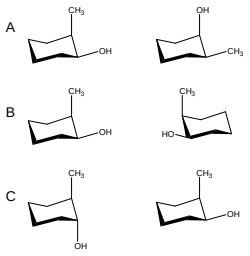
QUIZ

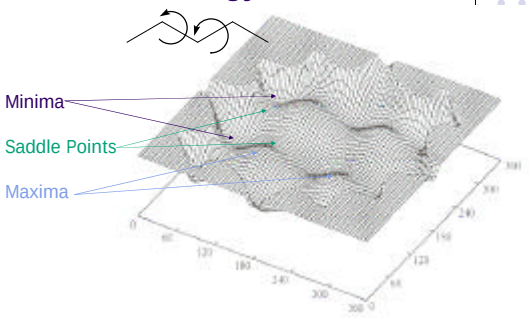
- Should MM energies be the same or different for the structure pairs shown?



Energy Minimization

CHEM 8711/7711

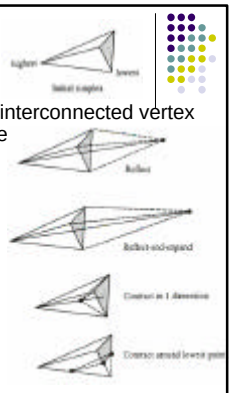
Potential Energy Surfaces



Energy Minimization Methods

- Energy Minimization is used synonymously with geometry optimization
- Derivative-based
  - Optimization algorithms that use derivatives of the energy function
- Non derivative-based
  - Optimization algorithms that do not use derivatives of the energy function

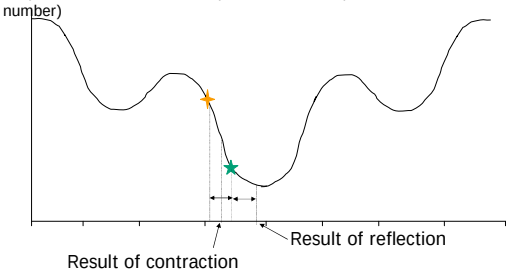
Simplex Algorithm



- Simplex: A figure with one more interconnected vertex than the energy function has dime
- A non-derivative method
- Requires 4 vertices for Cartesian optimization
- Three basic strategies
  - Reflection
  - Expansion
  - Contraction
- Effective for bad geometries, very slow near minima

Simplex Example

1D energy function = central torsion angle in butane
Starting position = 135°
Simplex needs 2 vertices, next point is 135 ± x° (x is a small, often random number)

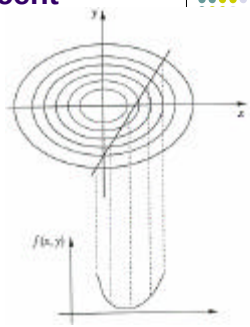


Derivative Minimization Methods

- First derivative
  - Indicates slope of energy surface = gradient
  - Gradient = 0 indicates maxima and saddle points as well as the minima we usually want
- Second derivative
  - Differentiates between types of points with gradient = 0, indicates curvature
  - Positive curvature = minima
  - Negative curvature = maxima
  - Zero curvature = saddle points
- Methods are assigned an order based on the highest derivative that they use

Steepest Descent

- A first-order method
- Direction of net force is followed with:
  - An arbitrary step size
  - Line search



Line Search

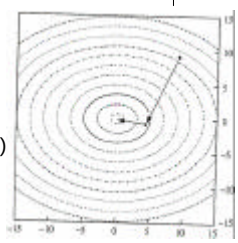
- Requires three points that bracket the minima (second point must have lowest energy)
- Two strategies
  - Iteratively select points between two lower-energy points (lots of function evaluations necessary
  - Fit a curve to the three points and use its minima as the next point selected

Limitations of Steepest Descent

- Can't differentiate between maxima, minima and saddle points
- Very slow at low gradient values (near minima)
- Very inefficient for long, narrow energy wells

Other Minimization Algorithms

- Conjugate Gradient
  - Also a first-order method (will have same problem as steepest descent with maxima/minima/saddle points)
  - Uses gradients from two successive points to determine direction after first step – behaves in a less oscillatory fashion



Other Minimization Algorithms II

- Newton-Raphson, a second order method
  - Suitable for relatively small systems (~100 atoms) due the the way the derivatives are handled
- Truncated Newton
  - Solves for the second derivative iteratively (truncated after some number of iterations)
  - Method of choice except for highly strained systems

Reading

- Chapter 5 through the end of 5.8 in Leach
- (from last week – Chapter 4 in Leach)

Class Exercise

- Build a flat cyclohexane (important that it be perfectly symmetrical)
  - Launch MOE
  - Click the Builder button on the left
  - Click '6' under the heading 'Carbon Ring' (leave sp^2 selected)
  - Delete the hydrogen atoms (select multiple atoms by holding down shift as you click on them)
  - Select the carbon atoms, and select sp^3 in the builder window
  - Save the structure (File -> Save, select name)

Class Exercise (cont'd)

- Use the Steepest Descent method to minimize the structure
  - Compute->Energy Minimize
  - Set the iteration limit for all algorithms other than steepest descent to 0
  - Set the gradient test for steepest descent to .01 or less
  - Take note of the molecule's shape, energy and number of steps required for minimization (record of minimization available in the command window)

Class Exercise (cont'd)

- Manually distort the structure and minimize again (with steepest descent alone)
  - Select a few atoms
  - Hold down shift, alt, and the right mouse button to translate only the selected atoms
  - Take note of the molecular geometry and final energy

Class Exercise 2

- Open your original flat benzene structure (File -> Open, pick from the file list on the left)
- Minimize it using the conjugate gradient method (set iteration limit for all others to zero, set the gradient test for conjugate gradient to the value you previously used for steepest descent minimization)
- Take note of the final geometry, energy, and number of iterations required for minimization

Class Exercise 3

- Open your original flat benzene structure
- Minimize it using the truncated Newton method (set iteration limit for all others to zero, set the gradient test for truncated Newton to the value you previously used for other minimizations)
- Take note of the final geometry, energy, and number of iterations required for minimization