TÜBİTAK

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METU

EURO^2

Electronic structure calculations by Gaussian 16

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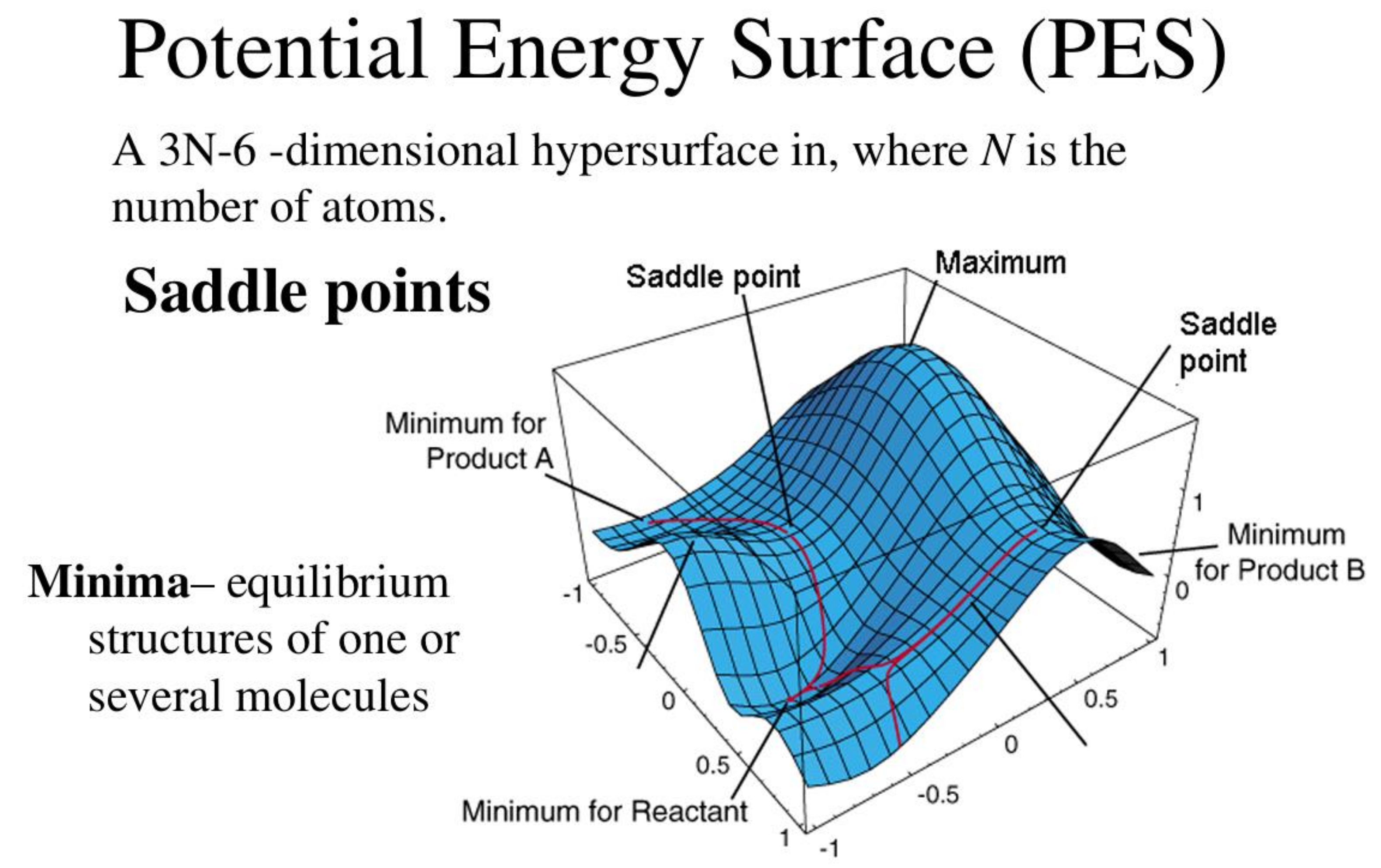
Reaction Mechanism by using Transition State Theory in Gaussian

https://www.tau.ac.il/~ephraim/TranState.pdf



Potential Energy Surface (PES)

A 3N-6 -dimensional hypersurface in, where *N* is the number of atoms.

