Computational Material Science
Part I

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Aim of Part I

- Get familiar with the computational methodologies often used and properties often predicted in molecular- or cluster-based research.
- With the basic understanding acquired, hopefully, you will have the ability to read literature and conduct your own calculations when needed in research.

Outline

- Potential energy surface: energy minimization and stationary point characterization
- Overview and comparison of methods
- Classical modeling: force field calculations (molecular mechanics; MM); solvation
- Quantum mechanical modeling (QM); qualitative molecular orbital analysis, various molecular orbital-based methods, calculation of chemical and physical properties
- Molecular dynamic (MD) and Monte Carlo (MC) calculations
- QM/MM

Grading

- 15% -- take home assignments
- 15% -- oral presentation
- 20% -- final examination

Useful Structure Database

CSD -- organic and metal-organic crystal structure database (350,000 compounds)

ICSD -- inorganic crystal structure database

CRYSTMET -- metals (alloys, intermetallics and minerals) structure database

--available at NCHC (NCHC: National Center for High-Performance Computing)

Useful Books

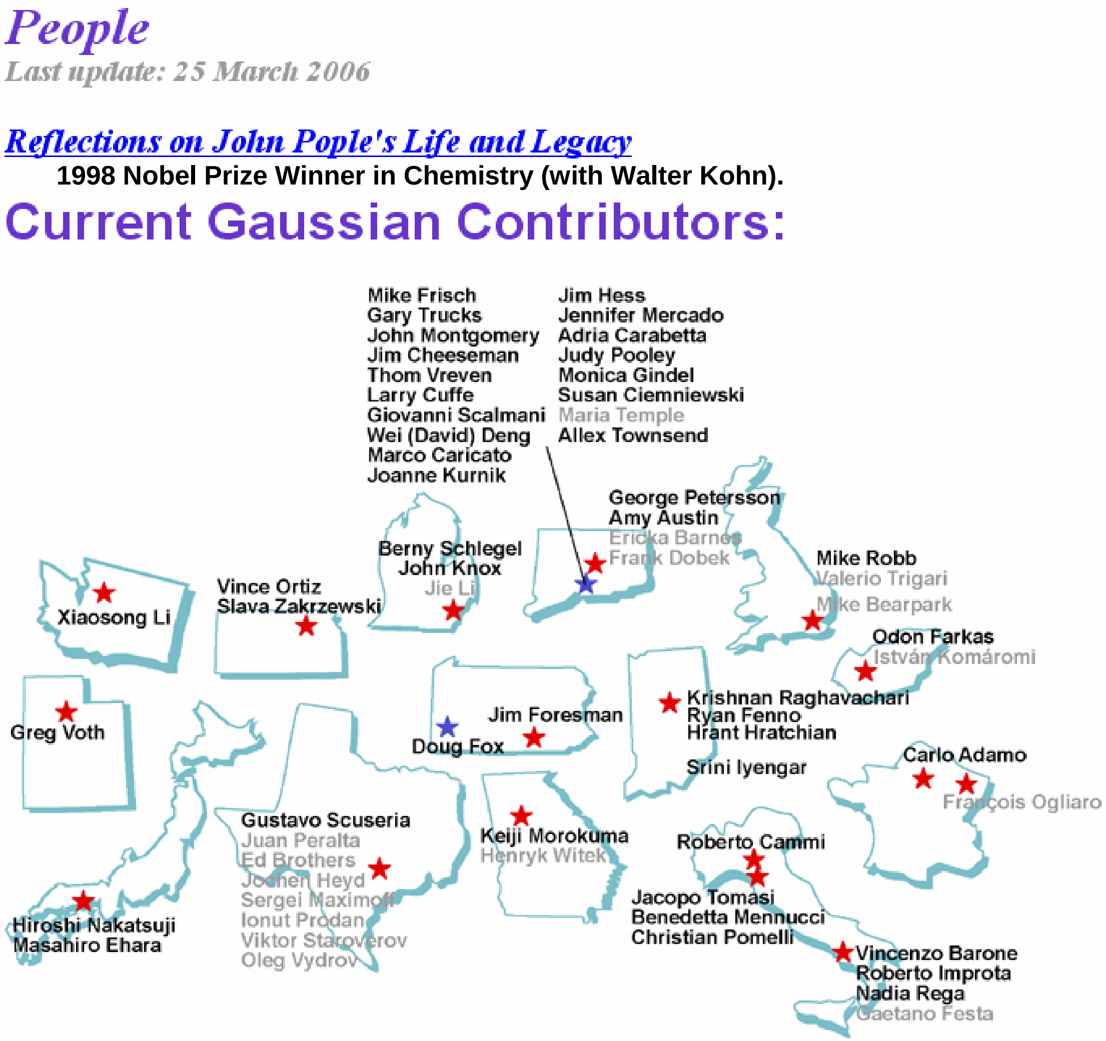
- “Molecular Modelling: Principles and Applications”, 2nd Ed., A. R. Leach / Prentice Hall (2001)
- “Essentials of Computational Chemistry: Theory and Models”, C. J. Cramer / Wiley (2004)
- “Molecular Modeling Techniques in Material Sciences”, J.-R. Hill, L. Subramanian, and A. Maiti / Taylor & Francis (2005)
- “Molecular Modelling for Beginners”, A. Hinchliffe/Wiley (2003)
- “Encyclopedia of Computational Chemistry”, P. v. R. Schleyer, Ed. / Wiley (1998)

Program Used

Gaussian 03
GaussView

Home:
http://www.gaussian.com

Capability
http://www.gaussian.com.g_brochures/g03_intro.htm



People
Last update: 25 March 2006

Reflections on John Pople's Life and Legacy
1998 Nobel Prize Winner in Chemistry (with Walter Kohn).

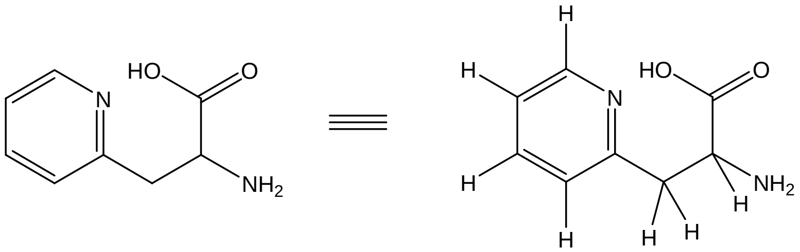
Current Gaussian Contributors:

Gaussian Citation

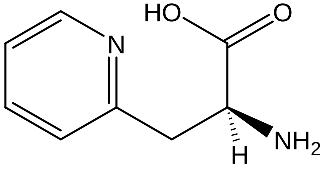
- Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

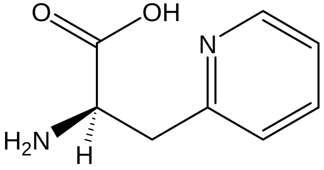
Chemical drawing

- H atoms next to C atoms are often omitted



- Three-dimensional effects





S-form **R-form**

Same molecular formula, different optical activity

Coordinate Systems

➢ Cartesian coordinates

C	0.0	0.0	0.0
O	0.0	1.22	0.0
H	0.94	-0.54	0.0
H	-0.94	-0.54	0.0

➢ Z-matrix coordinates

1	C						
2	C	1	1.54				
3	H	1	1.0	2	109.5		
4	H	2	1.0	1	109.5	3	180.0
5	H	1	1.0	2	109.5	4	60.0
6	H	2	1.0	1	109.5	5	-60.0
7	H	1	1.0	2	109.5	6	180.0
8	H	2	1.0	1	109.5	7	60.0

