cryslatt documentation

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1 Introduction

The *cryslatt* script performs the lattice parameter optimization of a crystal using the Boys-Bernardi counterpoise correction, according to the chosen level of theory. It may be used for both Hartree-Fock (HF) or Density Functional Theory (DFT) calculations and employs the quantum chemistry program CRYSTAL [1]. Calculations are launched using the external Python script ACMxc.

In order to obtain an energy-volume curve, a range of lattice constants is chosen and for each value L two calculations are run: one for the bulk, the other one for a single atom surrounded by ghost atoms as in the bulk structure. The total energy per atom $E^{\mathrm{bulk}}(L)$ of the bulk system, as well as the total energy $E^{\mathrm{atom}}(L)$ for the atom surrounded by ghost atoms, are computed and their difference is considered:

$$E^{\mathrm{coh}}(L) = E^{\mathrm{bulk}}(L) - E^{\mathrm{atom}}(L)$$

The resulting energy-volume curve is fitted using an equation of state, and the optimal lattice constant, bulk modulus and cohesive energy are computed.

2 Prerequisites

The *cryslatt* script requires some external programs and libraries:

- Python 3 (or newer);
- CRYSTAL;
- ACMxc (available on GitHub).

Adiabatic Connection Model (ACM) calculations require the values of the W_∞ and W'_∞, which are not currently provided by the latest CRYSTAL official version. This feature will be added in a future CRYSTAL version. Meanwhile, if you already own a CRYSTAL licence, the currently working version may be requested directly to the CRYSTAL developers, along with the launching scripts.

The script requires the following environment variables:

- `CRY23_UTILS`, which contains the path of the directory containing the CRYSTAL scripts;
- `PYTHONBIN`, containing the path of the Python 3 executable.

Furthermore, the variable `STORE`, defined in the script, must coincide with the path of the directory which contains the reference directories for calculations.

These reference directories must have the following structure:

```
<system_name>.SAVE
├─ ATOM
│  ├─ inputatom.d12
│  └─ inputatom.d3
├─ input.d12
├─ input.d3
└─ reference
```

The name of the reference system directory must have the `.SAVE` extension. Bulk input files are contained in that directory and must have the names `input.d12` and `input.d3`, while atomic ones must be contained in a subdirectory called `ATOM` and their names must be `inputatom.d12` and `inputatom.d3`. If a file called `METAL` is present in either the bulk or atom directory, ACMxc will be run in metallic mode for the corresponding calculation (namely $E^{\mathrm{MP2}} = -\infty$).

The CRYSTAL input files (ending with `.d12`) are modified by the *cryslatt* script and have the following form:

`input.d12`:

```
sodium bcc
CRYSTAL
0 0 0
229
3.79
1
11 0. 0. 0.
END
[BASIS SET]
END
DFT
FFFF
XXLGRID
#END
TOLDEE
CCCC
SHRINK
18 36
EXCHGENE
GUESSP
END
GEOM
CRYSTAL
0 0 0
229
LLLL
1
11 0. 0. 0.
END
```

`inputatom.d12`:

```
sodium bcc
CRYSTAL
0 0 0
229
4.0
1
11 0. 0. 0.
CLUSTER
0. 0. 0. AAAA 10
0 0
0
END
[BASIS SET]
END
DFT
FFFF
XXLGRID
#END
UHF
SPINLOCK
1 6
ATOMSPIN
1
1 1
TOLDEE
CCCC
EXCHGENE
GUESSP
FIXINDEX
END
GEOM
CRYSTAL
0 0 0
229
LLLL
1
11 0. 0. 0.
ATOMBSSE
1
AAAA 10
END
```

In the code above, the elements highlighted in red are modified by the *cryslatt* script. The dummy variable `FFFF` is replaced with the name of the DFT functional; if DFT is not used, the whole DFT block is deleted. The dummy variable `CCCC` is replaced with the tolerance on the total energy, `LLLL` is substituted by the lattice constant, `AAAA` by the number of ghost atoms shells. The keyword `GUESSP` is deleted if no guess density matrix is available.

