TORQUE – PROGRAM

VERSION 1.0.4 (2019)
USER MANUAL
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Overview and Input Summary

The TORQUE program determines rotational equilibrium of crystallization water orientations in ionic crystals. Crystallization water refers to molecular H_2O units that are network fillers rather than network formers. The forces are derived from a combination of point charge electrostatics of the host crystal and TIP3P (Jorgensen *et al.*, 1983), TIP4P/2005 (Abascal & Vega, 2005), TIP5P (Mahoney & Jorgensen, 2000) for the water molecules. The program input consists of a (arbitrary) named single file that specifies:

- Lattice parameters and positions.
- Atomic species and charges.
- Indicator which oxygens and hydrogen atoms belong to H_2O to be optimized.
- Type of water model (TIP3P, TIP4P/2005, TIPS5P).
- Symmetry operations and centering information.
- (optional) Occupancy of sites and/or positions.
- (optional) Seed for random number generator for initial placement of hydrogen.
- (optional) Range of rotation angle and threshold of minimum torque.
- Number of iterations, in the case user needs more than one iteration.

Feedback and suggestions are welcome and should be directed to:
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License

Installation and Program Execution

Requirements and notes

- Linux computer.
- Fortran 95 compiler. Program was tested with intel compiler 17.0.4 and gfortran 6.2.0
- The program does not require any external math libraries.
- The modular structure makes facilitates adaption of the torque program.

Installation Instructions

Download the source code file from:
https://github.com/ayat-ghazi/TORQUE

You should see the following content in the directory:

- The main program file: TORQUE_method_program.f90

• The subroutines file: sub_tools.f90

• The module files: module_dictionary.f90; module_input.f90; module_structure_symmetry_all.f90

• The makefile.

• The LICENSE file.

• The "InputFiles_Samples" subdirectory contains some example input files for various structures.

• The "MakeFiles" subdirectory contains two versions of makefiles suitable for intel fortran compiler and gfortran.

Compile the program using this command:
Make
This will generate an executable called: "TQ" (without quotes) in the same directory where the source code resides. If an error occurs edit the provided makefile. This default makefile is suitable for gfortran compiler, however, users can find a suited version for intel fortran compiler ("makefile_ifort") in the "Make" subdirectory. It needs to be copied in the main program directory and rename to "makefile" (without quotes).

Running the TORQUE program and examples

The program can be executed from command line by executing
PATH_TO_EXECUTABLE/TQ input_file
where "input_file" is a placeholder for the user provided file with the runtime parameters, described below, and "PATH_TO_EXECUTABLE" points to the directory where the executable resides. Sample input and output files are available in the subdirectory "InputFiles_Samples".

Detailed Input Instructions

General notes

• Different input sections are delimited by keywords. For example, the section between "LATTICE_MATRIX_" and END_LATTICE_MATRIX_" refers to the input section for the lattice of the crystal structure.

• Any line starting with ('#', '!', 'c') is considered as a comment by the program and will be skipped.

• The input file used here for illustration can be found as "inputfile_Grimselite" in the "InputFiles_Samples" directory. Grimselite (Li & Burns, 2001) crystallizes in space group $P\bar{6}2c$ (#190 International Table of Crystallography A)(Hahn, 2005).

Lattice: a=9.3020 Å b=9.3020 Å c=8.2600 Å α=90.0˚ β=90.0˚ γ=120.0˚
atom x y z occupancy

U	0.6667	0.3333	0.7500	1.0
K	0.2921	0.0000	0.0000	1.0
Na	0.3333	0.6667	0.7500	1.0
O1	0.9694	0.4797	0.7500	1.0
O2	0.8485	0.6315	0.7500	1.0
O3	0.6667	0.3333	0.9673	1.0
O4	0.1274	0.757	0.7500	1.0
O5	0.0000	0.0000	0.1277	0.5
C	0.9883	0.6282	0.7500	1.0

Input Deck

Lattice

Each ***row*** of the input lattice matrix contains one lattice vector in cartesian coordinates. Example:

LATTICE_MATRIX_
9.3020 0.0000 0.0000
-4.6510 8.0558 0.0000
0.0000 0.0000 8.2600
END_LATTICE_MATRIX_

Atomic species

The second section defines atomic species (second column) with their associated oxidation state (third column). First column is an identifier integer number (IN1) which distinguish different atomic species or the same atomic species with different symmetries. Charges for the oxygen and hydrogen atoms of crystallization water can be set, but the program will reset value to the selected water model. Framework oxygen is treated as any other ion in the structure and has the same syntax. Note that program reads the charges as real values, so users are not limited to integer oxidation numbers:

ATOMIC_SPECIES_CHARGES_
1 U 6.0
2 K 1.0
3 Na 1.0
4 O - 2.0
5 O -2.0
6 O -2.0
7 O -2.0
8 O -2.0
9 C 4.0
END_ATOMIC_SPECIES_CHARGES_

Atomic positions

The next section lists atomic positions and their occupancy numbers. Each line begins with a integer number (IN1), and follows by a position coordination and an occupation number. IN1 is the identifier number which was defined in previous section. Positions that belong to the same crystallographically equivalent set have the same integer number. In the case of partial occupancy, users can exclude atoms in this section by deletion or inserting comment lines. Alternatively, average structures can be specified through occupation numbers for each site. If a position randomly occupied by several different atom species, its coordination must be repeated in the following section with different IN1s and corresponding occupation numbers to have a proper average structure.

