Lecture 2
Molecular Geometry Optimization

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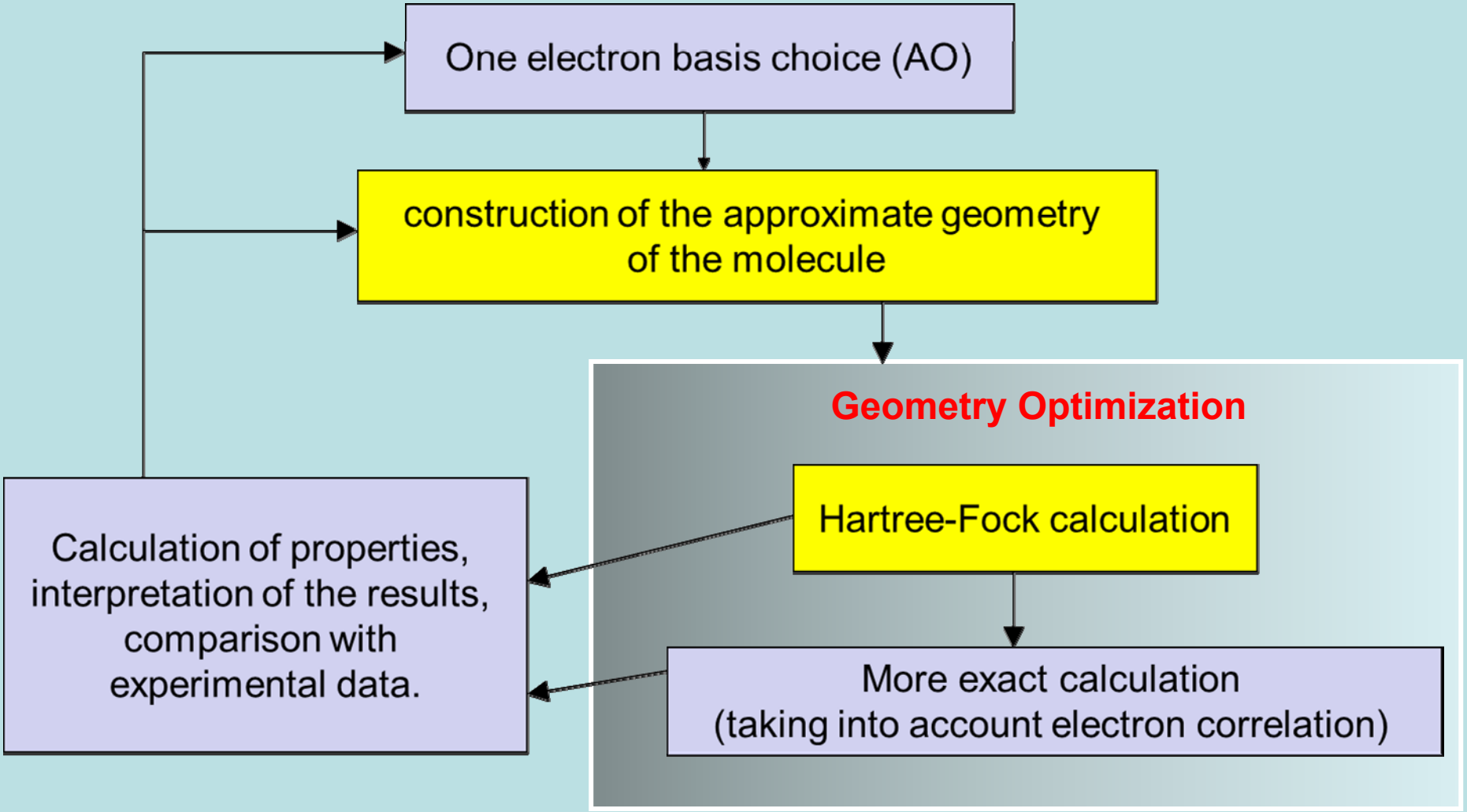