The `reference` file contains the experimental data for the system, in the order shown by the following example file and using the units of measurement in parentheses:

`reference`:

```
4.214  ! lattice constant (Angstroem)
7.7    ! bulk modulus (Gigapascal)
1.119  ! cohesive energy (electronvolt)
A2     ! lattice type (strukturbericht type)
```

Only the first element of each row of the `reference` file is read by the *cryslatt* script.

3 Details

3.1 Functions

The following functions are used in the script:

- `make_scaling_factors_nomin`: prepare values to be added to the starting lattice constant, if the initial minimization procedure is not active
- `make_scaling_factors`: prepare values to be added to the starting lattice constant, if the initial minimization procedure is active
- `prepare_crystal_input`: prepare the CRYSTAL input files for both bulk and atom calculations
- `run_guessp`: run CRYSTAL and `properties` using the CRYSTAL scripts
- `run_program`: run CRYSTAL calculations for bulk and atom
- `get_ene_cyc_dee`: read values of SCF energy, number of cycles and tolerance of energy from CRYSTAL output files
- `extract_results`: read values from ACMxc output files
- `make_fit`: call the fit.py script for fitting the energy-volume curve with the equation of state
- `run_at_lat`: run calculation at a specific lattice constant
- `run_lat_range`: run calculation on selected range of lattice constants
- `find_parabolic_minimum`: use a parabolic fit to estimate the starting lattice constant, if the initial minimization procedure is active
- `check_parabolic_convergence`: check if another parabolic fit is needed
- `vol2lat`: obtain volume from lattice constant
- `lat2vol`: obtain lattice constant from volume
- `make_latrange`: obtain the final range of lattice constants to perform calculations on
- `shrink_latrange`: reduce the number of lattice constant of the range if previous calculations are already present

3.2 Options

The following options can be used:

- `-f THEORY`: use the THEORY level of theory. Possible values: pbe, HF (default: HF)
- `-readonly`: read results of existing calculations only
- `-rerun`: run again all calculations
- `-r SYST`: perform calculations on system SYST. SYST must coincide with the name of a directory contained in `REFDIR`, not including the `.SAVE` extension
- `-n NUM`: use `NUM` processors (default: 10)
- `-conv NUM`: convergence on total energy ($10^{-\texttt{NUM}}$) (default: 9)
- `-copyprev`: use the density matrix of previous calculations
- `-nocopyprev`: do not use the density matrix of previous calculations

- `-forcedmetal`: assume the system is metallic (it does not compute the MP2 correlation energy)
- `-do_min`: use the initial minimization procedure (active by default)
- `-nodo_min`: do not use the initial minimization procedure
- `-center LAT`: use `LAT` as the starting lattice constant when no initial minimization procedure is used. It must be used along with `-nodo_min` (default: the reference lattice constant is used)
- `-npnt NUM`: compute `NUM` points of the energy-volume curve, if the initial minimization procedure is used (default: 12)
- `-npnt_nomin NUM`: compute `NUM` points of the energy-volume curve, if the initial minimization procedure is not used (default: 13)
- `-ashell NUM`: use `NUM` shells of ghost atoms (default: 3)
- `-w METH, -wfunc METH`: use the METH correlation energy approximation. Possible values: pc, hpc, lda (default: hpc)
- `-acm FUNC`: use the `FUNC` ACM functional (default: genisi)
- `-h, -help`: display help menu

References

[1] A. Erba, J. K. Desmarais, S. Casassa, B. Civalleri, L. Donà, I. J. Bush, B. Searle, L. Maschio, L. Edith-Daga, A. Cossard, C. Ribaldone, E. Ascrizzi, N. L. Marana, J.-P. Flament, and B. Kirtman. Crystal23: A program for computational solid state physics and chemistry. *Journal of Chemical Theory and Computation*, 19(20):6891–6932, 2023. PMID: 36502394.