
# Universal Structure Predictor:
# Evolutionary Xtallography

**A.R. Oganov, C.W. Glass, A.O. Lyakhov, Q. Zhu, G.-R. Qian, H.T. Stokes, M.S. Rakitin, M. Davari, P. Bushlanov, Z. Allahyari, S. Lepeshkin**

with contributions from
**R. Agarwal, X. Dong, P. Pertierra, Z. Raza, M.A. Salvado, D. Dong, Q. Zeng**

## MANUAL

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http://uspex.stonybrook.edu

# Contents

# 1 Features, aims and history of USPEX

## 1.1 Overview

USPEX stands for *Universal Structure Predictor: Evolutionary Xtallography*... and in Russian "uspekh" means "success", which is appropriate given the high success rate and many useful results produced by this method! The USPEX code possesses many unique capabilities for computational materials discovery. Here is a list of features: ...

From the beginning in 2004, non-empirical crystal structure prediction was the main aim of the USPEX project. In addition to this, USPEX also allows one to predict a large set of robust metastable structures and perform several types of simulations using various degrees of prior knowledge. Starting from 2010, our code explosively expanded to other types of problems, and from 2012 includes many complementary methods.

The problem of crystal structure prediction is very old and does, in fact, constitute the central problem of theoretical crystal chemistry. In 1988 John Maddox[1] wrote that:

> "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition... Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken".

It is immediately clear that the problem at hand is that of global optimization, *i.e.*, finding the global minimum of the free energy of the crystal (per mole) with respect to variations of the structure. To get some feeling of the number of possible structures, let us consider a simplified case of a fixed cubic cell with volume $V$, within which one has to position $N$ identical atoms. For further simplification let us assume that atoms can only take discrete positions on the nodes of a grid with resolution $\delta$. This discretization makes the number of combinations of atomic coordinates $C$ finite:

$$C = \frac{1}{(V/\delta^3)} \frac{(V/\delta^3)!}{[(V/\delta^3)-N]!N!} \tag{1}$$

If $\delta$ is chosen to be a significant fraction of the characteristic bond length (e.g., $\delta = 1$ Å), the number of combinations given by eq. 1 would be a reasonable estimate of the number of local minima of the free energy. If there are more than one type of atoms, the number of different structures significantly increases. Assuming a typical atomic volume $\sim$10 Å$^3$, and taking into account Stirling's formula ($n! \approx \sqrt{2\pi n}(n/e)^n$), the number of possible structures for an element A (compound AB) is $10^{11}$ ($10^{14}$) for a system with 10 atoms in the unit cell, $10^{25}$ ($10^{30}$) for a system with 20 atoms in the cell, and $10^{39}$ ($10^{47}$) for a system with 30 atoms in the unit cell. These numbers are enormous and practically impossible to deal with even for small systems with a total number of atoms $N \sim 10$.

Even worse, complexity increases exponentially with $N$. It is clear then, that point-by-point exploration of the free energy surface going through all possible structures is not feasible, except for the simplest systems with ∼1-5 atoms in the unit cell.

USPEX[2;3] employs an evolutionary algorithm devised by A.R. Oganov and C.W. Glass, with major subsequent contributions by A.O. Lyakhov and Q. Zhu. Its efficiency draws from the carefully designed variation operators, while its reliability is largely due to the use of state-of-the-art *ab initio* simulations inside the evolutionary algorithm. The strength of evolutionary simulations is that they do not require any system-specific knowledge (except the chemical composition) and are self-improving, i.e. in subsequent generations increasingly good structures are found and used to generate new structures. This allows a "zooming in" on promising regions of the energy (or property) landscape (Fig. 1). Furthermore, by carefully designing variation operators, it is very easy to incorporate additional features into an evolutionary algorithm.

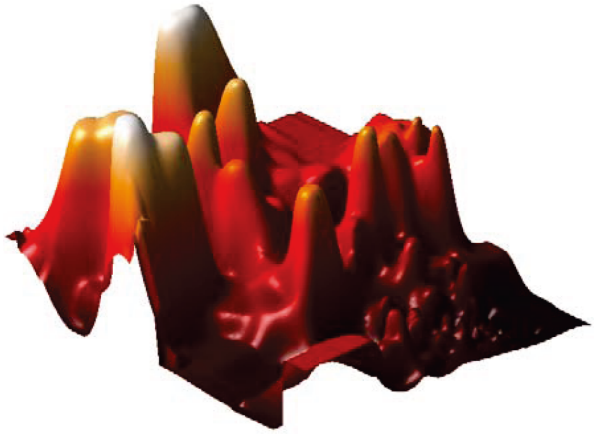


Figure 1: **2D projection of the reduced landscape of $Au_8Pd_4$, showing clustering of low-energy structures in one region.** The landscape was produced using the method of Oganov & Valle (2009).

A major motivation for the development of USPEX was the discovery of the post-perovskite phase of $MgSiO_3$ (Fig. 2), which was made in 2004[4;5] and has significantly changed models of the Earth's internal structure. In mid-2005 we had the first working version of USPEX. By September 2010, when USPEX was publicly released, the user community numbered nearly 200, over 800 users in May 2012, and over 2100 in December 2014.

The popularity of USPEX is due to its extremely high efficiency and reliability. This was shown in the First Blind Test for Inorganic Crystal Structure Prediction[6], where USPEX outperformed the other methods it was tested against (simulated annealing and random sampling). Random sampling (a technique pioneered for structure prediction by Freeman and Schmidt in 1993 and 1996, respectively, and since 2006 revived by Pickard[7] under the name AIRSS) is the simplest, but also the least successful and computationally the most expensive strategy. Even for small systems, such as GaAs with 8 atoms/cell, these

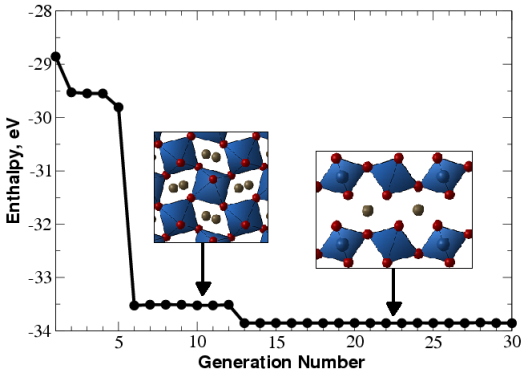



Figure 2: **Prediction of the crystal structure of $MgSiO_3$ at 120 GPa (20 atoms/cell).** Enthalpy of the best structure as a function of generation is shown. Between the $6^{th}$ and $12^{th}$ generations the best structure is perovskite, but at the $13^{th}$ generation the global minimum (post-perovskite) is found. This simulation was performed in 2005 using one of the first versions of USPEX combined with *ab initio* calculations. It used no experimental information and illustrates that USPEX can find both the stable and low-energy metastable structures in a single simulation. Each generation contains 30 structures. This figure illustrates the slowest of ∼10 calculations performed by the very first version of USPEX — and even that was pretty fast!

advantages are large (random sampling requires on average 500 structure relaxations to find the ground state in this case, while USPEX finds it after only ∼ 30 relaxations! (Fig. 3)). Due to the exponential scaling of the complexity of structure search (eq. 1), the advantages of USPEX increase exponentially with system size. For instance, 2 out of 3 structures of $SiH_4$ predicted by random sampling to be stable[7], turned out to be unstable[8]; and similarly random sampling predictions were shown[9] to be incorrect for nitrogen[10] and for $SnH_4$ (compare predictions[11] of USPEX and of random sampling[12]).

For larger systems, random sampling tends to produce almost exclusively disordered structures with nearly identical energies, which decreases the success rate to practically zero, as shown in the example of $MgSiO_3$ post-perovskite with 40 atoms/supercell — random sampling fails to find the correct structure even after 120,000 relaxations, whereas USPEX finds it after several hundred relaxations (Fig. 4).

Random sampling runs can easily be performed with USPEX — but we see this useful mostly for testing. Likewise, the Particle Swarm Optimization (PSO) algorithm for cluster and crystal structure prediction (developed by A.I. Boldyrev and re-implemented by Wang, Lu, Zhu and Ma) has been revamped and implemented on the basis of USPEX with minor programming work as a corrected PSO (corPSO) algorithm, which outperforms previous versions of PSO. Still, any version of PSO is rather weak and we see the PSO approach suitable mostly for testing purposes, if anyone wants to try. A very powerful new method, complementary to our evolutionary algorithm, is evolutionary metadynamics[13], a hybrid of Martoňák's metadynamics and the Oganov-Glass evolutionary approach. This method is powerful for global optimization and for harvesting low-energy metastable structures, and even for finding possible phase transition pathways. For detailed investiga-

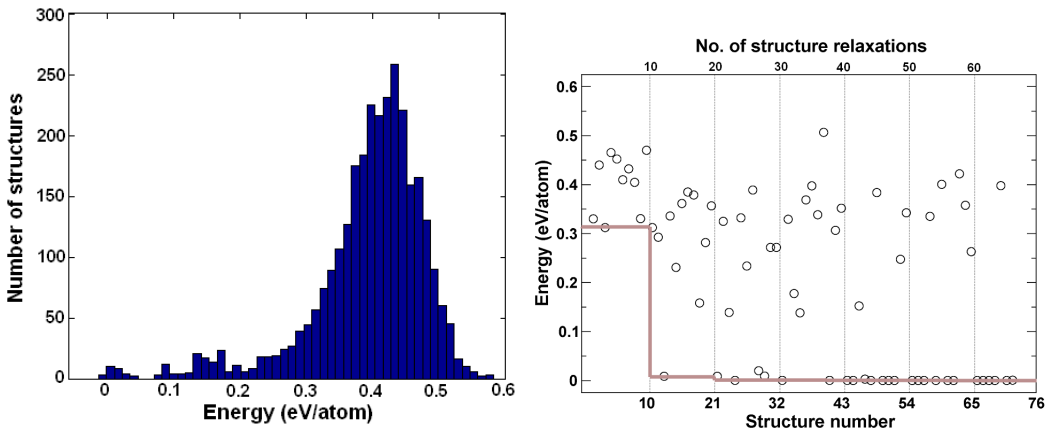



Figure 3: **Structure prediction for GaAs.** a) Energy distribution for relaxed random structures, b) progress of an evolutionary simulation (thin vertical lines show generations of structures, and the grey line shows the lowest energy as a function of generation). All energies are relative to the ground-state structure. The evolutionary simulation used 10 structures per generation. In addition, the lowest-energy structure of the previous generation survived into the next generation.

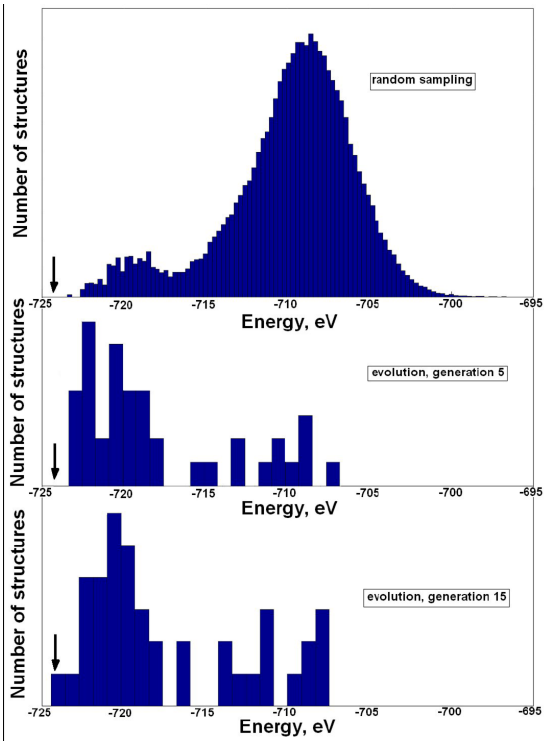



Figure 4: **Sampling of the energy surface: comparison of random sampling and USPEX for a 40-atom cell of $MgSiO_3$ with cell parameters of post-perovskite.** Energies of locally optimized structures are shown. For random sampling, $1.2 \times 10^5$ structures were generated (none of which corresponded to the ground state). For USPEX search, each generation included 40 structures and the ground-state structure was found within 15 generations. The energy of the ground-state structure is indicated by the arrow. This picture shows that "learning" incorporated in evolutionary search drives the simulation towards lower-energy structures.

tions of phase transition mechanisms, additional methods are implemented: variable-cell NEB method[14] and transition path method[15] in the version[16].

## 1.2 Features of USPEX

- Prediction of the stable and metastable structures knowing only the chemical composition. Simultaneous searches for stable compositions and structures are also possible.
- Incorporation of partial structural information is possible:
  - constraining search to fixed experimental cell parameters, or fixed cell shape, or fixed cell volume (Subsection 4.6);
  - starting structure search from known or hypothetical structures (Subsection 8.4);
  - assembling crystal structures from predefined molecules, including flexible molecules (Subsection 5.1).
- Efficient constraint techniques, which eliminate unphysical and redundant regions of the search space. Cell reduction technique (Oganov & Glass, 2008).
- Niching using fingerprint functions (Oganov & Valle, 2009; Lyakhov, Oganov, Valle, 2010). Subsection 4.9 for details.
- Initialization using fully random approach, or using space groups and cell splitting techniques (Lyakhov, Oganov, Valle, 2010).
- On-the-flight analysis of results — determination of space groups (and output in CIF-format) (Subsection 4.11), calculation of the hardness, order parameters, *etc.*
- Prediction of the structure of nanoparticles and surface reconstructions. See Section 5.2 for details.
- Restart facilities, enabling calculations to be continued from any point along the evolutionary trajectory (Subsection 4.7).
- Powerful visualization and analysis techniques implemented in the STM4 code (by M. Valle), fully interfaced with USPEX (Subsection 8.1).
- USPEX is interfaced with VASP, SIESTA, GULP, LAMMPS, DMACRYS, CP2K, Quantum Espresso, FHI-aims, ATK, CASTEP, Tinker, MOPAC codes. See full list of supported codes in Subsection 2.5. Interfacing with other codes is easy.
- Submission of jobs from local workstation to remote clusters and supercomputers is possible. See Section 8.9 for details.

- Options for structure prediction using the USPEX algorithm (default), random sampling, corrected particle swarm optimization (Subsection 5.5), evolutionary metadynamics (Subsection 5.4), minima hopping-like algorithm. Capabilities to predict phase transition mechanisms using evolutionary metadynamics, variable-cell NEB method (Subsection 6.1), and TSP method (Subsection **??**).

- Options to optimize physical properties other than the energy — *e.g.*, hardness (Lyakhov & Oganov, 2011), density (Zhu et al., 2011), band gap and dielectric constant (Zeng et al., 2014), and many other properties.

- For ease of programming and use, USPEX is written in MATLAB and it also works under Octave (a free MATLAB-like environment) — you do not need to compile anything, just plug and play! To enhance MATLAB-version compatibility, only basic MATLAB commands have been used. The code has been developed and tested under Matlab 2012 to 2015 and Octave 3.4 (*newer Octave versions are not supported yet!*).

- Starting from version 9.4.1, USPEX has an installer (`install.sh` file) and a Python-based runner of MATLAB code (`USPEX` Python module), providing a number of useful command line options.

## 1.3 Key USPEX method and application papers

1. Oganov A.R., Glass C.W. (2006). Crystal structure prediction using evolutionary algorithms: principles and applications. *J. Chem. Phys.*, **124**, 244704.

2. Oganov A.R., Stokes H., Valle M. (2011). How evolutionary crystal structure prediction works — and why. *Acc. Chem. Res.*, **44**, 227–237.

3. Lyakhov A.O., Oganov A.R., Stokes H., Zhu Q. (2013). New developments in evolutionary structure prediction algorithm USPEX. *Comp. Phys. Comm.*, **184**, 1172–1182.

4. Zhu Q., Oganov A.R., Glass C.W., Stokes H. (2012). Constrained evolutionary algorithm for structure prediction of molecular crystals: methodology and applications. *Acta Cryst. B*, **68**, 215–226.

5. Zhu Q., Li L., Oganov A.R., Allen P.B. (2013). Evolutionary method for predicting surface reconstructions with variable stoichiometry. *Phys. Rev. B*, **87**, 195317.

6. Zhu, Q., Sharma V., Oganov A.R., Ramprasad R. (2014). Predicting polymeric crystal structures by evolutionary algorithms. *J. Chem. Phys.*, **141**, 154102.

7. Zhou X.-F., Dong X., Oganov A.R., Zhu Q., Tian Y., Wang H.-T. (2014). Semimetallic Two-Dimensional Boron Allotrope with Massless Dirac Fermions. *Phys. Rev. Lett.*, **112**, 085502.

8. Lyakhov A.O., Oganov A.R., Valle M. (2010). Crystal structure prediction using evolutionary approach. In: Modern methods of crystal structure prediction (ed: A.R. Oganov), Berlin: Wiley-VCH.

9. Oganov A.R., Ma Y., Lyakhov A.O., Valle M., Gatti C. (2010). Evolutionary crystal structure prediction as a method for the discovery of minerals and materials. *Rev. Mineral. Geochem.*, **71**, 271–298.

10. Duan, D., Liu, Y., Tian, F., Li, D., Huang, X., Zhao, Z., Yu, H., Liu, B., Tian, W., Cui, T. (2014). Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-$T_c$ superconductivity. *Sci. Rep.*, **4**.

## 1.4 Version history (only important versions listed)

**v.1** — Evolutionary algorithm without local optimization. Real-space representation, interface with VASP. Experimental version. October 2004.

**v.2** — CMA-ES implementation (CMA-ES is a powerful global optimization method developed by N. Hansen). Experimental version. January 2005.

**v.3** — Evolutionary algorithm with local optimization.

**v.3.1** — Working versions, sequential. Major basic developments.

3.1.4-3.1.5 — First production version. Based largely on heredity with slice-shifting and with minimum-parent contribution (hard-coded to be 0.25). May 2005.

3.1.8 — Adaptive $k$-point grids. 15/10/2005.

3.1.11 — Restart from arbitrary generation. Experimental version. 04/11/2005.

3.1.12 — Production version based on v.3.1.11, variable slice-shift mutation. 11/11/2005.

3.1.13 — Adaptive scaling volume. 29/11/2005.

3.1.14 — Basic seed technique. 29/11/2005 (debugged 6/12/2005).

**v.3.2** — Massively parallel version.

**v.4** — Unified parallel/sequential version.

4.1.1 — Lattice mutation. 20/12/2005 (debugged 10/01/2006).

4.2.1 — Interfaced with SIESTA. Initial population size allowed to differ from the running population size. 24/01/2006 (debugged 20/04/2006).

4.2.3 — Relaxation of best structures made optional. Version with fully debugged massive parallelism. 25/04/2006.

4.4.1 — Interfaced with GULP. 08/05/2006.

**v.5** — Completely rewritten and debugged version, clear modular structure of the code.

5.1.1 — Atom-specific permutation, code interoperability, on-the-fly reading of parameters from `INPUT_EA.txt`. 20/12/2006.

5.2.1 — SIESTA-interface for Z-matrix, rotational mutation operator. 01/03/2007.

**v.6** — Production version.

6.1.3 — To efficiently fulfill hard constraints for large systems, an optimizer was implemented within USPEX. 07/06/2007.

6.2 — Development version.

6.3.1–6.3.2 — Introduced angular constraints for cell diagonals. Completely rewritten remote submission. Improved input format. Further extended standard tests. 07/12/2007.

6.3.3 — X-com grid interface (with participation of S. Tikhonov and S. Sobolev). 05/03/2008.

6.4.1 — Fingerprint functions for niching. 07/04/2008.

6.4.4 — Space group recognition. Fast fingerprints (from tables). 05/05/2008.

6.5.1 — Split-cell method for large systems. Easy remote submission. Variable number of best structures (clustering). 16/07/2008.

6.6.1 — A very robust version — improved fingerprint and split-cell implementations. 13/08/2008.

6.6.3 — Heredity with multiple parents implemented. 01/10/2008.

6.6.4 — Added a threshold for parents participating in heredity (niching). 03/10/2008.

6.6.6 — First implementation of multicomponent fingerprints. 04/12/2008.

6.6.7, 6.7.1 and 6.7.2 — Implemented quasi-entropy to measure the diversity of the population. 10/12/2008.

**v.7** — Production version, written to include variable composition.

7.1.1–7.1.7 — Series of improved versions. Version 7.1.7 has been distributed to ∼200 users. Variable composition partly coded, most known bugs fixed, improved tricks based on energy landscapes. Improved cell splitting, implemented pseudo-subcells. Implemented multicomponent fingerprints (much more sensitive to the structure than one-component fingerprints). 28/04/2009 (version finalized 28/05/2009).

7.2.5 — First fully functional version of the variable-composition method. Introduced transmutation operator and compositional entropy. 06/09/2009.

7.2.7 — Thoroughly debugged, improved restart capabilities, improved seeding, introduced perturbations within structure relaxation. 25/09/2009, further improved in versions 7.2.8/9.

7.3.0 — Full fingerprint support in the variable-composition code, including niching. "Fair" algorithm for producing the first generation of compositions. 22/10/2009.

7.4.1 — Introduced coordinate mutation based on local order[17]. Heredity and transmutation are also biased by local order. Introduced computation of the hardness and new types of optimization by hardness and density. 04/01/2010.

7.4.2 — Implementation of multiple-parents heredity biased by local order. 15/01/2010.

7.4.3 — Implementation of new types of optimization (to maximize structural order and diversity of the population). Implemented antiseeds, eliminated parameters `volTimeConst`, `volBestHowMany`. 24/01/2010.

**v.8** — Production version, written to include new types of optimization.

8.1.1–8.2.8 — Development versions. Local order and coordinate mutation operator. Softmutation operator. Calculation and optimization of the hardness. Optimization of the dielectric susceptibility. Prediction of the structure of nanoparticles and surfaces. Implementation of point groups. Greatly improved overall performance. Option to perform PSO simulations (not recommended for applications, due to PSO's inferior efficiency — so use only for testing purposes). Parameter `goodBonds` transformed into a matrix and used for building nanoparticles. 22/09/2010.

8.3.1 — Optimization of dielectric constants, cleaned-up input. 08/10/2010.

8.3.2 — For clusters, introduced a check on connectivity (extremely useful), `dynamicalBestHM`=2 option improved, as well as mechanism for producing purely softmutated generations. Improved fingerprints for clusters. Interface to Quantum Espresso and CP2K codes. 11/10/2010.

8.4 — Improved antiseed functionalities and several improvements for nanoparticles. Development branches for surface reconstructions, pseudo-metadynamics, molecular crystals.

8.5.0 — Initialization of the first random generation using the space group code of H. Stokes added. New formulation of metadynamics implemented and finalized, for now in a separate code. Several debugs for varcomp, antiseeds, nanoparticles, computation of hardness. 18/03/2011.

8.5.1 — Space group initialization implemented for cases of fixed unit cell, variable composition, and subcells. 20/04/2011.

8.6.0 — Added space group determination program from H. Stokes. Merger with the updated code for molecular crystals (including space group initialization). Fixed a bug for SIESTA (thanks to D. Skachkov). 06/05/2011.

8.6.1–8.7.2 — Improved symmetric initialization for the case of a fixed cell. Implemented optimization of dielectric constants (using GULP and VASP), band gap (using VASP), and DOS at the Fermi level (VASP). Graphical output enabled. Improved softmutation (by using better criteria for mode and directional degeneracies) and heredity (by using energy-order correlation coefficient and cosine formula for the number of trial slabs) operators. Most variables now have default values, which enables the use of very short input files. Shortened and improved the format of log-files. 13/11/2011.

8.7.5 — Graphical output now includes many extra figures. Added utility to extract all structures close to convex hull for easier post-processing. 21/03/2012.

**v.9** — Production version, made more user-friendly and written to include new types of functionality and to set the new standard in the field.

9.0.0 — Evolutionary metadynamics and vc-NEB codes added to USPEX package, added tensor version of metadynamics, added additional figures and post-processing tools, cleaned the code output. A few parameters removed from the input. Improved softmutation. April 2012.

9.1.0 — Release version. Cleaned up, documented. The user community is >800 people. Released 28/05/2012.

9.2.0 — Working GEM. Constant development of the GEM code. Space group determination tolerance is now an input parameter. Improved default for number of permutations. July-August 2012.

9.2.1–9.2.3 — Improved GEM, more diverse populations and supercell sizes, improved mode

selection. September-October 2012.

9.2.4–9.2.6 — (9.2.4 is a release version). Intelligent defaults for most input parameters. Improved symmetric initialization for clusters. Order-enhanced heredity for nanoparticles. New parameter to tune the tolerance for the space group determination. New property (quasientropy) can be optimized. Fully integrated vc-NEB code. November-December 2012.

9.2.7. — Release version. Enabled optimization of order for alloys, without structure relaxation (for easy creation of quasirandom structures, based on the more general definition than the so-called "special quasi-random structures"). Symmetry generation was improved (particularly important for fixed-cell calculations). For fixed-cell calculations, one can now specify the cell parameters, not only in the form of a $3 \times 3$ matrix, but also as a row of six values (three lengths in Angstroms and three angles in degrees). For the maximum number of permutation swaps (parameter `howManySwaps`), we have introduced an intelligent default. Added new tests, and cleaned and reran the old ones. Added interface to CASTEP (thanks to Z. Raza, X. Dong and AL). User community 1160 people. 30/12/2012.

9.3.0–9.3.3 — Fixed a bug in generation of random symmetric structures (this bug appeared in 9.2.7). Significantly simplified input and output. Created file `OUTPUT.txt` with the most important information. Enabled split-cell trick for molecular crystals. Improved variable-composition calculations by allowing one to specify initial compositions. Added interface to CASTEP and LAMMPS. Added new test cases. 20/03/2013.

9.3.4 — Release version, cleaned up. 25/03/2013.

9.3.5 — Added code for prediction of 2D-crystals. 19/04/2013.

9.3.6 — Incorporated plane groups for 2D-crystals. 29/04/2013.

9.3.8 — Incorporated plane groups for 1D-polymer crystals, improved variables of stoichiometry for surfaces. 19/06/2013.

9.3.9 — Released version. Significantly improved version, improved user-friendliness, new functionalities (2D-crystals, GEM) made more robust, improvements in the variable-composition algorithm (and enabled support for single-block calculations, *i.e.* fixed-composition searches with variable number of atoms in the cell), fully functional surface calculations, new optimization types (can optimize band gaps, dielectric constants, and newly invented figure of merit of dielectric materials). Interfaces with LAMMPS and ATK are documented in new test cases. Continuously updated with minor debugs (last debug 10/02/2014). 19/07/2013.

