Single Point Energies And Geometry Optimizations

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Single Point Energy Calculations

- Solution of Schrödinger Equation for Molecule with Specified Geometric Structure
  - *E* and geometry
  - *v* and thermodynamic properties
  - NMR
  - Electronic distributions
  - Other static properties
- Validity
  - Reasonable structure
  - Choice of level
  - Choice of basis set

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- Purpose
  - Only “affordable” calculation
  - Starting point for optimization
  - Estimate time of optimization
  - Calculate specific molecular properties after optimization
  - Calculate accurate values of *E* and related properties at a higher level of theory following lower level optimization

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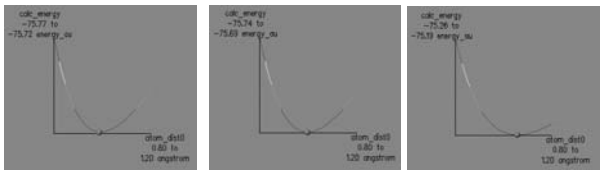
Potential Energy Surfaces (PES)

E and other properties are function of geometry

- Mathematical relationship of *E* as a function of structure
- Surface has as many dimensions as number of internal degrees of freedom in molecule
  - Diatomic molecule AB
    - r_{AB}
  - Nonlinear triatomic molecule ABC
    - r_{AB} and r_{BC} (unless identical)
    - A-B-C bond angle

Diatomic Molecule PES

Two-dimensional Potential Energy Well with Bond Length as Variable



$r(OH^-)$ = 0.99 Å (0.9628)

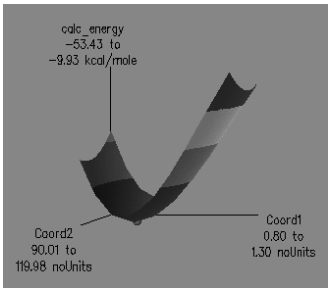
$r(OH)$ = 1.00 Å (0.9706)

$r(OH^+)$ = 1.06 Å (1.0289)

B88-LYP/DZVP

Triatomic Molecule PES

Surface with Bond Length and Bond Angle as Variables



$r(OH)$ = 0.950 Å (0.958)

H-O-H = 107.7° (104.5°)

PM3

PES Features

- Minima
  - Bottom of "Valley" on PES
    - Changing any geometric parameter increases *E*
  - Equilibrium structures of molecule
    - Different conformers
    - Structural isomers
    - Reactant and product

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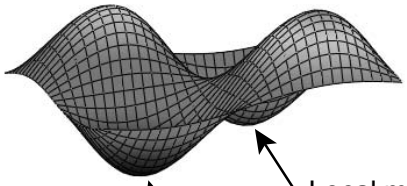

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- Maxima
  - Top of "mountain" on PES
    - Changing any geometric parameter decreases *E*
- Saddle Point
  - Maximum for one molecular parameter and minimum for another
    - Transition structure between two equilibrium structures

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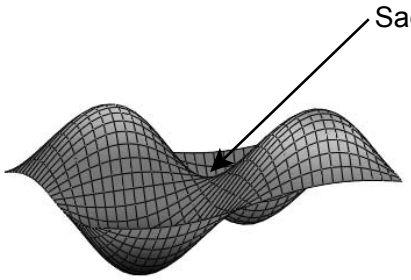

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Geometry Optimization

- Locating Extremum of PES
  - Minimization gives equilibrium structure(s)
  - Saddle point corresponds to transition structure
- Calculus at Extremum for Multidimensional Function
  - Gradient = $\mathbf{g}_i = \partial E/\partial \mathbf{v}_i = 0$
    - Force = -(gradient) = 0
    - "stationary point" is location on PES where forces = 0
  - Force constant = $\partial^2 E/\partial \mathbf{v}_i^2$
    - Specifies "curvature" of surface at point
    - All > 0 at stationary point
    - All > 0 except one < 0 at (1st order) saddle point
    - "Hessian" is matrix of second derivatives

