Lecture 4

Molecular Vibrations

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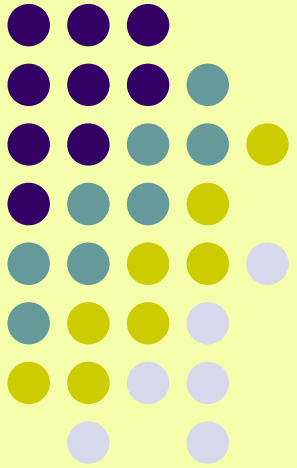
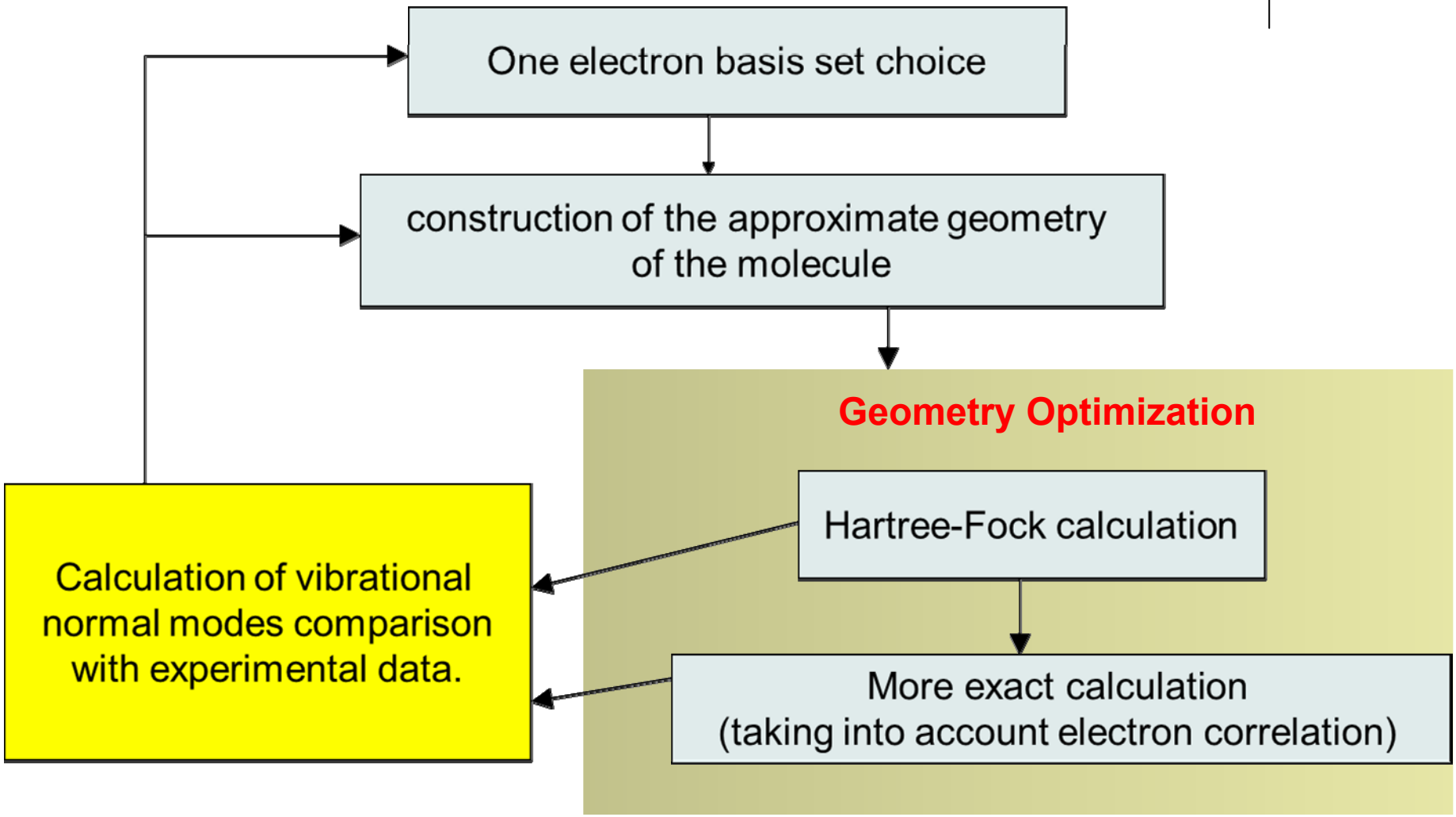
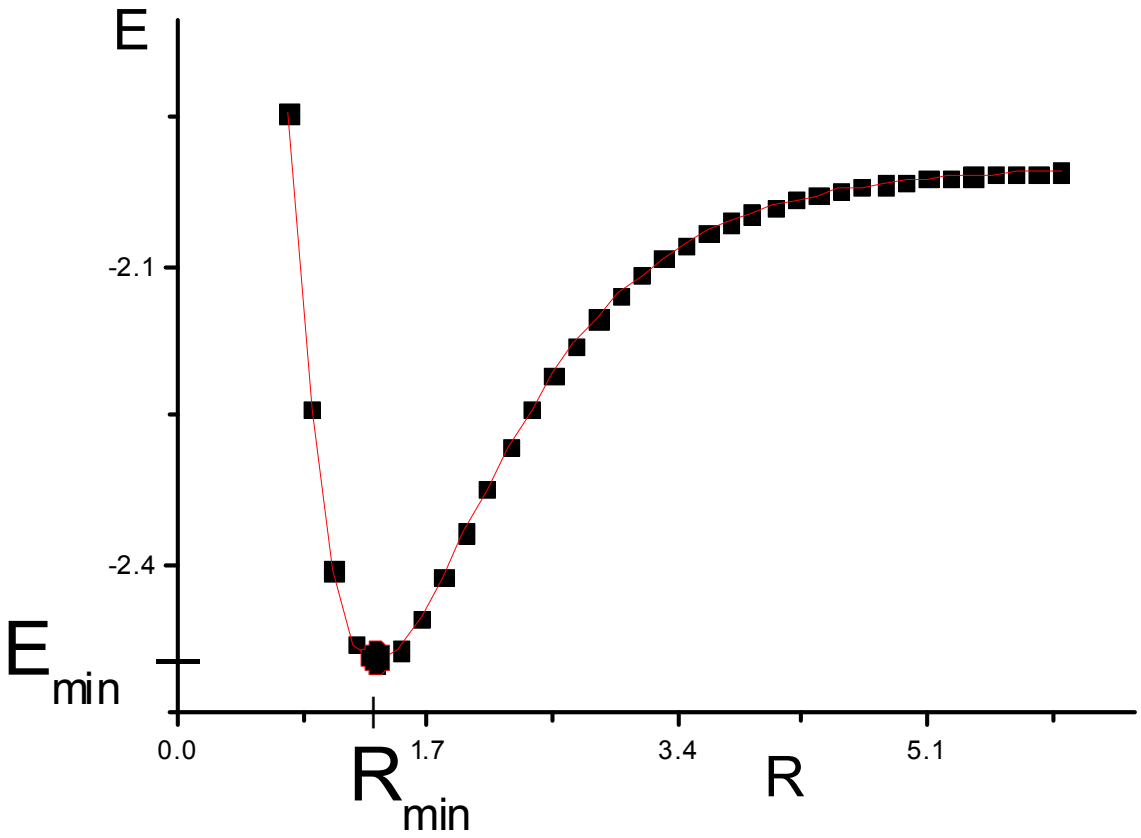