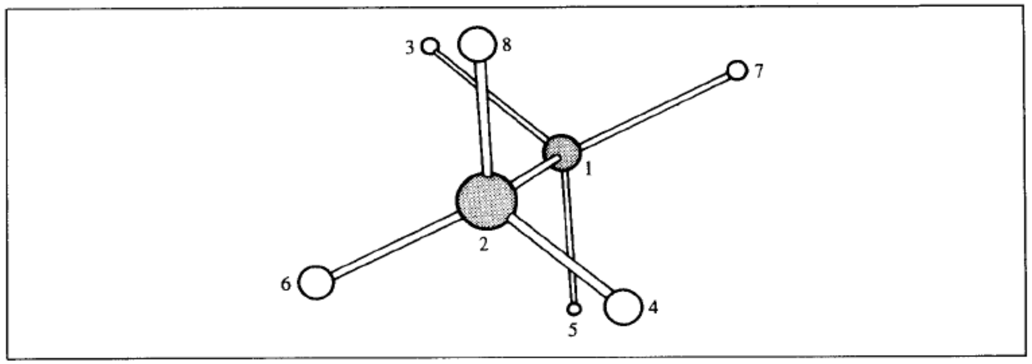


Fig. 1.1: The staggered conformation of ethane.

as follows:

Goal of Modelling

- Develop an understanding of the relation between a material’s properties and the underlying atomic structure
- A basic property: Energy!

Potential Energy Surfaces

- Born-Oppenheimer approximation
  - The much smaller mass of the electrons make them adjust rapidly to any change in the nuclear positions: Enables the electronic and nuclear motions to be separated.
  - Consequently, the energy of a molecule in its ground electronic state can be considered a function of the nuclear coordinates only.

Potential Energy Dependence on Nuclear Coordinates

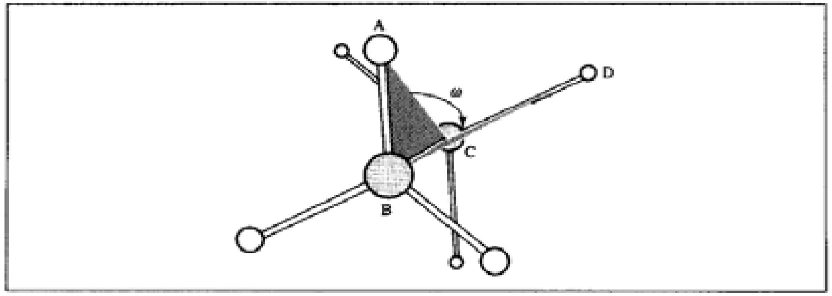


Fig. 1.2: A torsion angle A–B–C–D is defined as the angle between the planes A, B, C and B, C, D. A torsion angle can vary through 360° although the range −180° to +180° is most commonly used. We shall adopt the IUPAC definition of a torsion angle in which an eclipsed conformation corresponds to a torsion angle of 0° and a trans or anti conformation to a torsion angle of 180°. The reader should note that this may not correspond to some of the definitions used in the literature, where the trans arrangement is defined as a torsion angle of 0°. If one looks along the bond B–C, then the torsion angle is the angle through which it is necessary to rotate the bond AB in a clockwise sense in order to superimpose the two planes, as shown.

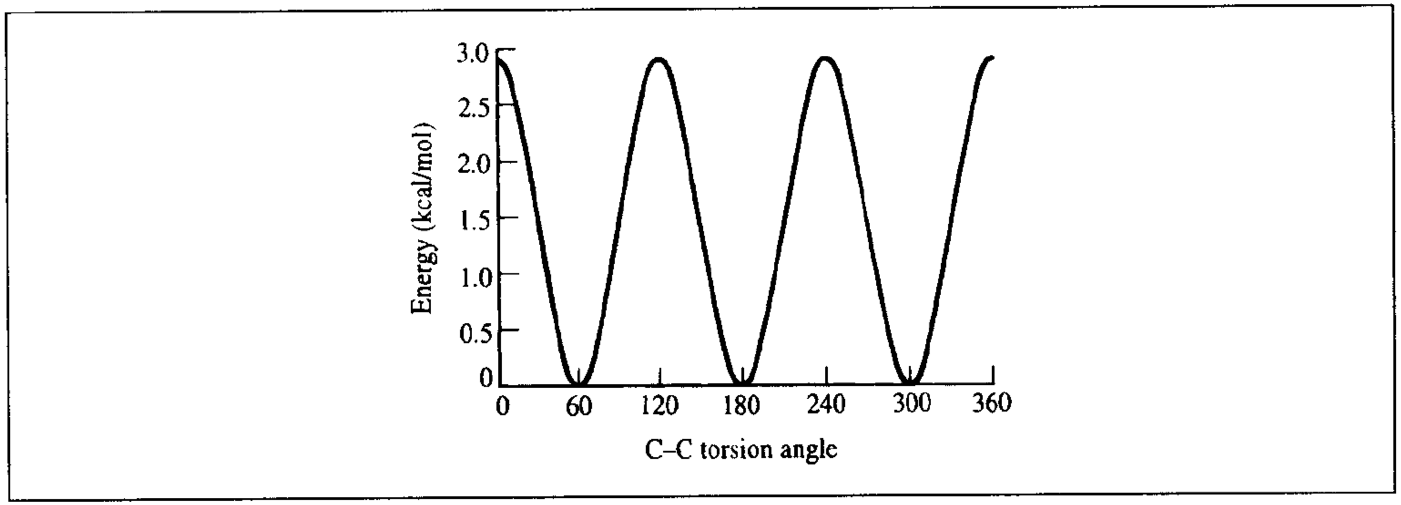
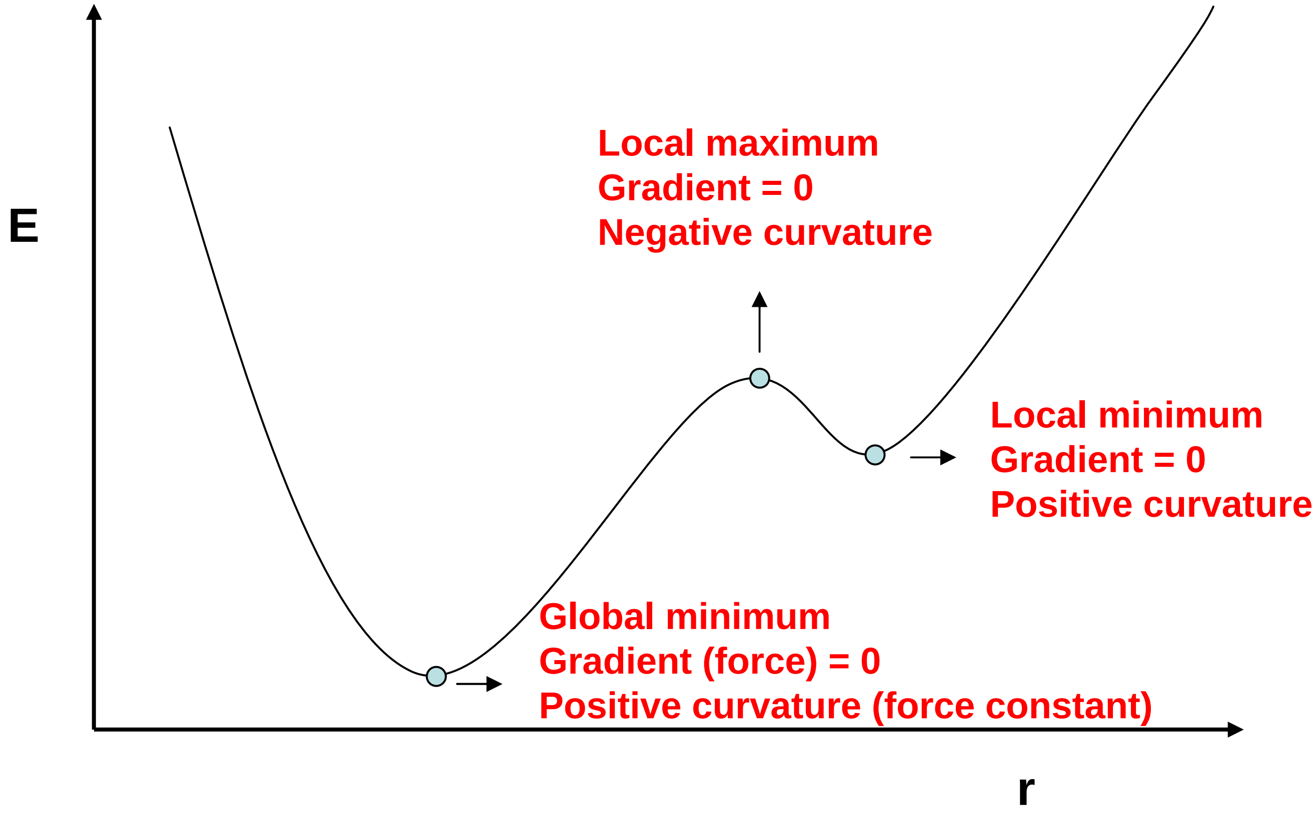