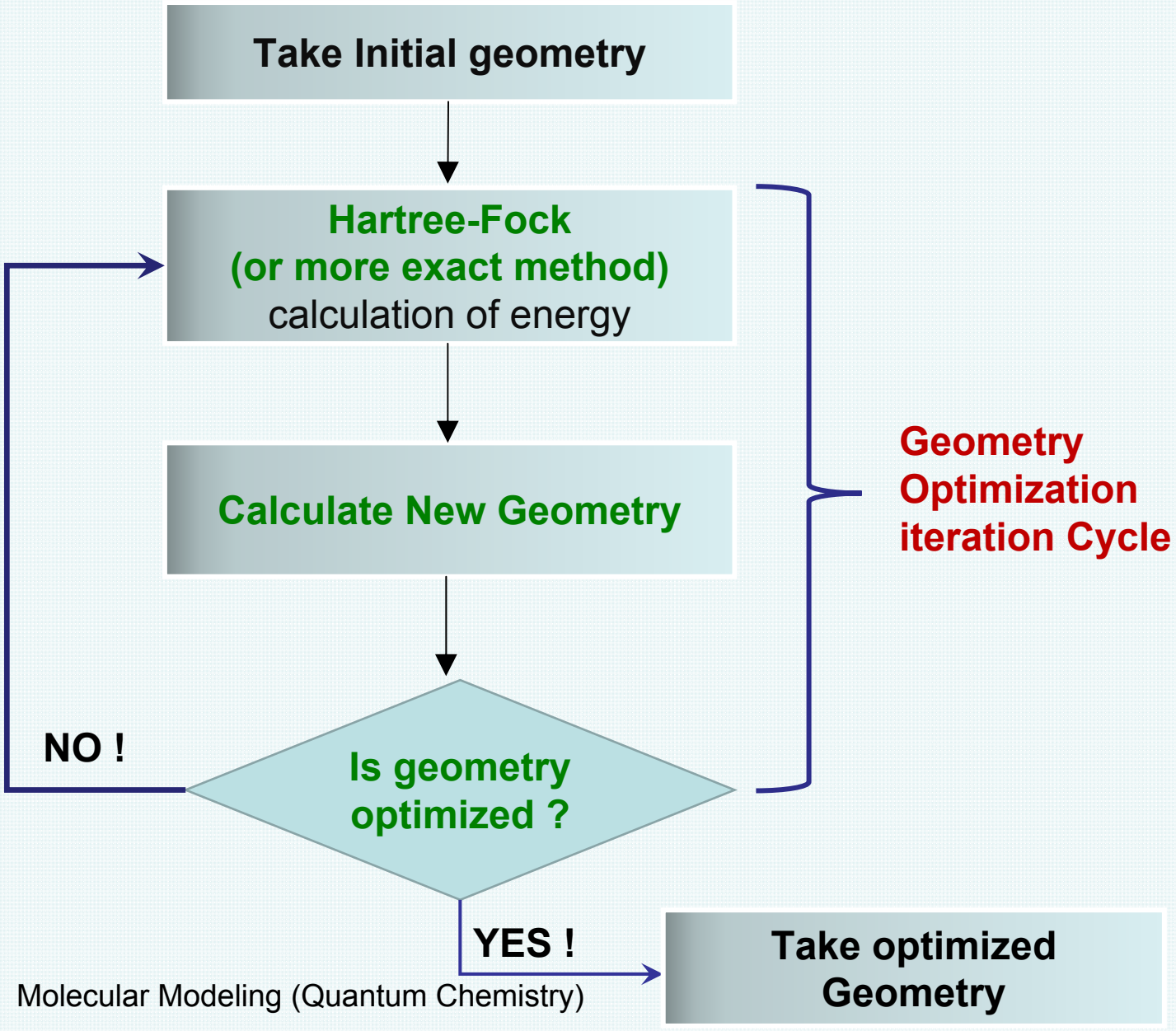
Typical scheme of Quantum Chemistry (*ab initio*) calculation