Saddle points

Minima– equilibrium structures of one or several molecules

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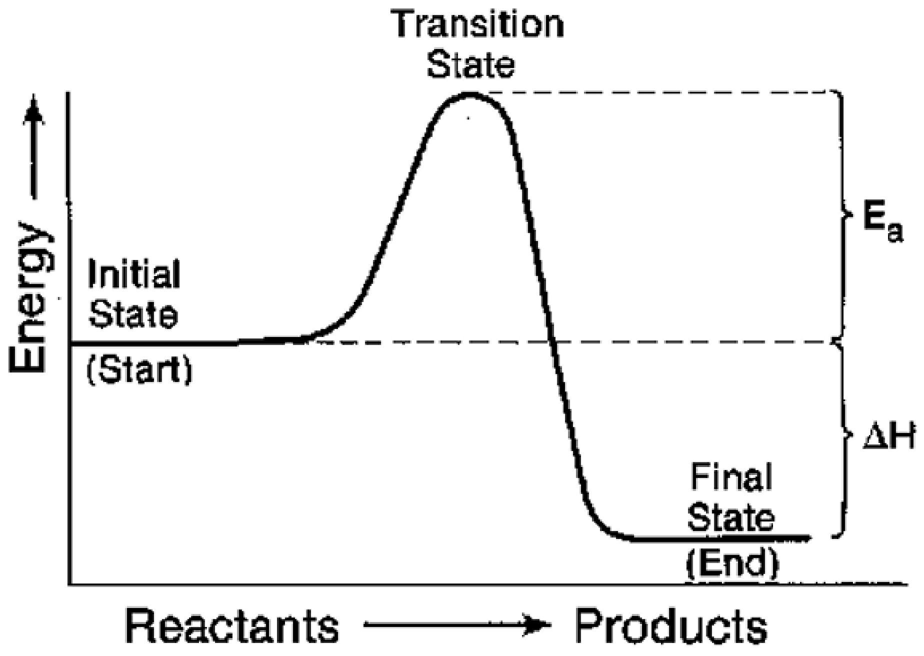

Arrhenius equation

$$k = Ae^{-E_A / k_b T}$$

k - rate constant
E_A – activation energy
T – temperature
k_b – Boltzmann constant

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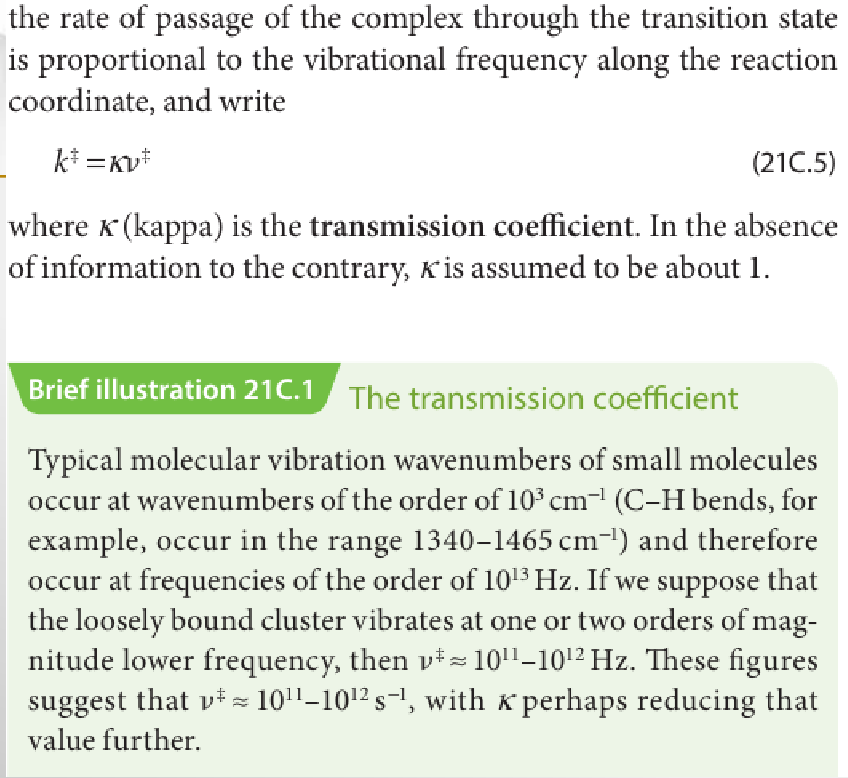