Fig. 1.3: Variation in energy with rotation of the carbon–carbon bond in ethane.

Stationary Points (○) on Potential Energy Surface



Local maximum
Gradient = 0
Negative curvature

Local minimum
Gradient = 0
Positive curvature

Global minimum
Gradient (force) = 0
Positive curvature (force constant)

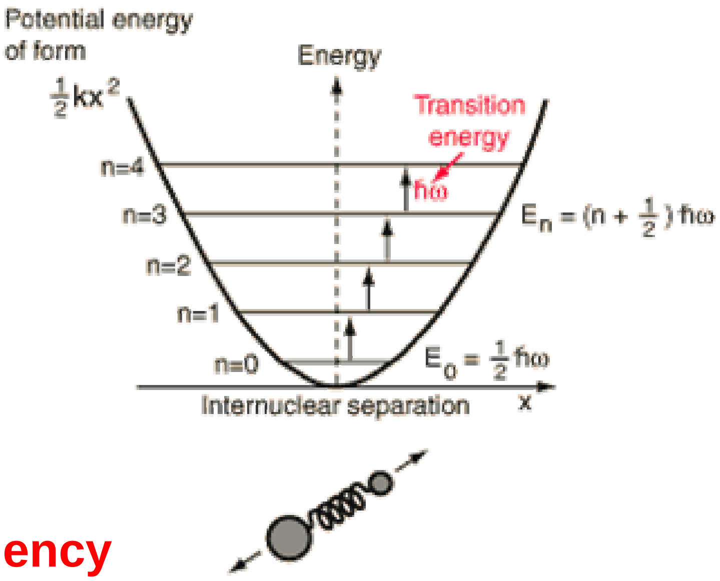
Characterization of Stationary Points

- An optimization procedure deemed "converged" when $(\frac{\partial E}{\partial r}) \approx 0$
- Stationary points are further characterized by $\frac{\partial^2 E}{\partial r^2}$.

Harmonic oscillator approximation of a diatomic molecule

$$\frac{\partial^2 E}{\partial r^2} = k$$

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$



x=0 represents the equilibrium separation between the nuclei.

If in a frequency analysis, imaginary frequency obtained $\Rightarrow$ not at a local minimum

Characterization of Stationary Points

2-D case

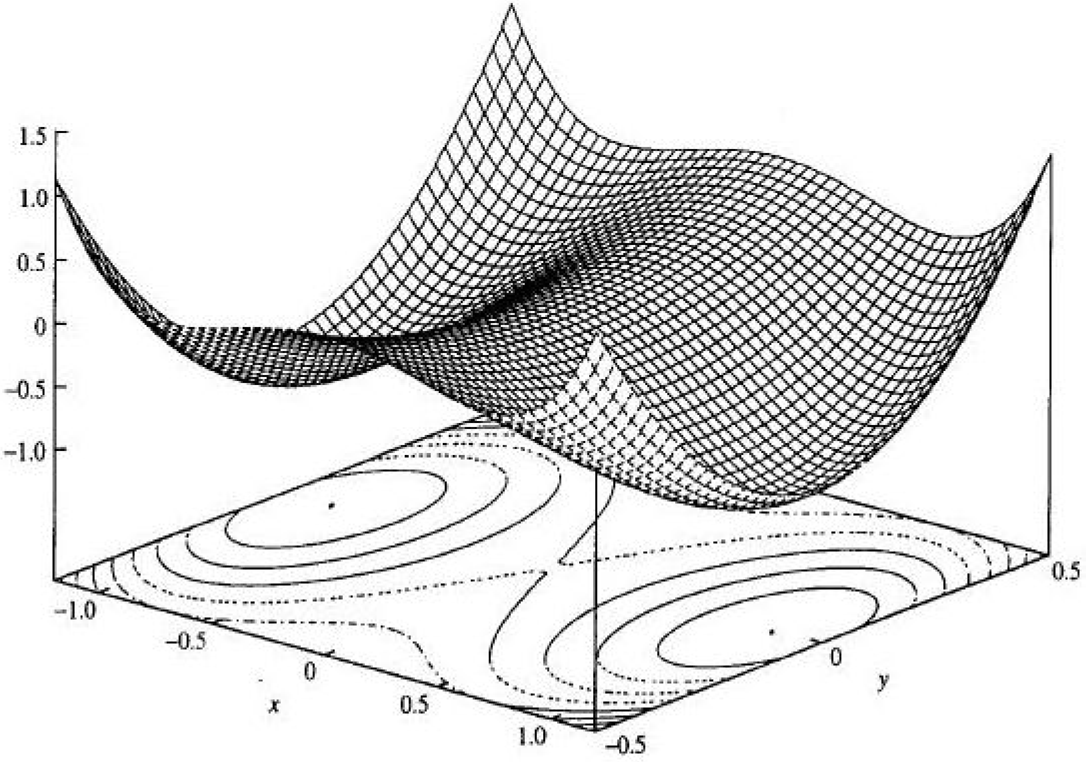


Fig. 4.24 The function $f(x, y) = x^4 + 4x^2y^2 - 2x^2 + 2y^2$ has a saddle point at (0, 0) and minima at (1, 0) and (−1, 0).