9.4.1 — A major upgrade, greatly improved user-friendliness (automatic estimate of volumes and of percentages of variation operators for each case), new functionalities (optimization of elastic properties and Chen's model of hardness, prediction of polymeric structures, anti-compositions, automatic analysis of statistics, improved seed technique), first release of GEM (generalized evolutionary metadynamics), provided a set of real-life examples of USPEX calculations, test cases, documentation. More than 2100 users. Released 30/12/2014.

9.4.2 — Release version, compatible with Octave 3.4. Convex hull code rewritten. Interface with MOPAC implemented. Default values for `goodBonds`, `valences`, `IonDistances` enabled. More robust for ternary, quaternary, and more complex variable-composition searches. Robust TPS implementation (only for developers, will be available for users soon). More than 2200 users. Released 21/03/2015.

9.4.3 — Release version. It includes fixing a number of bugs (which should slightly speed up performance), interface with MOPAC, improved documentation. Released 10/08/2015.

9.4.4 — Release version. It includes fix for space group determination and other problems reported by users, improved documentation and examples, full Octave 3.4 compatibility and partial Octave 3.6/3.8/4.0 support. This version should be nearly bug-free and is a milestone towards a very major upgrade, which will be made available in version 10. Released 05/10/2015.

# 2 Getting started

## 2.1 How to obtain USPEX

USPEX is an open source code, and can be downloaded at:

http://uspex.stonybrook.edu

In the download page, there are separate packages for USPEX source code, example and manual files.

## 2.2 Necessary citations

Whenever using USPEX, in all publications and reports you must cite the original papers, for example, in the following way:

> "Crystal structure prediction was performed using the USPEX code[2;13;18], based on an evolutionary algorithm developed by Oganov, Glass, Lyakhov and Zhu and featuring local optimization, real-space representation and flexible physically motivated variation operators".

Consult the `OUTPUT.txt` file for some of the most important references.

## 2.3 Bug reports

Like any large code, USPEX may have bugs. If you see strange behavior in your simulations, please report it to us in USPEX Google group at:

https://groups.google.com/forum/#!forum/uspex

Please describe your problem in details and attach `INPUT.txt`, `OUTPUT.txt`, `log` and other related files when you report a problem. You can also send the questions or problem descriptions to USPEX master (currently — Qiang Zhu (alecfans@gmail.com)).

## 2.4 On which machines can USPEX be run

USPEX can be used on any unix-based platform — all you need is one CPU where MATLAB or Octave can be run under Linux or Unix — using its special remote submission mechanism, USPEX will be able to connect to any remote machine (regardless of whether MATLAB is installed there) and use it for calculations.

## 2.5 Codes that can work with USPEX

Trial structures generated by USPEX are relaxed and then evaluated by an external code interfaced with USPEX. Based on the obtained ranking of relaxed structures, USPEX generates new structures — which are again relaxed and ranked. Our philosophy is to use existing well-established *ab initio* (or classical forcefield) codes for structure relaxation and energy calculations. Currently, USPEX is interfaced with:

- VASP — `https://www.vasp.at/`
- SIESTA — `http://departments.icmab.es/leem/siesta/`
- GULP — `http://nanochemistry.curtin.edu.au/gulp/`
- LAMMPS — `http://lammps.sandia.gov/`
- DMACRYS — `http://www.chem.ucl.ac.uk/basictechorg/dmacrys/index.html`
- CP2K — `http://www.cp2k.org/`
- Quantum Espresso — `http://www.quantum-espresso.org/`
- FHI-aims — `https://aimsclub.fhi-berlin.mpg.de/`
- ATK — `http://quantumwise.com/`
- CASTEP — `http://www.castep.org/`
- Tinker — `http://dasher.wustl.edu/tinker/`
- MOPAC — `http://openmopac.net/`

The choice of these codes was based on 1) their efficiency for structure relaxation; 2) robustness; and 3) popularity. Of course, there are other codes that can satisfy these criteria, and in the future we can interface USPEX to them.

## 2.6 How to install USPEX

After you download the archive with USPEX, you need to unpack it and run the following command to install USPEX to a user's or system-wide location:

```
bash ./install.sh
```

The installer does not require root privileges. You will be asked to select MATLAB or Octave (if it is found in the system), installation directory and to confirm creation/using of that directory. Then you will be provided with information about environmental variables, which must be set to make USPEX available in the system. For example:

```
For Bash shell system, add these lines in ~/.bashrc or ~/.profile or /etc/profile:
  export PATH=/home/user/bin/USPEX:$PATH
  export USPEXPATH=/home/user/bin/USPEX/src

For C shell system, add these lines in ~/.cshrc or ~/.profile or /etc/profile:
  setenv PATH "/home/user/bin/USPEX:$PATH"
  setenv USPEXPATH "/home/user/bin/USPEX/src"
```

If you want to change the path of MATLAB or Octave, you can edit the file `CODEPATH` in the installation directory of USPEX.

## 2.7 How to run USPEX

To run USPEX, you need to have MATLAB (preferred) or Octave and to have the executable of the external code on the compute nodes that you use for relaxing structures and computing their energies (see Subsection 2.5 for a list of supported codes). To set up your calculation, find an example (see Appendix 9.1 for a list of examples), similar to what you want to do, and start by editing `INPUT.txt`. The variables of this crucial file are described in Section 4 below. Then, gather the files needed for the external code performing structure relaxation in the `Specific/` folder — the executable (*e.g.*, `vasp`), and such files as `INCAR_1`, `INCAR_2`, ..., `INCAR_N`, and `POTCAR_A`, `POTCAR_B`, ..., where `A`, `B`, ... are the short symbols of the chemical elements described in the corresponding `POTCAR` files.

There are two ways to run the code — old and new, and both work.

(i) In the old way, you need to have the entire USPEX code (file `USPEX.m`, directory `FunctionFolder`, etc.) in your execution folder. Then type

```
nohup matlab < USPEX.m > log &
```

or, if you use Octave, type

```
nohup octave < USPEX.m > log &
```

(ii) In the new way, if you used the USPEX installer for the Python-based runner, all you need to execute the code is just type:

```
nohup USPEX -r > log &
```

or, if you use Octave, type

```
nohup USPEX -r -o > log &
```

File `log` will contain information on the progress of the simulation and, if any, errors (send these to us, if you would like to report a bug).

File `OUTPUT.txt` will contain details of the calculation and an analysis of each generation.

For the USPEX runner, we have a number of user-friendly options:

**-v, --version**: show program's version number and exit

**-h, --help**: show this help message and exit

**-p, --parameter**: specify parameter to get help. If no value or 'all' value is specified, all INPUT.txt parameters will be shown

**-e, --example**: show USPEX example details. If no value or 'all' value is specified, all examples will be shown

**-c NUM, --copy=NUM**: copy the INPUT.txt file and Specific Folder of ExampleXX.

**-g, --generate**: generate directories for preparing an USPEX calculation, including AntiSeeds, Seeds, Specific, Submission folders

**-r, --run**: run USPEX calculation

**-o, --octave**: run USPEX calculation with Octave instead of MATLAB

**--clean**: clean calculation folder

When running USPEX in the massively parallel mode, the user needs to do minimal work to configure files to the user's computers (hence, we cannot guarantee support for solving problems with massively parallel mode).

There are two modes for job submission — (1) local submission and (2) remote submission, depending on whether you submit *ab initio* calculations on the same machine where you run USPEX and MATLAB, or if you send your jobs to a remote supercomputer. See the keyword `whichCluster` and Subsection 8.9 of this Manual.

Please note, that you shoud have `bash` shell set by default to make USPEX working correctly. Users frequently report issues when running USPEX on a machine with `csh` shell, where "`echo -e ...`" command might not be supported.

## 2.8 Running USPEX examples: a mini-tutorial

Once you have downloaded the USPEX package and installed it, you can run the first USPEX example. The description of the examples is listed in Appendix 9.1. The required external codes to run the examples (except EX13) are shown below:

- GULP: EX02, EX03, EX08, EX12, EX15 (VC-NEB), EX16
- VASP: EX01, EX07, EX09, EX14 (META)
- LAMMPS: EX04
- ATK: EX05
- CASTEP: EX06
- DMACRYS: EX10
- Tinker: EX11

Now, let us start our first USPEX experience:

### 2.8.1 Test the USPEX python runner

To get the version information, you can use the following command:

```
>> USPEX -v
```

You should get the following information:

```
  USPEX Version 9.4.2 (19/03/2015)
```

If it does not work, please check your installation procedure and environment settings as described above.

### 2.8.2 Run the EX13-3D_special_quasirandom_structure_TiCoO

EX13 does not require any external code, you can run it to get familiar with the USPEX running procedure. The calculation would take ∼30 minutes. To start the calculation, first create a test folder, copy the example files and then run the calculation through the USPEX Python runner, with the following commands:

```
>> mkdir EX13
>> cd EX13
>> USPEX -c 13
>> USPEX -r
```

Meanwhile you have some time to get more details about example EX13. In EX13, the structural order is optimized (minimized) with the evolutionary algorithm. Therefore in `INPUT.txt` the following is set:

```
USPEX : calculationMethod
-4    : optType
```

and these parameters are used below:

```
300   : calculationType

% atomType
Co Ti O
% EndAtomType

% numSpecies
16 16 64
% EndNumSpecies
```

to specify USPEX to evaluate the $Co_{16}Ti_{16}O_{64}$ system. To reduce calculation time of EX13, you can reduce `populationSize` and `numGenerations`, for example:

```
5    : populationSize
5    : numGenerations
```

However, with such a small `populationSize` and `numGenerations`, you cannot expect USPEX to find the structure with the lowest order. Since you do not need to use any external code, you can simply set

```
% abinitioCode
0
% ENDabinit
```

The `Seeds/POSCARS` file contains the initial $Ti_{16}Co_{16}O_{64}$ structure.

When you find the `USPEX_IS_DONE` file, congratulations, you have successfully finished your first USPEX example. Next, you can run calculations using external codes.

### 2.8.3 Run an example using external code

In this step, we suggest to run examples interfaced with GULP or VASP, starting from EX02 or EX01. You will also use USPEX runner to get the example information of EX02, create a separate folder and copy the files, with commands:

```
>> mkdir EX02
>> cd EX02
>> USPEX -c 2
```

Since in example EX02 GULP code is used, set:

```
% abinitioCode
3 3 3 3
% ENDabinit
```

To run a serial job without a job batch system, you should change the following parameters in the INPUT.txt below:

```
0     : whichCluster
1     : numParallelCalcs
```

In the example INPUT.txt file whichCluster=QSH, where QSH is our group's cluster name. We also provide the same way to help users to define their own cluster. For more details, please see Section 8.9.

In INPUT.txt, we do not specify how to run GULP, because we assume all users use the same command:

```
% commandExecutable
gulp < input > output
% EndExecutable
```

But make sure, this command also works on your machine. If you want to run EX01 with a parallel version of VASP, you should set something like:

```
% abinitioCode
1 1 1 1
% ENDabinit

% commandExecutable
mpirun -np 8 vasp
% EndExecutable
```

With wrong commandExecutable settings, you will fail to start the USPEX calculation. When everything is set correctly, we can run the calculation through USPEX runner using the command:

```
>> USPEX -r
```

### 2.8.4 Checking the results

After starting the command, you can check the output files in results1/ folder.

Now, you have a basic experience of using USPEX to run simple calculations. Please read the following sections of this manual to get more insight into USPEX.

# 3 Overview of input and output files

Input/output files depend on the external code used for structure relaxation.

An important technical element of our philosophy is the multi-stage strategy for structure relaxation. Final structures and energies must be high-quality, in order to correctly drive evolution. Most of the newly generated structures are far from local minimum and their high-quality relaxation is extremely expensive. This cost can be avoided if the first stages of relaxation are done with cruder computational conditions — only at the last stages of structure relaxation is there a need for high-quality calculations. The first stages of structure relaxation can be performed with cheaper approaches. You can change the computational conditions (basis set, $k$-points sampling, pseudopotentials or PAW potentials) or the level of approximation (interatomic potentials *vs.* LDA *vs.* GGA) or even the structure relaxation code (see Subsection 2.5 for a list of supported codes) during structure relaxation of each candidate structure. We strongly suggest that you initially optimize the cell shape and atomic positions at constant unit cell volume, and only then perform full optimization of all structural variables. While optimizing at constant volume, you do not need to worry about Pulay stresses in plane-wave calculations — thus it is OK to use a small basis set; however, for variable-cell relaxation you will need a high-quality basis set. For structure relaxation, you can often get away with a small set of $k$-points — but don't forget to sufficiently increase this at the last stage(s) of structure relaxation, to get accurate energies.

## 3.1 Input files

Suppose that the directory where the calculations are performed is ∼/`StructurePrediction`. This directory will contain:

- file `INPUT.txt`, thoroughly described in Section 4.
- Subdirectory ∼/`StructurePrediction/Specific/` with VASP, SIESTA or GULP (*etc.*) executables, and enumerated input files for structure relaxation — `INCAR_1`, `INCAR_2`, ..., and pseudopotentials.
- Subdirectory ∼/`StructurePrediction/Seeds` — contains files with seed structures and with a list of compositions/anti-compositions. Seed structures should be in VASP5 POSCAR format and concatenated in a file called `POSCARS` or `POSCARS_gen` (`gen` is the generation number). The `compositions` and `Anti-compositions` files are used to control the compositions during variable-composition or single-block calculations.
- Subdirectory ∼/`StructurePrediction/AntiSeeds` — you may put here particular structures that you wish to penalize, or use antiseed technique without specifying any structures explicitly (and penalize structures found during the run).

## 3.2 Output files

There usually is a result folder ∼/StructurePrediction/results1 for storing the results of a USPEX calculation. If this is a new calculation, results2, results3, ... (if the calculation has been restarted or run a few times), there will be a separate results* folder for each calculation.

The subdirectory ∼/StructurePrediction/results1 contains the following files:

- OUTPUT.txt — summarizes input variables, structures produced by USPEX, and their characteristics.
- Parameters.txt — this is a copy of the INPUT.txt file used in this calculation, for your reference.
- Individuals — gives details of all produced structures (energies, unit cell volumes, space groups, variation operators that were used to produce the structures, $k$-points mesh used to compute the structures' final energy, degrees of order, *etc.*). File BESTIndividuals gives this information for the best structures from each generation. Example of Individuals file:

```
Gen   ID    Origin   Composition    Enthalpy   Volume  Density   Fitness   KPOINTS  SYMM  Q_entr A_order S_order
                                       (eV)     (A^3)  (g/cm^3)
  1    1   Random    [   4  8 16 ]  -655.062   201.062   4.700   -655.062 [ 1  1  1]   1   0.140  1.209  2.632
  1    2   Random    [   4  8 16 ]  -650.378   206.675   4.572   -650.378 [ 1  1  1]   1   0.195  1.050  2.142
  1    3   Random    [   4  8 16 ]  -646.184   203.354   4.647   -646.184 [ 1  1  1]   1   0.229  0.922  1.746
  1    4   Random    [   4  8 16 ]  -649.459   198.097   4.770   -649.459 [ 1  1  1]   9   0.128  0.958  2.171
  1    5   Random    [   4  8 16 ]  -648.352   202.711   4.662   -648.352 [ 1  1  1]   2   0.154  1.014  2.148
  1    6   Random    [   4  8 16 ]  -643.161   206.442   4.577   -643.161 [ 1  1  1]   1   0.234  0.946  1.766
  1    7   Random    [   4  8 16 ]  -647.678   207.119   4.562   -647.678 [ 1  1  1]   1   0.224  1.108  2.106
  1    8   Random    [   4  8 16 ]  -644.482   203.844   4.636   -644.482 [ 1  1  1]   1   0.215  0.952  1.857
  1    9   Random    [   4  8 16 ]  -647.287   204.762   4.615   -647.287 [ 1  1  1]  40   0.136  1.142  2.563
  1   10   Random    [   4  8 16 ]  -649.459   198.097   4.770   -649.459 [ 1  1  1]   9   0.128  0.958  2.171
. . . . . .
```

- convex_hull — only for variable-composition calculations, where it gives all thermodynamically stable compositions, and their enthalpies (per atom). Example:

```
---- generation  1 -------
  10   0     -8.5889
   0  14     -8.5893
  11   3     -8.7679
---- generation  2 -------
  10   0     -8.5889
   0  14     -8.5893
  11   3     -8.8204
---- generation  3 -------
  10   0     -8.5889
   0  14     -8.5893
  12   4     -8.9945
. . . . . .
```

- gatheredPOSCARS — relaxed structures (in the VASP5 POSCAR format). Example:

```
EA1     9.346  8.002  2.688 90.000 90.000 90.000 Sym.group:    1
1.0000
    9.346156     0.000000     0.000000
    0.000000     8.002181     0.000000
    0.000000     0.000000     2.688367
   Mg   Al  O
   4    8   16
```

```
Direct
    0.487956     0.503856     0.516443
    0.777565     0.007329     0.016443
    0.987956     0.507329     0.016443
    0.277565     0.003856     0.516443
    0.016944     0.178753     0.016443
    0.019294     0.833730     0.516443
    0.746227     0.333730     0.516443
    0.748577     0.678753     0.016443
    0.516944     0.832431     0.516443
    0.519294     0.177455     0.016443
    0.246227     0.677455     0.016443
    0.248577     0.332431     0.516443
    0.416676     0.241774     0.516443
    0.559871     0.674713     0.016443
    0.205650     0.174713     0.016443
    0.348845     0.741774     0.516443
    0.613957     0.380343     0.016443
    0.804054     0.542164     0.516443
    0.113957     0.630842     0.516443
    0.304054     0.469021     0.016443
    0.848845     0.269411     0.016443
    0.705650     0.836472     0.516443
    0.059871     0.336472     0.516443
    0.916676     0.769411     0.016443
    0.651564     0.130842     0.516443
    0.461467     0.969021     0.016443
    0.151564     0.880343     0.016443
    0.961467     0.042164     0.516443
EA2     9.487  4.757  4.580 90.243 90.188 89.349 Sym.group:    1
1.0000
    9.486893     0.000000     0.000000
    0.054041     4.756769     0.000000
   -0.014991    -0.019246     4.579857
   Mg   Al  O
   4    8   16
Direct
    0.499837     0.633752     0.011361
    0.500082     0.131390     0.482012
    0.813573     0.257696     0.494520
    0.326111     0.625491     0.501746
    0.995267     0.254346     0.992293
    0.160822     0.689054     0.001270
    0.995907     0.760753     0.498354
    0.159742     0.192300     0.491958
    0.811206     0.761223     0.997857
    0.325692     0.125479     0.987935
    0.656355     0.695175     0.503322
    0.656596     0.199917     0.991605
    0.487990     0.763078     0.627771
    0.845518     0.645378     0.347890
    0.623474     0.895186     0.185946
    0.616379     0.395875     0.308861
    0.093745     0.991831     0.185467
    0.092669     0.494591     0.309957
    0.847697     0.118765     0.113434
    0.475636     0.251449     0.875207
    0.327510     0.787484     0.116764
    0.720411     0.975740     0.706398
    0.200804     0.880147     0.683027
    0.975416     0.612789     0.852917
    0.986131     0.108285     0.644081
    0.204805     0.364607     0.830780
    0.718464     0.496262     0.817031
    0.323904     0.257705     0.340590
. . . . . .
```

- `BESTgatheredPOSCARS` — the same data for the best structure in each generation.
- `gatheredPOSCARS_unrelaxed` — gives all structures produced by USPEX before relaxation.
- `enthalpies_complete.dat` — gives the enthalpies for all structures in each stage of relaxation.
- `origin` — shows which structures originated from which parents and through which variation operators. Example:

```
 ID    Origin    Enthalpy   Parent-E   Parent-ID
   1   Random     -23.395   -23.395  [         0]
   2   Random     -23.228   -23.228  [         0]
   3   Random     -23.078   -23.078  [         0]
   4   Random     -23.195   -23.195  [         0]
   5   Random     -23.155   -23.155  [         0]
   6   Random     -22.970   -22.970  [         0]
   7   Random     -23.131   -23.131  [         0]
   8   Random     -23.017   -23.017  [         0]
   9   Random     -23.117   -23.117  [         0]
  10   Random     -23.195   -23.195  [         0]
. . . . . . . . . . . . . . . . . . . . . . . . . .
```

- `gatheredPOSCARS_order` — gives the same information as `gatheredPOSCARS`, and in addition for each atom it gives the value of the order parameter (Ref.[17]). Example:

```
EA1     9.346  8.002  2.688 90.000 90.000 90.000 Sym.group:    1
1.0000
    9.346156     0.000000     0.000000
    0.000000     8.002181     0.000000
    0.000000     0.000000     2.688367
   Mg   Al  O
   4    8   16
Direct
    0.487956     0.503856     0.516443     1.1399
    0.777565     0.007329     0.016443     1.1399
    0.987956     0.507329     0.016443     1.1399
    0.277565     0.003856     0.516443     1.1399
    0.016944     0.178753     0.016443     1.1915
    0.019294     0.833730     0.516443     1.2474
    0.746227     0.333730     0.516443     1.2474
    0.748577     0.678753     0.016443     1.1915
    0.516944     0.832431     0.516443     1.1915
    0.519294     0.177455     0.016443     1.2474
    0.246227     0.677455     0.016443     1.2474
    0.248577     0.332431     0.516443     1.1915
    0.416676     0.241774     0.516443     1.2914
    0.559871     0.674713     0.016443     1.1408
    0.205650     0.174713     0.016443     1.1408
    0.348845     0.741774     0.516443     1.2914
    0.613957     0.380343     0.016443     1.2355
    0.804054     0.542164     0.516443     1.2161
    0.113957     0.630842     0.516443     1.2355
    0.304054     0.469021     0.016443     1.2161
    0.848845     0.269411     0.016443     1.2914
    0.705650     0.836472     0.516443     1.1408
    0.059871     0.336472     0.516443     1.1408
    0.916676     0.769411     0.016443     1.2914
    0.651564     0.130842     0.516443     1.2355
    0.461467     0.969021     0.016443     1.2161
    0.151564     0.880343     0.016443     1.2355
    0.961467     0.042164     0.516443     1.2161
EA2     9.487  4.757  4.580 90.243 90.188 89.349 Sym.group:    1
1.0000
    9.486893     0.000000     0.000000
    0.054041     4.756769     0.000000
   -0.014991    -0.019246     4.579857
   Mg   Al  O
   4    8   16
Direct
    0.499837     0.633752     0.011361     0.9368
    0.500082     0.131390     0.482012     1.0250
    0.813573     0.257696     0.494520     0.9805
    0.326111     0.625491     0.501746     0.9437
    0.995267     0.254346     0.992293     0.9241
    0.160822     0.689054     0.001270     1.1731
    0.995907     0.760753     0.498354     0.9696
    0.159742     0.192300     0.491958     1.2666
    0.811206     0.761223     0.997857     1.0215
    0.325692     0.125479     0.987935     1.0353
    0.656355     0.695175     0.503322     1.2291
    0.656596     0.199917     0.991605     1.2547
    0.487990     0.763078     0.627771     1.1199
    0.845518     0.645378     0.347890     0.9725
    0.623474     0.895186     0.185946     0.9990
    0.616379     0.395875     0.308861     1.0141
    0.093745     0.991831     0.185467     1.1451
    0.092669     0.494591     0.309957     1.1164
    0.847697     0.118765     0.113434     0.8821
    0.475636     0.251449     0.875207     1.0609
    0.327510     0.787484     0.116764     1.0451
    0.720411     0.975740     0.706398     0.9539
    0.200804     0.880147     0.683027     0.9398
    0.975416     0.612789     0.852917     1.1191
```

```
   0.986131     0.108285     0.644081     0.9803
   0.204805     0.364607     0.830780     1.0915
   0.718464     0.496262     0.817031     1.0663
   0.323904     0.257705     0.340590     1.1471
. . . . . .
```

- `goodStructures_POSCARS` and `extended_convex_hull_POSCARS` (for fixed- and variable-composition calculations correspondingly) are files, made available in v.9 of USPEX. These files are extremely convenient for analysis; they report all of the different structures in order of decreasing stability, starting from the most stable structure and ending with the least stable.

- `compositionStatistic` is a file containing statistic of the compositions in terms of which variation operators produced these compositions. Example:

```
     Comp/Ratio        Total     Random Heredity Mutation Seeds  COPEX  Best/Convex
[  0.0000  1.0000  ]   30( 63)      21       8       1       0       0      33
       0     8          4(  4)       2       2       0       0       0       0
       0     9          2(  2)       2       0       0       0       0       0
       0    10          5(  5)       3       2       0       0       0       0
       0    11          2(  2)       0       1       1       0       0       0
       0    12          6( 35)       6       0       0       0       0      29
       0    13          2(  3)       1       1       0       0       0       1
       0    14          0(  0)       0       0       0       0       0       0
       0    15          2(  2)       2       0       0       0       0       0
       0    16          5(  8)       5       0       0       0       0       3
       0     3          1(  1)       0       1       0       0       0       0
       0     4          1(  1)       0       1       0       0       0       0
[  0.1250  0.8750  ]   52( 52)      32       9      11       0       0       0
       1     7         20( 20)       4       8       8       0       0       0
       2    14         32( 32)      28       1       3       0       0       0
[  0.1111  0.8889  ]   25( 25)       9      14       2       0       0       0
       1     8         25( 25)       9      14       2       0       0       0
[  0.1000  0.9000  ]   16( 16)       9       5       2       0       0       0
       1     9         16( 16)       9       5       2       0       0       0
[  0.0909  0.9091  ]   11( 11)       5       4       2       0       0       0
       1    10         11( 11)       5       4       2       0       0       0
[  0.0833  0.9167  ]   17( 17)       8       2       7       0       0       0
       1    11         14( 14)       8       2       4       0       0       0
       2    22          3(  3)       0       0       3       0       0       0
. . . . . .
```

- graphical files (`*.pdf`) — for rapid analysis of the results:

  - `Energy_vs_N.pdf` (`Fitness_vs_N.pdf`) — energy (fitness) as a function of structure number;
  - `Energy_vs_Volume.pdf` — energy as a function of volume;
  - `Variation-Operators.pdf` — energy of the child *vs.* parent(s) energy; different operators are marked with different colors (this graph allows one to assess the performance of different variation operators);
  - `E_series.pdf` — correlation between energies from relaxation steps $i$ and $i+1$; helps to detect problems and improve input for relaxation files.
  - For variable compositions there is an additional graph `extendedConvexHull.pdf`, which shows the enthalpy of formation as function of composition.
  - `compositionStatistic.pdf` — visualization of `compositionStatistic` file.

## 3.3 `Specific/` folder

Executables and enumerated input files for structure relaxation should be put in subdirectory ∼`/StructurePrediction/Specific/` for different interfaced code, such as VASP, SIESTA, GULP, *etc.*.