Geometry Optimization procedure



Number of degrees of freedom of a molecule (geometry)

For an N atomic molecule, the number of possible shifts of atoms = 3N

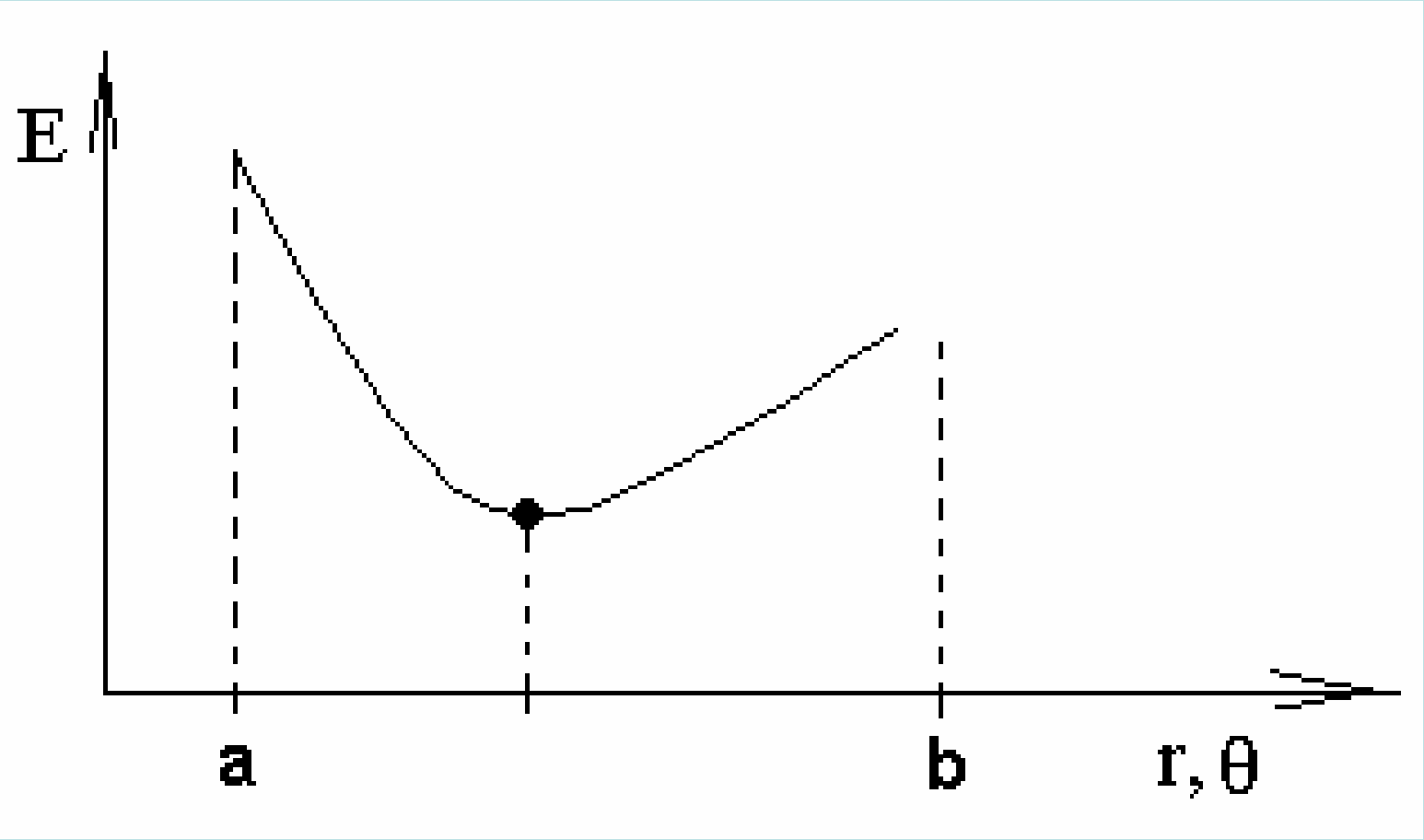
Translation of the molecule as a whole - 3
Rotation of a nonlinear molecule as a whole – 3
Rotation of a linear molecule as a whole – 2

