Manual of input file for crystal structure prediction

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Contents

1 Introduction

Input data is organized as several namelists, followed by other fields (“cards”) introduced by the names. The names of fields begin the symbol of “&”, and all the following caracters are upper case. In each field, ordered parameters are given behind a keyword, and the order of keywords is arbitrary.

2 Definitions

In MARICI, ionic chemical element is defined as the chemical element with formal charge. A symbol of ionic chemical element is written as follows: After the chemical element symbol, write the formal charge as “Ca2+”, “Hg+”, “Te2-”, or “Cl-”. If you do not write any formal charge, the ionic chemical element is regarded as the chemical element without formal charge.

3 Essential field to computer settings

This field designates the compter environment and how to output the results. **You must designate two parameters in this field as listed in Table 1** , while you do not have to write other optional parameters listed in Table 2. If you do not write a parameter line or leave blank after the keywords, the default value is used. **Note that you must enclose a path to a directory in double quotation marks.** The example is written below, and all the optional parameters are set to be default.

```
&CRYSTAL_PREDICTION_COMPUTER_SETTINGS
Maximum.Number.of.Total.Threading                  10
Work.Folder.Path                                   ”C:/Work/Marici++”
Maximum.Number.of.Threading.per.Crystal.Design     1
MD.Record.Frequency                                0
Infeasible.Crystal.Data.Outputs                    OFF
P1.Symmetry.Crystal.Data.Outputs                   OFF
Exceptional.Crystal.Data.Outputs                   OFF
Space.Group.Precision                              0.7
```

Table 1: The essential parameters in the field of computer settings.

Keyword	Definition
Maximum.Number.of.Total.Threading	The available number of threading for MARICI.
Work.Folder.Path	In the work folder path, designed crystals, reports, and structural optimization process (optional) are made.

Table 2: The optional parameters in the field of computer settings.

Keyword	Definition
Maximum.Number.of.Threading.per.Crystal.Design	The number of threading for structural optimization. In the latest version, the value must be one.
MD.Record.Frequency	If you need the record of structural optimization, assign a value more than one. Structures are taken snapshots of every the value steps in optimization.
Infeasible.Crystal.Data.Outputs	If you need infeasible structures, write “ON”. Otherwise, write “OFF” or leave blank.
P1.Symmetry.Crystal.Data.Outputs	If you need optimal structures with no symmetry, write “ON”. Otherwise, write “OFF” or leave blank.
Exceptional.Crystal.Data.Outputs	If you need structures making exceptional errors, write “ON”. Otherwise, write “OFF” or leave blank.
Space.Group.Precision	The value corresponds to “symprec” in SPGLIB library which determines a space group. The unit is Angstrom.

4 Essential field to ionic radius

Since the current MARICI does not have a table for default ionic radii of each ionic chemical element, you must designate them. **After the symbol of an ionic chemical element, you must write the minimum ionic radius, the maximum ionic radius, and the minimum ionic repulsion radius in this order.** Note that unit is Angstrom. The example is written below.

```
&IONIC_RADIUS
Ca2+          1.0          1.2          1.8
O2-           1.4          1.4          1.4
```

5 Essential field to feasible coordination compositions

Since the current MARICI does not have a table for the feasible compositions of coordination polyhedra of each ionic chemical element, you must designate them. **After the symbol of an ionic chemical element, you must write the list of the feasible compositions of coordination polyhedra around the ionic chemical element**. Note that a composition of coordination polyhedron is defined as the set of the coordination numbers corresponding to each chemical element, and you cannot designate ionic chemical element in place of chemical element. The composition is written as follows: After each chemical element symbol, write the coordination number of the element. You can connect the coordinations of different chemical elements without any symbol. The example is written below.

```
&FEASIBLE_COORDINATION_COMPOSITIONS
Hg+        O8         O6S2       N8         O6N2
Ca2+       O8         O9         O10F2      O11        O12
Si4+       O4
```

6 Essential field to covalent coordination numbers

The developer will implement covalent bonding to predict not only chalcogenides but also mixed-anion compounds and Zintl phase. To tell you the truth, covalent bonding has already been implemented, but the developer has not checked whether all the bug are removed or not, and besides, the developer think that the rule to treat covalent bonding should be refined. Then, although it is inconvenient, **you must assign the number of covalent bonding of each anion being zero if you predict ionic crystal structures as shown below**.

```
&FEASIBLE_COVALENT_COORDINATION_NUMBERS
O2-                          0
Cl-                          0
```