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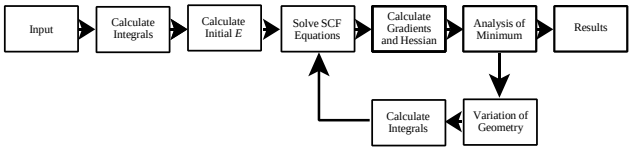

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- Analysis
  - Convergence criteria
    - Forces = 0 or less than chosen cut-off value
    - Next structure change is very small or below chosen cut-off value
    - Often additional criteria are used
  - Optimization methods for structure change based on decrease in *E*
    - Use gradient and force constant values
    - More later...

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- Optimization Results
  - Was a minimum determined?
    - Check by doing a single point calculation of vibrational frequencies (all positive)
  - Was a global minimum determined?
    - Check PES map
    - More later...
  - Was a saddle point determined?
    - Check by doing a single point calculation of vibrational frequencies (all positive except one is negative/imaginary)

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Optimization Methods

"Simple" Method

- Procedure
  - Minimize *E* with respect to only one variable holding all others constant
  - Change variable to optimum value
  - Repeat minimization with respect to a second variable holding all others constant
  - Change second variable to optimum value
  - Continue for each variable

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- Problems
  - Variables are not independent
    - Linear molecules like acetylene are often problems
  - Several cycles are needed
  - "Expensive" for large molecules
- "Real" methods
  - Use all variables
  - Three general approaches: SD, CG, NR

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Optimization Methods

Steepest Descent (SD)

- Change coordinates in direction opposite the maximum of gradient using a unit vector $\mathbf{s}_i = -\mathbf{g}_i / |\mathbf{g}_i|$
- Line search method for distance
  - Find 3 points such that inner point is lower in *E* than outer points
  - Thus at least one minimum lies between outer points
  - Iterate decreasing distance
  - Recalculate $\mathbf{g}_{i+1}$ and repeat

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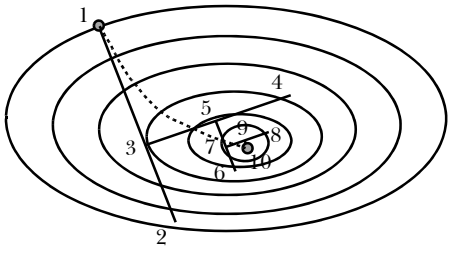

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- Advantages of SD
  - Always locate (local) minimum
- Problems of SD
  - $\mathbf{g}_{i+1}$ is perpendicular to $\mathbf{g}_i$
    - Lose any further *E* lowering possible by $\mathbf{g}_i$
    - Path oscillates around minimum path
  - Rate of convergence decreases near minimum
  - Undesireable behavior in long, narrow valley

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- Modifications of SD
  - Fit 3 points to function
    - Differentiate to find minimum
  - Arbitrary step size
    - Start with predetermined value or value proportional to $\mathbf{g}_i$
    - Calculate *E* at new position
    - If *E* is less
      - Increase step size
      - Calculate *E* at new position
      - Repeat until *E* increases
    - If *E* is greater or increases
      - Decrease step size
      - Calculate *E* at new position
      - Iterate

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Optimization Methods

Conjugate Gradient Method (CG)

- Mixture of current gradient and previous search direction
- Procedure
  - First step: SD
  - Subsequent steps: $\mathbf{v}_{i+1} = -\mathbf{g}_{i+1} + \gamma_{i+1}\,\mathbf{v}_i$
    - Fletcher-Reeves: $\gamma_{i+1} = (\mathbf{g}_{i+1} \bullet \mathbf{g}_{i+1})/(\mathbf{g}_i \bullet \mathbf{g}_i)$
    - Polak-Ribiere (common): $\gamma_{i+1} = [(\mathbf{g}_{i+1} - \mathbf{g}_i) \bullet \mathbf{g}_{i+1}]/(\mathbf{g}_i \bullet \mathbf{g}_i)$
    - Hestenes-Stifel: $\gamma_{i+1} = [(\mathbf{g}_{i+1} - \mathbf{g}_i) \bullet \mathbf{g}_{i+1}]/[\mathbf{v}_i \bullet (\mathbf{g}_{i+1} - \mathbf{g}_i)]$

