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.

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. If putting " C " at the end of the line that contains the coordinates of a certain atom the coordinate will be frozen 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 "FracCoord".

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

```
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.

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.

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.

Stepsize control

The options "MaxStre" and "MaxBend" 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

```
MaxBend=5.0
```

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