GAMESS, Avogadro, ChemCraft

A typical scheme of quantum chemical calculations (ab initio)



Potential Energy Surface (PES) concept



$$E(R=\infty)=E(A)+E(B)$$

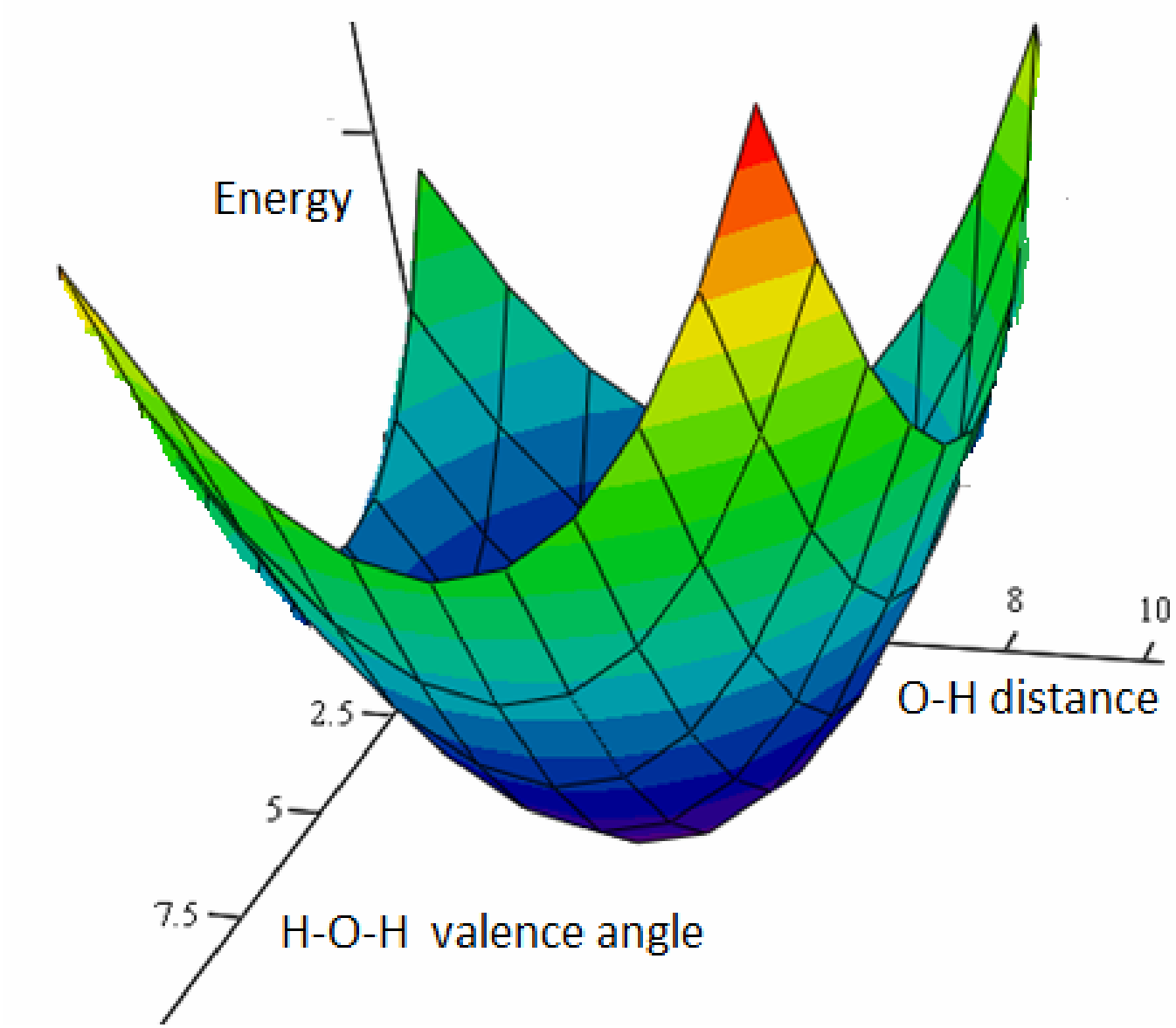
$$E(R_{min})=E_{min}$$

$$\left(\frac{dE}{dR}\right)_{R=R_{min}}=0$$

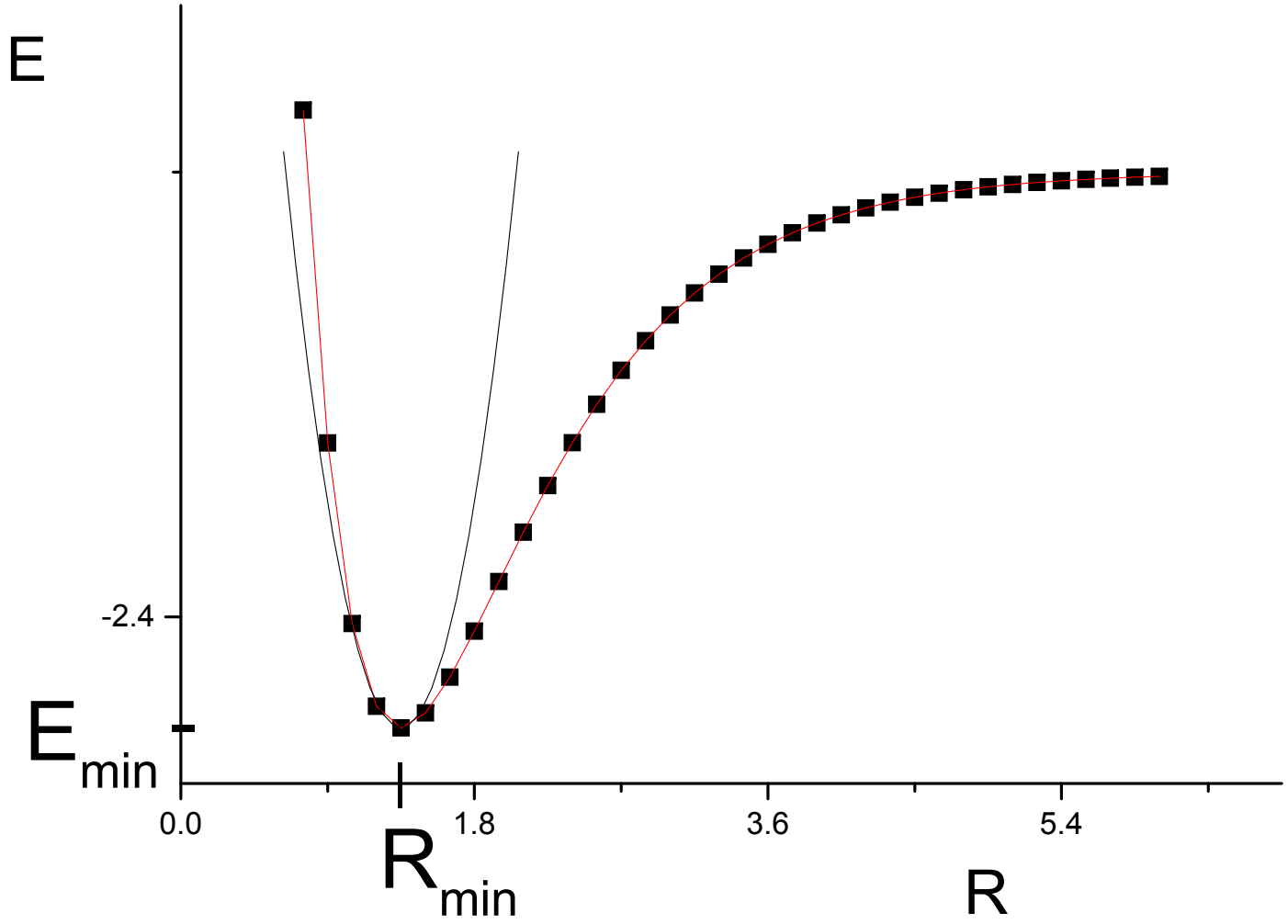
Force Constant

$$k=\left(\frac{d^2E}{dR^2}\right)_{R=R_{min}}>0$$

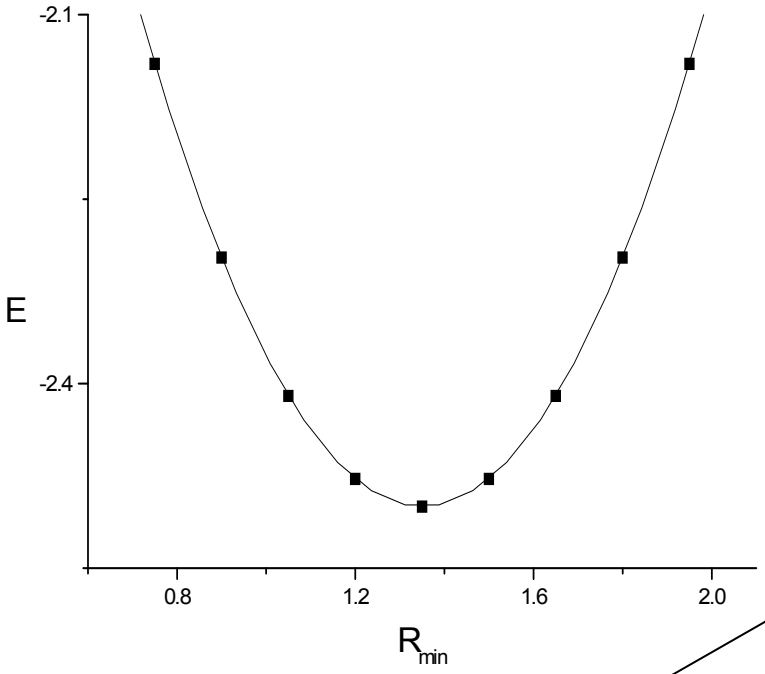
Potential Energy Surface (PES) for many-atomic systems



Harmonic Approximation
Dissociative curve of two atomic molecule



Harmonic approximation