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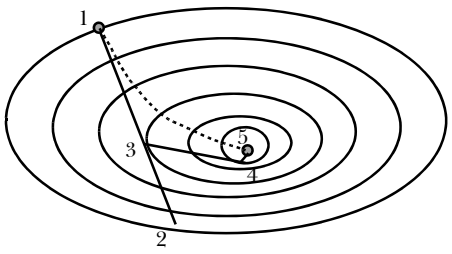

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- Advantages of CG
  - Better convergence
  - Always locate (local) minimum
- Problems of CG
  - Require additional computer resources to store $\mathbf{g}_i$ and $\mathbf{g}_{i+1}$
  - Expense scales as N^2

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Optimization Methods

Newton-Raphson (NR)

- Includes Hessian
- Advantages
  - Locates minima and saddle points
  - Convergence is second order near stationary point
- Problems
  - Control of step size
  - Calculation of Hessian required
- Several variations of NR

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Global Minimum

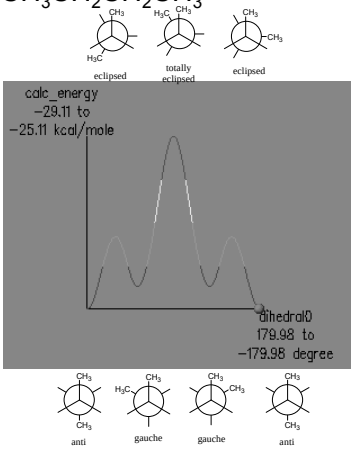
- Optimization Results
  - Above methods locate the “nearest” minimum (local?)
  - Conformers and transition structures are related to local minima and saddle points
  - Molecular properties are related to global minimum--the most stable structure
  - Several approaches to finding the global minimum
    - NO Guarantees!!!

Global Minimum Methods

Grid Search

- Simple
  - Calculate all possible energies
  - Prepare energy map or table
  - Choose best structure
- Problems
  - Number of minima increases exponentially with the number of variables
  - Not practical for large or biomolecules
    - Build structures from optimized fragments
    - Optimize portions of molecule

Example: $CH_3CH_2CH_2CH_3$



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Example: $CH_3(CH_2)_{n+1}CH_3$

$n = 1$	$N = 3^1 = 3$	t = 3 s
$n = 2$	$N = 3^2 = 9$	t = 9 s
$n = 5$	$N = 3^5 = 243$	t = ~4 min
$n = 10$	$N = 3^{10} = 59$ k	t = ~16 h
$n = 15$	$N = 3^{15} = 14$ M	t = ~160 d

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Global Minimum Methods

Other

- Monte Carlo
  - Usually start at a minimum
  - Randomly change one or several angles or bond lengths to generate new geometry
  - Calculate *E*
    - If *E* is lower, accept new geometry
    - If *E* is greater, retain or reject based on a Boltzmann distribution related to the energy change and *T*
  - Many variations

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- Molecular Dynamics
  - Based on Newton's equations of motion for atoms
  - Molecule overcomes barrier between minima if kinetic energy is great enough
    - Similar to climbing out a valley over a mountain
  - Kinetic energy is proportional to *T*
    - Use elevated temperatures (600 - 1200 K)
    - High temperatures reduce chance of trapping molecule in a local minimum
  - Essentially searches PES in the region of the starting minimum

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- Simulated Annealing
  - Molecular dynamics variation
  - Start with high *T* (2000 - 3000 K)
  - Reduce *T*
    - Molecule trapped in a minimum
      - Similar to playing roulette
      - Very slow cooling might give global minimum
    - Repeat to get many results
    - Choose best
- Genetic Algorithm
  - Use several low energy structures as “parents” to generate “off spring” that might be better
- Distance Geometry
  - Based on establishing minimum and maximum distances between all pairs of atoms