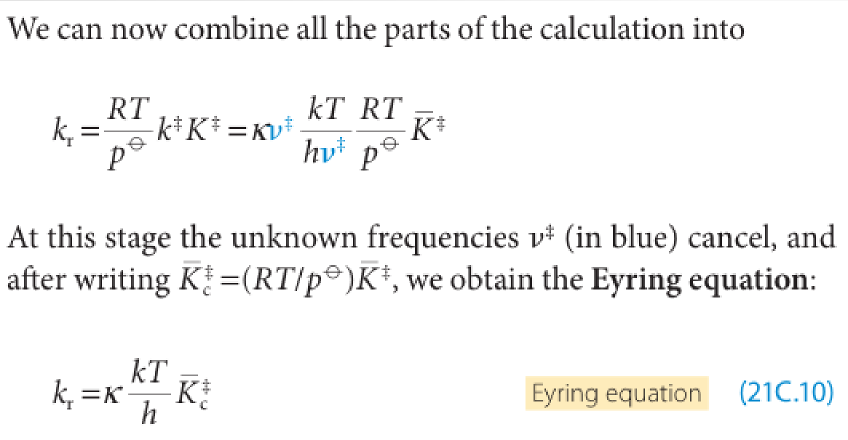
the rate of passage of the complex through the transition state is proportional to the vibrational frequency along the reaction coordinate, and write

$$k^{\ddagger} = \kappa\nu^{\ddagger} \tag{21C.5}$$

where κ (kappa) is the **transmission coefficient**. In the absence of information to the contrary, κ is assumed to be about 1.

Brief illustration 21C.1 The transmission coefficient

Typical molecular vibration wavenumbers of small molecules occur at wavenumbers of the order of $10^3\,\mathrm{cm^{-1}}$ (C–H bends, for example, occur in the range 1340–1465 $\mathrm{cm^{-1}}$) and therefore occur at frequencies of the order of 10^{13} Hz. If we suppose that the loosely bound cluster vibrates at one or two orders of magnitude lower frequency, then $\nu^{\ddagger} \approx 10^{11}$–$10^{12}$ Hz. These figures suggest that $\nu^{\ddagger} \approx 10^{11}$–$10^{12}\,\mathrm{s^{-1}}$, with κ perhaps reducing that value further.