$3N-6$	Number of degrees of freedom of a **nonlinear N - atomic** molecule
$3N-5$	Number of degrees of freedom of a **linear N - atomic** molecule

The Energy is function of 3N – 6 geometrical parameters for Nonlinear molecule

$$\mathbf{E} = \mathbf{E}(\underbrace{r_{C\text{-}C}, r_{C\text{-}H}, r_{C\text{-}N}, \ldots\ldots, \theta_{C\text{-}C\text{-}C}, \theta_{C\text{-}C\text{-}H}, \ldots\ldots D_{C\text{-}C\text{-}C\text{-}C}, D_{C\text{-}C\text{-}O\text{-}H}, D_{C\text{-}C\text{-}N\text{-}N}, \ldots\ldots}_{3N-6\text{ parameters}})$$

PES – potential energy surface



$$E(r_i,....\theta_k,....), \quad \{i,k\} = 3N-6$$

Stationary Point Characteristics (minimum)

$$\min \quad f(x)$$

$$\frac{\partial f}{\partial x} = 0$$

$$\frac{\partial^2 f}{\partial x^2} > 0$$

$$\min \quad E = E(x_1, x_2, \ldots . x_{3N-6})$$

$$\frac{\partial E}{\partial x_1} = \frac{\partial E}{\partial x_2} = \ldots = \frac{\partial E}{\partial x_{3N\text{-}6}} = \text{small} \approx 10^{-5}$$

$$H = \begin{pmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N-6}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_{3N-6}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial^2 E}{\partial x_{3N-6} \partial x_1} & \frac{\partial^2 E}{\partial x_{3N-6} \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_{3N-6} \partial x_{3N\text{-}6}} \end{pmatrix}$$

Diagonal representation of Hessian matrix

$$\begin{pmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N-6}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_{3N-6}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial^2 E}{\partial x_{3N-6} \partial x_1} & \frac{\partial^2 E}{\partial x_{3N-6} \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_{3N-6} \partial x_{3N-6}} \end{pmatrix} \rightarrow \begin{pmatrix} \frac{\partial^2 E}{\partial z_1 \partial z_1} & 0 & \cdots & 0 \\ 0 & \frac{\partial^2 E}{\partial z_2 \partial z_2} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \frac{\partial^2 E}{\partial z_{3N-6} \partial z_{3N-6}} \end{pmatrix}$$