- For VASP, files `INCAR_1`, `INCAR_2`, ..., *etc.*, defining how relaxation and energy calculations will be performed at each stage of relaxation (we recommend at least 3 stages of relaxation), and the corresponding `POTCAR_*` files with pseudopotentials. *E.g.*, `INCAR_1` and `INCAR_2` perform very crude structure relaxation of both atomic positions and cell parameters, keeping the volume fixed, `INCAR_3` performs full structure relaxation under constant external pressure with medium precision, `INCAR_4` performs very accurate calculations. Each higher-level structure relaxation starts from the results of a lower-level optimization and improves them. `POTCAR` files can alternatively be defined by just putting the files for the elements in `Specific/` folder, for instance `POTCAR_C`, `POTCAR_O`, *etc.*
- For SIESTA, you need the pseudopotentials files and input files `input_1.fdf`, `input_2.fdf`, ...
- For GULP, files `goptions_1`, `goptions_2`, ..., and `ginput_1`, `ginput_2`, ... must be present. The former specify what kind of optimization is performed, the latter specify the details (interatomic potentials, pressure, temperature, number of optimization cycles, *etc.*).
- For DMACRYS, `fort.22` is the file for general control parameters. The classical force field is given by the file of `fit.pots`. File `cutoff` defines the maximum bond length of the intra-molecular bonds.
- For CASTEP, structural files are given by `cell_1`, `cell_2`, ..., while the computational parameters are given by `param_1`, `param_2`, .... The corresponding pseudopotential files must be present as well.
- For CP2K, files `cp2k_options_1`, `cp2k_options_2`, ..., must be present. All files should be normal CP2K input files with all parameters **except** atom coordinates and cell parameters (these will be written by USPEX together with the finishing line "`&END FORCE_EVAL`"). The "`name of the project`" should always be USPEX, since the program reads the output from files `USPEX-1.cell` and `USPEX-pos-1.xyz`. We recommend performing relaxation at least in three steps (similarly to VASP) — first optimize only the atom positions with the lattice fixed, and then do a full relaxation.
- For Quantum Espresso, files `QEspresso_options_1`, `QEspresso_options_2`, ..., must be present. All files should be the normal QE input files with all parameters except atom coordinates, cell parameters and $k$-points (these will be written by

USPEX at the end of the file). We recommend performing a multi-step relaxation. For instance, `QEspresso_options_1` does a crude structure relaxation of atomic positions with fixed cell parameters, `QEspresso_options_2` does full structure relaxation under constant external pressure with medium precision; and `QEspresso_options_3` does very accurate calculations.

## 3.4 `INCAR_*` files in `Specific/` folder for VASP

To run USPEX correctly, there are some hints on the files in `Specific/` folder to control the structure relaxation in USPEX. We take example of VASP as an external code:

- Your final structures have to be well relaxed, and energies — precise. The point is that your energy ranking has to be correct (to check this, look at `E_series.pdf` file in the output).
- Your `POTCAR` files: To yield correct results, the cores of your pseudopotentials (or PAW potentials) should not overlap by more than 10–15%.
- To have accurate relaxation at low cost, use the multistage relaxation with at least three stages of relaxation for each structure, *i.e.* at least three `INCAR` files (`INCAR_1`, `INCAR_2`, `INCAR_3`, ...). We usually set 4–5 stages of relaxation.
- Your initial structures will be usually very far from local minima, in such cases it helps to relax atoms and cell shape at constant volume first (`ISIF`=4 in `INCAR_1,2`), then do full relaxation (`ISIF`=3 in `INCAR_3,4`), and finish with a very accurate single-point calculation (`ISIF`=2 and `NSW`=0 in `INCAR_5`).

  **Exceptions:** when you do fixed-cell predictions, and also in evolutionary metadynamics (except full relaxation) you must have `ISIF`=2.
- When your volume does not change, you can use default plane wave cutoff. When you use `ISIF`=3, you must increase it by 30–40%, otherwise you get a large Pulay stress. Also your convergence criteria can be loose in the beginning, but have to be tight in the end: *e.g.*, `EDIFF`=1e-2 and `EDIFFG`=1e-1 in `INCAR_1`, gradually tightening to `EDIFF`=1e-4 and `EDIFFG`=1e-3 in `INCAR_4`. The maximum number of timesteps (`NSW`) should be sufficiently large to enable good relaxation, but not too large to avoid wasting computer time on poor configurations. The larger your system, the larger `NSW` should be.
- Choosing an efficient relaxation algorithm can save a lot of time. In VASP, we recommend to start relaxation with conjugate gradients (`IBRION`=2 and `POTIM`=0.02) and when the structure is closer to local minimum, switch to `IBRION`=1 and `POTIM`=0.3.
- Even if you study an insulating system, many configurations that you will sample are going to be metallic, so to have well converged results, you must use "metallic"

treatment — which works both for metals and insulators. We recommend the Methfessel-Paxton smearing scheme (ISMEAR=1). For a clearly metallic system, use ISMEAR=1 and SIGMA=0.1–0.2. For a clearly insulating system, we recommend ISMEAR=1 and SIGMA starting at 0.1 (INCAR_1) and decreasing to 0.03–0.04.

Here we provide an example of INCAR files for carbon with 16 atoms in the unit cell, with default ENCUT=400 eV in POTCAR:

```
INCAR_1:
    PREC=LOW
    EDIFF=1e-2
    EDIFFG=1e-1
    NSW=65
    ISIF=4
    IBRION=2
    POTIM=0.02
    ISMEAR=1
    SIGMA=0.10
```

```
INCAR_2:
    PREC=NORMAL
    EDIFF=1e-3
    EDIFFG=1e-2
    NSW=55
    ISIF=4
    IBRION=1
    POTIM=0.30
    ISMEAR=1
    SIGMA=0.08
```

```
INCAR_3:
    PREC=NORMAL
    EDIFF=1e-3
    EDIFFG=1e-2
    ENCUT=520.0
    NSW=65
    ISIF=3
    IBRION=2
    POTIM=0.02
    ISMEAR=1
    SIGMA=0.07
```

```
INCAR_4:
    PREC=NORMAL
    EDIFF=1e-4
    EDIFFG=1e-3
    ENCUT=600.0
    NSW=55
    ISIF=3
    IBRION=1
    POTIM=0.30
    ISMEAR=1
    SIGMA=0.06
```

```
INCAR_5:
    PREC=NORMAL
    EDIFF=1e-4
    EDIFFG=1e-3
    ENCUT=600.0
    NSW=0
    ISIF=2
    IBRION=2
    POTIM=0.02
    ISMEAR=1
    SIGMA=0.05
```

The philosophy of METADYNAMICS is very similar to USPEX, except that we DO NOT change the cell shape during the META evolution. Therefore, we need to put ISIF=2 for all META steps. If the full relaxation mode is on, we can put ISIF=3 for the steps of full relaxation. Therefore, if we have the following set up:

```
% abinitioCode
1 1 1 (1 1)
% ENDabinit
```

the ISIF should be "2 2 2 3 3" for INCAR_1, . . . , INCAR_5 correspondingly.

Different from USPEX, VC-NEB method doesn't need a structure relaxation from the external codes, which runs the structure relaxation in VC-NEB itself with the forces from external code calculation. Thus, there are some differences in the files. Take VASP `INCAR` files for example, we need to set `NSW`=0 to avoid the structure relaxation, but with `ISIF`=2 or 3 to extract the forces on the atoms, and the stress tensor on the lattice in VASP. We also suggest to use `PREC`=Accurate to have a good estimation for the forces and stress to accelerate the calculations for VC-NEB. An example of `INCAR` file for VC-NEB is presented below:

```
INCAR_1:
    PREC=Accurate
    EDIFF=1e-4
    EDIFFG=1e-3
    ENCUT=600.0
    NSW=0
    ISIF=2
    IBRION=2
    POTIM=0.02
    ISMEAR=1
    SIGMA=0.05
```

# 4 Input options. The INPUT.txt file

A typical INPUT.txt file is given in the Appendix ??. Below we describe the most important parameters of the input. Most of the parameters have reliable default values, which will be used if you skip them in the input file (this allows you to have extremely short input files!). Those options that have no default, and should always be specified. Please consult online utilities at http://han.ess.sunysb.edu — these help to prepare the INPUT.txt file, molecular files, and analyze some of results. Section 7 of this Manual briefly discusses these utilities.

## 4.1 Type of run and system

▷ *variable* calculationMethod

*Meaning*: Specifies the method of calculation

Possible values (characters):

- USPEX — evolutionary algorithm for crystal structure prediction
- META — evolutionary metadynamics
- VCNEB — transition path determination using the variable-cell nudged elastic band method
- PSO — corrected PSO algorithm
- TPS — transition path sampling method (not yet released)
- MINHOP — minima hopping method (not yet released)
- COPEX — another new technique, to be released soon

*Default*: USPEX

*Format*:

```
USPEX : calculationMethod
```

▷ *variable* calculationType

*Meaning*: Specifies type of calculation, *i.e.*, whether the structure of a bulk crystal, nanoparticle, or surface is to be predicted. This variable consists of three indices: *dimensionality*, *molecularity* and *compositional variability*:

- dimensionality:

"3" — bulk crystals

"2" — surfaces, "–2" — 2D-crystals

"1" — polymers

"0" — nanoparticles

- molecularity:

  "0" — non-molecular

  "1" — molecular calculations

- variability of chemical composition in the calculation:

  "0" — fixed composition

  "1" — variable composition

*Default*: `300`

*Format*:

```
301 :  calculationType
```

**Note:** If `calculationType`=310, *i.e.*, a prediction for a molecular crystal is to be performed, then USPEX expects you to provide files `MOL_1`, `MOL_2`, ... with molecular geometries for all types of molecules, and these molecules will be placed in the newly generated structures as whole objects. Available options: 300, 301, 310, 000, 200, 201, –200 (and not yet released: 110, 311).

▷ *variable* `optType`

*Meaning*: This variable allows you to specify the property that you want to optimize.

Possible values (characters):

| Value | Number | Description |
|---|---|---|
| enthalpy | 1 | to find the stable phases |
| volume | 2 | volume minimization<br>(to find the densest structure) |
| hardness | 3 | hardness maximization<br>(to find the hardest phase) |
| struc_order | 4 | maximization of the degree of order<br>(to find the most ordered structure) |
| aver_dist | 5 | maximization of average structural differences within a generation |
| diel_sus | 6 | maximization of the static dielectric susceptibility<br>(only for VASP and GULP) |
| gap | 7 | maximization of the band gap<br>(only for VASP) |
| diel_gap | 8 | maximization of electrical energy storage capacity<br>(only for VASP) |
| mag_moment | 9 | maximization of the magnetization<br>(only for VASP) |
| quasientropy | 10 | maximization of structural quasientropy |

Elasticity-related properties ("11**"):

| Value | Number | Description |
|---|---|---|
| K, Bulk Modulus | 1101 | maximization of bulk modulus |
| G, Shear Modulus | 1102 | maximization of shear modulus |
| E, Young's Modulus | 1103 | maximization of Young's modulus |
| v, Poisson's ratio | 1104 | maximization of Poisson's ratio |
| G/K, Pugh's modulus ratio | 1105 | maximization of Pugh's modulus ratio |
| Hv, Vickers hardness | 1106 | maximization of Vickers hardness |
| Kg, Fracture toughness | 1107 | maximization of fracture toughness |
| D, Debye temperature | 1108 | maximization of Debye temperature |
| Vm, sound velocity | 1109 | maximization of sound velocity |
| S-wave velocity | 1110 | maximization of S-wave velocity |
| P-wave velocity | 1111 | maximization of P-wave velocity |

**Note:** Elasticity-related properties are supported only for VASP (starting from VASP 5.1) and GULP. For VASP users, you need to add one more `INCAR_*` file to the `Specific/` folder with the parameters `IBRION`=6, `ISIF`$\geq$3 and `NFREE`=4. The estimates of bulk, shear and Young's moduli are the Voigh-Reuss-Hill (VRH) averages. The Vickers hardness is calculated with the Chen-Niu model[19]. Fracture toughness optimization uses the lowest theoretical fracture toughness as fitness.

*Default*: `enthalpy`

*Format*:

```
enthalpy :  optType
```

**Notes:**

(1) If you want to do the opposite optimization, add a minus sign. For instance, to minimize the static dielectric constant, put "`-diel_sus`".

(2) If `optType=gap` or `diel_gap`, instead of the gap we use an extended function that also behaves continuously for metals — namely, $\Delta E_g - g(E_F)/N$, where $\Delta E_g$ is the gap, $g(E_F)$ is the density of states at the Fermi level (for metals) and $N$ is the number of atoms in the unit cell. Thanks to the continuity of this function, global maximization of gap-related quantities can even be performed for metallic solutions. For metals it is equal to the DOS at the Fermi level, for semiconductors and insulators — to the band gap.

Fig. 5 gives an example of hardness maximization for $TiO_2$ (`optType`=hardness), showing maximum possible hardness ~14 GPa[20] and refuting claims of Dubrovinsky (2001) about ultrahardness of $TiO_2$[21]. A good example of how a simple USPEX run can resolve a long-standing dispute.

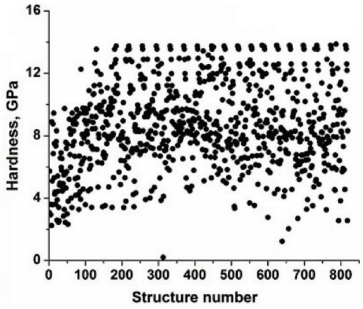



Figure 5: **Predictions of the hardest structure of $TiO_2$.**

Now, you need to specify what you know about the system.

▷ *variable* `atomType`

*Meaning*: Describes the identities of each type of atom.

*Default*: none, must specify explicitly

*Format*:

If you prefer to use the atomic numbers from Mendeleev's Periodic Table of the Elements, specify:

```
% atomType
12 14 8
% EndAtomType
```

Or, if you prefer to use atomic names, specify:

```
% atomType
```

```
Mg Si O
% EndAtomType
```

You can alternatively specify the full names of the elements, for example:

```
% atomType
Magnesium Silicon Oxygen
% EndAtomType
```

▷ *variable* numSpecies

*Meaning*: Describes the number of atoms of each type.

*Default*: none, must specify explicitly

*Format*:

```
% numSpecies
4 4 12
% EndNumSpecies
```

This means there are 4 atoms of the first type, 4 of the second type, and 12 of the third type.

**Notes:** For variable-composition calculations, you have to specify the compositional building blocks as follows:

```
% numSpecies
2 0 3
0 1 1
% EndNumSpecies
```

This means that the first building block has formula $A_2C_3$ and the second building block has formula BC, where A, B and C are described in the block `atomType`. All structures will then have the formula $xA_2C_3 + yBC$ with $x$, $y$ = (0,1,2,...) — or $A_{2x}B_yC_{3x+y}$. If you want to do prediction of all possible compositions in the A-B-C system, you should specify:

```
% numSpecies
1 0 0
0 1 0
0 0 1
% EndNumSpecies
```

You can also do fixed-composition calculations with a variable number of formula units; in this case set just one line (and `calculationType`=301), for example for compound $A_2BC_4$:

```
% numSpecies
2 1 4
% EndNumSpecies
```

▷ *variable* ExternalPressure

*Meaning*: Specifies external pressure at which you want to find structures, in GPa.

*Default*: 0

*Format*:

```
100 :  ExternalPressure
```

**Note:** As of USPEX 9.4.1 pressure value (in GPa) is set by the tag `ExternalPressure` in the `INPUT.txt` file. Please NO LONGER specify it in relaxation files in the `Specific/` folder.

▷ *variable* valences

*Meaning*: Describes the valences of each type of atom. Used only to evaluate bond hardnesses, which are used for computing the approximate dynamical matrix (for softmutation) and hardness of the crystal.

*Default*: USPEX has a table of default valences (see Appendix 9.8). Beware, however, that for some elements (*e.g.*, N, S, W, Fe, Cr, *etc.*) many valence states are possible. Unless you calculate hardness, this is not a problem and you can use the default values. If you do calculate the hardness, you need to carefully specify the valence explicitly.

*Format*:

```
% valences
2 4 2
% EndValences
```

▷ *variable* goodBonds

*Meaning*: Specifes, in the matrix form, the minimum bond valences for contacts that will be considered as important bonds. Like the `IonDistances` matrix (see below), this is a square matrix cast in an upper-triangular form. This is only used in calculations of hardness and in softmutation. One can estimate these values for a given bond type taking `goodBonds`$=\frac{valence}{max\_coordination\_number}$ or slightly smaller.

*Default*: USPEX can make a reasonable default estimation of `goodBonds`, you will see the values in `OUTPUT.txt` file. This should be sufficient for most purposes, but for hardness calculations you may need to carefully examine these values and perhaps set them manually. For more details, see Appendix 9.9

*Format*:

```
% goodBonds
10.0 10.0 0.2
0.0 10.0 0.5
0.0 0.0 10.0
% EndGoodBonds
```

**Notes:** The dimensions of this matrix must be equal to either the number of atomic species or unity. If only one number is used, the matrix is filled with this number. The matrix above reads as follows: to be considered a bond, the Mg–Mg distance should be short enough to have bond valence of 10 or more, the same for Mg–Si, Si–Si, and O–O bonds (by using such exclusive criteria,

we effectively disregard these interactions from the softmutation and hardness calculations), whereas Mg–O bonds that will be considered for hardness and softmutation calculations will have a bond valence of 0.2 or more, and the Si–O bonds will have a bond valence of 0.5 or more.

▷ *variable* checkMolecules

*Meaning*: Switches on/off post-relaxation check that original molecules (files MOL_1, MOL_2, ...) are intact. Useful for molecular crystals (calculationType=310, 311).

Possible values (integer):

- 0 — check is not performed, structures with broken or merged molecules are considered. (We strongly suggest users not to use this.)
- 1 — check is performed, all the structures with broken or merged molecules are discarded.

*Default*: 1

*Format*:

```
1 :  checkMolecules
```

▷ *variable* checkConnectivity

*Meaning*: Switches on/off hardness calculation and connectivity-related criteria in softmutation.

Possible values (integer):

- 0 — connectivity is not checked, no hardness calculations;
- 1 — connectivity is taken into account, hardness is calculated.

*Default*: 0

*Format*:

```
1 :  checkConnectivity
```

## 4.2 Population

▷ *variable* populationSize

*Meaning*: The number of structures in each generation; initial generation can be set separately, if needed.

*Default*: $2 \times N$ rounded to the closest 10, where $N$ is the number of atoms/cell (or `maxAt` for variable composition). The upper limit is 60. Usually, you can trust these default settings.

*Format*:

```
20 :  populationSize
```

▷ *variable* `initialPopSize`

*Meaning*: The number of structures in the initial generation.

*Default*: equal to `populationSize`.

*Format*:

```
20 :  initialPopSize
```

**Note:** In most situations, we suggest that these two parameters be equal. Sometimes (especially in variable-composition calculations) it may be useful to specify `initialPopSize` to be larger than `populationSize`. It is also possible to have a smaller initial population, and this is useful if one wants to generate the first population entirely from a few seed structures.

▷ *variable* `numGenerations`

*Meaning*: Maximum number of generations allowed for the simulation. The simulation can terminate earlier, if the same best structure remains unchanged for `stopCrit` generations.

*Default*: `100`

*Format*:

```
50 :  numGenerations
```

▷ *variable* `stopCrit`

*Meaning*: The simulation is stopped if the best structure did not change for stopCrit generations, or when `numGenerations` have expired — whichever happens first.

*Default*: total number of atoms for fixed-composition runs, maximum number of atoms `maxAt` for variable-composition runs.

*Format*:

```
20 :  stopCrit
```

## 4.3 Survival of the fittest and selection

▷ *variable* `bestFrac`

*Meaning*: Fraction of the current generation that shall be used to produce the next

generation.

*Default*: 0.7

*Format*:

```
0.7 :  bestFrac
```

**Note:** This is an important parameter, values between 0.5–0.8 are reasonable.

▷ *variable* keepBestHM

*Meaning*: Defines how many best structures will survive into the next generation.

*Default*: 0.15×populationSize

*Format*:

```
3 :  keepBestHM
```

▷ *variable* reoptOld

*Meaning*: Defines reoptimization of the survived structures. If reoptOld=0, these structures will be left without reoptimization while if reoptOld=1, they will be reoptimized again. Usually reoptOld=0 is a reasonable choice (provided your structure relaxation was high quality).

*Default*: 0

*Format*:

```
1 :  reoptOld
```

## 4.4 Structure generation and variation operators

▷ *variable* symmetries

*Meaning*: Possible space groups for crystals, plane groups for 2D crystals/surfaces, or point groups for clusters. A certain number of structures will be produced using randomly selected groups from this list, using randomly generated lattice parameters and atomic coordinates. During this process special Wyckoff sites can be produced from general positions (Fig. 6).

*Default*:

- For 3D crystals: 2-230
- For 2D crystals/surfaces: 2-17
- For clusters: E C2 D2 C4 C3 C6 T S2 Ch1 Cv2 S4 S6 Ch3 Th Ch2 Dh2 Ch4 D3 Ch6 O D4 Cv3 D6 Td Cv4 Dd3 Cv6 Oh Dd2 Dh3 Dh4 Dh6 Oh C5 S5 S10 Cv5 Ch5

```
D5 Dd5 Dh5 I Ih
```

*Format*:

```
% symmetries
195-198 200 215-230
% EndSymmetries
```

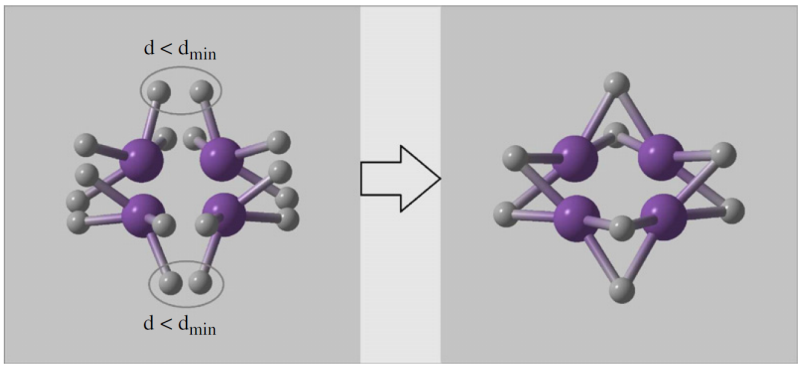



Figure 6: **Example of merging atoms onto special Wyckoff positions (from Ref.[13]).**

▷ *variable* fracGene

*Meaning*: Percentage of structures obtained by heredity; 0.1 means 10%, *etc.*

*Default*: 0.5

*Format*:

```
0.5 :  fracGene
```

▷ *variable* fracRand

*Meaning*: Fraction of the generation produced randomly from the space groups specified by the user.

*Default*: 0.2

*Format*:

```
0.20 :  fracRand
```

▷ *variable* fracPerm

*Meaning*: Percentage of structures obtained by permutation; 0.1 means 10%, *etc.*

*Default*: 0.1 if there is more than one type of atom/molecule; 0 otherwise.

*Format*:

```
0.1 :  fracPerm
```

▷ *variable* fracAtomsMut

*Meaning*: Specifies the percentage of structures obtained by softmutation or coormutation.

*Default*: 0.1

*Format*:

```
0.1 :  fracAtomsMut
```

**Note:** You can use softmutation or coormutation by specifying softMutTill.

▷ *variable* fracRotMut

*Meaning*: Percentage of structures obtained mutating molecular orientations; 0.1 means 10%, *etc.*

*Default*: 0.1 for molecular crystals; 0 otherwise.

*Format*:

```
0.1 :  fracRotMut
```

▷ *variable* fracLatMut

*Meaning*: Percentage of structures obtained from lattice mutations; 0.1 means 10%, *etc.*

*Default*: 0 for fixed cell prediction; 0.1 otherwise.

*Format*:

```
0.1 :  fracLatMut
```

**Note: If the sum of all the fractions (fracGene + fracRand + fracPerm + ...) is not equal to 1, they will be rescaled.**

▷ *variable* howManySwaps

*Meaning*: For permutation, the number of pairwise swaps will be randomly drawn from a uniform distribution between 1 and howManySwaps.

*Default*: 0.5×(maximum number of possible swaps). If atoms $Na$ and $Nb$, and atoms $Nc$ and $Nd$ are swappable, then the total number of possible swaps is $\min(Na, Nb) + \min(Nc, Nd)$, and the default for howManySwaps is $0.5 \times [\min(Na, Nb) + \min(Nc, Nd)]$. In most cases, it is a good idea to rely on this default.

*Format*:

```
5 :  howManySwaps
```

▷ *variable* specificSwaps

*Meaning*: Specifies which atom types you allow to swap in permutation.

*Default*: blank line, which means no specific swaps and all atoms are permutable.

*Format*:

```
% specificSwaps
1 2
% EndSpecific
```

**Note:** In this case, atoms of type 1 could be swapped with atoms of type 2. If you want to try all possible swaps, just leave a blank line inside this keyblock, or delete the block.

▷ *variable* mutationDegree

*Meaning*: The maximum displacement in softmutation in Å. The displacement vectors for softmutation or coormutation are scaled so that the largest displacement magnitude equals `mutationDegree`.

*Default*: 3×(average atomic radius)

*Format*:

```
2.5 :  mutationDegree
```

▷ *variable* mutationRate

*Meaning*: Standard deviation of the epsilons in the strain matrix for lattice mutation. The strain matrix components are selected randomly from the Gaussian distribution and are only allowed to take values between -1 and 1. Lattice mutation essentially incorporates the ideas of metadynamics into our method[6;22], where new structures are found by building up cell distortions of some known structure. Unlike in metadynamics, the distortions are not accumulated in our method, so the strain components should be large to obtain new structures.

*Default*: 0.5

*Format*:

```
0.5 :  mutationRate
```

It is a good idea to combine lattice mutation with a weak softmutation:

▷ *variable* DisplaceInLatmutation

*Meaning*: Specifies softmutation as part of lattice mutation and sets the maximum displacement in Å.

*Default*: 1.0

*Format*:

```
1.0 :  DisplaceInLatmutation
```

▷ *variable* AutoFrac

*Meaning*: Enables automatic evolution of variation operators (parameter control), which speeds up the calculation by up to ∼2 times. To switch to user defined variation operators, set AutoFrac=0.