7 Essential field to chemical compositions of which crystal structures are predicted

You must write all the ionic chemical compositions of which crystal structures are predicted. An ionic chemical composition is defined as the set of the numbers of ionic chemical elements per unit cell. It is written as follows: After the symbol of ionic chemical element, write “_” and the number of the ionic chemical element per unit cell in this order. If there are several kinds of ionic chemical elements, enumerate the compositions with space. Finally, write the number of crystal structure seeds for random sampling to search optimal structures. The example is written below.

```
&CRYSTAL_STRUCTURE_PREDICTION
Si4+_2 Os4+_4 O2-_8                    2000
Cl-                                    0
```

8 Essential field to numerical options for structural optimization

This field designates the numerical options for structural optimization. **You must designate only one parameter in this field, while you do not have to designate the other optional parameters.**

```
&CRYSTAL_PREDICTION_COMPUTER_SETTINGS
Maximum.Steps.of.Structural.Optimization                 200000
Maximum.Steps.of.Ceaseless.Global.Structural.Optimization 2500
Interatomic.Distance.Tracer.Timeout                       100
Unit.Cell.Reduction.Timeout                               200
Interatomic.Distance.Tracer.Cutoff.Ratio                  4.0
Interatomic.Distance.Constrainer.Cutoff.Ratio             2.0
```

Table 3: The essential parameters in the field of numerical options for structural optimization.

Keyword	Definition
Maximum.Steps.of.Structural.Optimization	The maximum number of structural optimization steps. If a structure cannot be an optimal solution through the optimization, the structure is regarded as an infeasible structure.

Table 4: The optional parameters in the field of numerical options for structural optimization.

Keyword	Definition
Maximum.Steps.of.Ceaseless.Global.Structural.Optimization	After the maximum steps, a structure is randomly distorted.
Interatomic.Distance.Tracer.Timeout	After the timeout, the list of tracking pairs of atoms is updated.
Unit.Cell.Reduction.Timeout	After the timeout, Delauney reduction is applied to the unit cell by SPGLIB library.
Interatomic.Distance.Tracer.Cutoff.Ratio	
Interatomic.Distance.Constrainer.Cutoff.Ratio	

9 Optional field to interatomic distance constraint

If you do not write this field or leave blanck after keywords, the default values are used, therefore, you can skip this section.

If any chemical bond is not formed between atom i and j, only the minimum distance between the pair of atoms is constrained as

$$d_{ij\boldsymbol{T}}^{(\mathrm{min})} \leq \left| \boldsymbol{x}_j + \boldsymbol{T} - \boldsymbol{x}_i \right| , \tag{1}$$

where $\boldsymbol{x}_i$ is the position of atom i and $\boldsymbol{T}$ is the a translation vector. When both the two atoms are anions or cations, the minimum distance is set to be

$$d_{ij\boldsymbol{T}}^{(\mathrm{min})} = r_i^{(\mathrm{IR})} + r_j^{(\mathrm{IR})}, \tag{2}$$

where $r^{(\mathrm{IR})}$ is the minimum ionic repulsion radius. When both two atoms have no formal charge, the minimum distance is set to be

$$d_{ij\boldsymbol{T}}^{(\mathrm{min})} = \gamma \left(R_i^{(\mathrm{C})} + R_j^{(\mathrm{C})} \right) , \tag{3}$$

where $R^{(\mathrm{C})}$ is the maximum covalent radius and γ is the constant named “Minimum.Exclusion.Distance.Ratio”. When the two atoms are ionic attractive, the minimum distance is set to be

$$d_{ij\boldsymbol{T}}^{(\mathrm{min})} = \gamma \left(R_i^{(\mathrm{I})} + R_j^{(\mathrm{I})} \right) , \tag{4}$$

where $R^{(\mathrm{I})}$ is the maximum ionic radius. **You can change the value of γ from the default if you use the field written below.**

```
&INTERATOMIC_DISTANCE_CONSTRAINTS
Minimum.Exclusion.Distance.Ratio          1.3
```

10 Optional parameters for initial structure generations

If you do not write this field or leave blanck after keywords, the default values are used, therefore, you can skip this section. Note that latest MARICI only support the complete random generations of initial structures.

A unit cell is defined by six parameters of $(a, b, c, \alpha, \beta, \gamma)$, where a, b, c are the length of lattice vector and α, β, γ are the angle between lattice vectors. First, unit cell is randomly generated under the constraints below:

$$
\begin{aligned}
&a = 1 \\
&1 \leq \frac{c}{a}, \frac{c}{a} \leq D \\
&b \leq \alpha, \beta, \gamma \leq B
\end{aligned}
$$

where D, b, B are constants. Second, all the atoms are randomly distributed in this unit cell. Finally, unit cell is expanded to satisfy the condition:

$$\phi = \frac{1}{\Omega} \sum_i \frac{4}{3} \pi R_i^3, \tag{5}$$

where ϕ is the given packing fraction, Ω is the volume of unit cell, and R_i is the radius of atom i.