$$q = R - R_{min}$$

$$E = k\frac{q^2}{2}$$

$$k = \left(\frac{d^2E}{dq^2}\right)_{R=R_{min}}$$

$$ma = F$$

$$m\ddot{q} = -kq$$ Hooke's Law:

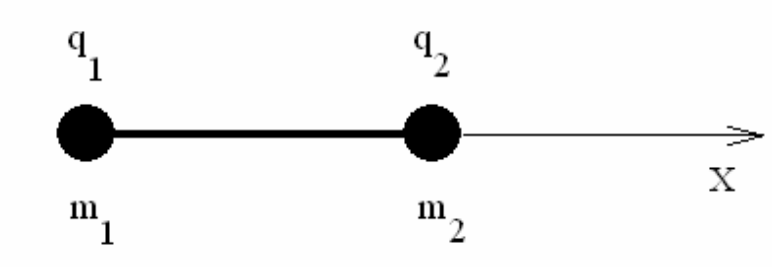
$$q(t) = \sin(\omega t + \theta)$$

ω-Frequency

Quantum task

Mechanical (classical) task,
«Small vibration theory»

Two atomic molecule vibrations in harmonic approximation



Hooke's Law: $\vec{F} = -k\,\vec{x}$

Si: N/m = kg/s²

CGS: Dyne/cm

[k]=[Force]/[displacement]

$$\begin{cases} m_1 \ddot{q}_1 = -k(q_1 - q_2) \\ m_2 \ddot{q}_2 = +k(q_1 - q_2) \end{cases}$$

Mass-weighted coordinates

$$q(t) = a\sin\left(\omega t + \theta\right)/\sqrt{m}$$

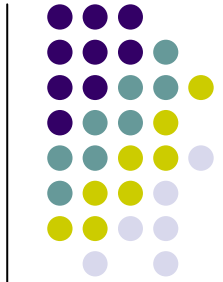
$$\begin{cases} -m_1\omega^2 q_1 = -kq_1 + kq_2 \\ -m_2\omega^2 q_2 = +kq_1 - kq_2 \end{cases}$$

$$\begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} \\ -\frac{k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \omega^2 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

Force Constant

Molecule	Frequency (cm^{-1})	k (10^5 dyne/cm)
H_2	4159.2	5.2
HF	3958.4	8.8
F_2	892	4.5
O_2	1556.3	11.4
N_2	2330.7	22.6
CO	2143.3	18.7
Li_2	246.3	1.3
NaCl	378	1.2
KCl	278	0.8