At points (1,0) and (-1,0)
eigenvalues of Hessian matrix
(i.e. force constant matrix)
all positive => minimum

At point (0,0)

eigenvalue	eigenvector
-4	(1,0)
+4	(0,1)

=> maximum along x direction
minimum along y direction

One negative eigenvalue:
1st order saddle point
(correspond to the transition state along a minimum energy path)

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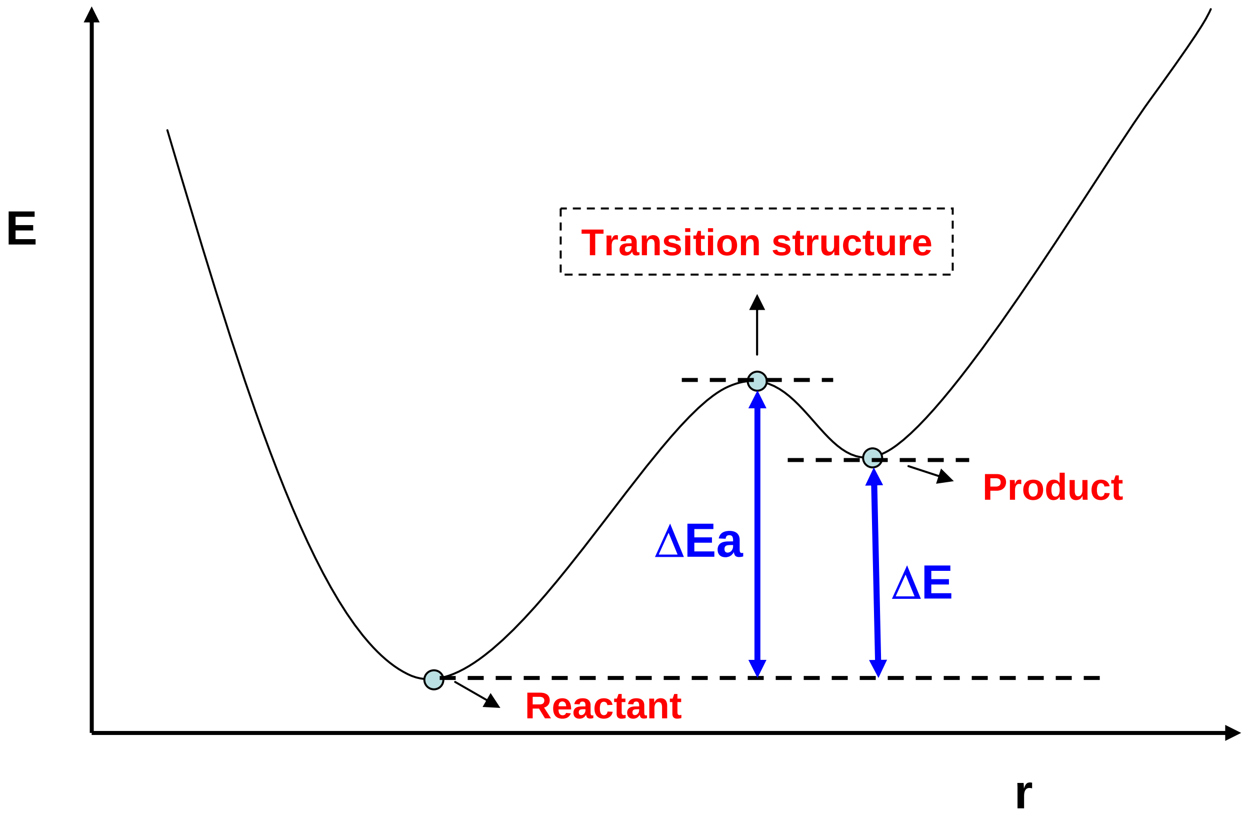
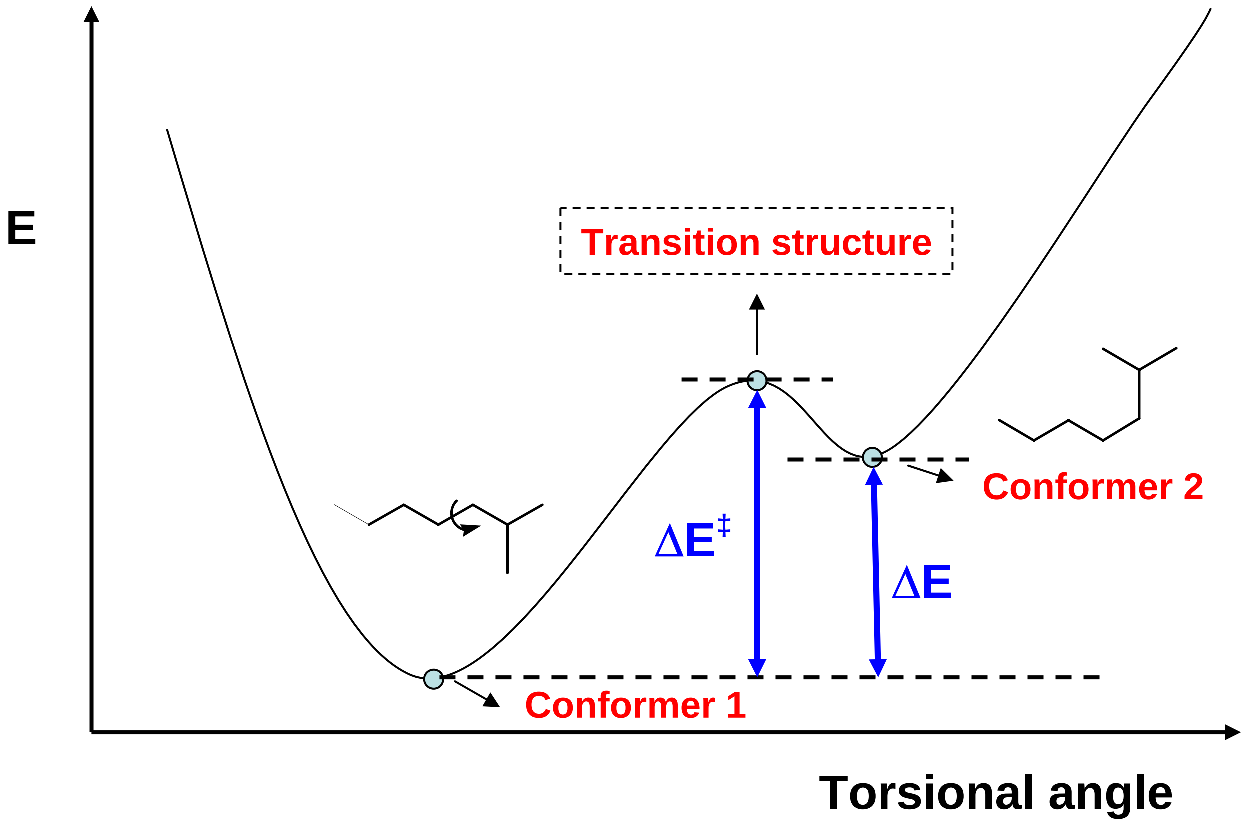
Significance of Stationary Points



ΔEa = activation energy; related to *reaction rate*

ΔE = *reaction energy*

Significance of Stationary Points



$\Delta E^{\ddagger}$ = rotational barrier

ΔE = energy difference of conformers

Energy Minimization

- Coordinates are gradually changed to produce configurations with lower and lower energies until the minimum is reached
- Algorithms are of two types: *with* the use of derivatives of the energy and *without*
- Why are derivatives important? – Reveal the shape of the energy surface, can significantly enhance the efficiency in searching the local minimum
- Why derivatives are not always used? – Could be time consuming if derived numerically

Energy Minimization

- Where you start the minimization decides what you get!