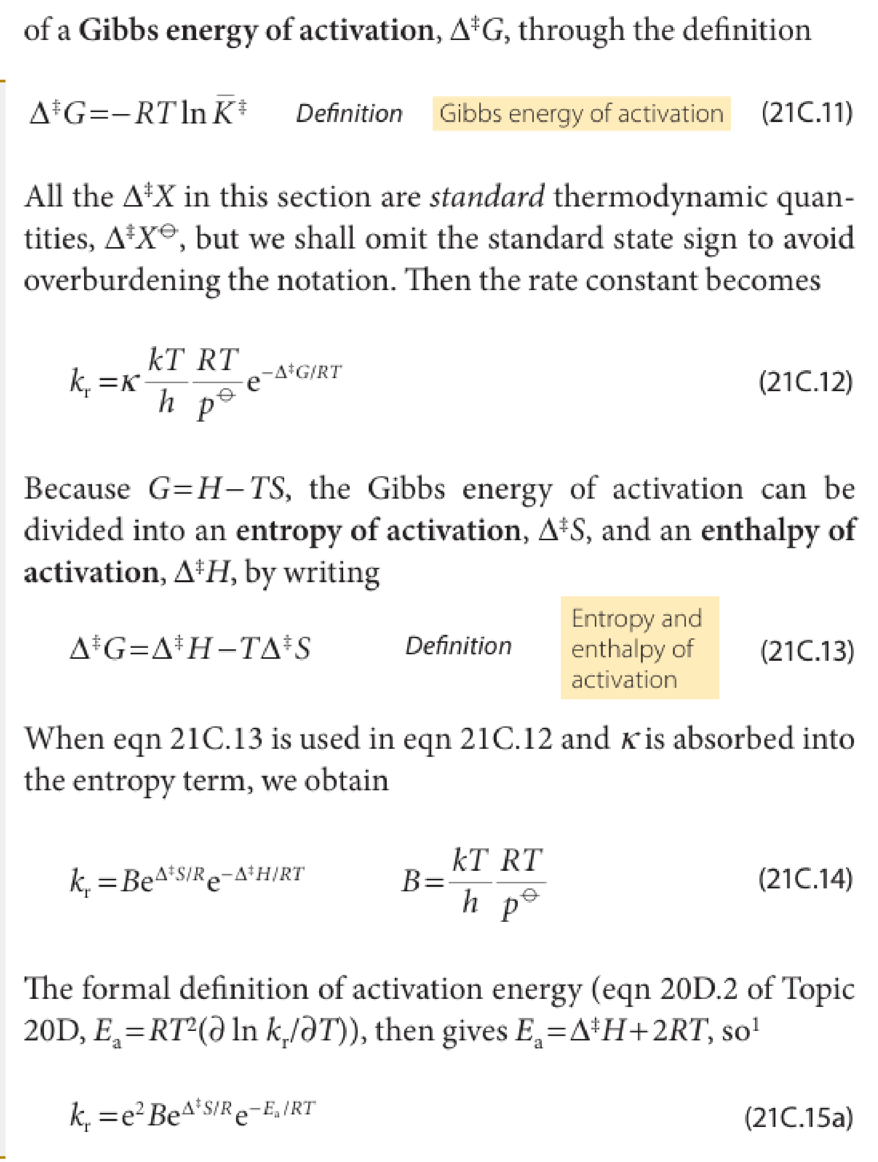
We can now combine all the parts of the calculation into

$$k_{\mathrm{r}} = \frac{RT}{p^{\ominus}} k^{\ddagger} K^{\ddagger} = \kappa\nu^{\ddagger}\frac{kT}{h\nu^{\ddagger}}\frac{RT}{p^{\ominus}}\bar{K}^{\ddagger}$$

At this stage the unknown frequencies $\nu^{\ddagger}$ (in blue) cancel, and after writing $\bar{K}_{\mathrm{c}}^{\ddagger} = (RT/p^{\ominus})\bar{K}^{\ddagger}$, we obtain the **Eyring equation**:

$$k_{\mathrm{r}} = \kappa\frac{kT}{h}\bar{K}_{\mathrm{c}}^{\ddagger} \tag{21C.10}$$

Eyring equation



of a **Gibbs energy of activation**, $\Delta^{\ddagger}G$, through the definition

$$\Delta^{\ddagger}G = -RT\ln\bar{K}^{\ddagger} \tag{21C.11}$$

Definition Gibbs energy of activation

All the $\Delta^{\ddagger}X$ in this section are *standard* thermodynamic quantities, $\Delta^{\ddagger}X^{\ominus}$, but we shall omit the standard state sign to avoid overburdening the notation. Then the rate constant becomes

$$k_{\mathrm{r}} = \kappa\frac{kT}{h}\frac{RT}{p^{\ominus}}\mathrm{e}^{-\Delta^{\ddagger}G/RT} \tag{21C.12}$$