*Default*: 0

*Format*:

```
1 :  AutoFrac
```

## 4.5 Constraints

The same structure can be represented in an infinite number of coordinate systems ("modular invariance"). Most of these equivalent choices will lead to very flat unit cells, which creates problems for structure relaxation and energy calculation (*e.g.*, a very large number of $k$-points are needed). The constraint, well known in crystallography, that the cell angles be between 60° and 120°, does not remove all redundancies and problematic cells (*e.g.*, thus allowed cells with $\alpha = \beta = \gamma \sim 120°$ are practically flat). Therefore, we developed[23;24] a special scheme to obtain special cell shapes with the shortest cell vectors. This transformation can be performed if there is at least one lattice vector whose projection onto any other cell vector or the diagonal vector of the opposite cell face is greater (by modulus) than half the length of that vector, *i.e.*, for pairs $\mathbf{a}$ and $\mathbf{b}$, or $\mathbf{c}$ and $(\mathbf{a}+\mathbf{b})$ these criteria are:

$$\left|\frac{\mathbf{a}\cdot\mathbf{b}}{|\mathbf{b}|}\right| > \frac{|\mathbf{b}|}{2} \tag{2}$$

$$\left|\frac{\mathbf{a}\cdot\mathbf{b}}{|\mathbf{a}|}\right| > \frac{|\mathbf{a}|}{2} \tag{3}$$

$$\left|\frac{\mathbf{c}\cdot(\mathbf{a}+\mathbf{b})}{|\mathbf{c}|}\right| > \frac{|\mathbf{c}|}{2} \tag{4}$$

$$\left|\frac{\mathbf{c}\cdot(\mathbf{a}+\mathbf{b})}{|\mathbf{a}+\mathbf{b}|}\right| > \frac{|\mathbf{a}+\mathbf{b}|}{2} \tag{5}$$

For instance, for the criterion 2 the new vector $\mathbf{a}^*$ equals:

$$\mathbf{a}^* = \mathbf{a} - \mathrm{ceil}\left(\frac{|\mathbf{a}\cdot\mathbf{b}|}{|\mathbf{b}|^2}\right)\mathrm{sign}(\mathbf{a}\cdot\mathbf{b})\mathbf{b} \tag{6}$$

This transformation is performed iteratively, completely avoids pathological cell shapes, and thus solves the problem. During this transformation, the atomic fractional coordinates are transformed so that the original and transformed structures are identical (during the transformation, the Cartesian coordinates of the atoms remain invariant).

▷ *variable* minVectorLength

*Meaning*: Sets the minimum length of a cell parameter of a newly generated structure.

*Default*: 1.8 × covalent diameter of the largest atom. For molecular crystals (calculationType = 310, 311) default value is 1.8 × max(MolCenters).

*Format*:

```
2.0 :  minVectorLength
```

Commonly used computational methods (pseudopotentials, PAW, LAPW, and many parametric forcefields) break down when the interatomic distances are too small. This situation needs to be avoided and you can specify the minimum distances between each pair of atoms using the IonDistances square matrix cast in an upper-triangular form:

▷ *variable* IonDistances

*Meaning*: Sets the minimum interatomic distance matrix between different atom types. Distances lower than IonDistances are considered entirely unphysical and will be strictly avoided.

*Default*: the IonDistances between atom A and B are estimated as $0.2 \times (V_A^{1/3} + V_B^{1/3})$ but not larger then 1.2 Å, and $0.45 \times (V_A^{1/3} + V_B^{1/3})$ in molecular calculations, where $V_A$ and $V_B$ are the default volumes of atom $A$ and $B$ estimated in USPEX.

*Format*:

```
% IonDistances
1.0 1.0 0.8
0.0 1.0 0.8
0.0 0.0 1.0
% EndDistances
```

**Note:** The dimensions of this matrix must be equal to the number of atomic species. If the compound in the example above is $MgSiO_3$, the matrix reads as follows: the minimum Mg–Mg distance allowed in a newly generated structure is 1.0 Å, the minimum Mg–Si, Si–Si and O–O distances are also 1.0 Å, and the minimum Mg–O and Si–O distances are 0.8 Å. You can use this keymatrix to incorporate further system-specific information: *e.g.*, if you know that Mg atoms prefer to be very far apart and are never closer than 3 Å in your system, you can specify this information. Beware, however, that the larger these minimum distances, the more difficult it is to find structures fulfilling these constraints (especially for large systems), so strive for a compromise and remember that IonDistances must be **much** smaller than the actual bond lengths.

▷ *variable* constraint_enhancement

*Meaning*: Allows one to apply the stricter constraints of the IonDistances matrix (by

constraint_enhancement times) for symmetric random structures (for all variation operators, unenhanced IonDistances matrix still applies). Only use it if you know what you are doing.

*Default*: 1

*Format*:

```
1 :  constraint_enhancement
```

For molecular crystals, the following keyblock is extremely important:

▷ *variable* MolCenters

*Meaning*: Matrix of minimal distances between the centers of molecules. Any distances lower than these indicate large overlap of the molecules, are unphysical and will be strictly avoided.

*Default*: zero-matrix for non-molecular calculations, no default for molecular crystals (must specify explicitly).

*Format*:

```
% MolCenters
5.5 7.7
0.0 9.7
% EndMol
```

**Note:** In the above example, there are two types of molecules. In all of the generated structures, the distance between the geometric centers of the molecules of the first type must be at least 5.5 Å (A–A distance), the distance between the centers of the molecules of the first and second type — 7.7 Å (A–B distance), and the distance between the molecules of the second type — 9.7 Å (B–B distance).

## 4.6 Cell

It is useful to create all new structures (before relaxing them) with a unit cell volume appropriate for given conditions. This can be specified in the Latticevalues keyblock:

▷ *variable* Latticevalues

*Meaning*: Specifies the initial volume of the unit cell or known lattice parameters.

*Default*: For cell volumes you don't have to specify values — USPEX has a powerful algorithm to find reasonable estimates at any pressure.

*Format*:

```
% Latticevalues
```

```
125.00
% Endvalues
```

**Notes:** (1) This volume is only used as an initial guess and only influences the first generation, each structure is fully optimized and adopts the volume corresponding to the (free) energy minimum. This keyblock also has another use: when you know the lattice parameters (*e.g.*, from experiment), you can specify them in the `Latticevalues` keyblock instead of unit cell volume, *e.g.*:

```
% Latticevalues
7.49 0.0 0.0
0.0 9.71 0.0
0.0 0.0 7.07
% Endvalues
```

You can also specify unit cell parameters just by listing `a`, `b`, `c`, $\alpha$, $\beta$, and $\gamma$ values:

```
% Latticevalues
10.1 8.4 12.5 90.0 101.3 90.0
% Endvalues
```

Attention: if you do a calculation with a fixed monoclinic cell, please use setting with special angle $\beta$ (standard setting).

(2) For variable-composition calculations, you have to specify the volume of end members of the compositional search space, *e.g.*:

```
% Latticevalues
12.5 14.0 11.0
% Endvalues
```

(3) Users no longer need to specify the unit cell or atomic volumes in the keyblock `Latticevalues` — a special algorithm has been implemented that accurately estimates it at the pressure of interest, without the need for the user to specify it. This option works well and is available for any `calculationType` where input volumes are required: 3**, 2D-crystals, 110, 000. You can also use online program http://han.ess.sunysb.edu/volume_estimation. The users can also input the volumes manually.

(4) If you study molecular crystals under pressure, you might sometimes need to increase the initial volumes somewhat, in order to be able to generate structures by the random symmetric algorithm.

▷ *variable* `splitInto`

*Meaning*: Defines the number of identical subcells or pseudosubcells in the unit cell. If you do not want to use splitting, just use the value 1, or delete the block. Use splitting only for systems with >25–30 atoms/cell.

*Default*: `1`

*Format*:

```
% splitInto (number of subcells into which the unit cell is split)
1 2 4
% EndSplitInto
```

Subcells introduce extra translational (pseudo)symmetry. In addition to this, each subcell can be built using a special space groups algorithm developed by A.R. Oganov and H.T. Stokes and implemented by H.T. Stokes (see Reference[13]).

## 4.7 Restart

If something goes wrong, you may want to continue the calculation from the point where it stopped — or from an earlier point. If all you want to do is continue the run from where it stopped, you do not need to change any settings (all information will be stored in the `*.mat` files) and it will be sufficient to remove the file `still_reading` and run USPEX again.

If you want to restart from a particular generation in a particular `results`-folder, then specify `pickUpGen` = number of the generation from which you want to start, `pickUpFolder` = number of `results`-folder (*e.g.*, 1 for `results1`, 2 for `results2`, ...) from which the restart needs to be initiated. If `pickUpGen`=0, then a new calculation is started. The default options for all three parameters are 0. For example, to restart a calculation performed in the folder `results5` from generation number 10, specify:

```
10 :  pickUpGen
5 :  pickUpFolder
```

## 4.8 Details of *ab initio* calculations

USPEX employs a powerful two-level parallelization scheme, making its parallel scalability exemplary. The first level of parallelization is performed within structure relaxation codes, the second level of parallelization distributes the calculation over the individuals in the same population (since structures within the same generation are independent of each other).

First, you must specify which code(s) you want to use for structure relaxation and fitness calculation:

▷ *variable* `abinitioCode`

*Meaning*: Defines the code used for every optimization step.

*Default*: `1` for every optimization step (VASP)

*Format*:

```
% abinitioCode
3 2 2 1 1
% ENDabinit
```

**Note:** Numbers indicate the code used at each step of structure relaxation (see Subsection 2.5 for a list of supported codes):

1 — VASP

2 — SIESTA

3 — GULP

4 — LAMMPS

5 — Neural Networks code (unused at the moment)

6 — DMACRYS

7 — CP2K

8 — Quantum Espresso

9 — FHI-aims

10 — ATK

11 — CASTEP

12 — Tinker

13 — MOPAC

▷ *variable* KresolStart

*Meaning*: Specifies the reciprocal-space resolution for $k$-points generation (units: $2\pi$Å$^{-1}$).

*Default*: from 0.2 to 0.08 linearly

*Format*:

```
 % KresolStart
0.2 0.16 0.12 0.08
% Kresolend
```

**Note:** You can enter several values (one for each step of structure relaxation), starting with cruder (*i.e.*, larger) values and ending with high resolution. This dramatically speeds up calculations, especially for metals, where very many $k$-points are needed. This keyblock is important if you use VASP or QuantumEspresso (with GULP it is not needed at all, and with SIESTA you will have to define KresolStart within SIESTA input files).

For **clusters**, **2D-crystals**, and **surfaces**, you have to specify the thickness of the vacuum region around the cluster (or around the surface slab):

▷ *variable* vacuumSize

*Meaning*: Defines the amount of vacuum added around the structure (closest distance in Å between neighboring clusters in adjacent unit cells). Used only for surfaces, 2D-crystals, and nanoparticles.

*Default*: 10 Å for every step of relaxation

*Format*:

```
% vacuumSize
10 10 15 20 20
% EndVacuumSize
```

▷ *variable* numParallelCalcs

*Meaning*: Specifies how many structure relaxations you want to run in parallel.

*Default*: 1

*Format*:

```
10 :  numParallelCalcs
```

You need to supply the job submission files or the names of executable files for each code/mode you are using.

▷ *variable* commandExecutable

*Meaning*: Specifies the name of the job submission files or executables for a given code.

*Default*: no default, has to be specified by the user.

*Format*:

```
% commandExecutable
gulp < input > output
mpirun -np 8 vasp > out
mpirun -np 8 vasp > out
mpirun -np 8 vasp > out
% EndExecutable
```

**Note:** Every line corresponds to a stage of relaxation — the first line describes the execution of the first stage of relaxation, *etc.* For example, `abinitioCode` equal to "`3 1 1 1`" means that the first relaxation step will be performed with GULP, while the subsequent steps will be performed using VASP via the command "`mpirun -np 8 vasp > out`". If only one line is present in `commandExecutable`, then the same execution will be performed for all steps of relaxation.

You can actually use USPEX on virtually any platform in the remote submission mode. All you need is MATLAB/Octave to be running on your workstation. In that case, your workstation will prepare input (including jobs), send them to the remote compute nodes, check when the calculations are complete, get the results back, analyze them, and prepare new input. The amount of data being sent to and fro is not large, so the network does not need to be very fast. Job submission is, of course, machine-dependent.

▷ *variable* whichCluster

*Meaning*: Specifies the types of job submission.

Possible values (integer):

- 0 — no-job-script;
- 1 — local submission;
- 2 — remote submission.

*Default*: 0

*Format*:

```
1 :  whichCluster
```

▷ *variable* remoteFolder

*Meaning*: Folder on the remote supercomputer where the calculation will be performed. This keyword is activated only if whichCluster=2.

*Default*: none

*Format*:

```
Blind_test :  remoteFolder
```

**Note:** there is a similar parameter specified in the remote submission file — homeFolder. The actual path to the calculation will be *homeFolder*/*remoteFolder*/CalcFolderX where X=1, 2, 3,. . . .

▷ *variable* PhaseDiagram

*Meaning*: Enables calculation of a phase diagram for calculationType=300 and 301. It gives an idea (crude one — just to get a rough idea!) of which the new phases may be at higher and lower pressures, and a rough idea of transition pressures.

*Default*: 0

*Format*:

```
1 :  PhaseDiagram
```

## 4.9 Fingerprint settings

Before changing the following parameters, we encourage you to read the methodological papers first, so you understand what you are doing (Oganov & Valle, 2009[17]).

▷ *variable* RmaxFing

*Meaning*: The distance cutoff (in Å).

*Default*: 10.0

*Format*:

```
10.0 :  RmaxFing
```

▷ *variable* deltaFing

*Meaning*: The discretization (in Å) of the fingerprint function.

*Default*: 0.08

*Format*:

```
0.10 :  deltaFing
```

▷ *variable* sigmaFing

*Meaning*: The Gaussian broadening of interatomic distances.

*Default*: 0.03

*Format*:

```
0.05 :  sigmaFing
```

`toleranceFing` (default=0.008) and `toleranceBestHM` (default=0.02) specify the minimal cosine distances between structures that qualify them as non-identical — for participating in the production of child structures and for survival of the fittest, respectively. They depend on the precision of structure relaxation and the physics of the system (for instance: for ordering problems, fingerprints belonging to different structures will be very similar, and these tolerance parameters should be made small). `toleranceBestHM` is used only if `dynamicalBestHM`=1 (which we don't use anymore), so this parameter is essentially obsolete.

## 4.10 Antiseed settings

A family of antiseed techniques have been developed and implemented in USPEX, all based on the idea of penalizing already sampled structures to ensure that the simulation is not stuck in a local minimum. Here, time-dependent fitness is the sum of the actual enthalpy (or another fitness property of interest) and a history-dependent term, which is the sum of the Gaussian potentials added to already sampled parts of the energy landscape:

$$f = f_0 + \sum_a W_a \exp\left(-\frac{d_{ia}^2}{2\sigma_a^2}\right),$$

where $f$ is fitness ($f_0$ — the true fitness, $f$ — history-dependent fitness), $W_a$ is the height and $\sigma_a$ is the width of the Gaussian. In our approach, Gaussian parameters change depending on the population diversity and energy spread at each generation.

There are three ways to use this technique. In the first, you can put the structure that you wish to penalize in the `AntiSeeds` folder. For example, this can be the ground state structure — in this case, USPEX will try to find the second lowest-enthalpy structure.

In the second and third methods, you don't specify antiseed structure(s) — the calculation either uses all sampled structures as antiseeds (well tested; the recommended approach) or just the best structure in each generation. You need to specify a few settings:

▷ *variable* antiSeedsActivation

*Meaning*: Specifies from which generation the antiseed mode will be switched on. When antiSeedsActivation $= N > 0$, Gaussians are added to all structures starting from generation $N$, and when $N < 0$ — Gaussians are only added to the best structure of each generation, starting from generation $N$. When $N = 0$, Gaussians are only added to the structures put in the `AntiSeeds` folder. If you don't want to use antiseeds, specify very large `antiSeedsActivation` (for example, 5000) and `antiSeedsMax`=0.0.

*Default*: `5000`

*Format*:

```
1 :  antiSeedsActivation
```

▷ *variable* antiSeedsMax

*Meaning*: Specifies the height of the Gaussian, in units of the mean square deviation of the enthalpy in the generation (computed only among `bestFrac` structures, *i.e.*, among potential parents). We recommend `antiSeedsMax`=0.01.

*Default*: `0.000`

*Format*:

```
0.005 :  antiSeedsMax
```

▷ *variable* antiSeedsSigma

*Meaning*: Specifies the width of the Gaussian, in units of the average distance between structures in the generation (computed only among `bestFrac` structures, *i.e.*, among potential parents). We recommend `antiSeedsSigma`=0.005.

*Default*: `0.001`

*Format*:

```
0.005 :  antiSeedsSigma
```

Fig. 7 shows an example of use of antiseed technique.

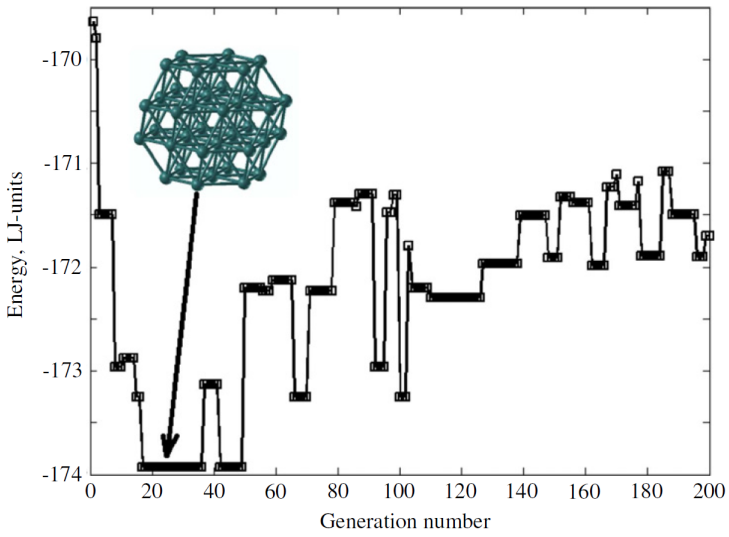



Figure 7: **Example of a calculation of a Lennard-Jones cluster with 38 atoms with the use of antiseeds.** The energy of the best structure in every generation is plotted. One can clearly see that the algorithm does not get stuck for a long time to any of the candidate minima and quickly finds the ground state. Here we used `antiSeedsActivation`=1, `antiSeedsMax`=0.01, `antiSeedsSigma`=0.001.

## 4.11 Space group determination

▷ *variable* `doSpaceGroup`

*Meaning*: Determines space groups and also writes output in the crystallographic `*.CIF`-format (this makes your life easier when preparing publications, but beware that space groups may sometimes be under-determined if the relaxation was not very precise and if very stringent tolerances were set for the symmetry finder). This option is enabled thanks to the powerful symmetry code provided by H.T. Stokes.

*Default*: `1`, if `calculationType=3**` (`300`, `301`, `310`, `311` — bulk crystals) and `0` otherwise.

*Format*:

```
1 :  doSpaceGroup (0 - no space groups, 1 - determine space groups)
```

▷ *variable* `SymTolerance`

*Meaning*: Precision for symmetry determination using the symmetry finder code of H.T. Stokes. Can be specified either as a number (in Å) or as `high | medium | low` (= `0.05 | 0.10 | 0.20`)

*Default*: `medium`

*Format*:

```
medium :  SymTolerance
```

## 4.12 Keywords for developers

▷ *variable* repeatForStatistics

*Meaning*: Number of automatically executed USPEX runs. USPEX simulations are stochastic, and redoing the simulation with the same input parameters does not necessarily yield the same results. While the final result — the ground state — is the same (hopefully!), the number of steps it takes to reach it and the trajectory in chemical space differ from run to run. To compare different algorithms, you MUST collect some statistics — do not rely on just a single run (which may be lucky or unlucky... USPEX does not rely on luck!). This option is only of interest to developers and it only makes sense to collect statistics with simple potentials (*e.g.*, using GULP).

*Default*: `1` (*i.e.*, no statistics will be gathered)

*Format*:

```
20 : repeatForStatistics
```

▷ *variable* stopFitness

*Meaning*: Specifies the fitness value so that the calculation will stop after reaching fitness $\leq$ `stopFitness`.

*Default*: no default, has to be specified by the user.

*Format*:

```
90.912 : stopFitness
```

**Note:** Automatic analysis of statistics is enabled when `stopFitness` is specified. It is recommended to set `repeatForStatistics` keyword to values >1 to collect the statistics of reachability of `stopFitness`. Sample output is:

```
Number of files to be processed: 20
Target enthalpy: 90.912

Generation: 23    Number: 1326    Enthalpy:    90.9119    Mat-file: /home/USPEX/01/results1/USPEX.mat
Generation: 22    Number: 1224    Enthalpy:    90.9119    Mat-file: /home/USPEX/02/results1/USPEX.mat
Generation: 60    Number: 3451    Enthalpy:    90.9119    Mat-file: /home/USPEX/03/results1/USPEX.mat
Generation: 30    Number: 1739    Enthalpy:    90.9119    Mat-file: /home/USPEX/04/results1/USPEX.mat
Generation: 17    Number:  956    Enthalpy:    90.9119    Mat-file: /home/USPEX/05/results1/USPEX.mat
Generation: 36    Number: 2055    Enthalpy:    90.9119    Mat-file: /home/USPEX/06/results1/USPEX.mat
Generation: 35    Number: 1987    Enthalpy:    90.9119    Mat-file: /home/USPEX/07/results1/USPEX.mat
Generation: 22    Number: 1241    Enthalpy:    90.9119    Mat-file: /home/USPEX/08/results1/USPEX.mat
Generation: 18    Number: 1002    Enthalpy:    90.9119    Mat-file: /home/USPEX/09/results1/USPEX.mat
Generation: 29    Number: 1641    Enthalpy:    90.9119    Mat-file: /home/USPEX/10/results1/USPEX.mat
Generation: 21    Number: 1197    Enthalpy:    90.9119    Mat-file: /home/USPEX/11/results1/USPEX.mat
Generation: 27    Number: 1542    Enthalpy:    90.9119    Mat-file: /home/USPEX/12/results1/USPEX.mat
Generation: 44    Number: 2519    Enthalpy:    90.9119    Mat-file: /home/USPEX/13/results1/USPEX.mat
Generation: 32    Number: 1821    Enthalpy:    90.9119    Mat-file: /home/USPEX/14/results1/USPEX.mat
Generation: 15    Number:  835    Enthalpy:    90.9119    Mat-file: /home/USPEX/15/results1/USPEX.mat
Generation: 43    Number: 2477    Enthalpy:    90.9119    Mat-file: /home/USPEX/16/results1/USPEX.mat
Generation: 40    Number: 2278    Enthalpy:    90.9119    Mat-file: /home/USPEX/17/results1/USPEX.mat
Generation: 24    Number: 1358    Enthalpy:    90.9119    Mat-file: /home/USPEX/18/results1/USPEX.mat
Generation: 14    Number:  757    Enthalpy:    90.9119    Mat-file: /home/USPEX/19/results1/USPEX.mat
Generation: 27    Number: 1532    Enthalpy:    90.9119    Mat-file: /home/USPEX/20/results1/USPEX.mat

Found structures numbers : 1326 1224 3451 1739  956 2055 1987 1241 1002 1641 1197 1542 2519 1821  835 2477 2278 1358  757 1532
Found generations numbers:   23   22   60   30   17   36   35   22   18   29   21   27   44   32   15   43   40   24   14   27

Success rate: 100 percent
Average number of generations to get E=90.912: 29
```

```
Average number of structures  to get E=90.912: 1647
Standard deviation: 670
```

▷ *variable* collectForces

*Meaning*: Enable to collect all relaxation information in USPEX calculation, including forces on the atoms, atomic positions, lattice parameters and stress tensors during the structure optimizations. The information is stored in FORCE.mat file. Only VASP is supported.

*Default*: 0

*Format*:

```
1 :  collectForces
```

## 4.13 Seldom used keywords

▷ *variable* ordering_active

*Meaning*: Switch on the biasing of variation operators by local order parameters.

*Default*: 1

*Format*:

```
1 :  ordering_active
```

▷ *variable* symmetrize

*Meaning*: Switches on a transformation of all structures to standard symmetry-adapted crystallographic settings.

*Default*: 0

*Format*:

```
1 :  symmetrize
```

▷ *variable* valenceElectr

*Meaning*: Number of valence electrons for each type of atoms.

*Default*: these numbers are constants for all atoms, and we have tabulated them, no need to specify explicitly.

*Format*:

```
% valenceElectr
2 6
% EndValenceElectr
```

▷ *variable* percSliceShift

*Meaning*: Probability of shifting slabs (used in heredity) in all dimensions, 1.0 means 100%.

*Default*: 1.0

*Format*:

```
0.5 :  percSliceShift
```

▷ *variable* dynamicalBestHM

*Meaning*: Specifies whether the number of surviving best structures will vary during the calculation, with keepBestHM as the upper limit.

Possible values (integer): 0 = no variation, 1 and 2 = see note

*Default*: 2

*Format*:

```
1 :  dynamicalBestHM
```

**Note:** If you set dynamicalBestHM=1, the code will choose up to keepBestHM lowest-energy structures (without duplicate structures, which are defined as having fingerprint distance below user-defined toleranceBestHM). If dynamicalBestHM=2 (our preferred choice), then clustering algorithm selects exactly keepBestHM maximally different structures in the entire energy interval corresponding to bestFrac, and optimum toleranceBestHM is determined automatically — this promotes diversity while retaining memory of good structures.

▷ *variable* softMutOnly

*Meaning*: How many generations should be produced by softmutation only.

*Default*: 0

*Format*:

```
% softMutOnly
1-5
% EndSoftOnly
```

**Note:** In the example above, the generations up to $5^{th}$ generation (excluding, of course, the first generation) are produced by softmutation alone. Note that upon softmutation, each parent produces TWO softmutants. You can also specify particular generations to be softmutated throughout the run, for example to softmutate every $10^{th}$ generation you can write:

```
% softMutOnly
2 12 22 32 42
```

```
% EndSoftOnly
```

▷ *variable* maxDistHeredity

*Meaning*: Specifies the maximal cosine distances between structures that participate in heredity. This specifies the radius on the landscape within which structures can mate. Use with care (or do not use at all).

*Default*: 0.5

*Format*:

```
0.5 :  maxDistHeredity
```

▷ *variable* manyParents

*Meaning*: Specifies whether more than two slices (or more than two parent structures) should be used for heredity. This may be beneficial for very large systems.

Possible values (integer):

0 — only 2 parents are used, 1 slice each.

1 — many structures are used as parents, 1 slice each.

2 — two structures are used as parents, many slices (determined dynamically using parameters minSlice and maxSlice) are chosen independently from each one.

3 — two structures are used as parents, many slices (determined dynamically using parameters minSlice and maxSlice) are cut from the cell with a fixed offset. This is the preferred option for large systems. For example, we cut both structures into slices of approximately the same thickness and then choose the even slices from parent 1 and odd slices form parent 2, making a multilayered "sandwich", or a "zebra".