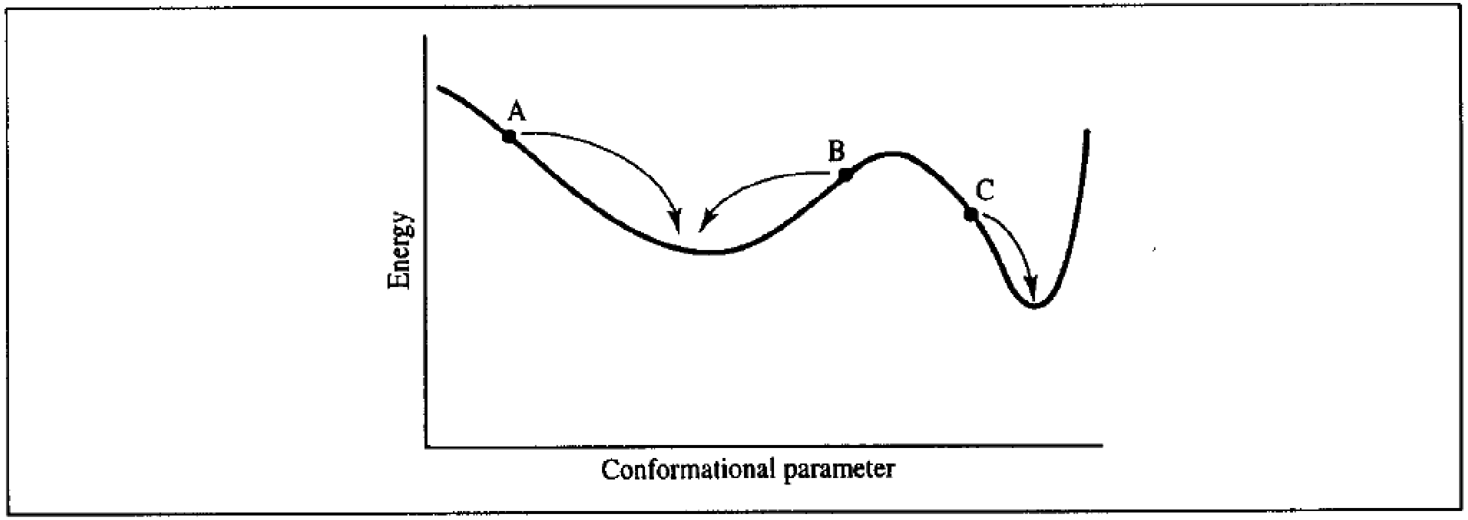


Fig. 5.3: A schematic one-dimensional energy surface. Minimisation methods move downhill to the nearest minimum. The statistical weight of the narrow, deep minimum may be less than a broad minimum which is higher in energy.

If you start at a local maximum, you may be trapped there since gradient = 0
⇒Must do frequency analysis to confirm the nature of the stationary point!
⇒Ex: corannulene ***

- No algorithm has yet proved capable of locating the global energy minimum from an arbitrary starting position

Minimization Methods

- Non-derivative minimization methods
  - The simplex method
  - The sequential univariate method
- First-order minimization methods
  - The steepest descents method
    - Line search
    - Arbitrary step approach
  - Conjugate gradients minimization
- Second derivative methods
  - The Newton-Raphson Method
  - Variants on the Newton-Raphson Method
  - Quasi-Newton methods (Variable metric methods)

The simplex method

- A simplex is a geometrical figure with M +1 vertices; M is the dimensionality of the energy function (for E(x,y,z), M = 3)
- In the simplex method, the figure moves on the potential energy surface (imagine an amoeba)

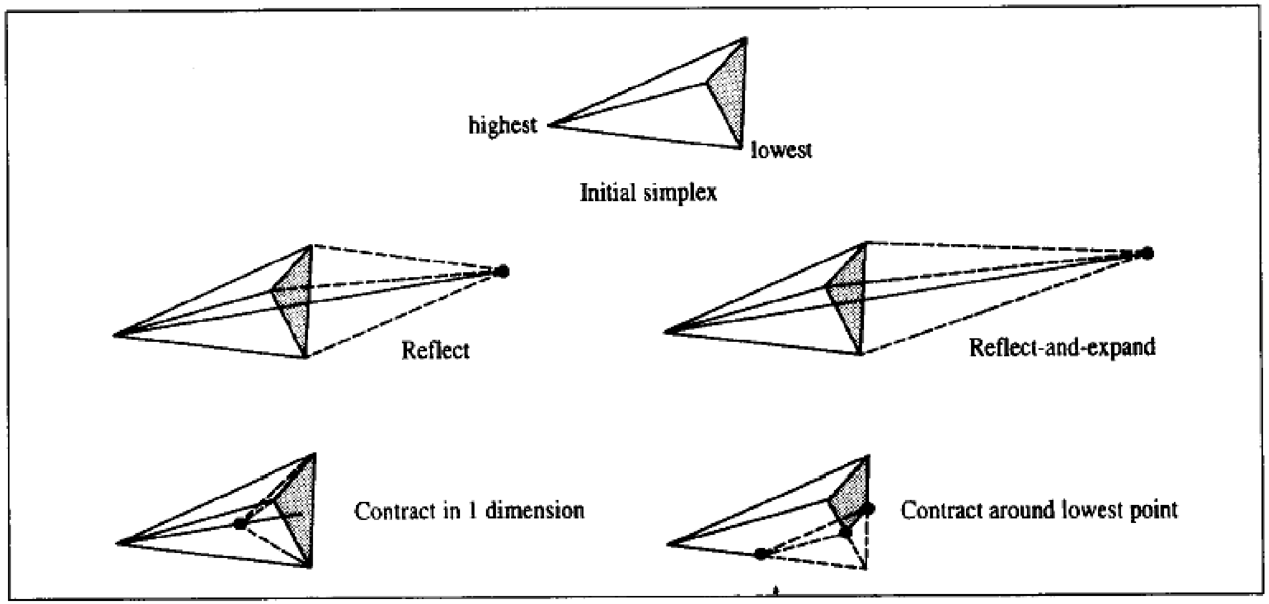
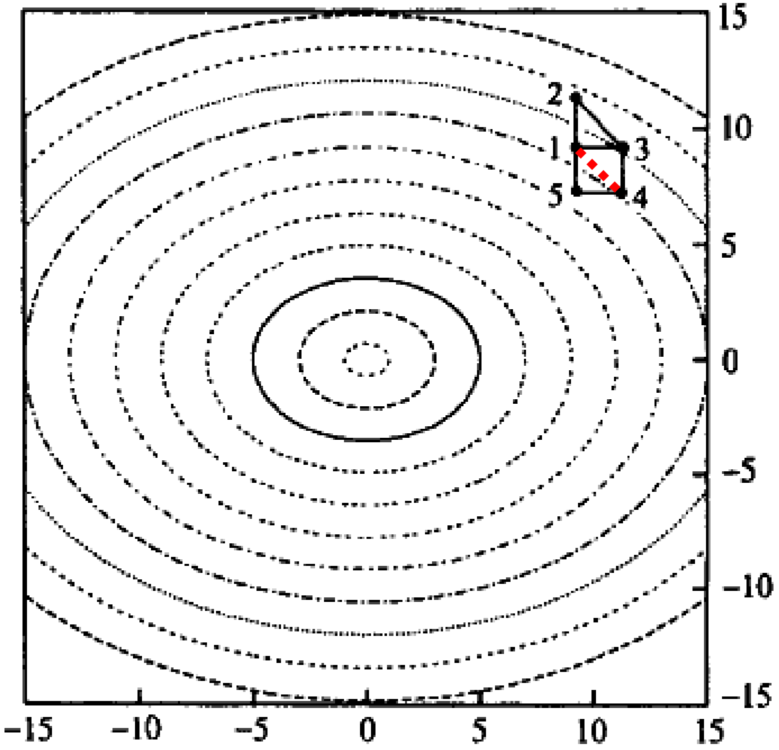


Fig. 5.4: The three basic moves permitted to the simplex algorithm (reflection, and its close relation reflect-and-expand; contract in one dimension and contract around the lowest point). (Figure adapted from Press W H, B P Flannery, S A Teukolsky and W T Vetterling 1992. Numerical Recipes in Fortran. *Cambridge, Cambridge University Press.)*

The simplex method



pt. 2 is highest in energy among pts. 1,2,3

=> Use pt. 2 to generate pt. 4

Pt. 3 is highest Among pts 1,3,4

=> Use pt.3 to generate pt.5

Note: pt. 5 is moving downhill!