$$z = \sum_{i=1}^{3N-6} C_i x_i$$

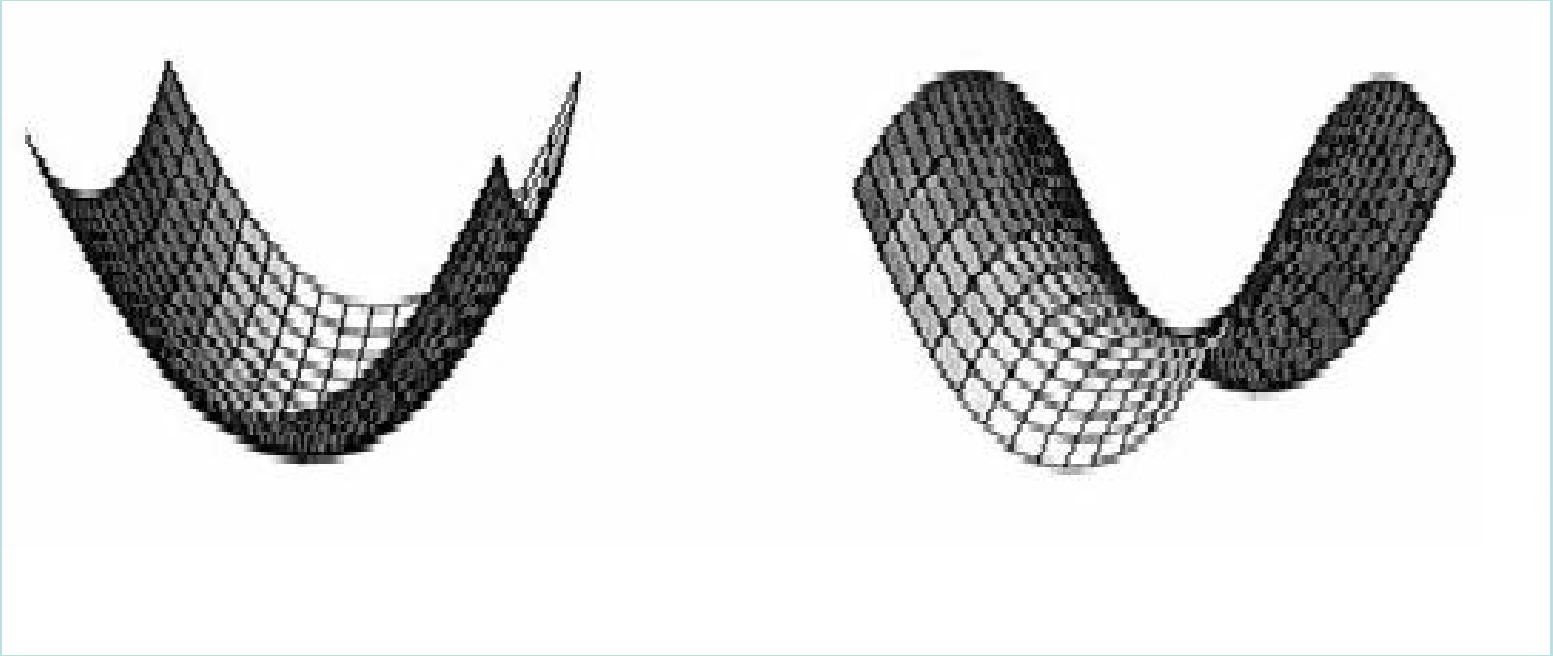
$$\frac{\partial^2 E}{\partial z_i \partial z_i}$$

[positive, negative, zero]

In minimum (optimal geometry) [N,0,0]

Minimum

Transition state



[N, 0, 0]

[N-1, 1, 0]

Gradient

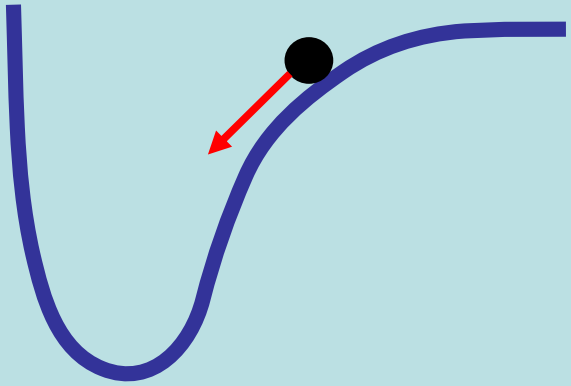
$$E(r_i, \theta_k) \quad X = \{ r_i, \theta_k \}$$

$$X = \begin{pmatrix} X_1 \\ X_2 \\ \cdots\cdots \\ X_{3N-6} \end{pmatrix} \qquad g_i = \frac{\partial E}{\partial X_i} \equiv \begin{pmatrix} \frac{\partial E}{\partial X_1} \\ \frac{\partial E}{\partial X_2} \\ \cdots\cdots \\ \frac{\partial E}{\partial X_{3N-6}} \end{pmatrix}$$

