

Definitions

Minimisation algorithm	Identifies geometries corresponding to minimum points on the energy surface
Saddle point	Highest points on the path between two minima/maxima i.e. a transition structure

At a minimum point, first derivatives are zero, and second derivatives are positive

Parameter	Molecular mechanics –
coordi-	Cartesian (3N)
nates	Quantum mechanics –
	Internal (3N-6)

Categories of min algo	1. Derivative
	2. Non-derivative

Derivative methods	- Obtained analytically or numerically
	- Analytical preferred
	- If only numerical, non-derivative may be more effective

Numerical derivative	Change in energy divided by change in coordinates
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Non-derivative methods

Simplex method	- Non derivative (zeroth order)
	- Locates minimum on energy surface by moving around like an amoeba

Simplex	M cartesian coord => M+1 vertices
	M internal coord => M-5 vertices

- Direction of first derivative => Minima location

- Magnitude of deriv. => Steepness of local slope

Movements	Reflection -
	Reflection and Expansion -
	Contraction -

Derivative methods

- Direction of first derivative => Minima location
- Magnitude of deriv. => Steepness of local slope
- Second derivative => curvature of function

$$\text{Force} = -dV(r)/dr$$

First order algos	- steepest descent
	- conjugate gradient

STEEPEST DESCENT

- moves in dir. || net force (walking straight downhill)
- both gradient and direction orthogonal
- 1) line search (2) arbitrary step (3) lanrange multipliers
- robust when starting point is far from minimum
- relieves highest energy features

1D Line search	- bracket search
	- computationally expensive

Arbitrary step	- random step size
	- if lower energy, step size increased by multiplication factor
	- higher energy, step size reduced
	- more steps but less function evaluations

Cons	- forced to make right angles
	- path oscillates, overcorrects, and reintroduces errors

CONJUGATE GRADIENT

- no oscillation
- gradient orthogonal but direction **conjugate**
- for quadratic function of M variables, min reached in M steps
- can be used from 2nd step (1st step SD)



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