Vibrational Calculations



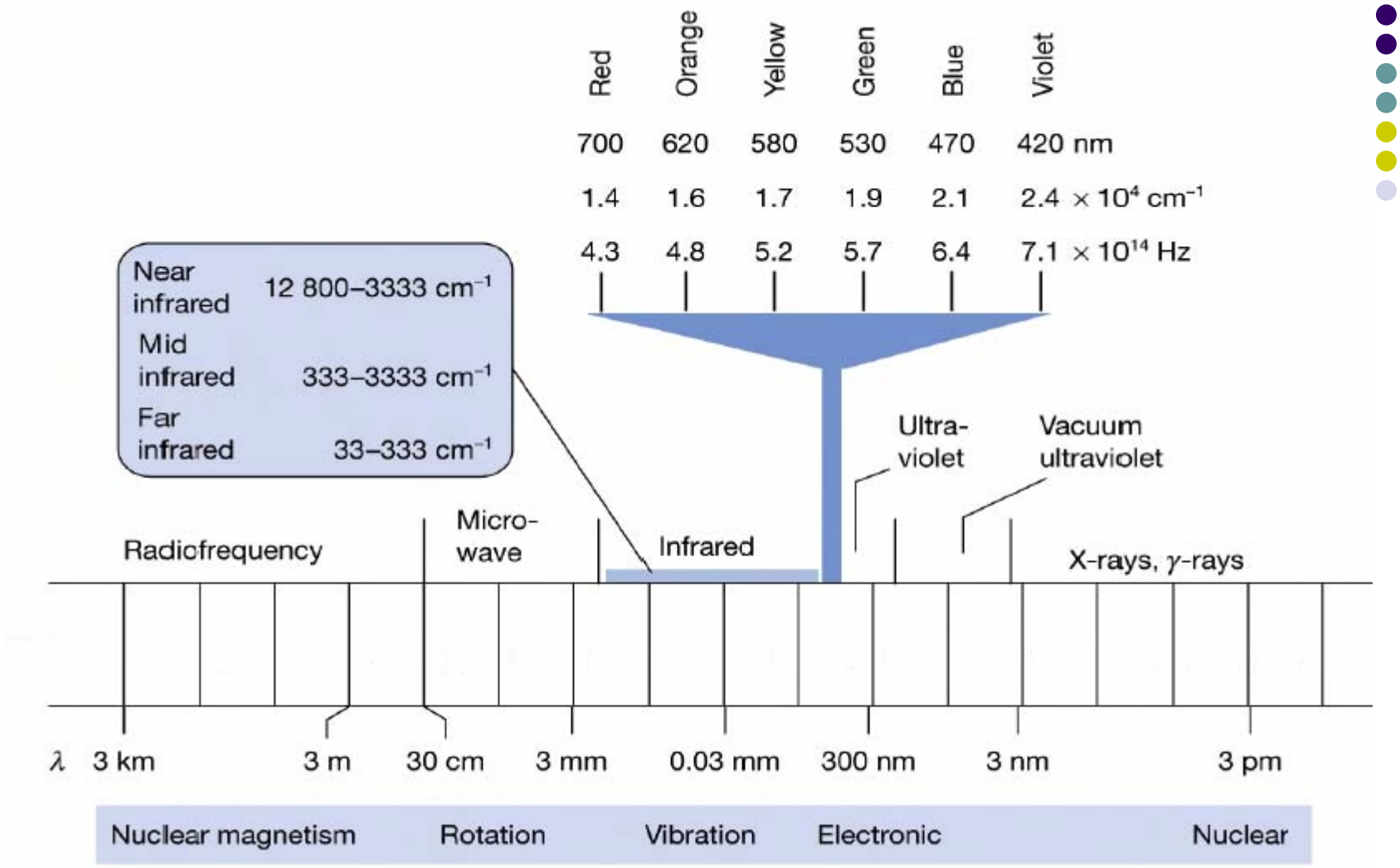
$$\begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} \\ -\frac{k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \omega^2 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