*Default*: 0

*Format*:

```
3 :  manyParents
```

minSlice, maxSlice: Determines the minimal and maximal thickness of the slices in Å that will be cut out of the parent structures to participate in creation of the child structure. We want the slices to be thick enough to carry some information about the parent (but not too thick to make heredity ineffective). Reasonable values for these parameters are around 1 and 6 Å, respectively.

For clusters, you can directly specify the number of parents participating in heredity (but we found this to be of little use):

▷ *variable* numberparents

*Meaning*: Defines the number of parents in heredity for clusters.

*Default*: 2

*Format*:

```
2 :  numberparents
```

# 5 Additional input for special cases

## 5.1 MOL_1, MOL_2, ... files for molecular crystals

### 5.1.1 Molecular Crystals, calculationType=310/311

For a molecular crystal, the MOL_1 file describes the structure of the molecule from which the structure is built. This file also defines which torsion angles will be mutated if the molecule is flexible. This file and its format differ from SIESTA's Z_Matrix file (MOL_1 gives the Cartesian coordinates of the atoms, whereas Z_Matrix file defines the atomic positions from bond lengths, bond angles and torsion angles). The Z_Matrix file is created using the information given in the MOL_1 file, *i.e.*, bond lengths and all necessary angles are calculated from the Cartesian coordinates. The lengths and angles that are important should be used for the creation of Z_Matrix — this is exactly what columns 5–7 specify. Let's look at the MOL_1 file for benzene $C_6H_6$:

```
Benzene
Number of atoms: 12
H    0.0000    0.0000    0.0000   0    0    0    1
C    1.0600    0.0000    0.0000   1    0    0    1
C    1.7550    1.2038    0.0000   2    1    0    1
C    3.1450    1.2038    0.0000   3    2    1    0
C    3.8400   -0.0000    0.0000   4    3    2    0
C    3.1450   -1.2038    0.0000   5    4    3    0
C    1.7550   -1.2038    0.0000   6    5    4    0
H    1.2250    2.1218    0.0000   3    2    1    0
H    3.6750    2.1218    0.0000   4    3    8    0
H    4.9000    0.0000    0.0000   5    4    9    0
H    3.6750   -2.1218    0.0000   6    5   10    0
H    1.2250   -2.1218    0.0000   7    6   11    0
```

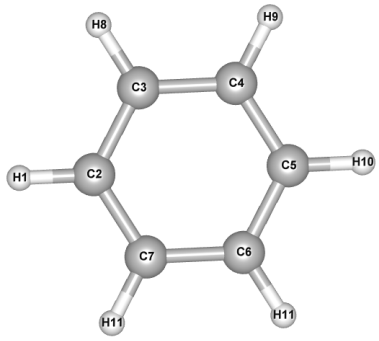



Figure 8: **Sample of MOL_1 file and illustration of the corresponding molecular structure.**

The $1^{st}$ atom is H, its coordinates are defined without reference to other atoms ("0 0 0").

The $2^{nd}$ atom is C, its coordinates (in molecular coordinate frame) in Z_matrix will be set only by its distance from the $1^{st}$ atom (*i.e.* H described above), but no angles — ("1 0 0").

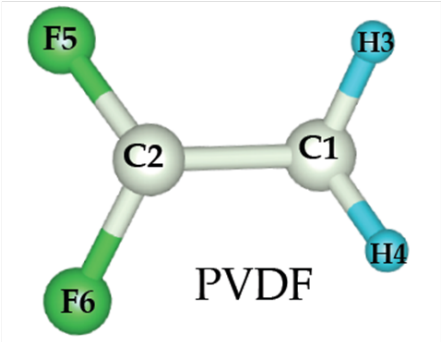
The $3^{rd}$ atom is C, its coordinates will be set by its distance from the $2^{nd}$ atom, and the bond angle 3-2-1, but not by torsion angle — hence we use "2 1 0".

The $4^{th}$ atom is C, its coordinates will be set by its distance from the $3^{rd}$ atom, bond angle 4-3-2, and torsion angle 4-3-2-1 — hence, we use "3 2 1" and so forth... until we reach the final, $12^{th}$ atom, which is H, defined by its distance from the $7^{th}$ atom (C), bond angle 12-7-6 and torsion angle 12-7-6-11 — hence "7-6-11".

The final column is the flexibility flag for the torsion angle. For example, in C4, the tosion angle is defined by 4-3-2-1. Ideally, this flag should be 1 for the first three atoms, and 0 — for the others. If any other flexible torsion angle exists, specify 1 for this column.

### 5.1.2 Polymeric Crystals, `calculationType`=110 ("linear chain model")

For polymers, the `MOL_1` file is used to represent the geometry of a monomeric unit, in the same style as for molecular crystals, except that we use the last column to specify the reactive atoms as shown in the `MOL_1` file for PVDF:




reactive atoms

```
PVDF-Trans
Number of atoms: 6
C   0.7237   7.2056   0.9499   0 0 0   1
C   1.5259   5.9752   1.3444   1 0 0   1
F   1.2809   8.3239   1.5697   1 2 0   0
F   0.8718   7.4605  -0.4197   1 2 3   0
H   1.0400   5.0789   0.9367   2 1 3   0
H   1.5489   5.8992   2.4434   2 1 3   0
```

Figure 9: **Sample of `MOL_1` file of PVDF and illustration of the corresponding monomeric structure.**

### 5.1.3 Additional inputs for classical forcefields

The above `MOL_1` files can be used for general cases in USPEX. However, some classical forcefield based codes need additional information. For instance, GULP needs to specify the chemical labels and charge. The `MOL_1` file for aspirin can be written in the following way:

```
Aspirin_charge
Number of atoms: 21
H_1     0.2310     3.5173     4.8778     0  0  0   1     0.412884
O_R     0.7821     4.3219     4.9649     1  0  0   1    -0.676228
C_R     0.4427     5.0883     6.0081     2  1  0   1     0.558537
O_2    -0.5272     4.5691     6.6020     3  2  1   0    -0.658770
C_R     1.0228     6.3146     6.3896     3  2  4   0     0.116677
C_R     2.1330     6.8588     5.6931     5  3  2   0     0.311483
C_R     0.4810     7.0546     7.4740     5  3  6   0    -0.119320
O_R     2.8023     6.2292     4.6938     6  5  3   0    -0.574557
C_R     2.6211     8.1356     6.0277     6  5  8   0    -0.083091
```

```
C_R     0.9966     8.3146     7.8237     7  5  3   0    -0.103442
H_2    -0.3083     6.6848     8.0128     7  5 10   0     0.198534
C_R     3.6352     5.1872     4.9079     8  6  5   0     0.609295
C_R     2.0623     8.8613     7.0940     9  6  5   0    -0.119297
H_2     3.3963     8.5283     5.4906     9  6 13   0     0.174332
H_2     0.5866     8.8412     8.6013    10  7 13   0     0.205960
O_2     3.9094     4.7941     6.0632    12  8  6   0    -0.588433
C_3     4.2281     4.5327     3.7638    12  8 16   0    -0.271542
H_2     2.4227     9.7890     7.3367    13  9 10   0     0.196738
H_2     3.4269     4.1906     3.1183    17 12  8   0     0.151315
H_2     4.8283     3.6848     4.0792    17 12 19   0     0.131198
H_2     4.8498     5.2464     3.2337    17 12 19   0     0.127726
```

Here, the keyword `charge` in the title tells the program to read the charge in the additional (last) column.

To work with Tinker, the additional column is used to specify the atomic label as follows:

```
Urea
Number of atoms: 8
C     0.000000    0.000000    0.000000   0 0 0 1  189
O     0.000000    0.000000    1.214915   1 0 0 1  190
N     1.137403    0.000000   -0.685090   1 2 0 1  191
N    -1.137403    0.000000   -0.685090   1 2 3 0  191
H     1.194247    0.000000   -1.683663   4 1 3 0  192
H    -1.194247    0.000000   -1.683663   4 1 3 0  192
H     1.998063    0.000000   -0.138116   2 1 3 0  192
H    -1.998063    0.000000   -0.138116   2 1 3 0  192
```

### 5.1.4 How to prepare the `MOL` files

There are plenty of programs which can generate Zmatrix style files, such as Molden, Avogadro, and so on. The experienced users might have their own way to prepare these files. For the users' convenience, we have created an online utility to allow one to generate the USPEX-style `MOL` file just from a file in XYZ format. Please try this utility at http://han.ess.sunysb.edu/zmatrix.

## 5.2 Surfaces

To perform a prediction of surface reconstructions, you have to:

- Specify `200` or `201` : `calculationType`.
- Provide a file containing substrate in VASP5 POSCAR format, as shown on Fig. 10.

- Specify the following parameters:

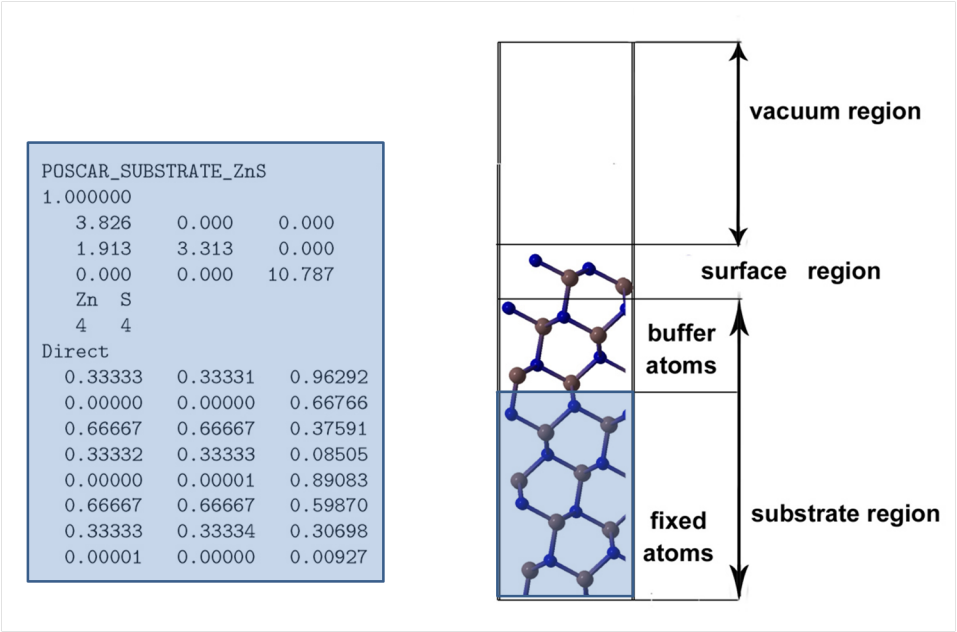



Figure 10: **The surface model used in USPEX.** Note that `POSCAR_SUBSTRATE` shall exactly represent the geometrical information of its bulk crystal without vacuum. If the input has large vacuum region, the program will automatically delete it and provide a new file called `POSCAR_SUBSTRATE_NEW`, and this file has to be used in the calculation (renamed as `POSCAR_SUBSTRATE`).

```
% symmetries
2-17
% endSymmetries
```

**Note:** If the `symmetries` tag is present, USPEX will try to generate structures using plane groups.

▷ *variable* `thicknessS`

*Meaning*: Thickness of surface region. Adatoms are allowed only in this region.

*Default*: `2.0` Å

*Format*:

```
3.5 :  thicknessS
```

▷ *variable* `thicknessB`

*Meaning*: Thickness of buffer region in substrate. This region is part of `POSCAR_SUBSTRATE`, allowed to relax.

*Default*: 3.0 Å

*Format*:

```
3.0 :  thicknessB
```

▷ *variable* reconstruct

*Meaning*: Maximum multiplications of the surface cell, to allow for complex reconstructions.

*Default*: 1

*Format*:

```
1 :  reconstruct
```

USPEX also provides the possibility of studying the stable configurations with variable number of surface atoms (to be released in USPEX 10.1). In this case, stable surface reconstructions are dictated by chemical potentials[25]. A typical set of input is the following:

```
########################################
#      TYPE OF RUN AND SYSTEM          #
########################################
USPEX  : calculationMethod (USPEX, VCNEB, META)
201    : calculationType (dimension: 0-3; molecule: 0/1; varcomp: 0/1)

% atomType
Si O
% EndAtomType

% numSpecies
2 4
% EndNumSpecies
```

Here we specify the maximum number of surface atoms in a $1 \times 1$ cell.

```
########################################
#              SURFACES                #
########################################
% symmetries
2-17
% endSymmetries

% StoichiometryStart
```

```
1 2
% StoichiometryEnd
```

This defines the stoichiometry of the bulk.

```
-23.7563 : E_AB (DFT energy of AmBn compound, in eV per formula unit)
-5.4254  : Mu_A (DFT energy of elemental A, in eV/atom)
-4.9300  : Mu_B (DFT energy of elemental B, in eV/atom)

3.5      : thicknessS (thickness of surface region, 2 A by default )
3.0      : thicknessB (thickness of buffer region in substrate, 3 A by default)
4        : reconstruct (maximum multiplications of cell)
```

At the moment, USPEX supports variable-composition calculation for the following cases of surfaces:

- Reconstructions of elemental surfaces (such as C@diamond(100) surface).
- Reconstructions of surfaces at binary compounds (such as GaN(0001) surface).
- Reconstructions involving foreign species on elemental surfaces (such as PdO@Pd(100) surface).

## 5.3 Variable-composition code

To switch on the variable-composition mode, you have to:

1. Specify `301` or `311` or `201 : calculationType`.
2. Specify compositional building blocks in `numSpecies` (see the description of `numSpecies` variable).
3. Optionally specify the approximate atomic volumes for each atom type (or for each compositional block) using keyblock `Latticevalues`.
4. Specify the following *varcomp-only* options:

▷ *variable* `firstGeneMax`

*Meaning*: How many different compositions are sampled in the first generation. If 0, then the number is equal to `initialPopSize`/4. For binaries, we recommend `firstGeneMax`=11, for ternaries a higher value is needed, *e.g.* 30.

*Default*: `11`

*Format*:

```
10 :  firstGeneMax
```

▷ *variable* minAt

*Meaning*: Minimum number of atoms (for `calculationType`=301/201/300) or molecules (for `calculationType`=311) in the unit cell for the first generation.

*Default*: `No default`

*Format*:

```
10 :  minAt
```

▷ *variable* maxAt

*Meaning*: Maximum number of atoms (for `calculationType`=301/201/300 or in META calculations) or molecules (for `calculationType`=311) in the unit cell for the first generation.

*Default*: `No default`

*Format*:

```
20 :  maxAt
```

▷ *variable* fracTrans

*Meaning*: Percentage of structures obtained by transmutation. In this operator, a randomly selected atom is transmuted into another chemical species present in the system — the new chemical identity is chosen randomly by default, or you can specify it in the block `specificTrans`, just like with specific permutation swaps.

*Default*: `0.1`

*Format*:

```
0.1 :  fracTrans
```

▷ *variable* howManyTrans

*Meaning*: Maximum percentage of atoms in the structure that are being transmuted (0.1 = 10%). The fraction of atoms that will be transmuted is drawn randomly from a homogeneous distribution bounded between 0 and the fractional parameter `howManyTrans`.

*Default*: `0.2`

*Format*:

```
0.2 :  howManyTrans
```

▷ *variable* `specificTrans`

*Meaning*: Specifies allowed transmutations.

*Default*: blank line (no specific transmutations)

*Format*:

```
% specificTrans
1 2
% EndTransSpecific
```

**Note:** In this case, atoms of type 1 could be transmuted into atoms of type 2 and vice versa. If you want to try all possible transmutations, just leave a blank line inside this keyblock.

In the case of variable-composition runs, parameter `keepBestHM` takes a new meaning — all structures on the convex hull (*i.e.*, thermodynamically stable states of the multicomponent system) survive, along with a few metastable states closest to the convex hull — the total number is `keepBestHM`.

For variable-composition runs, it is particularly important to set up the first generation wisely. Choose a suitably large initial generation size `initialPopSize`. Choose a reasonably large number of different compositions `firstGeneMax` to be sampled in the first generation (but not too large — each composition needs to be sampled several times at least). Finally, `minAt` and `maxAt` should not differ by more than 2 times, and you may need a few calculations with different system sizes: *e.g.*, 4–8, 8–16, 16–30 atoms, *etc.*

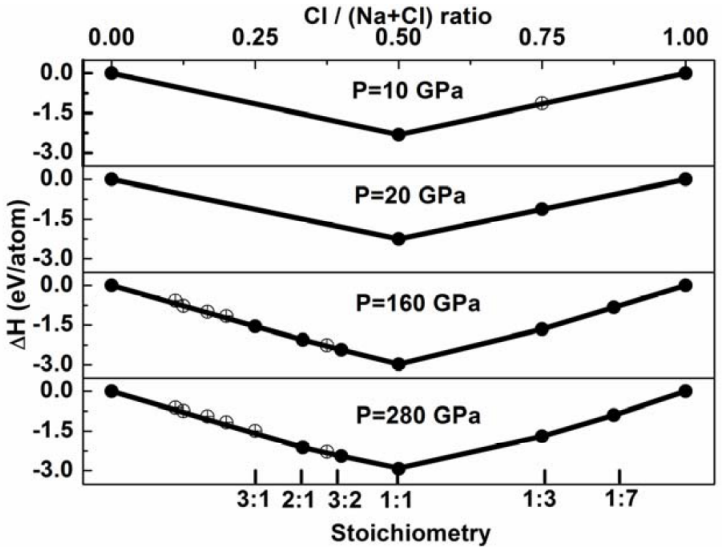



Figure 11: **Convex hull diagram for Na-Cl system at selected pressures.** Solid circles represent stable compounds; open circles — metastable compounds.

An additional comment for VASP users — if you want to perform a variable-composition run, let's say for the Na-Cl system, you should make sure the atomic types are given correctly in `INPUT.txt`, and put pseudopotential files `POTCAR_Na` and `POTCAR_Cl` in the folder

~/StructurePrediction/Specific/. USPEX will then recognize each atom and take each atom's POTCAR file appropriately for the calculations. Fig. 11 shows thermodynamics of stable sodium chlorides discovered using USPEX and confirmed by experiment[26].

## 5.4 Evolutionary metadynamics code

This is a very powerful method for finding the global minimum, as well as many low-energy metastable structures that are potentially kinetically accessible from the starting structure. The starting structure has to be high-quality and is given in the file POSCAR_1.

Evolutionary metadynamics is only enabled with the VASP and GULP codes at the moment.

To switch on the evolutionary metadynamics mode, you have to:

1. Specify

   ```
   META : calculationMethod
   ```

   ```
   300 :  calculationType
   ```

2. Create file POSCAR_1 in the VASP5 format in your folder (evolutionary metadynamics requires a good starting structure, relaxed at the pressure of interest).

3. Specify the population size (in this case, this is the number of softmutations at each metastep):

   ```
   30 :  populationSize
   ```

4. Specify the pressure:

   ▷ *variable* ExternalPressure

   *Meaning*: The pressure at which you want to perform the calculation, in GPa.

   *Default*: no default

   *Format*:

   ```
   10 :  ExternalPressure (GPa)
   ```

5. Specify the following metadynamics-only options:

▷ *variable* GaussianWidth

*Meaning*: The width of each of the Gaussians added to the energy surface to accelerate phase transitions. A good rule of thumb is to choose a value close to 0.10–0.15$L$, where $L$ is the minimum length of the unit cell, in Angstroms.

*Default*: $0.10 \times L$ (Å)

*Format*:

```
0.80 : GaussianWidth
```

▷ *variable* GaussianHeight

*Meaning*: The height of each of the Gaussians added to the energy surface to accelerate phase transitions. A good rule of thumb (Martoňák *et al.*, 2005) is to choose a value close to $L(\delta h)^2 G$, where $L$ is the average length of the unit cell in Angstroms, $\delta h$ is the Gaussian width in Angstroms (see below), and $G$ is the shear modulus in kbars.

*Default*: $1000 \times (0.10 \times L)^2 \times L = 10 \times L^3$ (Å$^3$kbar)

*Format*:

```
2000 : GaussianHeight
```

▷ *variable* FullRelax

*Meaning*: Metadynamics as such only relaxes structures within a fixed cell. For analysis, you need to perform complete structure relaxation (*i.e.* relaxing also the cell).

- `FullRelax`=0 — no full relaxation will be performed (very fast option, but inconvenient for analysis of the results).
- `FullRelax`=1 — only the best structure of the generation will be fully relaxed (also fast, sometimes sufficient).
- `FullRelax`=2 — all inequivalent structures are fully relaxed (still fast, only ∼2 times slower than `FullRelax`=1, but provides a lot more insight. Strongly recommended for most cases).

*Default*: `2`

*Format*:

```
2 : FullRelax
```

For full relaxation, when performing evolutionary metadynamics the format of the block `abinitioCode` is slightly different, for example:

```
abinitioCode
3 3 3 3 (3 3)
ENDabinit
```

In the example above, there are four stages of relaxation within a fixed cell, and two stages of full relaxation (in parentheses). Remember that in the last fixed-cell stage of

relaxation, pressure tensor must be accurate — this is what drives metadynamics. Only VASP, SIESTA, and GULP codes are supported at the moment.

▷ *variable* `maxVectorLength`

*Meaning*: Together with `minVectorLength` the boundary values for basic cell lengths in evolutionary metadynamics (note that this is a different meaning for `minVectorLength` from normal calculations, and `maxVectorLength` is only used in evolutionary metadynamics). When any of the basic cell lengths becomes smaller than `minVectorLength` or larger than `maxVectorLength`, we add a steep correction "force" in metadynamics, which drives cell evolution towards "good" values. The correction forces are exactly zero when all basic cell lengths are in the "good" range.

*Default*: `No default`

*Format*:

```
12.0 :  minVectorLength
```

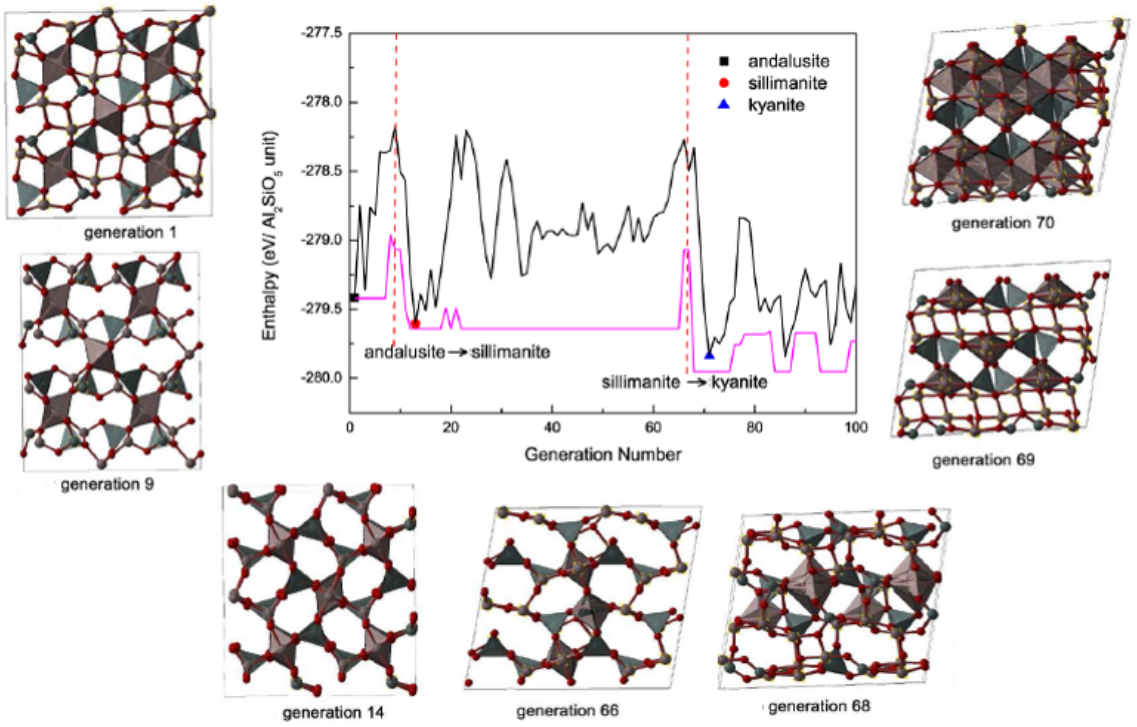



Figure 12: **Enthalpy evolution during the compression on andalusite ($Al_2SiO_5$) at 10 GPa (black line: enthalpies for best structures with constant h; magenta line: enthalpies for best structures after full relaxation).** Sequence of structures obtained in this run: generation 1 (andalusite) → generation 9 (sillimanite) → generation 14 → generation 66 → generation 68 → generation 69 → generation 70 (kyanite).

When you run metadynamics, additional files will be found in the `results1` folder, most importantly:

- `force.dat` — analysis of forces on the cell, internal (`f_c`) and from the Gaussians (`f_g`);
- `presten` — pressure tensor;
- `lattice.dat` — cell shape change during the simulation;
- `enthalpies` and `enthalpies_relaxed` — enthalpies of structures at each metastep at fixed cell and after full relaxation, respectively;
- `gatheredPOSCARS` and `gatheredPOSCARS_relaxed` — structures at fixed cell and after full relaxation, respectively.

Fig. 12 shows an example of use of evolutionary metadynamics: starting from one $Al_2SiO_5$ polymorph (andalusite), we obtained the other two known polymorphs (kyanite and sillimanite) and non-trivial phase transformation mechanisms.

## 5.5 Particle swarm optimization (PSO) code

In the field of crystal and cluster structure prediction, several approaches proved to be successful for small systems. Particle Swarm Optimization (PSO), pioneered in this field by Boldyrev[27], is a special class of evolutionary algorithms where a population (swarm) of candidate solutions (called "particles") is moved in the search space according to a few simple formulae. The movements of the particles are guided by their own best known position in the search space as well as the entire swarm's best known position. Initially, the coordinates $\chi$ and 'velocities' $\upsilon$ of the particles are generated randomly. Then at every step, the positions and velocities are updated according to the formulae:

$$\begin{aligned} \upsilon'_i &= \omega \cdot \upsilon_i + \varphi_p \cdot r_p \cdot (p_i - \chi_i) + \varphi_g \cdot r_g \cdot (g - \chi_i), \\ \chi'_i &= \chi_i + \upsilon'_i. \end{aligned} \tag{7}$$

Here $\omega$, $\varphi_p$ and $\varphi_g$ are weight factors that control the behavior and efficiency of the PSO algorithm; $r_p$ and $r_g$ are random numbers in the [0; 1] range generated separately for every particle at every step; $p_i$ is the best known position of particle $i$ and $g$ is the best known position of the entire swarm.