ATOMIC_POSITIONS_OCCUPANCY_
1 0.66670 0.33330 0.75000 1.0
1 0.33330 0.66670 0.25000 1.0
2 0.29210 0.00000 0.00000 1.0
2 0.00000 0.29210 0.00000 1.0
2 0.70790 0.70790 0.00000 1.0
2 0.29210 0.00000 0.50000 1.0
2 0.00000 0.29210 0.50000 1.0
2 0.70790 0.70790 0.50000 1.0

For brevity other sites are omitted. For more details see the file “inputfile_Grimselite” in “InputFiles_Samples”.

lines with IN1=8 show the coordinates of oxygen atoms of water molecule with half occupancy.
8 0.00000 0.00000 0.12770 0.5
8 0.00000 0.00000 0.37230 0.5
8 0.00000 0.00000 0.62770 0.5
8 0.00000 0.00000 0.87230 0.5

The following lines are the positions of hydrogen atoms which were taken from our DFT computations. These lines will be marked to be excluded from the calculations in the Crystallization water specification section.
Alternatively, the oxygen positions of crystallization water could be taken from experimental structure refinements.

```
10      0.016663        -0.078797       0.193012        1.0
11      -0.078894       0.017694        0.191793        1.0
12      -0.078797       0.016663        0.693012        1.0
13      0.017694        -0.078894       0.691793        1.0
END_ATOMIC_POSITIONS_OCCUPANCY_
```

The oxygen atoms of water molecules have index IN1=8. In Grimselite oxygen of crystallization water is located in crystallographic site 4e site (IN1=8 in the ATOM_POSITIONS_OCCUPANCY_ section of the input file, shown above with 50% occupancy. As it can be seen, the occupation numbers for these oxygen atoms are 0.5 in column 5. In this case, the program deals with average occupancies of the crystallographically equivalent positions. Alternatively, users can specify the two water locations explicitly and changing the occupation number for oxygen atoms to 1. The oxygen atoms that belong to water molecules must be identified with their IN1 number as shown in the following section:

Crystallization water specification

```
WATER_IDENTIFICATION_NUMBER_
8
END WATER_IDENTIFICATION_NUMBER_
```

In the next section, the user must indicate the IN1 numbers of hydrogen atoms of water molecules. The program does not consider those atom species which their IN1 number are listed here in the calculation of electrostatic forces. Here, the hydrogen atoms with IN1=10 to 13 are completing the description of the water molecule, and must be specified. If there is no information about the coordinates of hydrogen atoms of water molecules, this section could be blank or zero:

```
HYDROGEN_IDENTIFICATION_NUMBER_
10 11 12 13
END HYDROGEN_IDENTIFICATION_NUMBER_
```

Water model

The type of water models is defined in the next section. 0 = TIP3P, 1 = TIP4P/2005, 2 = TIP5P. Default is TIP3P.

```
WATER_MODEL_
0
END_WATER_MODEL_
```

Computational parameters

We have defined some default parameters for the minimum torque magnitude, maximum and minimum degree of angular rotation, seed value and number of program restarts with random water orientations.

```
PARAMETERS_
Threshold = 0.00001 ! Torque convergence threshold.
Max_Angle = 0.5 ! Rotation for maximum torque.
Min_Angle = 0.005 ! Minimum rotation.
Seed = 12345 ! Seed for random number generator.
Iteration=1 ! Number of trials for initial water orientations.
END_PARAMETERS_
```

Symmetry operations and centering
The symmetry operations are listed in this last section of the input files. These operators are combination of rotations/translations {R|t} and stored in a 2d array (sym). Each set of rotation/translation consists of three successive lines which labeled by the same number in the first column. Columns two to four are showing the components of the rotation matrix (by row), and the fifth column shows the non-symmorphic translation vector. For instance, there are three lines which are started with number 1 in the first column. 8

These three lines indicate an operator consist of a 3×3 rotation matrix and a 3×1 translation vector. As it can be seen here, the first line starts with number zero at the first column. Lines starting with zero in the first column are used to specify the origin of the space group as well as centering (P, F, I, C, A, R,…). "P" requires only one centering vector (0,0,0), so there is one line that starts with zero at the beginning as shown in the example. A "F" lattice in the conventional basis requires 4 lines in the block with zero in the first column to keep the coordination of the origin and possible centering vector(s), (0,0,0), (1/2,1/2,0), (1/2,0,1/2), (0,1/2,1/2) on each line in the columns two to four (fifth column is zero as well).

```
SYMMETRY_OPERATORS_
0        0.00000        0.00000        0.00000        0.00000
1        1.00000        0.00000        0.00000        0.00000
1        0.00000        1.00000        0.00000        0.00000
1        0.00000        0.00000        1.00000        0.00000
…
12       -1.00000       0.00000        0.00000        0.00000
12       -1.00000       1.00000        0.00000        0.00000
12       0.00000        0.00000        1.00000        0.50000
END_SYMMETRY_OPERATORS_
```

For a face-centered, "F" lattice, the first four lines read as follows:

```
0        0.00000        0.00000        0.00000        0.00000
0        0.50000        0.50000        0.00000        0.00000
0        0.50000        0.00000        0.50000        0.00000
0        0.00000        0.50000        0.50000        0.00000
```

Output
The program generates two output files. The complete optimized structure can be found in the "OUTPUT_Structure" file, formatted as human readable POSCAR/CONTCAR file, used in the Vienna *ab-initio* Simulation Package (VASP, Kresse & Furthmüller, 1996*a*,*b*). "OUTPUT_Results" is a log file that keeps track of the progress of the optimization, mean absolute error, and execution time.

Concluding remarks
- A complete listing of this input file as well as other examples can be found in the subdirectory "InputFiles_Samples".
- Comments/suggestions/feedback are welcome and should be directed to: Seyedayat Ghazisaeed: Email: ayatghz@outlook.com

References
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