$$\begin{pmatrix} \frac{\partial^2 E}{\partial q_1^2} & \frac{\partial^2 E}{\partial q_1 \partial q_2} & \ldots\ldots & \frac{\partial^2 E}{\partial q_1 \partial q_{3N-6}} \\ \frac{\partial^2 E}{\partial q_2 \partial q_1} & \frac{\partial^2 E}{\partial q_2^2} & \ldots\ldots & \ldots\ldots \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ \frac{\partial^2 E}{\partial q_{3N-6} \partial q_1} & \ldots\ldots & \ldots\ldots & \frac{\partial^2 E}{\partial q_{3N-6}^2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \ldots \\ a_{3N-6} \end{pmatrix} = \omega^2 \begin{pmatrix} a_1 \\ a_2 \\ \ldots \\ a_{3N-6} \end{pmatrix}$$

$$H\,\vec{a} = \omega^2 \vec{a} \qquad \mathrm{a} = \sum_i^{3N-6} a_i q_i$$

a – forms of vibrations (Normal Modes)

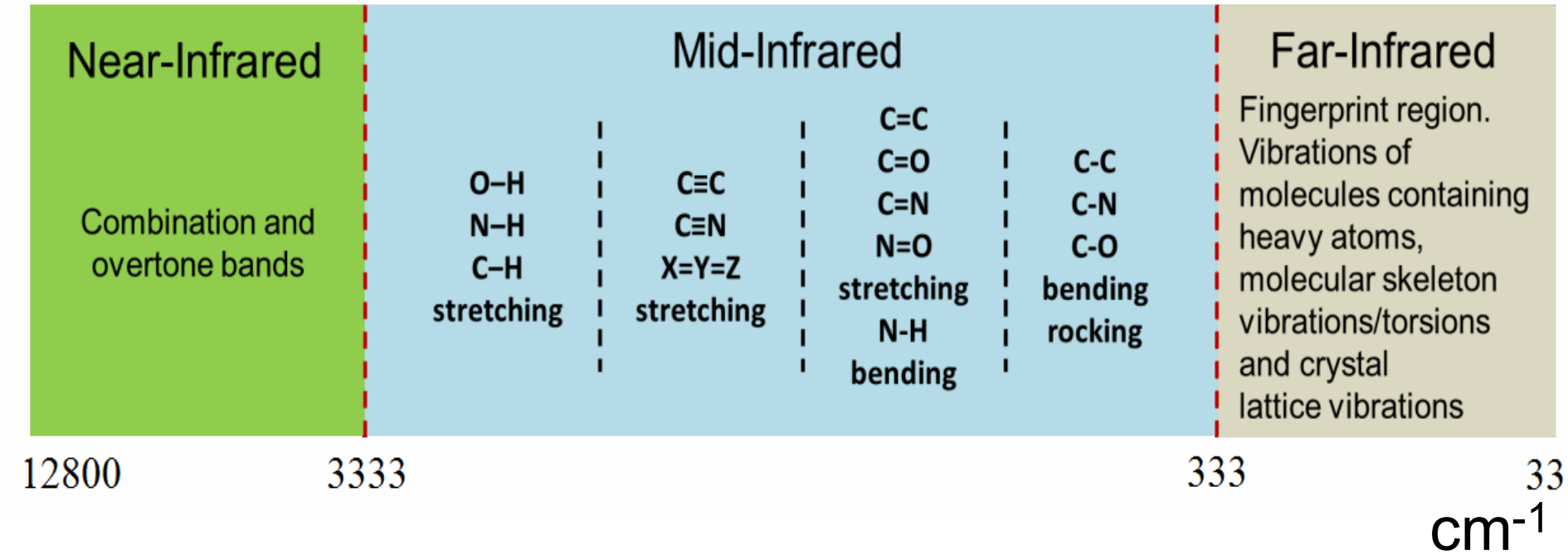
ω – **Frequency** or wave number is the number of wavelengths per unit distance, typically centimeters (cm^{-1}):



$$E = h\nu \qquad \lambda = c / \nu \qquad \tilde{\nu} = 1/\lambda \quad [\mathrm{cm^{-1}}]$$