Such an algorithm, despite its simplicity, can work[27]. Key points to improve with respect to previous implementations[27;28] are (1) metric of the search space (it is not trivial to map crystal structures uniquely onto a coordinate system) and (2) ways to evolve structures in PSO, *i.e.* variation operators.

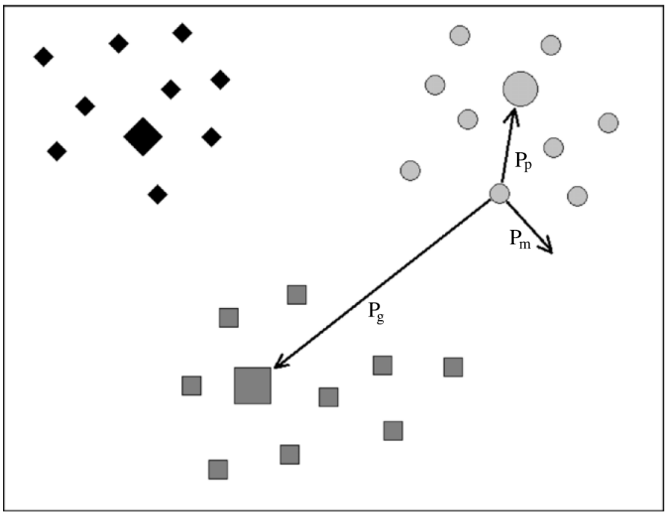



Figure 13: **Illustration of PSO-USPEX hybrid algorithm for the population of three individuals (marked by diamonds, squares and circles) after 10 generations.** Best position for each particle is marked by an enlarged symbol. The best structure is the big square. The structure shown by circle can be either mutated, create a child with its historically best position (large circle) or the best position of entire population (large square) using heredity operator with probabilities $P_m$, $P_p$ and $P_g$, respectively.

Evolving the particles by determining the speed $v_i$ (7) directly from coordinates of the atoms and cell parameters of two structures (as in Ref.[28]) cannot be productive. Our solution is to use fingerprint distances[17] as the most natural metric for the energy landscape, and variation operators of USPEX for evolving the 'PSO particles' (*i.e.* structures) as the most efficient unbiased ways to evolve a population of structures. Namely, the particle is either mutated (to imitate a random move), or participates in heredity with its best known position or in heredity with the best known population position (to imitate PSO moves in the direction of these positions). Instead of applying at each step all moves with some weights (see Eq. 7), we apply them one at a time with probabilities described by formulae:

$$P_m = \frac{\omega}{\Sigma}; \qquad P_p = \frac{\varphi_p \cdot r_p \cdot D_p}{\Sigma}; \qquad P_g = \frac{\varphi_g \cdot r_g \cdot D_g}{\Sigma}; \\ \Sigma = \omega + \varphi_p \cdot r_p \cdot D_p + \varphi_g \cdot r_g \cdot D_g, \tag{8}$$

where $D_p$ is a fingerprint distance between current and best position of a particle, while $D_g$ is a fingerprint distance between the current position of the particle and best known position of the entire population. Our tests, performed on a few diverse systems, show that this approach (which we call "cor-PSO", *i.e.* corrected PSO) is relatively successful and works better than previous versions of PSO, but still cannot compete with the USPEX algorithm[2;29] for success rate or efficiency.

The following variables are unique for `calculationMethod`=PSO:

▷ *variable* PSO_softMut

*Meaning*: Weight of softmutation ($\omega$ in eq. 8).

*Default*: 1

*Format*:

```
1 :  PSO_softMut
```

▷ *variable* PSO_BestStruc

*Meaning*: Weight of heredity with the best position of the same PSO particle ($\varphi_p$ in eq. 8).

*Default*: 1

*Format*:

```
1 :  PSO_BestStruc
```

▷ *variable* PSO_BestEver

*Meaning*: Weight of heredity with the globally best PSO particle ($\varphi_g$ in eq. 8).

*Default*: 1

*Format*:

```
1 :  PSO_BestEver
```

# 6 Prediction of Phase Transition Pathways

Phase transitions determine many aspects of the behavior of materials. Thus, it is essential to reveal possible mechanisms of structural phase transitions.

## 6.1 Variable-Cell Nudged-Elastic-Band (VCNEB) method

Prediction of a phase transition mechanism can be considered as a double-ended problem, in which the algorithm has to locate the intermediate states. The nudged elastic band (NEB)[30;31;32] method is a widely used technique for solving double-ended problems, an efficient and robust approach for seeking the reaction paths and the saddle points along the "minimum energy path" (MEP) on the potential energy surface between the two end-points. The NEB method has been successfully applied to molecular chemical reactions, surfaces, and defect migration, in particular it could provide the energy barrier between the given initial and final states of a phase transition process. Unfortunately, most of the problems treated by the NEB method are considered under the constraint of constant unit cell — which precludes it from being used for phase transitions (which involve the variation of the unit cell along the transition path).

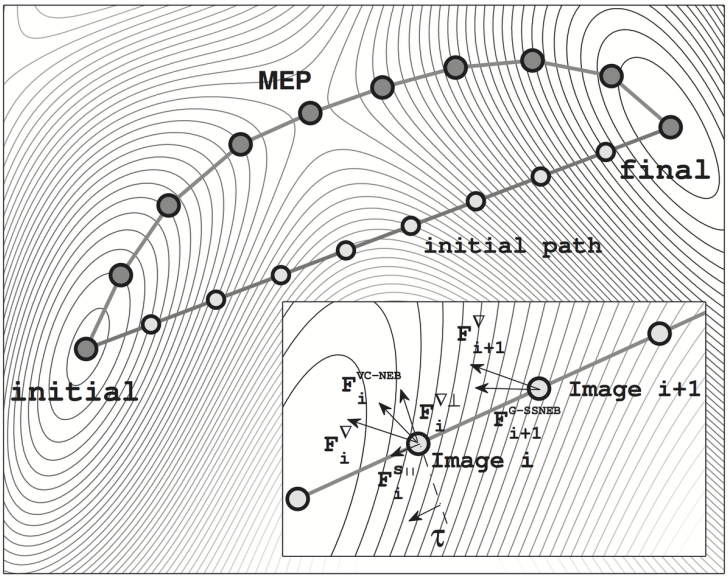



Figure 14: **The minimum energy path (line with gray circles) and initial path on a model 2D enthalpy surface.** The forces in the VC-NEB method on Image $i$ are shown in the inset. $\mathbf{F}_i^{\nabla}$ is the potential force in the gradient direction. $\mathbf{F}_i^{\nabla\perp}$ and $\mathbf{F}_i^{s\parallel}$ are the transverse component of $\mathbf{F}_i^{\nabla}$ and the spring force, respectively.

The variable cell NEB (VC-NEB) method[14], which we have developed with somewhat different formulation, treats the cell and atomic coordinates on an equal footing and operates in an expanded configuration space under the condition of constant pressure.

Our VC-NEB method within the first principles framework has been added to USPEX code as a new part. The VC-NEB method is a more general tool for exploring the activation paths between the two endpoints of a phase transition process within a larger configuration space. Every structure on the pathway in the VCNEB method is regarded as an "Image".

## 6.2 Input options for VCNEB

The VCNEB method is only enabled with the VASP, GULP and Quantum Espresso codes at the moment.

To switch on the VCNEB mode, you have to:

1. Specify

   `VCNEB : calculationMethod`

2. Create a file `Images` in the VASP4 format in your folder (VCNEB requires at least two structures, initial and final phases, to run the phase transition pathway prediction).

3. Specify the following VCNEB options:

▷ *variable* `vcnebType`

*Meaning*: Specifies type of the VCNEB calculation. This variable consists of three indices: *calculation option*, *Image number variability*, and *spring constant variability*:

- calculation option:

  "1" — the VCNEB method;

  "2" — structure relaxation mode with no VCNEB calculation.

- `Variable-Image-Number` method:

  "0" — the number of Images in VCNEB calculation is fixed;

  "1" — the number of Images in VCNEB calculation is variable.

- variability of spring constant:

  "0" — fixed spring constant;

  "1" — variable spring constant.

*Default*: `110`

*Format*:

```
111 :  vcnebType
```

**Note:** If `vcnebType`=111, *i.e.*, a calculation for VCNEB calculation with variable number of Images and variable spring constant is to be performed. We strongly suggest users to run a variable number of Images in VCNEB calculations when investigating the reconstructive phase transitions.

▷ *variable* `numImages`

*Meaning*: Initial number of Images to perform the calculation.

*Default*: `9`

*Format*:

```
13 :  numImages
```

▷ *variable* `numSteps`

*Meaning*: Maximum steps of performing the VCNEB calculation.

*Default*: `200`

*Format*:

```
500 :  numSteps
```

**Notes:** (1) When `numSteps`=-1, the initial pathway will only be generated without running energy calculations. (2) Convergence of VCNEB pathways is usually rather slow. We recommend to set `numSteps` to at least 500.

▷ *variable* `optReadImages`

*Meaning*: Options for reading the `Images` file:

- "0" — All images (`numImages`) are needed and specified in `Images` file;
- "1" — Only initial and final images are needed and would be read in `Images` file;
- "2" — The initial, final and any specified intermediate Images will be read in `Images` file.

*Default*: `2`

*Format*:

```
1 :  optReadImages
```

**Note:** In all options, the initial and final images must be specified. Automatic linear interpolation will be applied to generated the initial Images in option 1 and 2.

▷ *variable* optimizerType

*Meaning*: Optimization algorithm option of structure relaxation:

- "1" — Steep Descent (SD);
- "2" — FIRE (Fast Inertial Relaxation Engine) Algorithm[33].

*Default*: 1 (SD) — for VCNEB calculations; 2 (FIRE) — for structure relaxation

*Format*:

```
1 :  optimizerType
```

▷ *variable* optRelaxType

*Meaning*: Structure relaxation mode:

- "1" — relax only atomic positions (with cell fixed), *e.g.* as in the classical NEB method;
- "2" — relax only cell lattice (used only for testing);
- "3" — full relaxation of atomic positions and cell lattice.

*Default*: 3

*Format*:

```
3 :  optRelaxType
```

▷ *variable* dt

*Meaning*: Time step for structure relaxation.

*Default*: 0.05

*Format*:

```
0.1 :  dt
```

**Note:** If dt is very small, the calculations will be very slow. If dt is too large, the calculation will be unstable and often generate meaningless pathways.

▷ *variable* ConvThreshold

*Meaning*: Halting criteria condition for RMS (Root Mean Square forces) on images.

*Default*: 0.003 eV/Å

*Format*:

```
0.005 :  ConvThreshold
```

▷ *variable* VarPathLength

*Meaning*: Criterion for path length between Images for variable Image method. When the length between two neighbor images is larger than 1.5 times of `VarPathLength`, a new image will be added between the two images using linear interpolation; when less then 0.5 the value, the second image will be removed.

*Default*: The average pathlength between Images of the initial pathway

*Format*:

```
0.3 :  VarPathLength
```

▷ *variable* K_min

*Meaning*: Minimum spring constant, only used in variable-spring constant VCNEB (in $eV/Å^2$).

*Default*: `5`

*Format*:

```
3 :  K_min
```

▷ *variable* K_max

*Meaning*: Maximum spring constant, only used in variable-spring constant VCNEB (in $eV/Å^2$).

*Default*: `5`

*Format*:

```
6 :  K_max
```

▷ *variable* Kconstant

*Meaning*: Spring constant, Only used in fixed-spring constant VCNEB (in $eV/Å^2$).

*Default*: `5`

*Format*:

```
4 :  Kconstant
```

▷ *variable* optFreezing

*Meaning*: Option for freezing the Image structure. Image structure will be frozen when `ConvThreshold` is achieved if enabled. Image structure freezing options:

- "0" — no Images freeze any time;
- "1" — freeze when `ConvThreshold` is achieved.

*Default*: 0

*Format*:

```
1 :  optFreezing
```

▷ *variable* optMethodCIDI

*Meaning*: Option for Climbing-Image (CI) and Downing-Image (DI) method. This method is only suggested to be used when you have a reasonable and well converged pathway. CI/DI-Image method options:

- "0" — CI/DI method not used;
- "1" — single CI method, only the highest energy or user-provided transition state (TS) will be used for CI;
- "-1" — single DI method, only the lowest energy or user-provided local minimum state (LM) will be used for DI;
- "2" — mixed multi-CI/DI method, the sequential numbers of TS and LM states need to be provided;

*Default*: 0

*Format*:

```
1 :  optMethodCIDI
```

▷ *variable* startCIDIStep

*Meaning*: CI/DI method starting step number, only available when optMethodCIDI=1.

*Default*: 100

*Format*:

```
200 :  startCIDIStep
```

▷ *variable* pickupImages

*Meaning*: Images ID picked up for CI/DI-Image method.

*Default*: Image ID of transition state and local minimum state Images

*Format*:

```
% pickupImages
9 11 17
% EndPickupImages
```

**Note:** In this case, the $9^{th}$, $11^{th}$ and $17^{th}$ Images will be picked up for applying CI/DI-Image method. The Image at transition state will be applied with CI-Image method and the Image at local minimum state will be applied DI-Image method automatically.

▷ *variable* `FormatType`

*Meaning*: The format of structures in pathway output file, locates at `results1/PATH/`. Pathway structures output format:

- "1" — XCRYSDEN format (.xsf file);
- "2" — VASP POSCAR;
- "3" — XYZ format with cell lattice.

*Default*: `2`

*Format*:

```
1 :  FormatType
```

▷ *variable* `PrintStep`

*Meaning*: Save the VNCEB restart files locating at `results1/STEP/` every `PrintStep` steps.

*Default*: `1`

*Format*:

```
10 :  PrintStep
```

**Note:** For empirical code, such as GULP, we suggest users to set `PrintStep`=10 to reduce time cost of saving the restart files.

Fig. 15 shows an example of use of the VCNEB method: phase transition mechanism and energy barrier starting from the $Ibam \rightarrow P6/mmm$ transition of BH system at 168 GPa, we obtained a *Pbcm* intermediate phase.

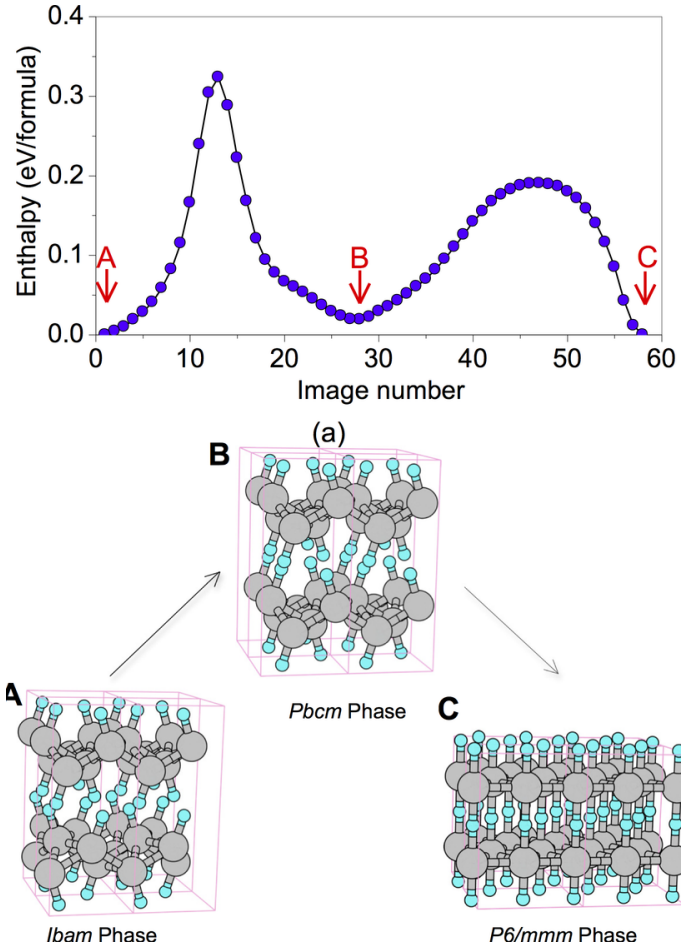



Figure 15: **The $Ibam \rightarrow P6/mmm$ transition of BH at 168 GPa[14]**. A $Pbcm$ intermediate phase is revealed. The saddle points on $Ibam \rightarrow Pbcm$ and $Pbcm \rightarrow P6/mmm$ segments have barriers of 0.32 and 0.19 eV/f.u., respectively.

## 6.3 How to set the initial pathway in the VC-NEB calculation

The VC-NEB method is very efficient for finding the phase transition path, but we must also carefully prepare the initial path. The cell rotations happen near the initial and final structures during the VC-NEB calculation, where the pathway includes a lot of identical structures near the initial and finial images. To remove these useless rotations, our improved `Variable-Image-Number` method will prevent cell rotations automatically, which saves quite a lot of time.

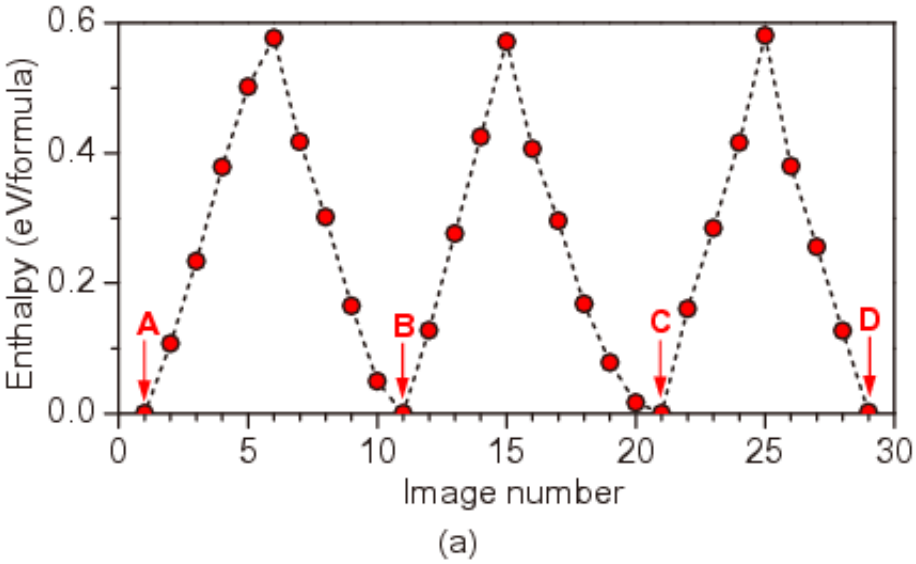
Alternatively, you can apply the rotation-avoiding technique before you apply the VC-NEB method when generating the initial image set. The general $3 \times 3$ rotation matrix with Euler angles $R(\phi, \theta, \psi)$ and the lattice mirror operator $M(x, y, z)$ matrix are defined. Before performing a VC-NEB calculation, the global numerical search in space of Euler angles and mirror operator are used to find the minimal lattice cell transformation distance $\Delta h$:

$$\Delta h = |h_{initial} - R(\phi, \theta, \psi) M(x, y, z) h_{final}| \,. \tag{9}$$

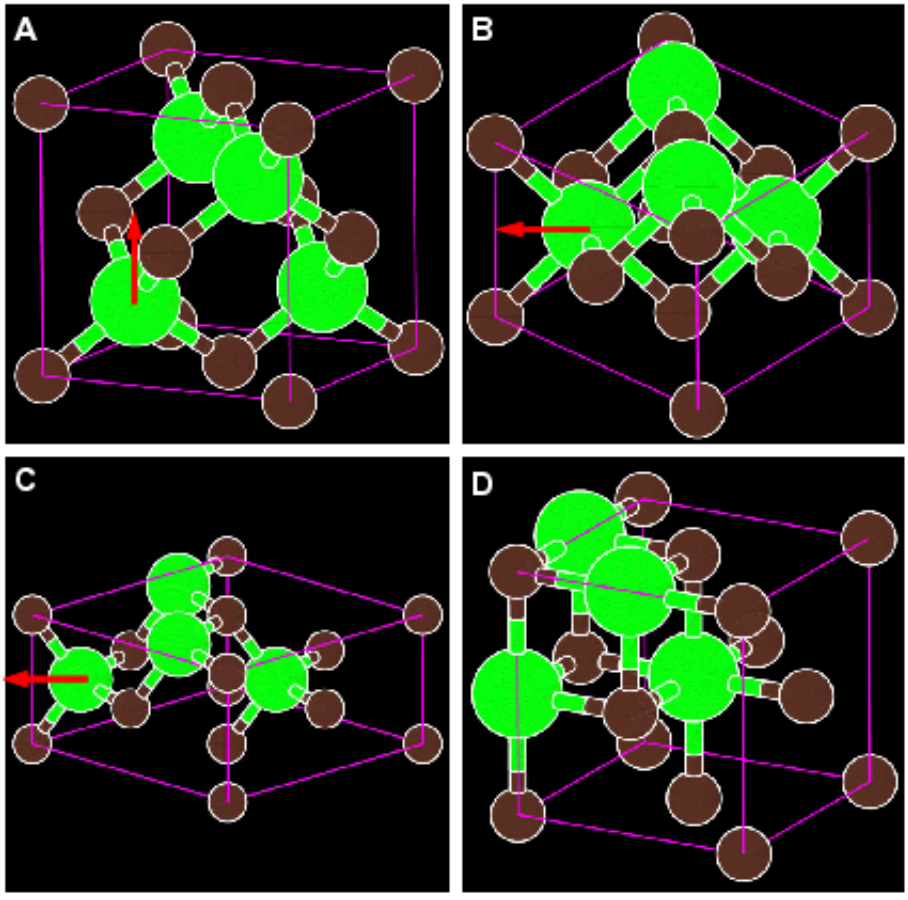
The rotation-avoiding lattice vector of the final image $\tilde{h}_{final}$ is assigned as the endpoint image:

$$\tilde{h}_{final} = R(\phi, \theta, \psi) M(x, y, z) h_{final}. \tag{10}$$

More important, we need to prevent the arbitrariness assigning the atomic fractional coordinates $\mathbf{r}_v$ of the initial and finial images (correctly mapping the atoms at the initial and final structures). Otherwise, the calculation will be hard to converge or several identical paths can be found in a calculation, as shown in Fig. 16. For more complicated systems, you will get some unreasonable or messy pathways if you don't have a good initial pathway. Global numerical search for minimizing the distance between the atoms from two endpoint images helps the VC-NEB method to reassign the atom sequence. The ability to automatically create model paths before the VC-NEB calculation is crucial for the stability and convergence of the algorithm, and is a prerequisite for studying large and complex systems.




(a)




(b)

Figure 16: **Identical pathways found when setting up a "bad" initial Image file**. The pathway is for the B3→B1 phase transition in GaN at the equilibrium pressure 45.0 GPa. At Images 11 and 21, B1 and B3 structures in a monoclinic cell are found during the MEP searching, respectively. The Ga atoms move along the arrow directions during the phase transition.

# 7 Online utilities

We have created a number of useful online utilities, which can be used for preparing USPEX input and for post-processing. The utilities are available at:

http://han.ess.sunysb.edu

Below you can find information about each one of them.

## 7.1 Structure characterization

Here we have 4 utilities:

- Fingerprints — the utility calculates and plots fingerprint function, which is a crystal structure descriptor, a 1D-function related to the pair correlation function and diffraction patterns. It does not depend on absolute atomic coordinates, but only on interatomic distances. Small deviations in atomic positions will influence fingerprints only slightly, *i.e.* they are numerically robust.
- Multifingerprint — the utility calculates average quasi-entropy, A-order and S-order for a set of structures. Also it filters unique structures by cosine distances difference $\geq 0.003$, identifies the symmetry of these structures and lists them in the `uniq_gatheredPOSCARS` file.
- POSCAR2CIF — determines space group and prepares a `CIF` file from a `POSCAR` file.
- CIF2POSCAR — prepares a `POSCAR` file from a `CIF` file.
- XSF2POSCAR — prepares a `POSCAR` file from a `XSF` (XCRYSDEN) file.

## 7.2 Properties calculation

Here we have 2 utilities:

- Hardness — the utility is to calculate hardness based on the Lyakhov-Oganov model.
- EELS — the utility calculates the Electron Energy Loss Spectrum (EELS). Written by Priya Johari.

## 7.3 Molecular crystals

Here we have 2 utilities:

- MOL precheck — the utility allows you to check `MOL_1` files before running USPEX calculations with `calculationType`=310/311/110.
- Zmatrix — the utility converts `XYZ` file to USPEX `MOL_1` file.

## 7.4 Surfaces

Substrate — a program which prepares a substrate from a `POSCAR`/`CIF` file and specified Miller indices, thickness of the layer, and shift. The resulting `POSCAR` file can be used for `calculationType`=200/201 as a substrate for surface calculations.

## 7.5 Miscellaneous

Here we have the following:

- Input generator — USPEX `INPUT.txt` generator. The utility can help beginners to create a correct input for USPEX calculations.
- Volume estimation — the utility estimates volumes of non-molecular and molecular crystals for USPEX (for `INPUT.txt` file).
- USPEX manual — online version of this manual.
- USPEX examples — archives with USPEX examples for versions 9.3.9 and 9.4.2.

# 8 Frequently Asked Questions

## 8.1 How can I visualize the results?

USPEX produces a large set of numbers (structures, energies, *etc*). Post-processing, or analysis of the data, is extremely important. Analysis of these data "by hand" can be quite tedious and time-consuming. By employing efficient visualization, analysis can be carried out much more quickly and can produce valuable additional insights. In this aspect USPEX occupies a unique niche, benefiting from an interface specifically developed for USPEX by Mario Valle to read and visualize USPEX output files using his STM4 visualization toolkit[34], which we recommend to use in conjunction with USPEX. This includes analysis of thousands of structures in a matter of a few minutes, determination of structure-property correlations, analysis of algorithm performance, quantification of the energy landscapes, state-of-the-art visualization of the structures, determination of space groups, *etc.*, including even preparation of movies showing the progress of the simulation! Fig. 17 shows typical figures produced by STM4. To use STM4, you need to have AVS/Express installed on your computer. AVS/Express is not public domain and requires a license. STM4 is available at http://mariovalle.name/STM4.