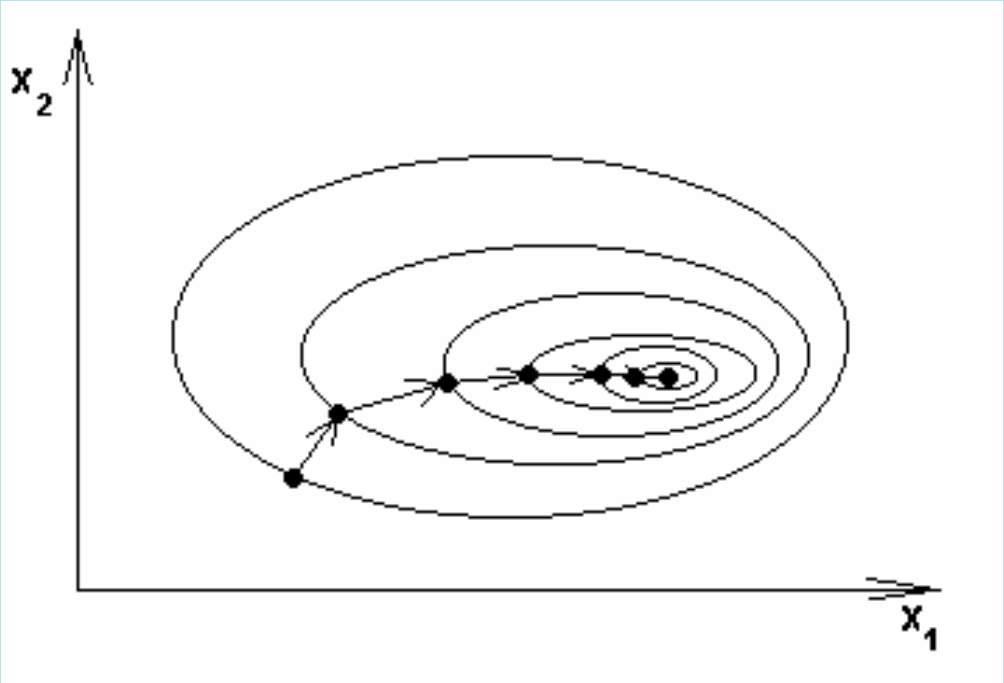
opttol parameter

$$\|g\| \le \text{opttol} = 10^{-5}$$

Kcal/(A mol)