Because $G = H - TS$, the Gibbs energy of activation can be divided into an **entropy of activation**, $\Delta^{\ddagger}S$, and an **enthalpy of activation**, $\Delta^{\ddagger}H$, by writing

$$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S \tag{21C.13}$$

Definition Entropy and enthalpy of activation

When eqn 21C.13 is used in eqn 21C.12 and κ is absorbed into the entropy term, we obtain

$$k_{\mathrm{r}} = B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-\Delta^{\ddagger}H/RT} \qquad B = \frac{kT}{h}\frac{RT}{p^{\ominus}} \tag{21C.14}$$

The formal definition of activation energy (eqn 20D.2 of Topic 20D, $E_{\mathrm{a}} = RT^2(\partial\ln k_{\mathrm{r}}/\partial T)$), then gives $E_{\mathrm{a}} = \Delta^{\ddagger}H + 2RT$, so[1]

$$k_{\mathrm{r}} = \mathrm{e}^2 B\mathrm{e}^{\Delta^{\ddagger}S/R}\mathrm{e}^{-E_{\mathrm{a}}/RT} \tag{21C.15a}$$

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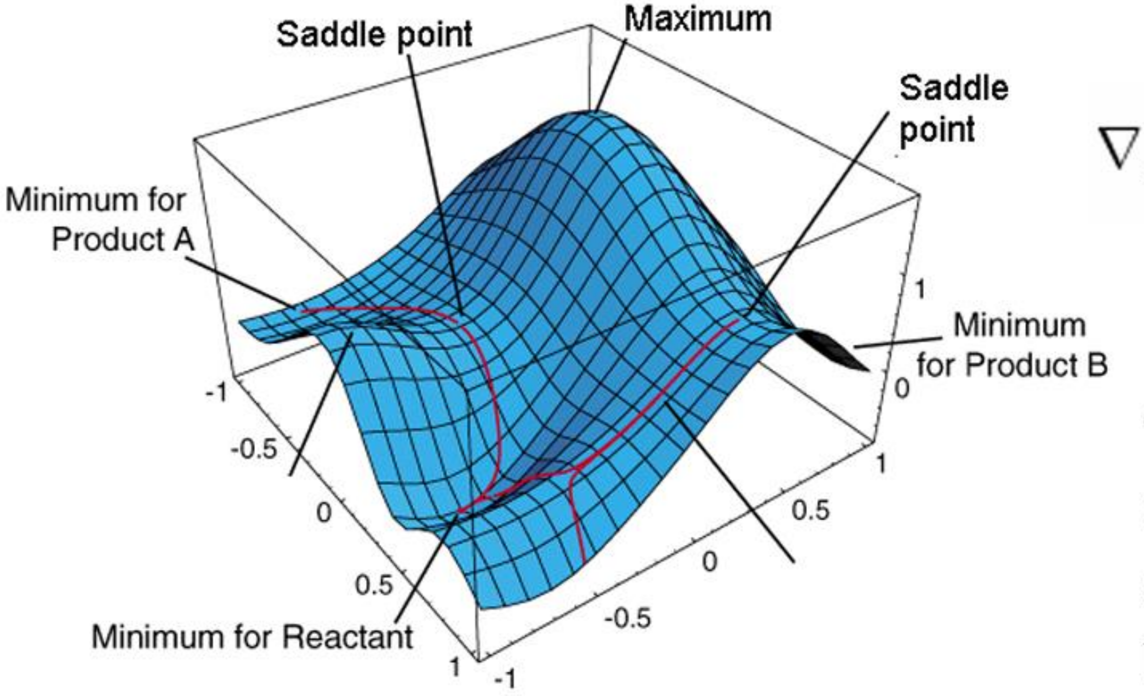

$$\nabla f = \left(\frac{\partial f}{\partial x_1}, \ldots, \frac{\partial f}{\partial x_n} \right)$$

- gradient

The coordinates can be Cartesian (x,y,z..), or internal, such as bondlength and angle displacements)

Force: $F = -\nabla E$ (Potential energy)

$\nabla f = 0$ - Stationary Point (minimum, maximum, or saddle point)