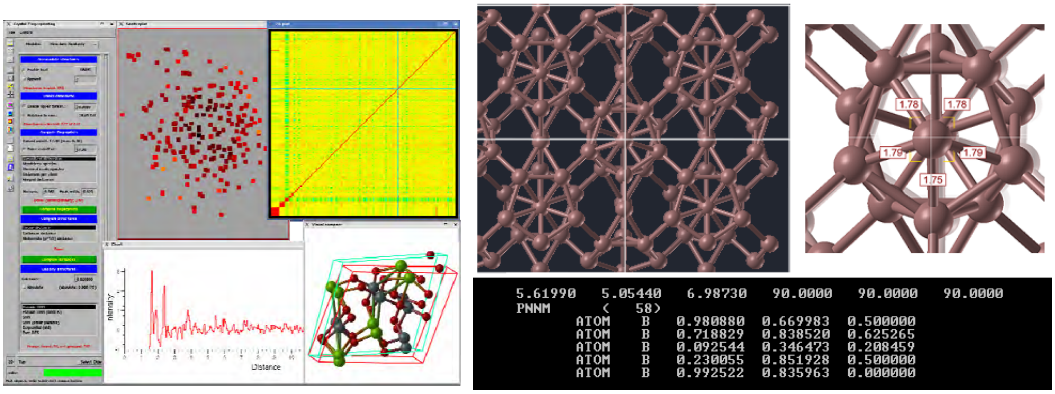



Figure 17: **STM4 interface for USPEX.**

Alternatively, you can visualize USPEX results with other software, *e.g.*, OpenDX, VESTA, *etc.* VESTA already includes a feature for reading USPEX structure files directly.

## 8.2 How can I avoid trapping?

First, use a sufficiently large population size. Second, USPEX by default uses a powerful fingerprint niching method. Anything that increases the diversity of the population will reduce the chances of trapping in a local minimum. To make sure that your simulation is not trapped, it is useful to run a second simulation with different parameters. A powerful trick to avoid trapping is the antiseed technique.

## 8.3 What is a single block calculation?

The single block feature was introduced in USPEX 9.3.9, and enables USPEX users to run structure predictions with a variable number of formula units of the same composition. For example:

```
% atomType
Si O
% EndAtomType

% numSpecies
1 2
% EndNumSpecies

12 : minAt
24 : maxAt
```

This means we sample structures of compound $SiO_2$ (with the ratio of 1:2) with a variable number of formula units with 12–24 atoms.

Starting from USPEX 9.4.1, the single block feature has been moved from `calculationType` = 301/311 to 300/310. The settings are still the same, users just need to set up the `minAt`, `maxAt` and `numSpecies` keywords.

## 8.4 How do I use the seed technique?

This technique is useful, if instead of starting with random structures, you would like to input some structures that you already know for the compound or related materials. Just create a file `Seeds/POSCARS` for the next generation, or `Seeds/POSCARS_gen` (`gen` is the generation number) for the specific generation of an USPEX calculation, in the format of concatenated `POSCAR` files in VASP5 format. Don't miss letter "`S`" in the file name.

Example:

```
EA33 2.69006 5.50602 4.82874 55.2408 73.8275 60.7535 no SG
1.0
2.690100  0.000000  0.000000
2.690100  4.804100  0.000000
1.344900  2.402100  3.967100
Mg Al O
1  2  4
Direct
0.799190  0.567840  0.859590
0.793520  0.230950  0.544750
0.793540  0.916090  0.174450
0.050972  0.816060  0.859610
0.172230  0.194810  0.859600
```

```
0.438250  0.655170  0.406880
0.438230  0.202440  0.312330
EA34 7.61073 2.85726 2.85725 60.0001 79.1809 79.1805 no SG
1.0
7.610700  0.000000  0.000000
0.536350  2.806500  0.000000
0.536330  1.352000  2.459300
Mg Al O
1  2  4
Direct
0.708910  0.507440  0.068339
0.374050  0.285730  0.846630
0.023663  0.069185  0.630090
0.889560  0.780560  0.341460
0.350470  0.626920  0.187820
0.597290  0.211310  0.772210
0.116440  0.371590  0.932500
```

One can add seeds at any time during the calculation. USPEX will look for new seeds at the beginning of each generation. The corresponding information will be recorded to `results1/Seeds_history` and the seeds files (`POSCARS` or `POSCARS_gen`) will be kept as `POSCARS_gen` in `Seeds/` folder.

Whenever seeds are added, we suggest users to check the `results1/Seeds_history` and `Warnings` files. There will be a warning message "`Meet a problem when reading Seeds - ...`" if your seeds are problematic. When an error appears in the seeds file, such as missing lines, the structures after the error point will not be added.

**Note:** Make sure you specified all atomic symbols at the $6^{th}$ line of each structure. For example, to add the $P6_3/mc$ $H_2$ structure to a H-O variable-composition calculation, you should edit the file as:

```
H_I-P63/mc
1
4.754726  -2.74514  0.000000
-0.00000  5.490285  0.000000
0.000000  0.000000  4.508715
H
16
Direct
...
(the atomic positions information is omitted here)
```

## 8.5 How do I play with the compositions?

For variable-composition and single block calculations, as soon as the calculation starts, it produces a file `Seeds/compositions` with all possible compositions, from which the code randomly takes compositions for the random structure generator. You can edit

this file, leaving the compositions you are most interested in — only these compositions will be used for random structure production in the second and subsequent generations. `Seeds/compositions` file lists the numbers of atoms of each type in the cell, *e.g.*, for the C-O system:

```
8 0
0 8
2 4
```

means that you are interested in randomly producing $C_8$, $O_8$, and $C_2O_4$ structures. Other compositions will be sampled too, thanks to the heredity and transmutation operators.

When you want to generate structures with specific compositions, you can use the anti-compositions feature — write the list of all unwanted compositions to the file named `Seeds/Anti-compositions`. There are three ways to do so:

1. For all unwanted compositions with the same ratios, you can write stoichiometric ratio to ban these compositions. For example, you can use "`1 2 1`" to ban all the composition with the same ratio, such as "`1 2 1`", "`2 4 2`", "`3 6 3`" and so on.
2. Only for the specific composition, but not for other compositions with the same ratio. You can write the compositions with a minus sign. For example, you can use "`-3 2 0`" or "`3 -2 0`" to ban the "`3 2 0`" composition, but not to ban "`6 4 0`" or "`9 6 0`" composition. (Notice: "`3 2 -0`" does not work for this case).
3. For all single/binary/ternary compounds. If you don't want to sample all single/binary/ternary compounds, just write the keyword `single/binary/ternary` in `Anti-compositions` file.

Example:

```
 single
 binary
 1 1 2
-2 2 1
```

If you don't clearly know what you are doing, please leave `Anti-compositions` file empty. For more information about the compositions you don't want, you can have a look at `results1/compositionStatistic` file.

**Note:**

- Even if `compositions` or `Anti-compositions` files exist before the calculation starts, they will be ignored. `Anti-compositions` file will be renamed to a backup file `Anti-compositions-back`. Therefore, please edit `compositions` or `Anti-compositions` files after the calculation starts.

- Please also be aware, that in USPEX calculations with compositional blocks, the compositions usually mean the numbers of these blocks. Therefore, to have the correct format of `Anti-compositions` file, please check `compositions` file first.

## 8.6 How do I set up a passwordless connection from a local machine to a remote cluster?

You will need to copy the public key from your local machine (directory `./ssh` or `./ssh2`) to the remote cluster. Here is the list of commands you need to execute:

```
local # ssh-keygen -t dsa
local # scp ~/.ssh2/id_dsa.pub oganov@palu.cscs.ch:~/.ssh/tmp.pub
remote # cd ~/.ssh/
remote # ssh-keygen -f tmp.pub -i >> authorized_keys
remote # rm tmp.pub
```

## 8.7 How do I restart a calculation with a corrupt `*.mat` file?

When there is a problem in file system, e.g. the disk is full, the file system is overloaded, USPEX could have a problem in writing these `*.mat` files correctly, and meet a message during the calculation like:

```
???Error using ==> load
Unable to read MAT file /home/USPEX/Current_POP.mat

File may be corrupt.
```

When you meet an error with a corrupt `*.mat` file, please recover the broken `*.mat` file with the backup one, delete the `matfilelocker` file, then restart the calculation. Unfortunately, when the backup `*.mat` file is empty or also corrupt, you have to restart the calculation with a generation pickup.

## 8.8 What should I do when USPEX is not running for a while?

When you found USPEX is not running for a while, with file `still_running` existing for a long time (usually longer than 30 minutes; use "`ls -l`" command to check the timestamp of the `still_running` file), you should consider that there is something wrong with the calculation. In this situation, what you need to do is to follow a checking procedure below:

- Make sure your MATLAB calculation is not running, use "`top`" command to check it. Sometimes USPEX can take long time in structure generation and softmutation. Once you are sure that MATLAB stopped, you can continue with the next step.

- Stop your crontab or job running script to avoid USPEX running during the checking procedure. This is very important, otherwise you will mess up your USPEX calculations.
- Delete the `still_running` file.
- Run USPEX with command "`USPEX -r`" or "`matlab < USPEX.m`" to check what will happen. If you meet errors or bugs, you can try to fix them, or report a bug to our USPEX Google forum.
- If everything is fine, just restart your crontab or job running script to continue the calculation.

## 8.9 How do I set up a calculation using a job submission script?

To set up a job submission script, we expect users to know some basic knowledge of MATLAB programing and your job submission systems, at least the basic idea of how to work with strings in MATLAB and how to get the job information.

There are two modes for job submission: **local** submission or **remote** submission, depending on whether you submit *ab initio* calculations to the local machine where you run USPEX and MATLAB, or to a remote supercomputer.

### 8.9.1 Step 1: Configuring files in `Submission/` folder

**Case I: Local submission.**

Please edit in `INPUT.txt` file the following tag:

```
1   : whichCluster (0: no-job-script, 1: local submission, 2: remote submission)
```

Then, go to the directory `Submission/`, where you need to edit two files: `submitJob_local.m` and `checkStatus_local.m`.

One can find the detailed instructions in these files. In general, one just needs to tell USPEX how to submit the job and check if the job has completed or not.

In `submitJob_local.m`:

```
function jobNumber = submitJob_local()
%-------------------------------------------------------------
%This routine is to check if the submitted job is complete or not
%One needs to do a little edit based on your own situation.
%1   : whichCluster (default 0, 1: local submission, 2: remote submission)
%-------------------------------------------------------------

%Step 1: to prepare the job script that is required by your supercomputer
fp = fopen('myrun', 'w');
```

```
fprintf(fp, '#!/bin/sh\n');
fprintf(fp, '#PBS -l nodes=1:ppn=8,walltime=1:30:00 -q cfn_short\n');
fprintf(fp, '#PBS -N USPEX\n');
fprintf(fp, '#PBS -j oe\n');
fprintf(fp, '#PBS -V \n');
fprintf(fp, 'cd ${PBS_O_WORKDIR}\n');
fprintf(fp, 'mpirun -np 4 vasp1 > vasp.out\n');
fclose(fp);

%Step 2: to submit the job with a command like qsub, bsub, llsubmit, etc.

[a,b]=unix(['qsub myrun'])

%Step 3: to get the jobID from the screen message
%It will output some message on the screen like '2350873.nano.cfn.bnl.local'

end_marker = findstr(b,'.');
jobNumber = b(1:end_marker(1)-1);
```

In `checkStatus_local.m`:

```
function doneOr = checkStatus_local(jobID)
%-------------------------------------------------------------------
%This routine is to check if the submitted job is complete or not
%One needs to do a little edit based on your own case.
1    : whichCluster (0: no-job-script, 1: local submission, 2: remote submission)
%-------------------------------------------------------------------

%Step1: the command to check job by ID.
    [a,b] = unix(['qstat ' jobID ''])

%Step2: to find the keywords from the screen message to determine if the job is complete
%Below is just a sample:
%-------------------------------------------------------------------------------------
%Job id                    Name             User            Time Use S Queue
%-------------------------- ---------------- --------------- -------- - ----------
%2455453.nano              USPEX            qzhu            02:28:42 R cfn_gen04
%-------------------------------------------------------------------------------------
%If the job is still running, it will show as above.
%If there are no key words like 'Q/R Cfn_gen04', it indicates the job is complete.
%Therefore, we can use a small MATLAB function findstr to apply this argument.
    if isempty(findstr(b,'R cfn_')) & isempty(findstr(b,'Q cfn_'))
       doneOr = 1
       unix('rm USPEX*');    % to remove the log file
  end
```

### Case II: Remote submission.

Please edit in `INPUT.txt` file the following tag:

```
2       : whichCluster (default 0, 1: local submission; 2: remote submission)
C-20GPa : remoteFolder
```

Finally, go to the directory `Submission/`, where you need to edit two files: `submitJob_remote.m` and `checkStatus_remote.m`

In `submitJob_remote.m`:

```
function jobNumber = submitJob_remote(USPEX, Index)
%-------------------------------------------------------
%This routine is to check if the submitted job is complete or not
%2    : whichCluster (default 0, 1: local submission; 2: remote submission)
%C-20GPa : remoteFolder
%-------------------------------------------------------

%-------------------------------------------------------
%Step1: To prepare the job script, runvasp.sh
  fp = fopen('runvasp.sh', 'w');
  fprintf(fp, '#!/bin/sh\n');
  fprintf(fp, '#PBS -l nodes=2:ppn=2,walltime=1:30:00\n');
  fprintf(fp, '#PBS -N USPEX\n');
  fprintf(fp, '#PBS -j oe\n');
  fprintf(fp, '#PBS -V \n');
  fprintf(fp, 'cd ${PBS_O_WORKDIR}\n');
  fprintf(fp, '/usr/local/pkg/openmpi-1.4.5/bin/mpirun -np 4 vasp1 > vasp.out\n');
  fclose(fp);
%-------------------------------------------------------------------------------
%Step 2: Copy the files to the remote machine

%Step2-1: Specify the PATH to put your calculation folder
Home = ['/nfs/user08/qiazhu']; %'pwd' of your home directory on remote machine
Address = 'qiazhu@seawulf.stonybrook.edu'; %your target server: username@address
Path = [Home '/' USPEX '/CalcFold' num2str(Index)];  %Just keep it

%Step2-2: Create the remote directory
% Please change the ssh/scp command if necessary!
% Sometimes you don't need the -i option
try
[a,b]=unix(['ssh -i ~/.ssh/seawulf ' Address ' mkdir ' USPEX ]);
catch
end

try
[a,b]=unix(['ssh -i ~/.ssh/seawulf ' Address ' mkdir ' Path ]);
catch
end

%Step2-3: Copy the necessary files (for VASP calculations, we need POSCAR, INCAR, POTCAR,
% KPOINTS and job script)
unix(['scp -i ~/.ssh/seawulf POSCAR   ' Address ':' Path]);
unix(['scp -i ~/.ssh/seawulf INCAR    ' Address ':' Path]);
unix(['scp -i ~/.ssh/seawulf POTCAR   ' Address ':' Path]);
unix(['scp -i ~/.ssh/seawulf KPOINTS  ' Address ':' Path]);
unix(['scp -i ~/.ssh/seawulf runvasp.sh ' Address ':' Path]);

%-------------------------------------------------------------------------------
%Step 3: to submit the job and get JobID, i.e., the exact command to submit the job.
[a,v]=unix(['ssh -i ~/.ssh/seawulf ' Address ' /usr/local/pkg/torque/bin/qsub '
            Path '/runvasp.sh'])

% format: Job 1587349.nagling is submitted to default queue <mono>
end_marker = findstr(v,'.');
if strfind(v,'error')
   jobNumber=0;
else
   jobNumber = v(1:end_marker(1)-1);
end
```

In `CheckStatus_remote.m`:

```
function doneOr = checkStatus_remote(jobID, USPEX, Folder)
%-------------------------------------------------------------
%This routine is to check if the submitted job is complete or not
%One needs to do a little edit based on your own situation.
%-------------------------------------------------------------

%Step1: Specify the PATH to put your calculation folder
Home = ['/nfs/user08/qiazhu']; %'pwd' of your home directory of your remote machine
Address = 'qiazhu@seawulf.stonybrook.edu'; %Your target: username@address.
Path = [Home '/' USPEX '/CalcFold' num2str(Folder)]; %just keep it
%Step2: Check JobID, the exact command to check job by jobID
[a,b]=unix(['ssh -i ~/.ssh/seawulf ' Address ' /path/to/qstat ' num2str(jobID)])
    tempOr1 = strfind(b, 'R batch');
    tempOr2 = strfind(b, 'Q batch');
    if isempty(tempOr1) & isempty(tempOr2)
      doneOr = 1;
% for vasp, we usually need OSZICAR for reading energy and CONTCAR for reading
%structure OUTCAR, EIGENVAL, DOSCAR might be needed for reading other properties.
%   unix(['scp -i ~/.ssh/seawulf ' Address ':' Path '/OUTCAR ./'])
%OUTCAR is not necessary by default
      unix(['scp -i ~/.ssh/seawulf ' Address ':' Path '/OSZICAR ./'])
%For reading enthalpy/energy
      unix(['scp -i ~/.ssh/seawulf ' Address ':' Path '/CONTCAR ./'])
%For reading structural info
end
```

It might take some time to correctly configure these files. To test if it works or not, you can type "`USPEX -r`" twice and then track the screen information. The first attempt is to check if the jobs are submitted, while the second attempt is to check if USPEX can correctly check the status of the submitted jobs. All of the related information can be found in the screen output message. If MATLAB exits without any errors, you are almost ready to go.

### 8.9.2 Step 2: Running USPEX periodically

The real calculation starts with the command "`USPEX -r > log`". Each time the MATLAB process will check the status of the running *ab initio* calculations. If the job is complete, MATLAB will go the the calculation folder to read the results, and then submit new calculations. After that, MATLAB will exit. Therefore, one needs to periodically call the command (for example, every 5 minutes). The periodic script can be executed by using either `crontab` or a shell script.

### 8.9.3 Crontab

This can be performed using a `crontab` daemon on your Linux machine. In your user home directory, there should now be the files:

`~/call_job`

`~/CronTab`

Here is an example of a 1-line `CronTab` file from one of our clusters:

```
*/5 * * * * sh call_job
```

It states that the interval between job submissions is 5 minutes and points to the file `call_job`, which should contain the address of the directory where USPEX will be executed, and the file `call_job` looks like this:

```
#!/bin/sh
source $HOME/.bashrc
cd /ExecutionDirectory
date >> log
USPEX -r >> log
```

To activate `crontab`, type

```
crontab ~/CronTab
```

If you want to terminate this run, either edit `call_job` or remove this `crontab` by typing

```
crontab -r
```

To check if crontab works well, one should also keep tracking the updates of the log file at the beginning of the calculation.

### 8.9.4 Shell script

You can also prepare the script by using the `sleep` command in Linux shell. Below is a rather simple script `run-uspex.sh`:

```
#!/bin/sh
while [ ! -f ./USPEX_IS_DONE ]; do
    date >> log
    USPEX -r >> log
    sleep 300
done
```

**Note:** keep in mind that this calculation can only be terminated by killing the process ID of this script.

## 8.10 How do I work with symmetry codes on 32-bit machines?

Execute "`./install-32bit.sh`" shell script under `FunctionFolder/Tool/32bit/` folder to replace the default 64-bit binary codes by the 32-bit executables.

# 9 Appendices

## 9.1 List of Examples

- `EX01-3D_Si_vasp`: Silicon (8 atoms/cell) at zero pressure. Variable-cell DFT calculation using VASP, PBE96 functional. Many thanks to G. Kresse for permission to include his PAW files (`POTCAR`) in our distribution.
- `EX02-3D_MgAl2O4_gulp`: $MgAl_2O_4$ (28 atoms/cell) at 100 GPa pressure. Variable-cell calculation using Buckingham potentials, GULP code. Beware that for reliable, you should better do *ab initio* calculations.
- `EX03-3D-const_cell_MgSiO3_gulp`: this example shows how to do structure prediction when you know cell parameters. $MgSiO_3$ (20 atoms/cell) with Buckingham potentials, GULP code. Cell parameters correspond to post-perovskite. The discovery of post-perovskite (*Oganov & Ono, Nature 2004; Murakami et al., Science 2004*) was a major breakthrough in Earth sciences.
- `EX04-3D_C_lammps`: this example shows how to do crystal structure prediction using USPEX together with the LAMMPS code. In this a simple example: 8 carbon atoms, and Tersoff potential.
- `EX05-3D_Si_atk`: Example of crystal structure prediction of Si with 8 atoms/cell using the density-functional tight binding approximation and ATK code.
- `EX06-3D_C_castep`: DFT-based prediction of the crystal structure of carbon with 8 atoms/cell at 10 GPa, using the CASTEP code.
- `EX07-2D_Si_vasp`: prediction of the 2D-crystal of silicon using DFT and VASP. Simple and powerful.
- `EX08-0D_LJ_gulp`: Nanoparticle structure prediction. Lennard-Jones nanoparticle with 30 atoms, using the GULP code.
- `EX09-3D-molecules_CH4_vasp`: methane with 4 molecules/cell, at the pressure of 20 GPa. DFT, VASP. Molecule is described in the file `MOL_1`.
- `EX10-3D-molecules_CH4_dmacrys`: methane with 8 molecules/cell, with forcefield and DMACRYS code, at normal pressure. Molecule is described in the file `MOL_1`, but note its slightly unusual format for DMACRYS calculations. Please put executables `dmacrys`, `neighcrys-pp`, `neighcrys-vv` in the `Specific/` folder.
- `EX11-3D-molecules_urea_tinker`: urea with 2 molecules/cell, with forcefield and TINKER code, at normal pressure. Molecule is described in the file `MOL_1`.
- `EX12-3D_varcomp_LJ_gulp`: Lennard-Jones binary system with fake "Mo" and "B" atoms, GULP, and variable-composition USPEX (*Lyakhov and Oganov, 2010*).

- `EX13-3D_special_quasirandom_structure_TiCoO`: USPEX can easily find the most disordered (or the most ordered) alloy structure. Here, this is shown for $Ti_xCo_{(1-x)}O$. You need to specify the initial structure in `Seeds/POSCARS` and use only the permutation operator. In this case, you don't need to use any external codes. In this example, we optimize (minimize) the structural order (*Oganov and Valle (2009); Lyakhov, Oganov, Valle (2010)*) without relaxation (`abinitioCode` = 0). Seed structure (supercell of Ti-Co-O-structure) is permutated to find the structure the minimum/maximum order. Minimizing order in this situation, one gets a generalized version of the "special quasirandom structure".

- `EX14-GeneralizedMetadynamics_Si_vasp`: simple example of a powerful capability to find complex low-energy structures starting with a simple seed structure (*Zhu et al, 2013*). Silicon, up to 16 atoms/cell, DFT, VASP. Pay special attention to `INCAR` files. Best of all, just keep the files that you see here, changing only `ENCUT`, perhaps `SIGMA`. Evolutionary metadynamics not only predicts low-energy structures, but also gives an idea of transition mechanisms between crystal structures.

- `EX15-VCNEB_Ar_gulp`: example of a variable-cell nudged elastic band (*VCNEB: Qian et al., 2013*) calculation fcc-hcp transition in a model system, argon, at 0 GPa pressure. Lennard-Jones potential, GULP code.

- `EX16-USPEX-performance_SrTiO3_gulp`: $SrTiO_3$ (50 atoms/cell) at zero pressure. Variable-cell calculation using Buckingham potentials, GULP code. Running this example you can see that even for such a relatively large system USPEX code scores a >90% success rate and remarkable efficiency. This contrasts with a 7-12% success rate reported for the same system and using the same potential by Zurek & Lonie. Clearly, USPEX outperforms the poor reimplementation of our method by Zurek and Lonie. We have witnessed excellent performance of our code also for much larger systems.

- `EX17-3D_DebyeTemp_C_vasp`: example of optimization of the elasticity-related properties (bulk or shear moduli, Poisson ratio, Chen-Niu hardness, or Debye temperature). In this example, we maximize the Debye temperature of carbon using the VASP code.

- `EX18-3D_varcomp_ZnOH_gulp`: as you know, USPEX has unique capabilities for variable-composition searches. This example shows a pretty challenging case — variable-composition calculation for the ternary system Zn-O-H. This calculation uses a ReaxFF forcefield in GULP code. USPEX can do calculations for any number of components — *e.g.* quaternary, quinternary, *etc.* systems are within its reach. Of course, the more components you have, the more expensive (and the more risky) your calculation is. No reference results at the moment.

- `EX19-Surface-boron111`: Prediction of (111) surface reconstruction of alpha-boron, with variable number of atoms (Zhou *et al.*, Phys. Rev. Lett. 113, 176101 (2014)).

- `EX20-0D_Cluster_C60_MOPAC`: Cluster structure prediction (000) for $C_{60}$ using MOPAC.
- `EX21-META_MgO_gulp`: Evolutionary metadynamics, with GULP code and Buckingham potentials, MgO with 8 atoms/cell. Starting structure is of rocksalt type, and evolutionary metadynamics finds a number of low-energy structures and structural relations.
- `EX22-GEM_MgO_gulp`: Generalized evolutionary metadynamics, with GULP code and Buckingham potentials. Starting structure is of rocksalt type, with 8 atoms/cell, the calculation is allowed to increase system size up to 16 atoms/cell, and generalized evolutionary metadynamics (GEM) finds a number of low-energy structures and structural relations.