1 nm $=10^{-9}$m [nm] = 10^{7} / [$\mathrm{cm^{-1}}$] 1 [eV]= 8065 [$\mathrm{cm^{-1}}$]

IR absorption regions

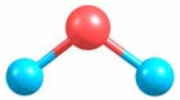


Types of Molecular Vibrations

- Valence: Stretching of bond
- Deformation of valence angle
  - Deformational Bending
  - Deformational Rocking
  - Deformational - scissor
- Dihedral

Totally vibrations for nonlinear molecule $3N-6$

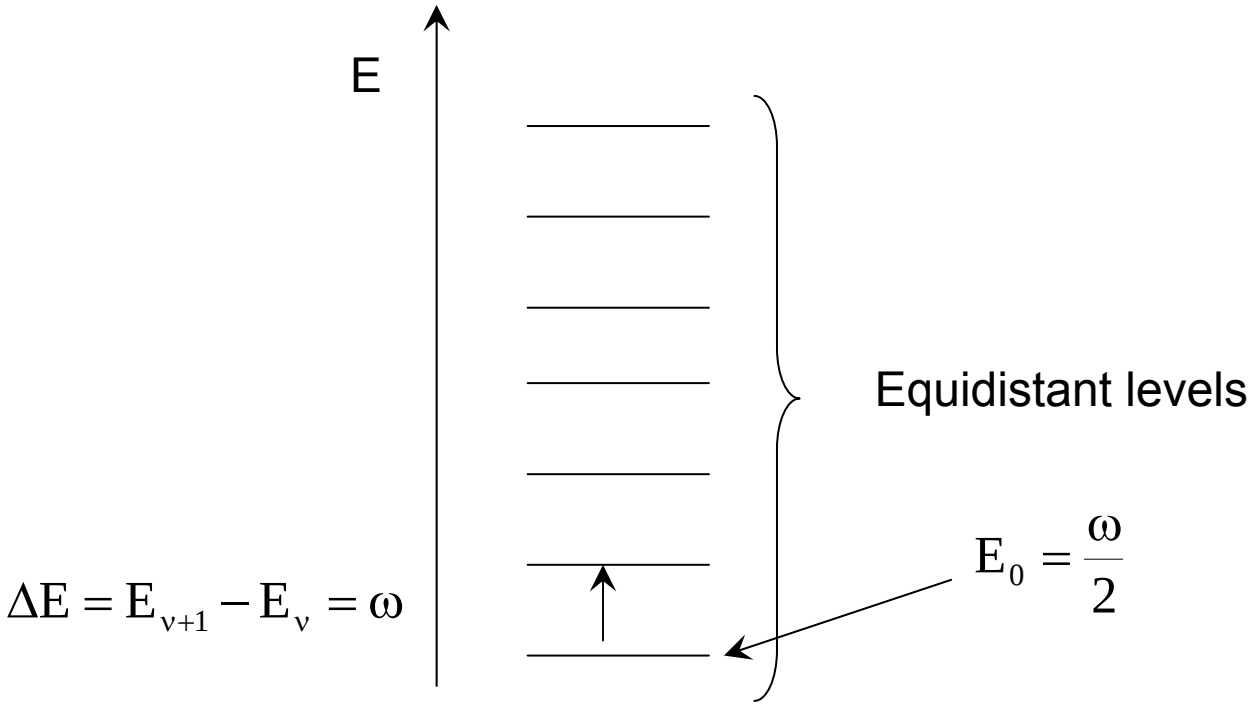
For the water molecule 3·3-6=3 vibrations

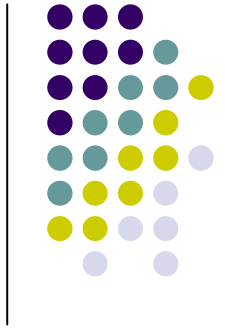




Quantum Theory of vibrations

$$E_\nu = \omega\left(\nu + \frac{1}{2}\right)$$ ν- Quantum Number

$$E_0 = \frac{\omega}{2}$$ Zero-point energy, ZPE





To be continued

Thermochemical calculations