Fig. 5.5: The first few steps of the simplex algorithm with the function $x^2 + 2y^2$*. The initial simplex corresponds to the triangle 123. Point 2 has the largest value of the function and the next simplex is the triangle 134. The simplex for the third step is 145.*

- **3N +1 vertices, lots of energy evaluations! (N: number of atoms)**
- **Rarely considered for quantum mechanical calculations**

The Sequential Univariate Method

- In each cycle, only one coordinate is varied. ($x_i + \delta x_i$ and $x_i + 2\delta x_i$: pts. 1,2,3)
- A parabola fitted through the three points
- The minimum of the quadratic function determined and the new starting point is changed to the position of the minimum (pt. 4)
- A new cycle start for the next coordinate (y : pts. 5, 6, 7)

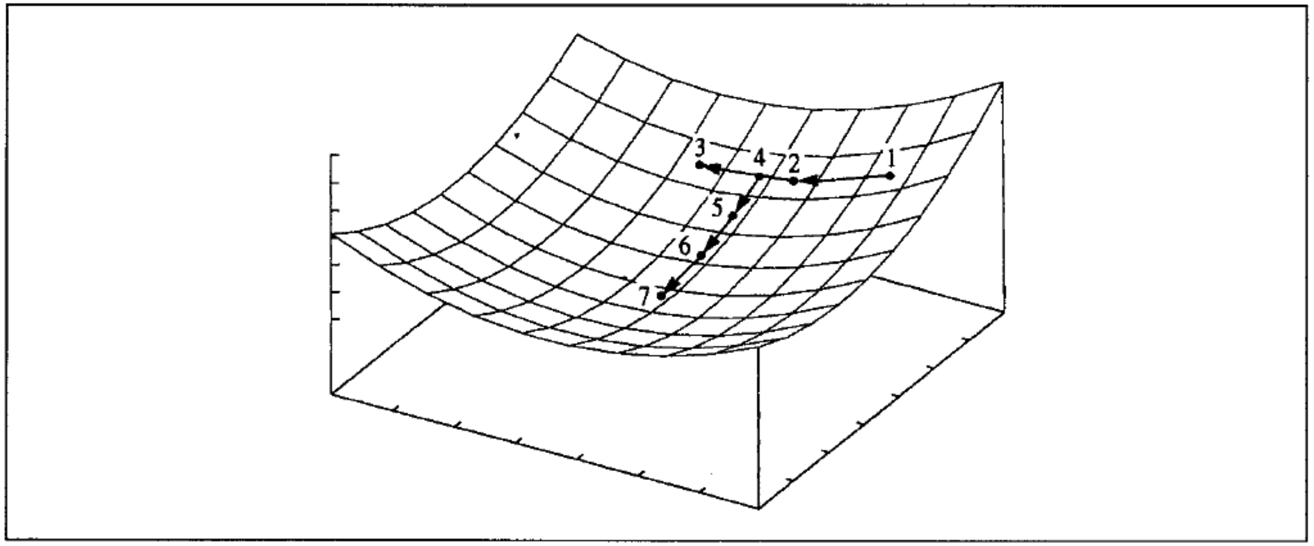


Fig. 5.6: The sequential univariate method. Starting at the point labelled 1 two steps are made along one of the coordinates to give points 2 and 3. A parabola is fitted to these three points and the minimum located (point 4). The same procedure is then repeated along the next coordinate (points 5, 6 and 7). (Figure adapted from Schlegel H B 1987. Optimization of Equilibrium Geometries and Transition Structures. In Lawley K P (Editor). Ab Initio Methods in Quantum Chemistry – I. *New York, John Wiley, pp. 249–286.)*

- **Fewer energy evaluation than simplex**
- **Could be problematic If strong coupling between coordinates**

The Steepest Descents Method

- Move along the gradient (force) direction
- Useful when gradient is large and far from minimum

With Line Search in One Dimension

- Multiple points to locate the minimum in the direction of the gradient

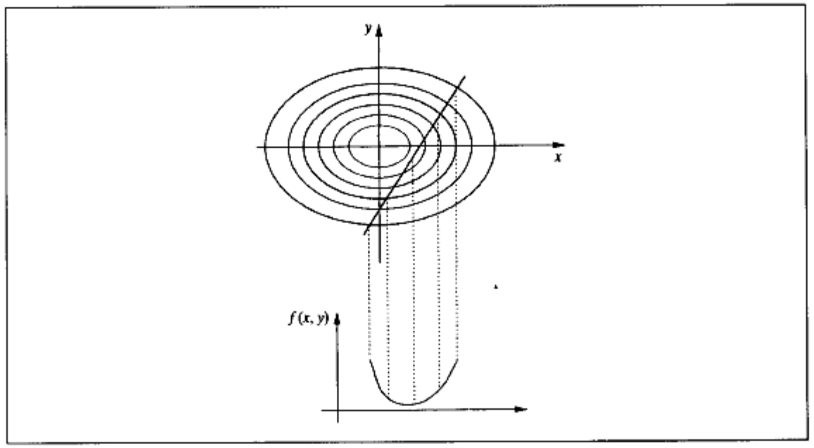


Fig. 5.7: A line search is used to locate the minimum in the function in the direction of the gradient.

Arbitrary Step Approach

- Step size decrease when energy does not decrease (assuming the valley has been leapt across)

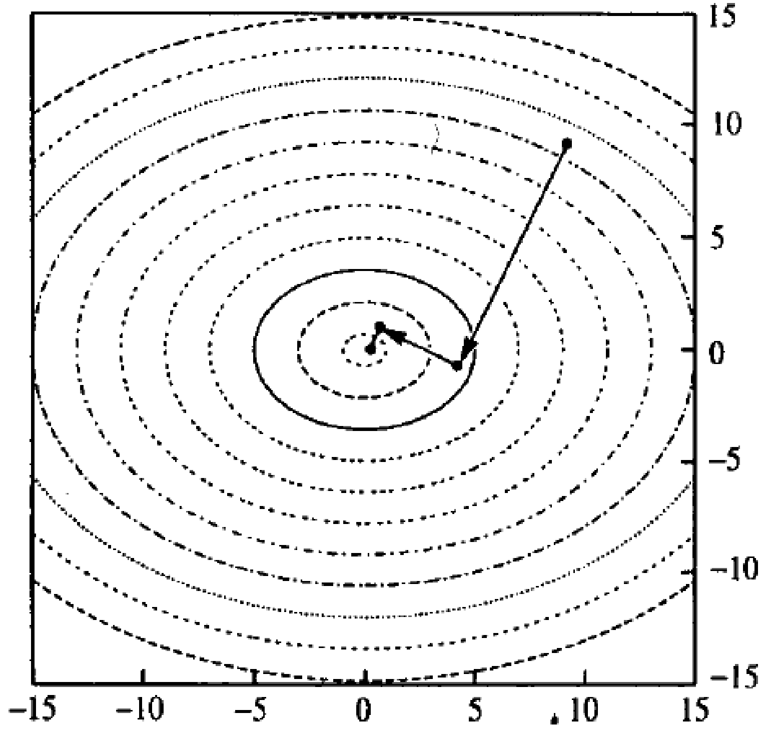


Fig. 5.9: Application of steepest descents to the function $x^2 + 2y^2$.