## 9.2 Test runs

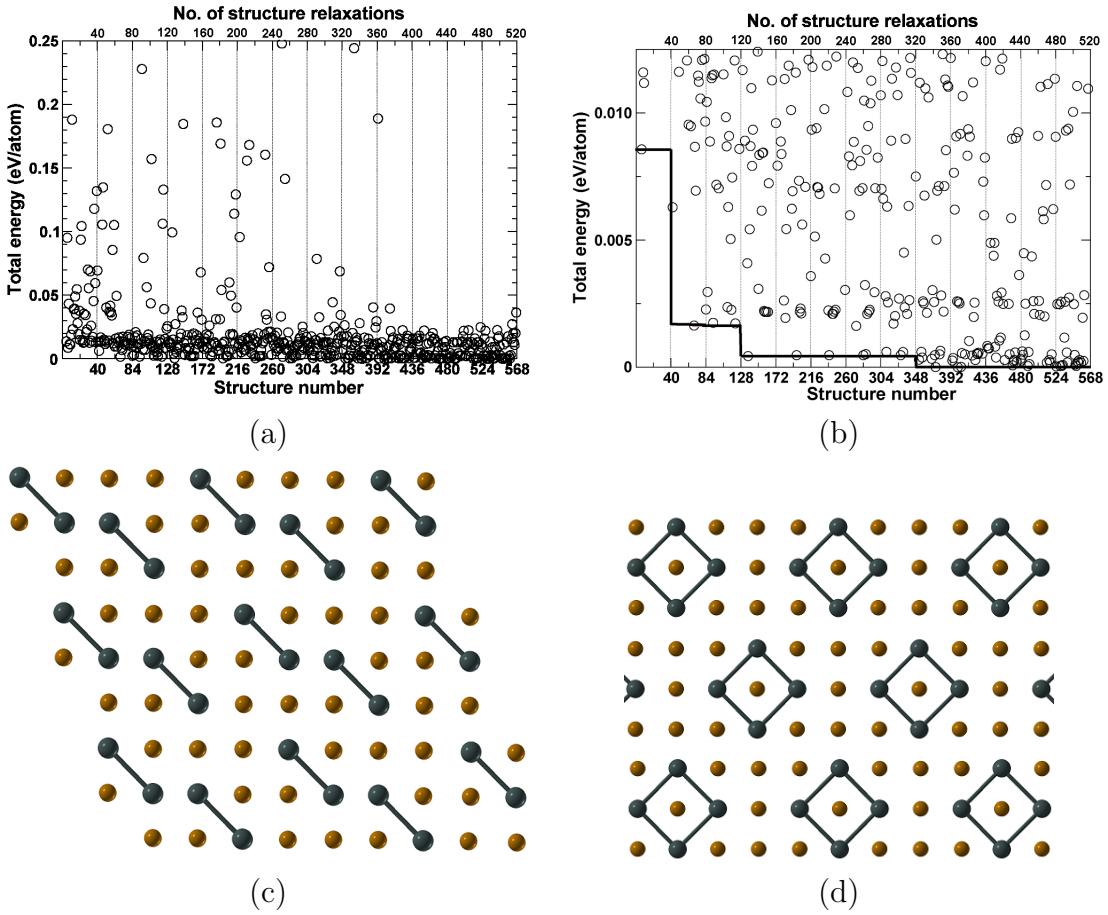



Figure 18: **Evolutionary structure search for $Au_8Pd_4$.** a, b — evolution of the total energy (for clarity, panel (b) zooms in on the lowest-energy region of the same data set), c — the lowest-energy structure found in our evolutionary simulation, and d — the lowest-energy structure found by cluster expansion calculations of Zunger. Note that our structure (c) is the lowest-energy known structure for this compound. This establishes the power of our method (even in its ancient, 2007, version).

## 9.3 Sample INPUT.txt files

### 9.3.1 Fixed-composition USPEX calculation (calculationType=300):

```
PARAMETERS EVOLUTIONARY ALGORITHM
% Example of the short input, using most options as defaults

% atomType
Mg Al O
% EndAtomType

% numSpecies
2 4 8
% EndNumSpecies

50    : numGenerations
50.0  : ExternalPressure

% abinitioCode
3 3 3 3 3
% ENDabinit

% commandExecutable
gulp < input > output
% EndExecutable
```

### 9.3.2 Variable-composition USPEX calculation (calculationType=301):

```
USPEX : calculationMethod (USPEX, VCNEB, META)
301   : calculationType (dimension: 0-3; molecule: 0/1; varcomp: 0/1)
1     : AutoFrac

% atomType
Mo B
% EndAtomType

% numSpecies
1 0
0 1
% EndNumSpecies

80    : populationSize
200   : initialPopSize
60    : numGenerations
20    : stopCrit

11    : firstGeneMax
8     : minAt
18    : maxAt

% abinitioCode
3 3 3
% ENDabinit

% commandExecutable
gulp < input > output
% EndExecutable
```

### 9.3.3 Evolutionary metadynamics (calculationMethod=META):

```
META   : calculationMethod (USPEX, VCNEB, META)
301    : calculationType (dimension: 0-3; molecule: 0/1; varcomp: 0/1)

% valences
4
% endValences

% IonDistances
1.2
% EndDistances

0.0001 : ExternalPressure

16     : maxAt
2.0    : minVectorLength
8.0    : maxVectorLength

15     : populationSize
40     : numGenerations
3.0    : mutationDegree
250.0  : GaussianHeight
0.3    : GaussianWidth
2      : FullRelax

abinitioCode
1 1 1 (1 1)
ENDabinit

% KresolStart
0.12 0.10 0.09 0.10 0.08
% Kresolend

% commandExecutable
mpirun -np 4 vasp > log
% EndExecutable
```

### 9.3.4 vcNEB calculation (calculationMethod=VCNEB):

```
VCNEB : calculationMethod

% numSpecies
4
% EndNumSpecies

% atomType
Ar
% EndAtomType

0.0    : ExternalPressure

111    : vcnebType
15     : numImages
500    : numSteps
1      : optimizerType
2      : optReadImages
3      : optRelaxType
0.25   : dt
0.003  : ConvThreshold

0.3    : VarPathLength
3      : K_min
6      : K_max
0      : optFreezing
0      : optMethodCIDI

2      : FormatType
10     : PrintStep

abinitioCode
3
ENDabinit

% commandExecutable
gulp < input > output
% EndExecutable
```

## 9.4 List of space groups

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | $P1$ | 2 | $P\text{-}1$ | 3 | $P2$ | 4 | $P2_1$ |
| 5 | $C2$ $(A2)^*$ | 6 | $Pm$ | 7 | $Pc$ $(Pa)^*$ | 8 | $Cm$ $(Am)^*$ |
| 9 | $Cc$ $(Aa)^*$ | 10 | $P2/m$ | 11 | $P2_1/m$ | 12 | $C2/m$ $(A2/m)^*$ |
| 13 | $P2/c$ $(P2/a)^*$ | 14 | $P2_1/c$ $(P2_1/a)^*$ | 15 | $C2/c$ $(A2/a)^*$ | 16 | $P222$ |
| 17 | $P222_1$ | 18 | $P2_12_12$ | 19 | $P2_12_12_1$ | 20 | $C222_1$ |
| 21 | $C222$ | 22 | $F222$ | 23 | $I222$ | 24 | $I2_12_12_1$ |
| 25 | $Pmm2$ | 26 | $Pmc2_1$ | 27 | $Pcc2$ | 28 | $Pma2$ |
| 29 | $Pca2_1$ | 30 | $Pnc2$ | 31 | $Pmn2_1$ | 32 | $Pba2$ |
| 33 | $Pna2_1$ | 34 | $Pnn2$ | 35 | $Cmm2$ | 36 | $Cmc2_1$ |
| 37 | $Ccc2$ | 38 | $Amm2$ $(C2mm)^*$ | 39 | $Aem2$ $(C2mb)^*$ | 40 | $Ama2$ $(C2cm)^*$ |
| 41 | $Aea2$ $(C2cb)^*$ | 42 | $Fmm2$ | 43 | $Fdd2$ | 44 | $Imm2$ |
| 45 | $Iba2$ | 46 | $Ima2$ | 47 | $Pmmm$ | 48 | $Pnnn$ |
| 49 | $Pccm$ | 50 | $Pban$ | 51 | $Pmma$ | 52 | $Pnna$ |
| 53 | $Pmna$ | 54 | $Pcca$ | 55 | $Pbam$ | 56 | $Pccn$ |
| 57 | $Pbcm$ | 58 | $Pnnm$ | 59 | $Pmmn$ | 60 | $Pbcn$ |
| 61 | $Pbca$ | 62 | $Pnma$ | 63 | $Cmcm$ | 64 | $Cmce$ $(Cmca)^*$ |
| 65 | $Cmmm$ | 66 | $Cccm$ | 67 | $Cmme$ $(Cmma)^*$ | 68 | $Ccce$ $(Ccca)^*$ |
| 69 | $Fmmm$ | 70 | $Fddd$ | 71 | $Immm$ | 72 | $Ibam$ |
| 73 | $Ibca$ | 74 | $Imma$ | 75 | $P4$ | 76 | $P4_1$ |
| 77 | $P4_2$ | 78 | $P4_3$ | 79 | $I4$ | 80 | $I4_1$ |
| 81 | $P\text{-}4$ | 82 | $I\text{-}4$ | 83 | $P4/m$ | 84 | $P4_2/m$ |
| 85 | $P4/n$ | 86 | $P4_2/n$ | 87 | $I4/m$ | 88 | $I4_1/a$ |
| 89 | $P422$ | 90 | $P42_12$ | 91 | $P4_122$ | 92 | $P4_12_12$ |
| 93 | $P4_222$ | 94 | $P4_22_12$ | 95 | $P4_322$ | 96 | $P4_32_12$ |
| 97 | $I422$ | 98 | $I4_122$ | 99 | $P4mm$ | 100 | $P4bm$ |
| 101 | $P4_2cm$ | 102 | $P4_2nm$ | 103 | $P4cc$ | 104 | $P4nc$ |
| 105 | $P4_2mc$ | 106 | $P4_2bc$ | 107 | $I4mm$ | 108 | $I4cm$ |
| 109 | $I4_1md$ | 110 | $I4_1cd$ | 111 | $P\text{-}42m$ | 112 | $P\text{-}42c$ |
| 113 | $P\text{-}42_1m$ | 114 | $P\text{-}42_1c$ | 115 | $P\text{-}4m2$ | 116 | $P\text{-}4c2$ |
| 117 | $P\text{-}4b2$ | 118 | $P\text{-}4n2$ | 119 | $I\text{-}4m2$ | 120 | $I\text{-}4c2$ |
| 121 | $I\text{-}42m$ | 122 | $I\text{-}42d$ | 123 | $P4/mmm$ | 124 | $P4/mcc$ |
| 125 | $P4/nbm$ | 126 | $P4/nnc$ | 127 | $P4/mbm$ | 128 | $P4/mnc$ |
| 129 | $P4/nmm$ | 130 | $P4/ncc$ | 131 | $P4_2/mmc$ | 132 | $P4_2/mcm$ |
| 133 | $P4_2/nbc$ | 134 | $P4_2/nnm$ | 135 | $P4_2/mbc$ | 136 | $P4_2/mnm$ |
| 137 | $P4_2/nmc$ | 138 | $P4_2/ncm$ | 139 | $I4/mmm$ | 140 | $I4/mcm$ |
| 141 | $I4_1/amd$ | 142 | $I4_1/acd$ | 143 | $P3$ | 144 | $P3_1$ |
| 145 | $P3_2$ | 146 | $R3$ | 147 | $P\text{-}3$ | 148 | $R\text{-}3$ |
| 149 | $P312$ | 150 | $P321$ | 151 | $P3_112$ | 152 | $P3_121$ |
| 153 | $P3_212$ | 154 | $P3_221$ | 155 | $R32$ | 156 | $P3m1$ |
| 157 | $P31m$ | 158 | $P3c1$ | 159 | $P31c$ | 160 | $R3m$ |
| 161 | $R3c$ | 162 | $P\text{-}31m$ | 163 | $P\text{-}31c$ | 164 | $P\text{-}3m1$ |
| 165 | $P\text{-}3c1$ | 166 | $R\text{-}3m$ | 167 | $R\text{-}3c$ | 168 | $P6$ |
| 169 | $P6_1$ | 170 | $P6_5$ | 171 | $P6_2$ | 172 | $P6_4$ |
| 173 | $P6_3$ | 174 | $P\text{-}6$ | 175 | $P6/m$ | 176 | $P6_3/m$ |
| 177 | $P622$ | 178 | $P6_122$ | 179 | $P6_522$ | 180 | $P6_222$ |
| 181 | $P6_422$ | 182 | $P6_322$ | 183 | $P6mm$ | 184 | $P6cc$ |
| 185 | $P6_3cm$ | 186 | $P6_3mc$ | 187 | $P\text{-}6m2$ | 188 | $P\text{-}6c2$ |
| 189 | $P\text{-}62m$ | 190 | $P\text{-}62c$ | 191 | $P6/mmm$ | 192 | $P6/mcc$ |
| 193 | $P6_3/mcm$ | 194 | $P6_3/mmc$ | 195 | $P23$ | 196 | $F23$ |
| 197 | $I23$ | 198 | $P2_13$ | 199 | $I2_13$ | 200 | $Pm\text{-}3$ |
| 201 | $Pn\text{-}3$ | 202 | $Fm\text{-}3$ | 203 | $Fd\text{-}3$ | 204 | $Im\text{-}3$ |
| 205 | $Pa\text{-}3$ | 206 | $Ia\text{-}3$ | 207 | $P432$ | 208 | $P4_232$ |
| 209 | $F432$ | 210 | $F4_132$ | 211 | $I432$ | 212 | $P4_332$ |
| 213 | $P4_132$ | 214 | $I4_132$ | 215 | $P\text{-}43m$ | 216 | $F\text{-}43m$ |
| 217 | $I\text{-}43m$ | 218 | $P\text{-}43n$ | 219 | $F\text{-}43c$ | 220 | $I\text{-}43d$ |
| 221 | $Pm\text{-}3m$ | 222 | $Pn\text{-}3n$ | 223 | $Pm\text{-}3n$ | 224 | $Pn\text{-}3m$ |
| 225 | $Fm\text{-}3m$ | 226 | $Fm\text{-}3c$ | 227 | $Fd\text{-}3m$ | 228 | $Fd\text{-}3c$ |
| 229 | $Im\text{-}3m$ | 230 | $Ia\text{-}3d$ | | | | |

*In the parentheses there are non-standard space groups used in the code.

## 9.5 List of plane groups

| Number | Group |
|---|---|
| 1 | p1 |
| 2 | p2 |
| 3 | pm |
| 4 | pg |
| 5 | cm |
| 6 | pmm |
| 7 | pmg |
| 8 | pgg |
| 9 | cmm |
| 10 | p4 |
| 11 | p4m |
| 12 | p4g |
| 13 | p3 |
| 14 | p3m1 |
| 15 | p31m |
| 16 | p6 |
| 17 | p6m |

## 9.6 List of point groups

List of all crystallographic and the most important non-crystallographic point groups in Schönflies and Hermann-Mauguin (international) notations.

*Crystallographic point groups:*

| Hermann-Maugin | Schönflies | In USPEX |
|---|---|---|
| 1 | $C_1$ | C1 or E |
| 2 | $C_2$ | C2 |
| 222 | $D_2$ | D2 |
| 4 | $C_4$ | C4 |
| 3 | $C_3$ | C3 |
| 6 | $C_6$ | C6 |
| 23 | T | T |
| $\overline{1}$ | $S_2$ | S2 |
| M | $C_{1h}$ | Ch1 |
| mm2 | $C_{2v}$ | Cv2 |
| $\overline{2}$ | $S_4$ | S4 |
| $\overline{3}$ | $S_6$ | S6 |
| $\overline{6}$ | $C_{3h}$ | Ch3 |
| m$\overline{3}$ | $T_h$ | Th |
| 2/m | $C_{2h}$ | Ch2 |
| mmm | $D_{2h}$ | Dh2 |
| 4/m | $C_{4h}$ | Ch4 |
| 32 | $D_3$ | D3 |
| 6/m | $C_{6h}$ | Ch6 |
| 432 | O | O |
| 422 | $D_4$ | D4 |
| 3m | $C_{3v}$ | Cv3 |
| 622 | $D_6$ | D6 |
| $\overline{4}$3m | $T_d$ | Td |
| 4mm | $C_{4v}$ | Cv4 |
| $\overline{3}$m | $D_{3d}$ | Dd3 |
| 6mm | $C_{6v}$ | Cv6 |
| m$\overline{3}$m | $O_h$ | Oh |
| $\overline{4}$2m | $D_{2d}$ | Dd2 |
| $\overline{6}$2m | $D_{3h}$ | Dh3 |
| 4/mmm | $D_{4h}$ | Dh4 |
| 6/mmm | $D_{6h}$ | Dh6 |
| m$\overline{3}$m | $O_h$ | Oh |

*Important non-crystallographic point groups*

| Hermann-Maugin | Schönflies | In USPEX |
|---|---|---|
| 5 | $C_5$ | C5 |
| 5/m | $S_5$ | S5 |
| $\overline{5}$ | $S_{10}$ | S10 |
| 5m | $Cv_{5v}$ | Cv5 |
| $\overline{10}$ | $Ch_{5h}$ | Ch5 |
| 52 | $D_5$ | D5 |
| $\overline{5}$m | $D_{5d}$ | Dd5 |
| $\overline{10}$2m | $D_{5h}$ | Dh5 |
| 532 | I | I |
| 5$\overline{3}$m | $I_h$ | Ih |

## 9.7 Table of univalent covalent radii used in USPEX

Table of covalent radii (in Å) used in USPEX (for hardness calculations, *etc.*):

| Z | Element | radius | Z | Element | radius | Z | Element | radius |
|---|---|---|---|---|---|---|---|---|
| 1 | H | 0.31 | 30 | Zn | 1.22 | 63 | Eu | 1.98 |
| 2 | He | 0.28 | 31 | Ga | 1.22 | 64 | Gd | 1.96 |
| 3 | Li | 1.28 | 32 | Ge | 1.20 | 65 | Tb | 1.94 |
| 4 | Be | 0.96 | 33 | As | 1.19 | 66 | Dy | 1.92 |
| 5 | B | 0.84 | 34 | Se | 1.20 | 67 | Ho | 1.92 |
| 6 | $Csp^3$ | 0.76 | 35 | Br | 1.20 | 68 | Er | 1.89 |
| | $Csp^2$ | 0.73 | 36 | Kr | 1.16 | 69 | Tm | 1.90 |
| | Csp | 0.69 | 37 | Rb | 2.20 | 70 | Yb | 1.87 |
| 7 | N | 0.71 | 38 | Sr | 1.95 | 71 | Lu | 1.87 |
| 8 | O | 0.66 | 39 | Y | 1.90 | 72 | Hf | 1.75 |
| 9 | F | 0.57 | 40 | Zr | 1.75 | 73 | Ta | 1.70 |
| 10 | Ne | 0.58 | 41 | Nb | 1.64 | 74 | W | 1.62 |
| 11 | Na | 1.66 | 42 | Mo | 1.54 | 75 | Re | 1.51 |
| 12 | Mg | 1.41 | 43 | Tc | 1.47 | 76 | Os | 1.44 |
| 13 | Al | 1.21 | 44 | Ru | 1.46 | 77 | Ir | 1.41 |
| 14 | Si | 1.11 | 45 | Rh | 1.42 | 78 | Pt | 1.36 |
| 15 | P | 1.07 | 46 | Pd | 1.39 | 79 | Au | 1.36 |
| 16 | S | 1.05 | 47 | Ag | 1.45 | 80 | Hg | 1.32 |
| 17 | Cl | 1.02 | 48 | Cd | 1.44 | 81 | Tl | 1.45 |
| 18 | Ar | 1.06 | 49 | In | 1.42 | 82 | Pb | 1.46 |
| 19 | K | 2.03 | 50 | Sn | 1.39 | 83 | Bi | 1.48 |
| 20 | Ca | 1.76 | 51 | Sb | 1.39 | 84 | Po | 1.40 |
| 21 | Sc | 1.70 | 52 | Te | 1.38 | 85 | At | 1.50 |
| 22 | Ti | 1.60 | 53 | I | 1.39 | 86 | Rn | 1.50 |
| 23 | V | 1.53 | 54 | Xe | 1.40 | 87 | Fr | 2.60 |
| 24 | Cr | 1.39 | 55 | Cs | 2.44 | 88 | Ra | 2.21 |
| 25 | Mn l.s. | 1.39 | 56 | Ba | 2.15 | 89 | Ac | 2.15 |
| | h.s | 1.61 | 57 | La | 2.07 | 90 | Th | 2.06 |
| 26 | Fe l.s | 1.32 | 58 | Ce | 2.04 | 91 | Pa | 2.00 |
| | h.s. | 1.52 | 59 | Pr | 2.03 | 92 | U | 1.96 |
| 27 | Co l.s. | 1.26 | 60 | Nd | 2.01 | 93 | Np | 1.90 |
| | h.s. | 1.50 | 61 | Pm | 1.99 | 94 | Pu | 1.87 |
| 28 | Ni | 1.24 | 62 | Sm | 1.98 | 95 | Am | 1.80 |
| 29 | Cu | 1.32 | | | | 96 | Cm | 1.69 |

*Source:* Cordero *et al.*, Dalton Trans. 2832-2838, 2008[35].

## 9.8 Table of default chemical `valences` used in USPEX

Table of chemical `valences` used in USPEX (for hardness calculations, *etc.*):

| Z | Element | valence | Z | Element | valence | Z | Element | valence |
|---|---|---|---|---|---|---|---|---|
| 1 | H | 1 | 35 | Br | 1 | 69 | Tm | 3 |
| 2 | He | 0.5 | 36 | Kr | 0.5 | 70 | Yb | 3 |
| 3 | Li | 1 | 37 | Rb | 1 | 71 | Lu | 3 |
| 4 | Be | 2 | 38 | Sr | 2 | 72 | Hf | 4 |
| 5 | B | 3 | 39 | Y | 3 | 73 | Ta | 5 |
| 6 | C | 4 | 40 | Zr | 4 | 74 | W | 4 |
| 7 | N | 3 | 41 | Nb | 5 | 75 | Re | 4 |
| 8 | O | 2 | 42 | Mo | 4 | 76 | Os | 4 |
| 9 | F | 1 | 43 | Tc | 4 | 77 | Ir | 4 |
| 10 | Ne | 0.5 | 44 | Ru | 4 | 78 | Pt | 4 |
| 11 | Na | 1 | 45 | Rh | 4 | 79 | Au | 1 |
| 12 | Mg | 2 | 46 | Pd | 4 | 80 | Hg | 2 |
| 13 | Al | 3 | 47 | Ag | 1 | 81 | Tl | 3 |
| 14 | Si | 4 | 48 | Cd | 2 | 82 | Pb | 4 |
| 15 | P | 3 | 49 | In | 3 | 83 | Bi | 3 |
| 16 | S | 2 | 50 | Sn | 4 | 84 | Po | 2 |
| 17 | Cl | 1 | 51 | Sb | 3 | 85 | At | 1 |
| 18 | Ar | 0.5 | 52 | Te | 2 | 86 | Rn | 0.5 |
| 19 | K | 1 | 53 | I | 1 | 87 | Fr | 1 |
| 20 | Ca | 2 | 54 | Xe | 0.5 | 88 | Ra | 2 |
| 21 | Sc | 3 | 55 | Cs | 1 | 89 | Ac | 3 |
| 22 | Ti | 4 | 56 | Ba | 2 | 90 | Th | 4 |
| 23 | V | 4 | 57 | La | 3 | 91 | Pa | 4 |
| 24 | Cr | 3 | 58 | Ce | 4 | 92 | U | 4 |
| 25 | Mn | 4 | 59 | Pr | 3 | 93 | Np | 4 |
| 26 | Fe | 3 | 60 | Nd | 3 | 94 | Pu | 4 |
| 27 | Co | 3 | 61 | Pm | 3 | 95 | Am | 4 |
| 28 | Ni | 2 | 62 | Sm | 3 | 96 | Cm | 4 |
| 29 | Cu | 2 | 63 | Eu | 3 | 97 | Bk | 4 |
| 30 | Zn | 2 | 64 | Gd | 3 | 98 | Cf | 4 |
| 31 | Ga | 3 | 65 | Tb | 3 | 99 | Es | 4 |
| 32 | Ge | 4 | 66 | Dy | 3 | 100 | FM | 4 |
| 33 | As | 3 | 67 | Ho | 3 | 101 | Md | 4 |
| 34 | Se | 2 | 68 | Er | 3 | 102 | No | 4 |

## 9.9 Table of default goodBonds used in USPEX

Table of default goodBonds used in USPEX (for hardness calculations, *etc.*):

| Z | Element | goodBonds | Z | Element | goodBonds | Z | Element | goodBonds |
|---|---|---|---|---|---|---|---|---|
| 1 | H | 0.20 | 35 | Br | 0.10 | 69 | Tm | 0.20 |
| 2 | He | 0.05 | 36 | Kr | 0.05 | 70 | Yb | 0.20 |
| 3 | Li | 0.10 | 37 | Rb | 0.05 | 71 | Lu | 0.20 |
| 4 | Be | 0.20 | 38 | Sr | 0.10 | 72 | Hf | 0.30 |
| 5 | B | 0.30 | 39 | Y | 0.20 | 73 | Ta | 0.40 |
| 6 | C | 0.50 | 40 | Zr | 0.30 | 74 | W | 0.30 |
| 7 | N | 0.50 | 41 | Nb | 0.35 | 75 | Re | 0.30 |
| 8 | O | 0.30 | 42 | Mo | 0.30 | 76 | Os | 0.30 |
| 9 | F | 0.10 | 43 | Tc | 0.30 | 77 | Ir | 0.30 |
| 10 | Ne | 0.05 | 44 | Ru | 0.30 | 78 | Pt | 0.30 |
| 11 | Na | 0.05 | 45 | Rh | 0.30 | 79 | Au | 0.05 |
| 12 | Mg | 0.10 | 46 | Pd | 0.30 | 80 | Hg | 0.10 |
| 13 | Al | 0.20 | 47 | Ag | 0.05 | 81 | Tl | 0.20 |
| 14 | Si | 0.30 | 48 | Cd | 0.10 | 82 | Pb | 0.30 |
| 15 | P | 0.30 | 49 | In | 0.20 | 83 | Bi | 0.20 |
| 16 | S | 0.20 | 50 | Sn | 0.30 | 84 | Po | 0.20 |
| 17 | Cl | 0.10 | 51 | Sb | 0.20 | 85 | At | 0.10 |
| 18 | Ar | 0.05 | 52 | Te | 0.20 | 86 | Rn | 0.05 |
| 19 | K | 0.05 | 53 | I | 0.10 | 87 | Fr | 0.05 |
| 20 | Ca | 0.10 | 54 | Xe | 0.05 | 88 | Ra | 0.10 |
| 21 | Sc | 0.20 | 55 | Cs | 0.05 | 89 | Ac | 0.20 |
| 22 | Ti | 0.30 | 56 | Ba | 0.10 | 90 | Th | 0.30 |
| 23 | V | 0.30 | 57 | La | 0.20 | 91 | Pa | 0.30 |
| 24 | Cr | 0.25 | 58 | Ce | 0.30 | 92 | U | 0.30 |
| 25 | Mn | 0.30 | 59 | Pr | 0.20 | 93 | Np | 0.30 |
| 26 | Fe | 0.25 | 60 | Nd | 0.20 | 94 | Pu | 0.30 |
| 27 | Co | 0.25 | 61 | Pm | 0.20 | 95 | Am | 0.30 |
| 28 | Ni | 0.15 | 62 | Sm | 0.20 | 96 | Cm | 0.30 |
| 29 | Cu | 0.10 | 63 | Eu | 0.20 | 97 | Bk | 0.30 |
| 30 | Zn | 0.10 | 64 | Gd | 0.20 | 98 | Cf | 0.30 |
| 31 | Ga | 0.25 | 65 | Tb | 0.20 | 99 | Es | 0.30 |
| 32 | Ge | 0.50 | 66 | Dy | 0.20 | 100 | FM | 0.30 |
| 33 | As | 0.35 | 67 | Ho | 0.20 | 101 | Md | 0.30 |
| 34 | Se | 0.20 | 68 | Er | 0.20 | 102 | No | 0.30 |

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