MANUAL TO USING THE QUICCA OPTIMIZER IN MONDO

Default operation

The input line to turn on the default options of the QUICCA optimizer looks like:

`Grad =(Optimize,PrimInt,NoBackTr,BiSect,NoGDIIS)`

The meaning of these options is the following:

`Optimize` : Find a local minimum on the potential energy surface of the actual molecule

`PrimInt` : Use primitive internal coordinates to carry out the optimization

`NoBackTr` : Do NOT do any energy-based backtracking during the optimization. The lack of this input-option automatically turns on the backtracking.

`BiSect` : This option turns on the QUICCA optimizer. An alternative of it is DiagHess, a simpler optimizer that uses a very rough diagonal Hessian.

`NoGDIIS` : Disables Cartesian geometric-DIIS. The lack of this option turns on GDIIS. The use of Cartesian coordinates based GDIIS is not recommended.

Minimization vs Stationary points

`DoGradNorm` : The option `DoGradNorm` when placed in the `Grad` line will result in finding the nearest stationary point close to the input structure, independent from the type of the stationary point (minimum or saddle point). This is due to the fact that `DoGradNorm` forces the optimization of the gradient norm while the default QUICCA optimizes the gradient curve so that the gradient curve will have a positiv derivative at the location of the optimized structure. This requirement on the slope of the gradient curve is omitted when `DoGradNorm` is used.

Constraints

For gas phase molecules, constraints can be applied to Cartesian position, internal coordinates as well as to their combinations.

For crystals, constraints can be applied to fractional coordinates, lattice parameters, internal coordinates and to their combinations.

Cartesian/fractional constraints

The input file contains Cartesian or fractional coordinates of atoms. Putting " C " at the end of the line (that contains the coordinates of a certain atom) freezes the coordinates pf the atom during the optimization.

E.g. the line

`N 3.500 -0.500 0.000 C`

has the meaning of keeping a "N" atom in the Cartesian position of "3.500 -0.500 0.000" during the optimization.

The same line, when being part of a crystal structure definition, means that the fractional coordinates of the same "N" atom will be kept fixed while the absolute Cartesian position is allowed to change as the lattice parameters change. This is independent from whether the input is given in "AtomCoord" or "Frac-Coord".

Input section for other constraints

To define other types of constraints the input section

`<BEGIN_ADD_INTERNALS>` and `<END_ADD_INTERNALS>`

must be defined, similar to `<BeginGeometry>` and `<EndGeometry>`.

Constraining lattice parameters

An example of how to constrain lattice parameters is given below. All these extra input lines must be entered between

`<BEGIN_ADD_INTERNALS>` and `<END_ADD_INTERNALS>`

The meaning of the following lines

`STRE_A 12.6`

`STRE_B 18.9`

`STRE_B 10.3`

`ALPHA 120.0`

`BETA 96.0`

`GAMMA 106.0`

is that the length of the lattice vectors A, B and C is constrained to be 12.6, 18.9 and 10.3 respectively. Also, the lattice angles ALPHA, BETA and GAMMA are constrained to be 120.0, 96.0 and 106.0.

Lattice constraints can be applied to only a few or all lattice parameters, in an arbitrary combination.

Constraining internal coordinates

The constraints on internal coordinates are very similar to those on the lattice parameters. Internal coordinate constraints can be defined for the following types of coordinates: STRE (stretching), BEND (bending), TORS (torsion), OUTP (out-of-plane), LINB (linear bending). Definitions of the constraits must also be placed between the lines of `<BEGIN_ADD_INTERNALS>` and `<END_ADD_INTERNALS>`.

For example

`STRE 15 26 1.3`

means that the streching coordinate between atoms 15 and 26 must take the value of 1.3 angstroems at the end of the optimization. Other constraints like

3

```
BEND 72 89 31 122.4
TORS 72 89 31 21 95.7
OUTP 1 25 65 43 0.15
LINB 1 5 16 8 180.0
```
have similar meaning: the BEND of atoms 72 89 31 (central atom 89) must become 122.4 degrees, the TORS of atoms 72 89 31 21 (central bond between 89 and 31) must become 95.7, the OUTP of 1 25 65 43 (with 25 as the central atom, and 1 as the 'apex' atom) must become 0.15 degrees, the LINB of 1 5 16 (5 is the central atom) must take the value of 180 degrees in the plane defined by atoms 8 16 and 5, after the 1 5 16 angle is projected onto this plane.

Note that if the above definitions of internal coordinates are entered without any constraint value (the last number) then they will be used as a flexible internal coordinate during the optimization.

In case of crystal optimizations internal coordinates bridging different cells can also be defined, similarly to the molecular case, but in addition the cell indices of atoms must be given. For example
```
TORS 72 89 31 21 CELL 0 0 0 1 0 0 1 0 1 1 1 1 95.7
```
defines a TORS coordinate whose 1st atom is in the central cell, the 2nd atom is in the [1 0 0] cell, the 3rd in the [1 0 1] and the 4th in the [1 1 1] cell. And this coordinate is constrained to be 95.7 degrees. Leaving out 95.7 from the end, the coordinate will be flexible during the optimization.

