.3667  0.9667  0.5000  T  T  F
0.6333  0.0333  0.5000  T  T  F
0.0333  0.6333  0.5000  T  T  F
0.9667  0.3667  0.5000  T  T  F
0.1333  0.4667  0.0000  T  T  F
0.8667  0.5333  0.0000  T  T  F

```

POS.4:

```

0.7333  0.0667  0.0000  T  T  F  - e1
0.2667  0.9333  0.0000  T  T  F
0.4333  0.2333  0.5000  T  T  F
0.5667  0.7667  0.5000  T  T  F
0.7667  0.5667  0.5000  T  T  F
0.2333  0.4333  0.5000  T  T  F
0.0667  0.7333  0.0000  T  T  F
0.9333  0.2667  0.0000  T  T  F

```

POS.5:

```

0.1833  0.1833  0.2498  T  T  T  - e1
0.8167  0.8167  0.2498  T  T  T
0.3167  0.6833  0.7498  T  T  T
0.6833  0.3167  0.7498  T  T  T
0.3167  0.6833  0.2502  T  T  T
0.6833  0.3167  0.2502  T  T  T
0.1833  0.1833  0.7502  T  T  T
0.8167  0.8167  0.7502  T  T  T

```


C Energy references of DFT pure elements in their stable state

In order to calculate the heat of formation of ordered compound or the mixing energy from SQS calculations, ZenGen uses the energy references given in the `install/pure` folder. All the references have been obtained by systematic calculations with VASP using GGA-PBE functional⁷.

H																	He																														
Li* Be*											B	C	N	O	F	Ne																															
Na* Mg*											Al	Si	P	S	Cl	Ar																															
K	Ca*	Sc*	Ti*	V*	Cr*	Mn*	Fe*	Co*	Ni*	Cu*	Zn	Ga	Ge*	As*	Se	Br	Kr																														
Rb	Sr	Y	Zr	Nb	Mo*	Tc*	Ru*	Rh*	Pd*	Ag*	Cd	In	Sn	Sb	Te	I	Xe																														
Cs	Ba		Hf*	Ta*	W*	Re*	Os*	Ir	Pt*	Au	Hg	Tl	Pb*	Bi	Po	At	Rn																														
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo																														
<table border="1" style="width: 100%; text-align: center;"> <tr> <td>La</td><td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> <tr> <td>Ac</td><td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td><td>Lr</td> </tr> </table>																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																	
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																	
X	Not considered																																														
Y	Investigated for the structures A1, A2, A3 and SER cut off energy: 300, 400, 500, 600, 800 eV & spin polarization																																														
Y*	With and without pseudo-core electrons																																														

Pure elements calculated in several structures (A1, A2, A3,...), at several cutoff energies (300, 400, 500, 600 & 800 eV) have been systematically considered without and with spin-polarization (symbolized by the `_m` suffix in tables for this later). The energies for the elements indicated in black filled square of the periodic table are provided. For some elements, indicated by a star, several pseudo-core electrons calculations have been considered. As an example, the listing of the pure elements in their stable state SER and in A3 phase calculated with a cutoff energy of 600 eV are shown below. Units are: energy in eV, cell parameter in Å, volume in Å³, magnetic moment in μ_B . As said previously, result listings of all sets of structure and cutoff are provided into the `install/pure` folder.

SER-600.out file:

# Eltm.	Struct.	Total-energy	mag=	a-conv	Vol-conv	Vol-at	r-at	b/a	c/a	CUT-OFF: 600 eV
Ac	A1-fcc	-4.04728 eV	0.000	5.672	182.47	45.62	2.22	1.000	1.000	
Ag	A1-fcc	-2.71722 eV	0.000	4.147	71.32	17.83	1.62	1.000	1.000	
Ag_pv	A1-fcc	-2.70313 eV	0.000	4.154	71.67	17.92	1.62	1.000	1.000	
Al	A1-fcc	-3.74653 eV	0.000	4.042	66.03	16.51	1.58	1.000	1.000	
Am	A1-fcc	-13.84306 eV	0.000	4.105	69.15	17.29	1.60	1.000	1.000	
As	A7-rho	-4.66991 eV	0.000	3.813	136.40	22.73	1.76	1.000	2.840	
As_d	A7-rho	-4.67909 eV	0.000	3.807	136.66	22.78	1.76	1.000	2.860	
Au	A1-fcc	-3.22003 eV	0.000	4.155	71.75	17.94	1.62	1.000	1.000	
B	hR36-B	-6.70480 eV	0.000	5.049	86.92	7.24	1.20	0.000	0.529	
Ba_sv	A2-bcc	-1.90828 eV	0.000	5.028	127.10	63.55	2.48	1.000	1.000	
Be	A3-hcp	-3.76622 eV	0.000	2.264	15.83	7.92	1.24	1.000	1.575	
Be_sv	A3-hcp	-3.76451 eV	0.000	2.264	15.82	7.91	1.24	1.000	1.575	
Bi	A7-rho	-3.87346 eV	0.000	4.582	221.19	36.86	2.06	1.000	2.655	
C	A4-dia	-8.08239 eV	0.000	3.635	48.03	6.00	1.13	1.000	1.000	
Ca_pv	A1-fcc	-1.92023 eV	0.000	5.524	168.59	42.15	2.16	1.000	1.000	
Ca_sv	A1-fcc	-1.92906 eV	0.000	5.528	168.90	42.22	2.16	1.000	1.000	
Cd	A3-hcp	-0.74607 eV	0.000	3.021	45.87	22.94	1.76	1.000	1.921	

⁷J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. Phys. Rev. Lett., 77:3865, 1996. J. P. Perdew, K. Burke, and M. Ernzerhof. Erratum: Generalized gradient approximation made simple. Phys. Rev. Lett., 78:1396, 1997

Ce	A1-fcc		-5.92536 eV		0.000		4.725	105.52	26.38	1.85	1.000	1.000
Ce_3	A1-fcc		-4.73202 eV		0.000		5.325	150.96	37.74	2.08	1.000	1.000
Ce_h	A1-fcc		-5.93196 eV		0.000		4.722	105.29	26.32	1.85	1.000	1.000
Co	A3-hcp		-7.03500 eV		1.593		2.490	21.61	10.80	1.37	1.000	1.615
Co_pv	A3-hcp		-7.03162 eV		1.596		2.494	21.70	10.85	1.37	1.000	1.615
Cr	A2-bcc		-9.48582 eV		0.000		2.836	22.80	11.40	1.40	1.000	1.000
Cr_m	A2-bcc		-9.49622 eV		0.000		2.853	23.22	11.61	1.40	1.000	1.000
Cr_pv	A2-bcc		-9.51023 eV		0.000		2.846	23.06	11.53	1.40	1.000	1.000
Cu	A1-fcc		-3.72720 eV		0.000		3.634	47.99	12.00	1.42	1.000	1.000
Cu_pv	A1-fcc		-3.74814 eV		0.000		3.619	47.41	11.85	1.41	1.000	1.000
Fe	A2-bcc		-8.23670 eV		2.196		2.830	22.65	11.33	1.39	1.000	1.000
Fe_pv	A2-bcc		-8.25688 eV		2.201		2.831	22.70	11.35	1.39	1.000	1.000
Fe_sv	A2-bcc		-8.34199 eV		2.159		2.813	22.25	11.12	1.38	1.000	1.000
...												

Vol-conv means the volume of the conventional cell, Vol-at divides Vol-conv by the number of atom and r-at is the atomic hard-sphere radius corresponding to the Vol-conv volume.

A3-hcp-SUM.out file:

```
## A3-hcp structure - VASPv5 - PBE - G21x21x15
## Elt s :      300 eV      400 eV      500 eV      600 eV      800 eV
## -----
Ac :      -4.038271      -4.038565      -4.038448      -4.038398      -4.038437
Ac_m :      -4.038269      -4.038565      -4.038447      -4.038398      -4.038435
Ag :      -2.722690      -2.713949      -2.714037      -2.713732      -2.713686
Ag_m :      -2.722598      -2.713861      -2.713947      -2.713643      -2.713599
Ag_pv :      -2.648143      -2.701533      -2.697242      -2.699615      -2.698820
Ag_pv_m :      -2.648143      -2.701533      -2.697242      -2.699615      -2.698820
Al :      -3.710065      -3.713283      -3.713629      -3.713708      -3.713815
Al_m :      -3.710065      -3.713283      -3.713629      -3.713708      -3.713815
Am :      -13.794876      -13.821198      -13.824619      -13.826964      -13.828194
Am_m :      -16.061918      -16.090146      -16.093417      -16.095324      -16.096468
As :      -4.171879      -4.171873      -4.171899      -4.171935      -4.171974
As_d :      -4.172353      -4.173440      -4.174321      -4.174287      -4.174330
As_d_m :      -4.172352      -4.173444      -4.174330      -4.174284      -4.174340
As_m :      -4.171879      -4.171873      -4.171899      -4.171935      -4.171974
Au :      -3.220477      -3.215166      -3.215165      -3.215059      -3.215029
Au_m :      -3.220477      -3.215166      -3.215165      -3.215059      -3.215027
B :      -5.126011      -5.138769      -5.138943      -5.140227      -5.141000
B_h :      -4.836355      -5.013159      -5.082323      -5.124104      -5.138507
...
```

A3-hcp-600.out file:

```
## A3-hcp structure - VASPv5 - PBE - G21x21x15 - 600 eV
## Total-energy | mag= | a Vol-hex Vol/at c/a
Ac :      -4.038398 eV | 0.000 | 4.02 91.20 45.60 1.615
Ac_m :      -4.038398 eV | 0.000 | 4.02 91.18 45.59 1.615
Ag :      -2.713732 eV | 0.000 | 2.93 35.70 17.85 1.647
Ag_m :      -2.713643 eV | 0.000 | 2.92 35.70 17.85 1.650
Ag_pv :      -2.699615 eV | 0.000 | 2.93 35.87 17.94 1.650
Ag_pv_m :      -2.699615 eV | 0.000 | 2.93 35.87 17.94 1.650
Al :      -3.713708 eV | 0.000 | 2.86 33.29 16.64 1.651
Al_m :      -3.713708 eV | -0.000 | 2.86 33.29 16.64 1.651
Am :      -13.826964 eV | 0.000 | 2.93 34.49 17.25 1.578
Am_m :      -16.095324 eV | 6.997 | 3.56 63.54 31.77 1.624
As :      -4.171935 eV | 0.000 | 3.00 38.59 19.30 1.651
As_d :      -4.174287 eV | 0.000 | 3.00 38.65 19.32 1.651
...
```