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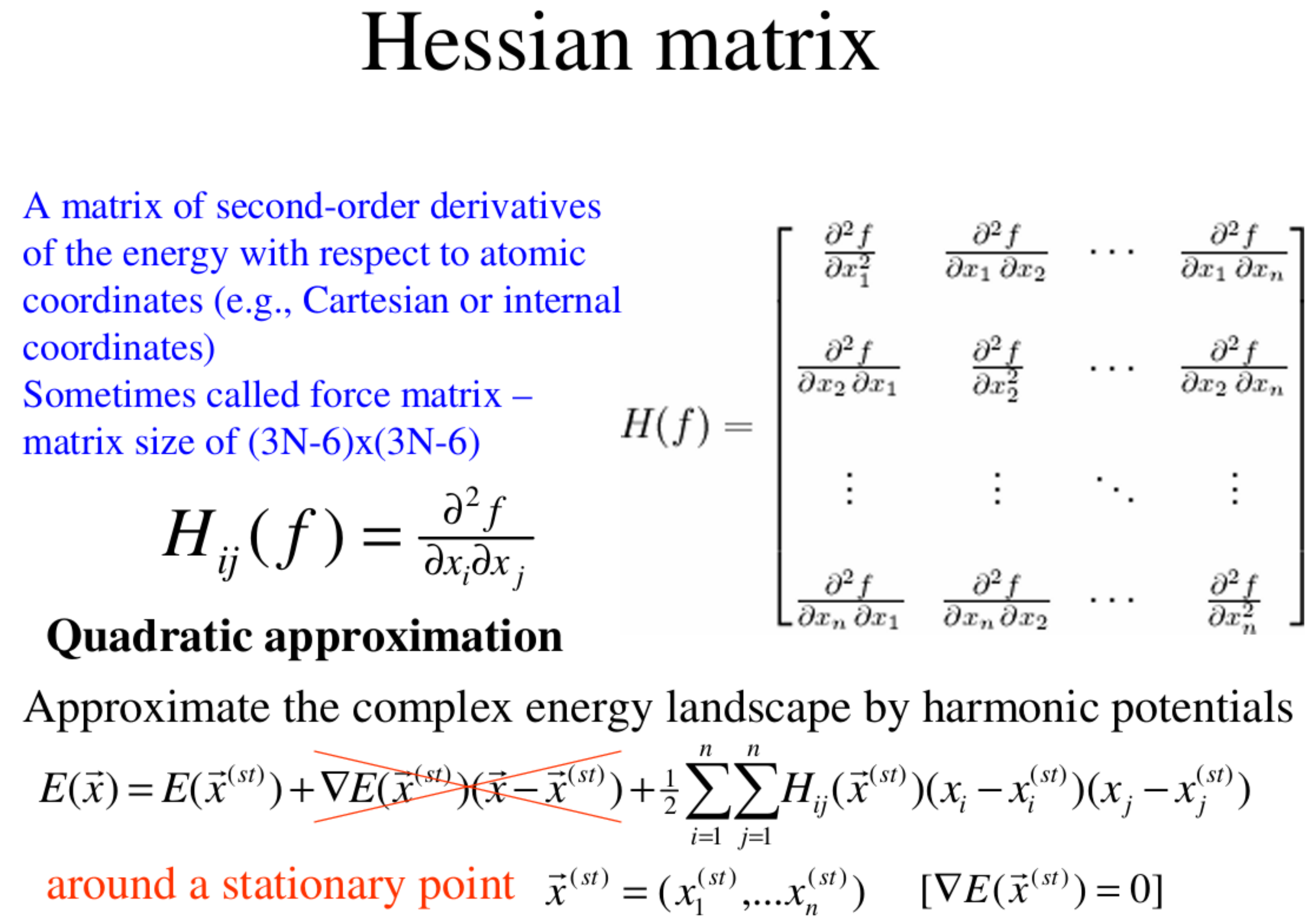

Hessian matrix

A matrix of second-order derivatives of the energy with respect to atomic coordinates (e.g., Cartesian or internal coordinates)