Conjugate Gradients Minimization

- Less oscillatory behavior in narrow valleys compared to steepest descents

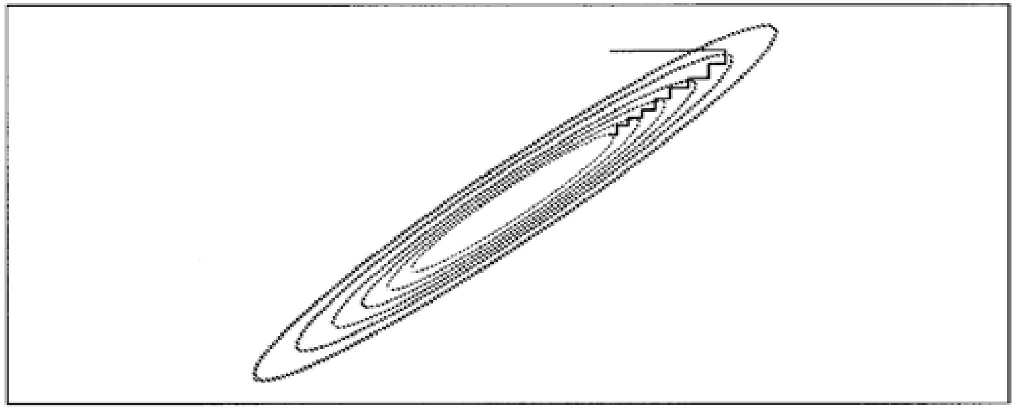


Fig. 5.10: The steepest descents method can give undesirable behaviour in a long narrow valley.

- Conjugate direction : new direction is computed from the gradient and the previous direction

$$\mathbf{v}_k = -\mathbf{g}_k + \gamma_k \mathbf{v}_{k-1} \qquad (5.6)$$

$$\gamma_k = \frac{\mathbf{g}_k \cdot \mathbf{g}_k}{\mathbf{g}_{k-1} \cdot \mathbf{g}_{k-1}} \qquad (5.7)$$

Fletcher-Reeves algorithm

Conjugate Gradients Minimization

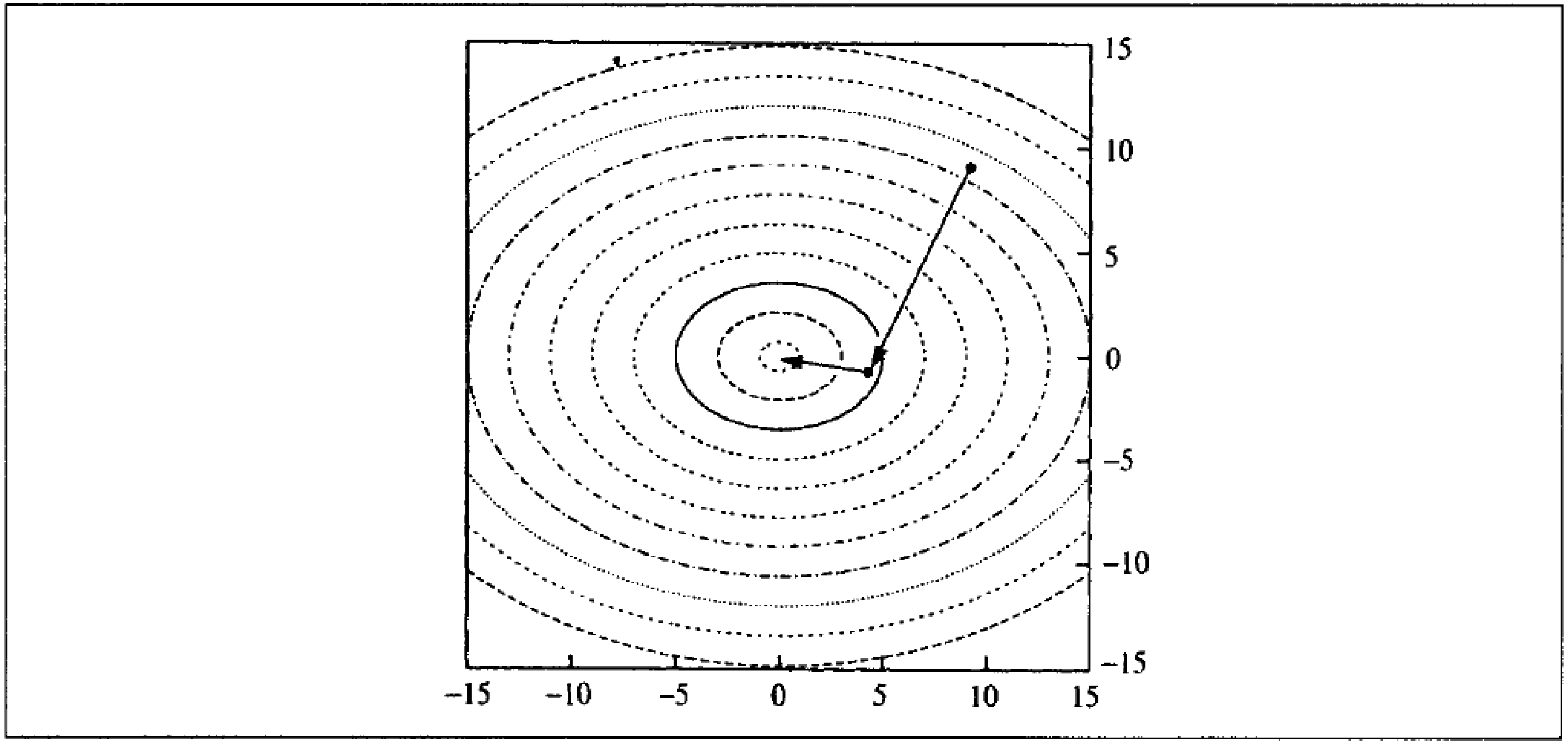


Fig. 5.11: Application of conjugate gradients method to the function $x^2 + 2y^2$.

- **Different algorithms have different definitions of the scalar constant**

Polak-Ribiere algorithm

$$\gamma_k = \frac{(\mathbf{g}_k - \mathbf{g}_{k-1}) \cdot \mathbf{g}_k}{\mathbf{g}_{k-1} \cdot \mathbf{g}_{k-1}}$$

The Newton-Raphson Method

Taylor series expansion about the point x_k

$$\mathscr{V}(x) = \mathscr{V}(x_k) + (x - x_k)\mathscr{V}'(x_k) + (x - x_k)^2\mathscr{V}''(x_k)/2 + \cdots \qquad (5.13)$$

$$\mathscr{V}'(x) = \mathscr{V}'(x_k) + (x - x_k)\mathscr{V}''(x_k) \qquad (5.14)$$

At local minimum, V’(x) is 0 => $x^* = x_k - \mathscr{V}'(x_k)/\mathscr{V}''(x_k)$

- **For multidimensional function, *$V''(x_k)$* correspond to the inverse Hessian Matrix of second derivatives** (3N x 3N in dimension) **: large storage needed if # of atoms exceed 100!**
- **Real surface is not quadratic, so multiple steps needed**
- **Quadratic approximation is more realistic near minimum, so N-R performs better around minimum**

Variants on the Newton-Raphson Method

- Update Hessian occasionally, but gradients recalculated at each iteration
- Block-diagonal Newton-Raphson method : only one atom is moved at each iteration (not effiecient when motions of some atoms are closely coupled, e.g. a phenyl ring.)