Steepest Descent

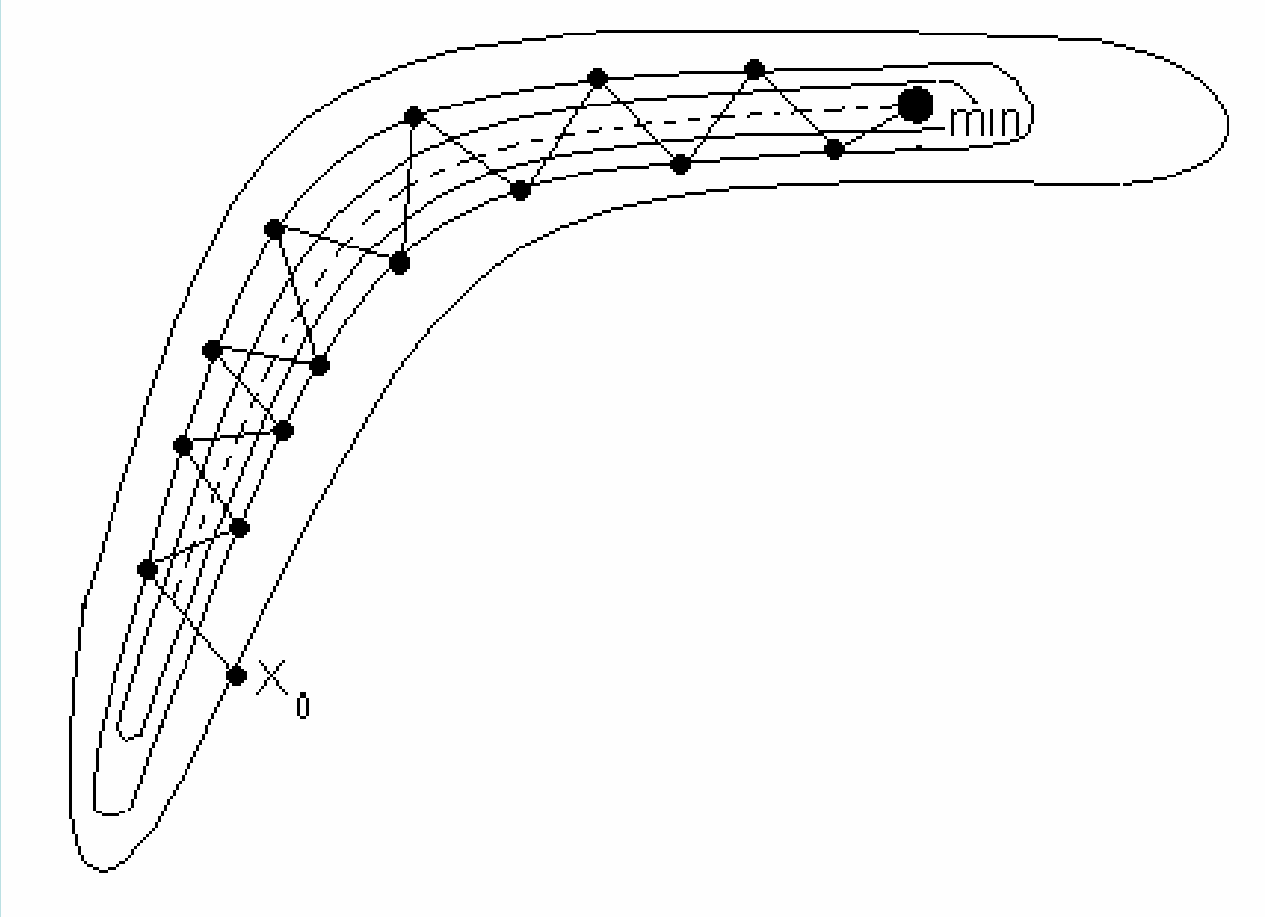


$$x_{(k)} = x_{(k-1)} - \alpha_{(k-1)} g_{(k-1)}$$

One can find α
By minimization of energy

$$x_{(0)} \rightarrow x_{(1)} \rightarrow x_{(2)} \rightarrow .... \rightarrow x_{*}$$