Sometimes called force matrix – matrix size of (3N-6)x(3N-6)

$$H_{ij}(f) = \frac{\partial^2 f}{\partial x_i \partial x_j}$$

$$H(f) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1\,\partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1\,\partial x_n} \\ \frac{\partial^2 f}{\partial x_2\,\partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2\,\partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n\,\partial x_1} & \frac{\partial^2 f}{\partial x_n\,\partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

Quadratic approximation

Approximate the complex energy landscape by harmonic potentials

$$E(\vec{x}) = E(\vec{x}^{(st)}) + \cancel{\nabla E(\vec{x}^{(st)})(\vec{x}-\vec{x}^{(st)})} + \tfrac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} H_{ij}(\vec{x}^{(st)})(x_i - x_i^{(st)})(x_j - x_j^{(st)})$$

around a stationary point $\vec{x}^{(st)} = (x_1^{(st)}, \ldots x_n^{(st)})$ $[\nabla E(\vec{x}^{(st)}) = 0]$

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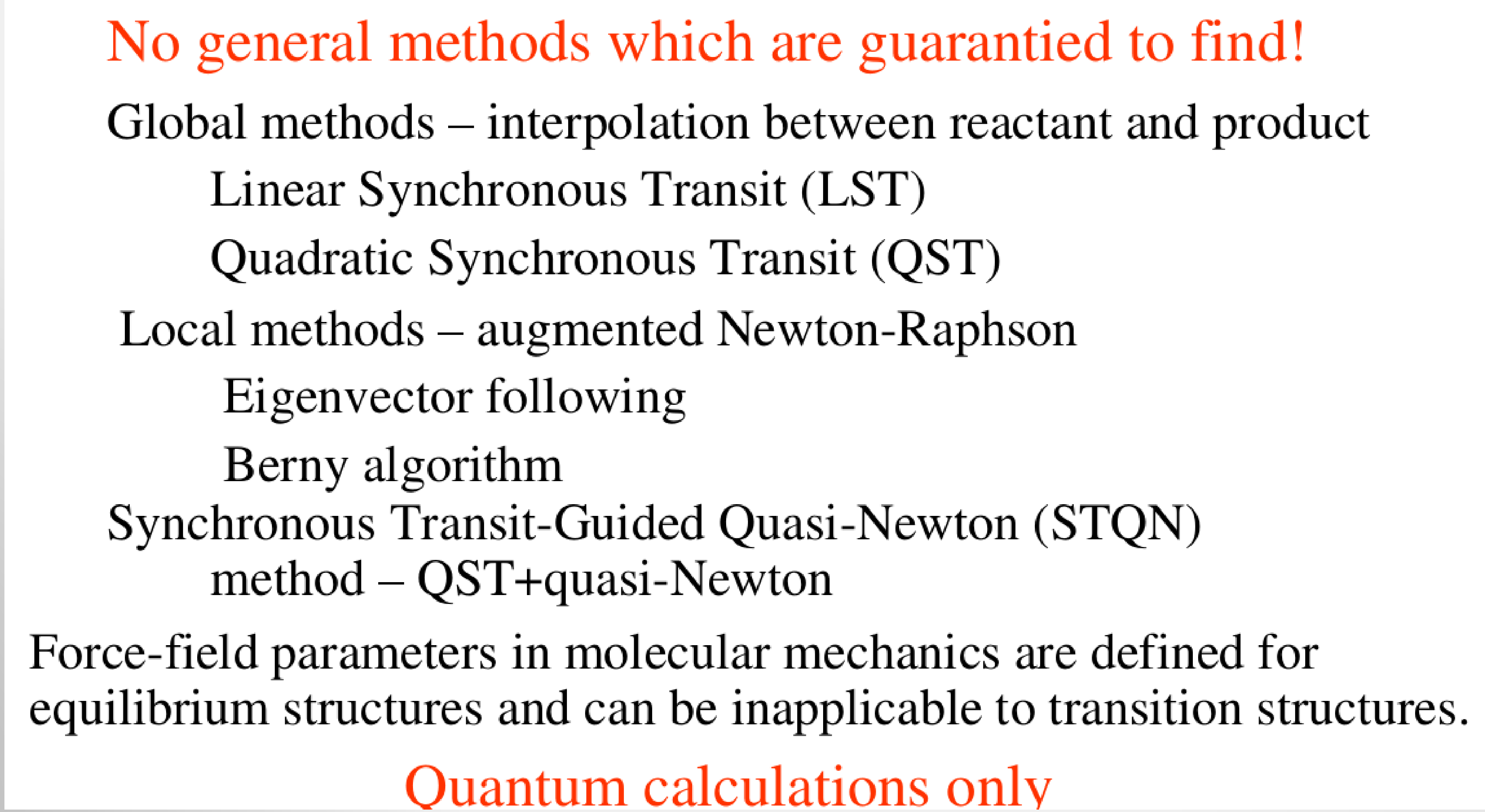