Quasi-Newton Methods

- The new position (x_{k+1}) are obtained from x_k, the gradient g_k and the approximated Hessian (H_k) Each algorithm has a unique definition of approximated Hessian. Commonly seen algorithm: DFP, BFGS, MS

Dvidon-Fletcher-Powell, Broyden-Fetcher-Goldfarb-Shanno, Murtaugh-Sargent

Convergence Criteria

- Changes in energy between successive steps < threshold value
- Changes in coordinate between successive steps < threshold
- Root-mean-square of gradient (force) < threshold (should also monitor the *maximum* value of the gradient)

Performance of Minimization Methods

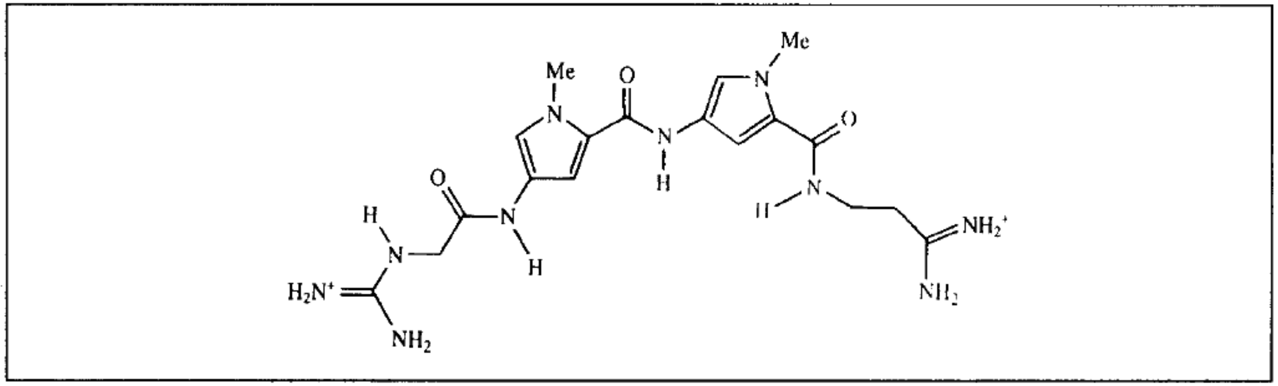
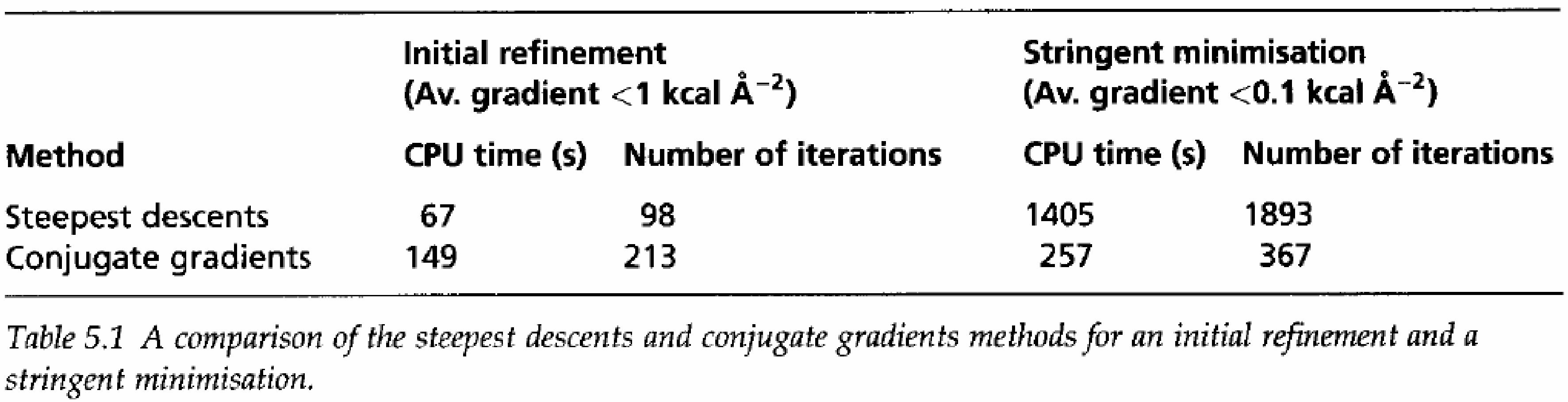


Fig. 5.12: The DNA inhibitor netropsin.



	Initial refinement (Av. gradient <1 kcal Å^{-2})		Stringent minimisation (Av. gradient <0.1 kcal Å^{-2})	
Method	**CPU time (s)**	**Number of iterations**	**CPU time (s)**	**Number of iterations**
Steepest descents	67	98	1405	1893
Conjugate gradients	149	213	257	367

Table 5.1 A comparison of the steepest descents and conjugate gradients methods for an initial refinement and a stringent minimisation.

Choosing Minimization Methods

- Size of the system?

  Newton-Raphson may not be good when too many atoms are present, due to the storage problem of Hessian matrix)

- Availability of analytical derivatives?

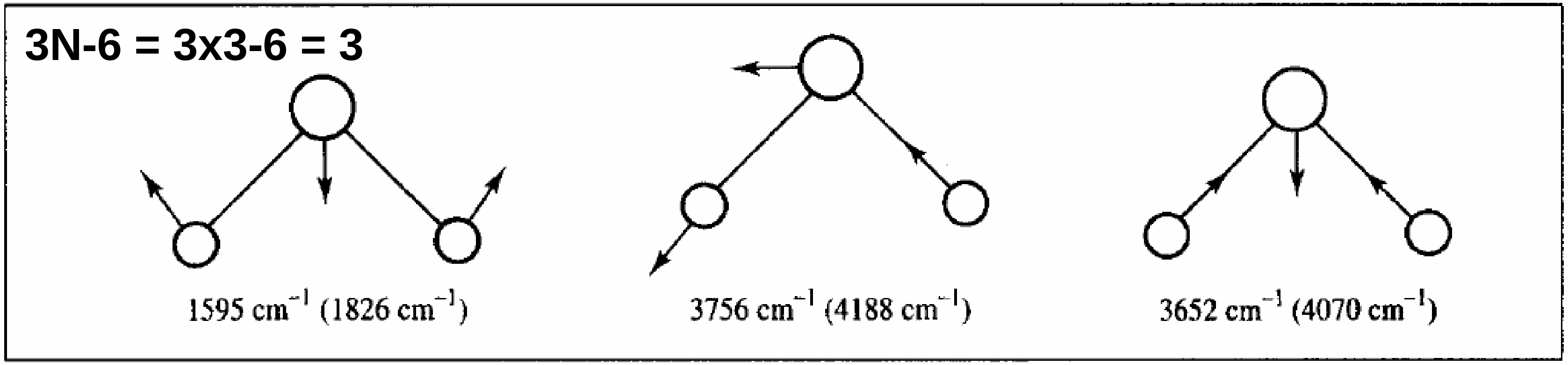
- Shape of the potential energy surface?

  Far from the minimum: Steepest descents could be good

  Close to the minimum: Newton-Raphson or conjugate gradients may be superior

Normal Mode Analysis and Thermodynamic properties

- Frequency analysis (diagonalisation of Hessian matrix based on mass-weighted coordinates) at the stationary point can get vibration normal modes (eigenvectors) and the corresponding vibration frequencies (eigenvalues)



3N-6 = 3x3-6 = 3

Fig. 5.15: Normal modes of water. Experimental and (calculated) frequencies are shown. Theoretical frequencies calculated using a 6-31G* basis set.

Normal Mode Analysis and Thermodynamic properties

- Energy from energy minimization corresponds to a hypothetical and motionless energy minimum at 0K

- Each normal mode is at the ground state at 0K

  => zero-point vibration energy ***

- To compare with experimental : need corrections!

  $U(T) = U_{trans}(T) + U_{rot}(T) + U_{vib}(T)$

  $H = U + RT$

  $G = H - TS$ ***