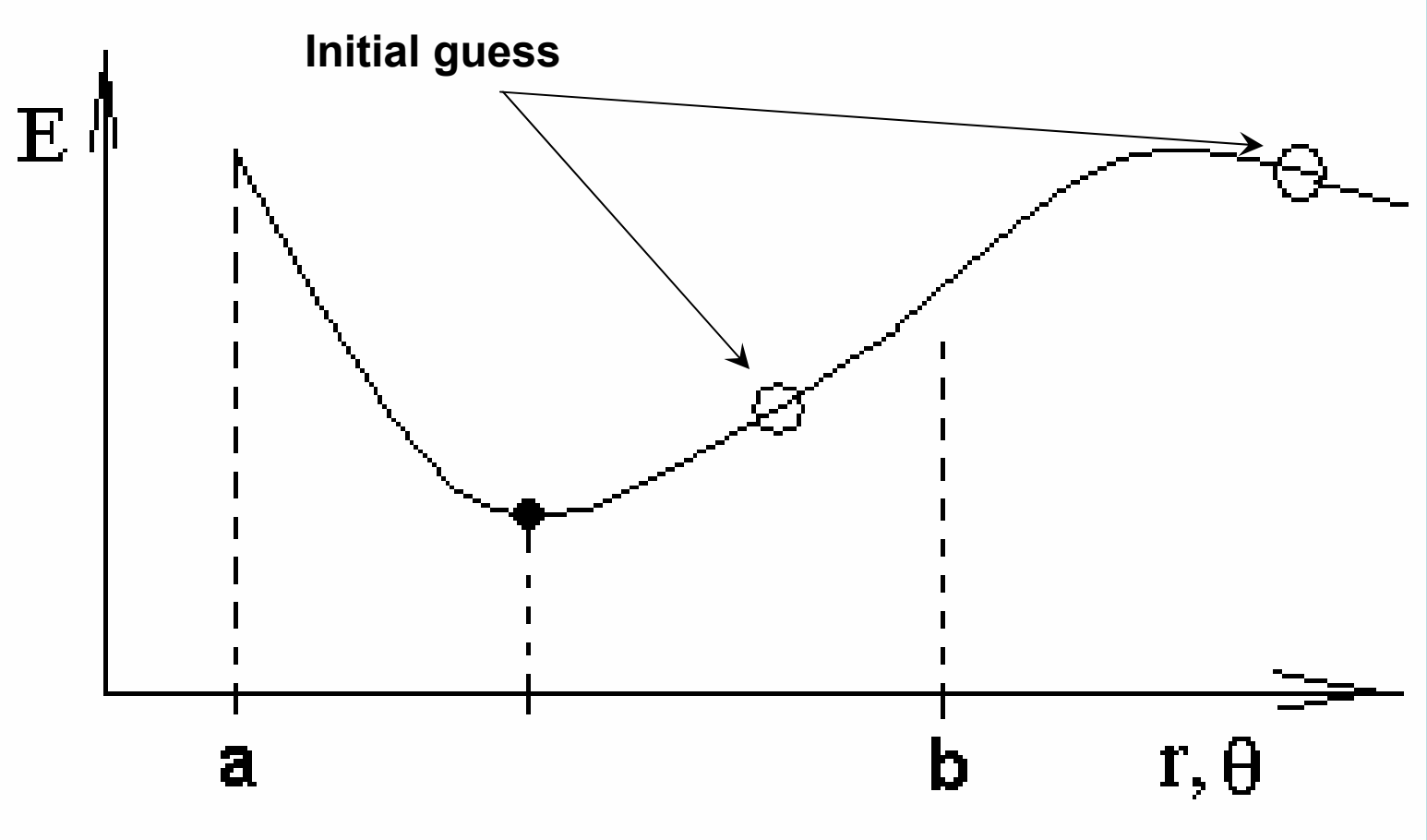
The problem of ravines



quasi-newtonian methods

$$x_{(k)} = x_{(k-1)} - \alpha_{(k-1)} H^{-1}_{(k-1)} g_{(k-1)}$$

It is important to choose a good initial geometry !!!



GAMESS options

gradient and Hessian can be found
Analytically (fast method)
Numerically (slow method)

$control numgrd=.true. **$end**

Accuracy of geometry optimization and number of optimization steps:

$statpt
opttol=1e-5 nstep=50
$end

NSERCH= **44** ENERGY= -1365.0182790

Energy of system !!!

GRADIENT (HARTREE/BOHR)

ATOM		ZNUC	DE/DX	DE/DY	DE/DZ
1	AL	13.0	0.0000041	-0.0000100	0.0000063
2	AL	13.0	-0.0000251	-0.0000263	0.0000152
3	O	8.0	0.0000059	0.0000024	-0.0000241
4	SI	14.0	-0.0000350	-0.0000317	0.0000005
5	SI	14.0	0.0000037	0.0000375	-0.0000201

MAXIMUM GRADIENT = 0.0000375 RMS GRADIENT = 0.0000161

***** EQUILIBRIUM GEOMETRY **LOCATED** *****

COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
AL	13.0	0.0722278997	0.0420774565	3.7713557809
AL	13.0	1.8600680440	1.4537918605	1.4466944061
O	8.0	1.2067051691	0.9524349136	2.9181865457
SI	14.0	-1.6729777729	-1.4110882472	1.4877902217
SI	14.0	0.0702419855	-0.0380169106	-0.7766354571

NSERCH= **200** ENERGY= -1365.232790

GRADIENT (HARTREE/BOHR)

ATOM	ZNUC	DE/DX	DE/DY	DE/DZ
1 AL	13.0	0.041000	-0.0000100	0.0000063
2 AL	13.0	-0.510000	-0.0000263	0.0000152
3 O	8.0	0.059000	0.0000024	-0.0000241
4 SI	14.0	-0.035000	-0.0000317	0.0000005
5 SI	14.0	0.0000037	0.0000375	-0.0000201

MAXIMUM GRADIENT = 0.375 RMS GRADIENT = 0.161

***** **FAIL** TO LOCATE STATIONAR POINT *****

COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
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To be Continued

Hartree-Fock Approach