No general methods which are guarantied to find!

- Global methods – interpolation between reactant and product
  - Linear Synchronous Transit (LST)
  - Quadratic Synchronous Transit (QST)
- Local methods – augmented Newton-Raphson
  - Eigenvector following
  - Berny algorithm
- Synchronous Transit-Guided Quasi-Newton (STQN) method – QST+quasi-Newton

Force-field parameters in molecular mechanics are defined for equilibrium structures and can be inapplicable to transition structures.

Quantum calculations only

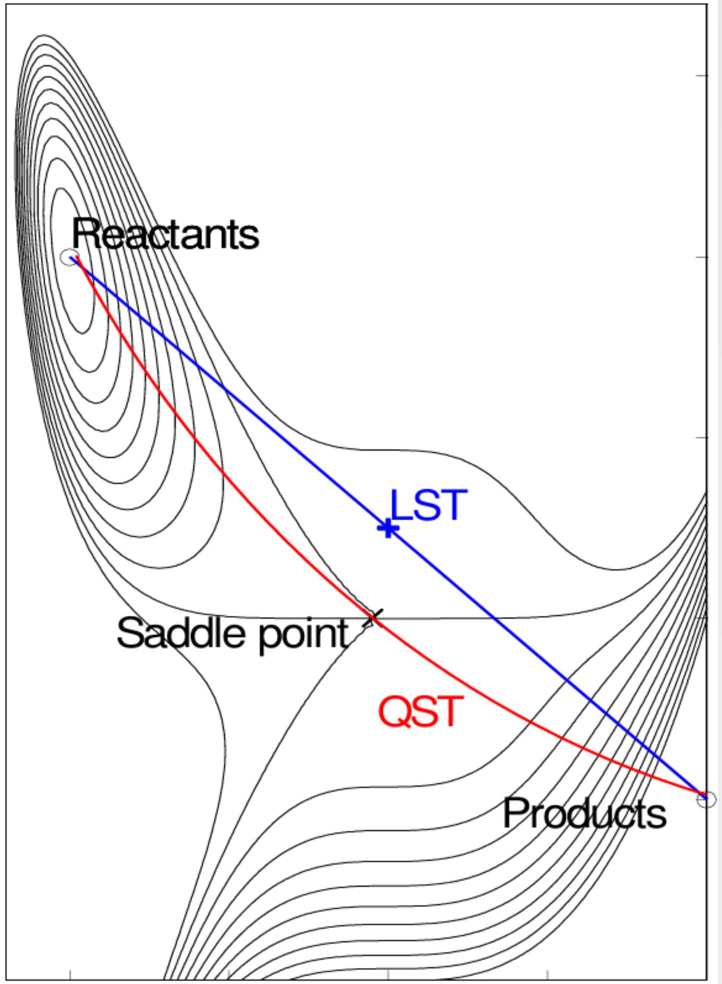
Reaction Mechanism by using Transition State Theory in Gaussian

Linear synchronous transit (LST)
- search for a maximum along a linear path between reactants and products

Quadratic synchronous transit (QST) - search for a maximum along an arc connecting reactants and products, and for a minimum in all directions perpendicular to the arc

Best case - the transition state is found.

General case – search is finished in a wrong saddle point or in a point with wrong number of negative eigenvalues (>1).



Thanks

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