Constraining individual Cartesian components

Individual components of the Cartesian coordinates can be constrained exactly the same way as internal coordinates, by using the labels CARTX, CARTY, CARTZ. Eg.
CARTX 34 1145.98
will constrain the X component of the atom 34 to 1145.98 angstroems. In case of crystal optimizations, the corresponding fractional coordinate will be fixed.

Alternating optimization

For crystal structure optimizations the alternation of atoms-only and lattice-only steps may be helpful.

Alternate : This option of the `Grad` line turns on the alternating optimizer. The default operation of alternate is first to optimize the structure by moving only fractional coordinates of atoms. Once the gradients on the fractional coordinates become smaller than the gradient accuracy threshold, the optimizer freezes the fractionals and releases the optimization of the lattice vectors. After a single step with the lattice vectors, the lattice becomes frozen again and the fractional coordinates are relaxed. These procedure is repeated until both lattice and fractional coordinates are relaxed.

LatticeStart : This option, when added to `Alternate` in the `Grad` line, forces the alternation to start with fixed fractionals and moving lattice vectors, otherwise "Alternate" works the same way as in the default scheme.

MaxAtomSteps : This option must be put into a separate line, e.g. `MaxAtomSteps=3` forces the alternating optimizer to do a maximum of 3 steps when in the fractionals-only phase.

MaxLatticeSteps : Similar to `MaxAtomSteps`. E.g. `MaxLatticeSteps=5` forces the optimizer to make no more than 5 steps when doing a lattice-only optimization. Any combination of `MaxAtomSteps` and `MaxLatticeSteps` is allowed. In the absence of these commands, the deafult operation works, i.e. `MaxAtomSteps=10000` and `MaxLatticeSteps=1`.

Symmetrization of lattice parameters

It usually has a convergence accelerating effect if the symmetry of the lattice parameters is preserved during the optimization. This can be done by constraining the ratio of lattice parameters by the following options.

`RatioABC` : ratios of lengths values of A, B and C.

`RatioAlpBetGam` : ratios of angle values of ALPHA, BETA and GAMMA.

Usage: E.g. `RatioABC 1.0 1.1 -1.0` in a separate input line will fix the ratio A:B=1:1.1 while C remains fully flexible. Fully flexible parameters should be marked with a negative number. `RatioAlpBetGam` is used similarly. These options can arbitrarily be combined with all other options available for geometry optimization.

Explicit lattice parameters

Crystal-lattice optimizations are carried out in the default procedure without any explicite internal coordinates for lattice parameters. It is however possible to get the lattice parameters explicitely involved into the crystal optimization by adding the option

`ExplLatt`

into the `Grad` line.

Recognition of weak bonds

Weak bonds, such as the Van der Waals bonds can be recognized difficultly, because it is not clear in what situation they should be used and in what not. The Van der Waals radii of atoms are used in a careful way in the default recognition algorithm, meaning that they are scaled dow to reduce the occurance of overly large number of internal coordinates. However, in cases when the molecule or crystal has a very large structural contribution from Van der Waals interaction (eg. sulphure crystal) it is recommended to increase the Van der Waals radii of atoms for the internal coordinate recognition. This can be done by using the option `VDWFact`. Eg.
`VDWFact=1.25`

multiplies the values of default VDW radii by 1.25 . The factor 1.25 activates the full length of tabulated atomic Van der Waals radii to be applied. The default VDW radii values are smaller to avoid the formation of an unnecessarily dense connectivity network.

Coordinates associated to weak bonds

Each weak bond can in principle form an edge of a BEND, TORS or OUTP. However, adding these extra coordinates would hugely increase the redundancy of the internal coordinate system and may even avoid convergence. Thus, in default, no BEND, TORS or OUTP is added along non-covalent bonds. This is usually correct for large proteins. In some cases, e.g. loose water clusters, the extra BENDs, etc. may be necessary. They can be added by the `Grad`-line options

`NonCovBend` (adds BEND and OUTP) and

`NonCovTors` (adds TORS).

If the

`HBondOnly`

option is added into the `Grad`-line, only the hydrogen-bonds of the non-covalent bonding system are recognized and other weak bonds are not.

In case of a cluster, isolated fragments may turn up. Isolated fragments are automatically recognized and and conncted via their nearest points. In some cases the user wants to define these connections by hand via the `<BEGIN_ADD_INTERNALS>` and `<END_ADD_INTERNALS>` options and the addition of extra internal coordinates. In this case the automatic fragment-connection is recommended to be turned off by the `Grad` line option

`NoFragmConnect` .

Stepsize control

The options "MaxStre" and "MaxAngle" allow external control over the maximum stepsize during an internal coordinate optimization. Eg.

```
MaxStre=0.1
```

sets the maximum allowed stepsize to 0.1 angstroems on stretches, while

```
MaxAngle=5.0
```

sets the maximum allowed stepsize on BEND, TORS, OUTP and LINB-s of the molecule to 5.0 degrees.