Optimizations

Useful to consider Taylor series of PES

$$E(x) = E(x_0) + E'(x_0)(x-x_0) + 1/2E''(x_0)(x-x_0)^2$$

Gradient (g) Hessian (H)

x, and g are vectors, H a matrix

- Steepest descents – step downhill in direction given by g

  Very inefficient

- Newton Raphson –

  $\Delta x = -H^{-1}g$

  Trouble if there is a zero eigenvalue of H (need to remove transl. and rot.)

  Wrong direction, if neg. eigenvalue

  If H is approximated - quasiNewton

Eigenmode following

- diagonalize H
- $\Delta x = - \Sigma F_i V_i / b_i$
- $\Delta E = - \Sigma F_i^2 / 2 b_i$
  - b_i = eigenvalue
  - V_i = eigenvector
  - F_i = comp. of g along V_i
  - Can be used to find TS's!
- $\Delta x = - \Sigma F_i V_i / (b_i - \lambda_i)$ <<shifting>>

The "berny" algorithm in G03 is similar to EF

- Default – simple guess for H
- Updates H as calculation proceeds
- Usually OK for locating minima
- If problems: opt=calcfc, opt=calchffc

  Can also partially evaluate numerically

Berny checks # neg. eigenvalues of H

Will stop if incorrect (can override)

Convergence

- Max force
- Rms force
- Max. step
- Rms step

To use with z-matrix: opt=z-matrix

```
# hf/3-21G opt=z-matrix test


Relaxed scan – will do 18 optimizations
0 1
O1
H 1 r1
C 1 r2 2 a2


R1 0.9 S 5 0.5
R2 1.1
A2 115.4 S 2 1.0
```

Transition states

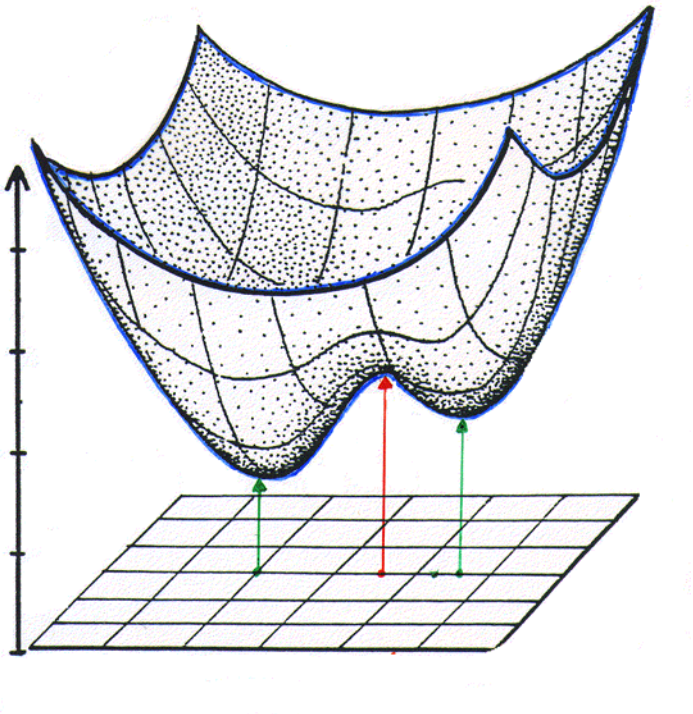
• Easy when determined by symmetry (e.g., OH rotation in phenol)

Can just use constrained minimization

• When not symmetry constrained – tougher than minimization

Need to have a good initial guess structure, and usually curvature info.

•Even when TS is found, non-trivial to find the associated minima



2-dim. PES with two minima and one TS

See: www.tau.ac.il/~becker/course/mini.html

Opt=

- TS (based on berny)

  Actually need curvature, e.g., opt=(ts, calcfc)

- (TS,EF)

  Useful if gradients are lacking

  Otherwise, no advantage over berny

- QST2 (uses reactant + product structures)

  Order of atoms must be same in R and P

  Linear interpol. in redundant internal coords.

  Will not work for HCN -> HNC

  See: http://www.chemie.uni-muenchen.de/oc/zipse/lv18099/stqn.html

- QST3 (uses reactant, product, and guess for TS)

- Path = M (optimizes discretized path)

  Should specify also qst2 or qst3

  Uses linear interpolation to get starting points

  Might need to use guess=always

  Might need to specify “BimolecularReactant” or “BimolecularProduct”

- NEB (coded up in Jordan group)

  Similar to "path"

  First derivatives only

Some general comments about TS opt. and G03

QST2 - Need to merge reactant and product files, the latter starting with title, and separated by blank line

Can run G03W directly

If you are on a computer with a full install, there are examples of inputs for about 350 different types of calculations.

Find the G03w directory
Look for the “examples” and “tests” subdirectories.
tests.idx gives a short description of the various tests.