&INTERATOMIC_DISTANCE_CONSTRAINTS	
Generation.Mode	RANDOM
Initial.Packing.Fraction	0.7
Maximum.Lattice.Length.Ratio	3.0
Maximum.Lattice.Angle	120
Minimum.Lattice.Angle	60

11 Optional field to structural optimization

If you do not write this field or leave blanck after keywords, the default values are used, therefore, you can skip this section.

11.1 Structural optimization algorithm

The inequality constraints are approximated by the hard-spherical potential as

$$d_\sigma \leq x_\sigma \;\Rightarrow\; U_{\min}\left(x_\sigma\right) \equiv \max\left[0, k_\downarrow\left(d_{ij} - x_\sigma\right)\right], \tag{6}$$

$$x_\sigma \leq D_\sigma \;\Rightarrow\; U_{\max}\left(x_\sigma\right) \equiv \max\left[0, k_\uparrow\left(x_\sigma - D_{ij}\right)\right], \tag{7}$$

where $k_\downarrow$ and $k_\uparrow$ are the repulsive and attractive force constants, respectively. Accordingly, the structural optimization problem is given by

$$\text{minimize} \quad H\left(\boldsymbol{X}\right) \equiv \sum_\sigma \left[U_{\min}\left(x_\sigma\right) + U_{\max}\left(x_\sigma\right)\right] + P\Omega, \tag{8}$$

with P being the pressure and Ω being the volume of unit cell. The minimization problem is solved as follows: Let $\Delta\boldsymbol{x}_i$ and $\Delta\boldsymbol{t}_i$ be the displacements of $\boldsymbol{x}_i$ and $\boldsymbol{t}_i$ calculated by

$$\Delta\boldsymbol{x}_i = -\xi_i \frac{\partial H\left(\boldsymbol{X}\right)}{\partial \boldsymbol{x}_i}, \qquad \Delta\boldsymbol{t}_i = -\zeta_i \frac{\partial H\left(\boldsymbol{X}\right)}{\partial \boldsymbol{t}_i}, \tag{9}$$

where the constants ξ_i and ζ_i are scaled to satisfy the condition given by

$$\left|\Delta\boldsymbol{x}_i\right| \leq \Delta x_s^{(\max)}, \qquad \left|\Delta\boldsymbol{t}_i\right| \leq \gamma\Delta x_s^{(\max)}, \tag{10}$$

with $\Delta x_s^{(\max)}$ being the maximum displacement of atoms in s-th optimization step and γ being a constant. $\Delta x_s^{(\max)}$ is calculated as

$$\Delta x_s^{(\max)} = \Delta x_0^{(\max)} \left(\frac{\Delta x_S^{(\max)}}{\Delta x_0^{(\max)}}\right)^{\frac{s}{S}}, \tag{11}$$

where S is the maximum number of optimization steps, and γ is defined as

$$\gamma = 0.02L \cdot \Delta x_s^{(\max)}, \tag{12}$$

with L being the number of atoms per unit cell.

11.2 Optional field to global structural optimization

Each default parameter for global structural optimization are written behind each keyword. Note that you do not have to write this field.

```
&GLOBAL_STRUCTURAL_OPTIMIZATION
Pressure                                        1.0
Attractive.Force.Constants                      30.0
Repulsive.Force.Constants                       -100
Initial.Maximum.Atomic.Displacement             0.5
Final.Maximum.Atomic.Displacement               0.5
Maximum.Unit.Cell.Displacement.Factor           0.02
Feasible.Geometrical.Constraint.Error.Rate      1.0
Number.of.Iterative.Balance.Steps               25

&LOCAL_STRUCTURAL_OPTIMIZATION
Pressure                                        1.0
Attractive.Force.Constants                      30.0
Repulsive.Force.Constants                       -100
Initial.Maximum.Atomic.Displacement             0.3
Final.Maximum.Atomic.Displacement               0.05
Maximum.Unit.Cell.Displacement.Factor           0.02
Feasible.Geometrical.Constraint.Error.Rate      0.1
Number.of.Iterative.Balance.Steps               2000

&PRECISE_STRUCTURAL_OPTIMIZATION
Pressure                                        1.0
Attractive.Force.Constants                      30.0
Repulsive.Force.Constants                       -100
Initial.Maximum.Atomic.Displacement             0.1
Final.Maximum.Atomic.Displacement               0.005
Maximum.Unit.Cell.Displacement.Factor           0.02
Feasible.Geometrical.Constraint.Error.Rate      0.05
Number.of.Iterative.Balance.Steps               4000
```