



L6 – Classical Mechanics 2

Molecular mechanics: harmonic approximation and normal modes

Electrons

Schrödinger equation
(Born-Oppenheimer approximation)

$$(T_{elec}(\mathbf{r}) + V(\mathbf{r}, \mathbf{R}))\varphi_n(\mathbf{r}; \mathbf{R}) = E_n(\mathbf{R})\varphi_n(\mathbf{r}; \mathbf{R})$$



Quantum
chemistry

Nuclei

Nuclear Newton's equation
(Classical approximation)

$$M_\alpha \frac{d^2 \mathbf{R}_\alpha}{dt^2} = -\nabla_\alpha E_n(\mathbf{R})$$



Molecular
mechanics

Molecular
mechanics

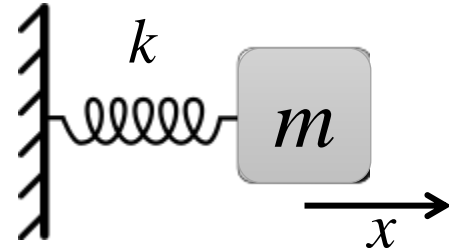
```
graph TD; A[Molecular mechanics] --> B[Normal mode analysis]; A --> C[Molecular dynamics];
```

Normal
mode
analysis

Molecular
dynamics

Harmonic approximation

Simple harmonic oscillator



$$F = -kx$$

$$m \frac{d^2 x}{dt^2} = F = -kx$$

$$x(t) = c \cos(\omega t + \varphi)$$

$$\omega = 2\pi f = \sqrt{\frac{k}{m}}$$



The initial conditions determine the amplitude c and the phase φ .

Hook's law

$$F = -kx$$

Hook's force is conservative

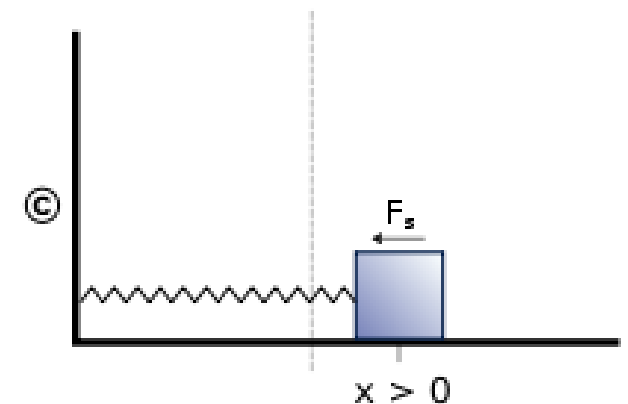
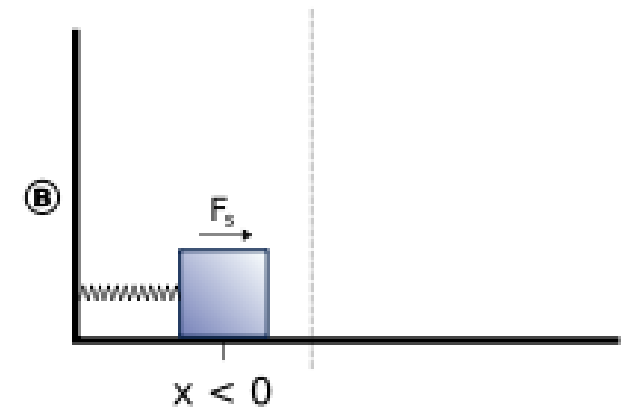
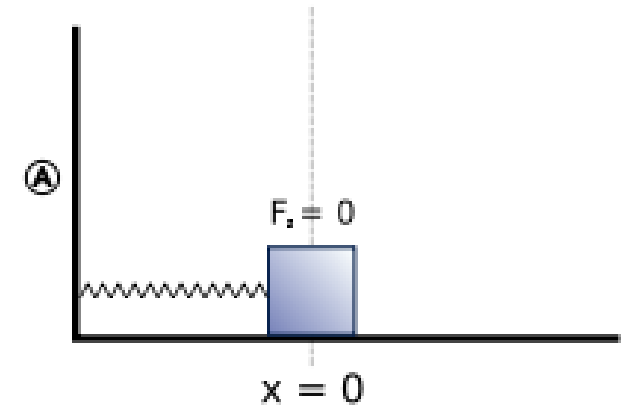
$$W_{\text{closed-circuit}} = 0$$

$$W_{\text{closed-circuit}} = W_{AB} + W_{BA}$$

$$= \int_A^B F(x) dx + \int_B^A F(x) dx$$

$$= -\int_A^B kx dx - \int_B^A kx dx$$

$$= -\left(\frac{kB^2}{2} - \frac{kA^2}{2}\right) - \left(\frac{kA^2}{2} - \frac{kB^2}{2}\right) = 0$$



Hook's law

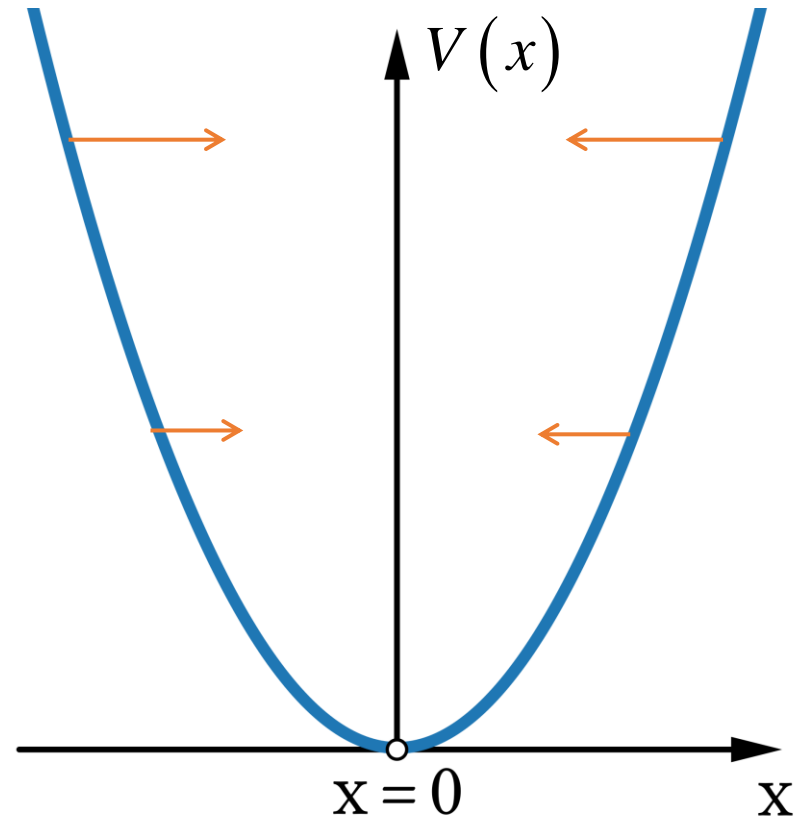
$$F = -kx$$

Harmonic potential energy

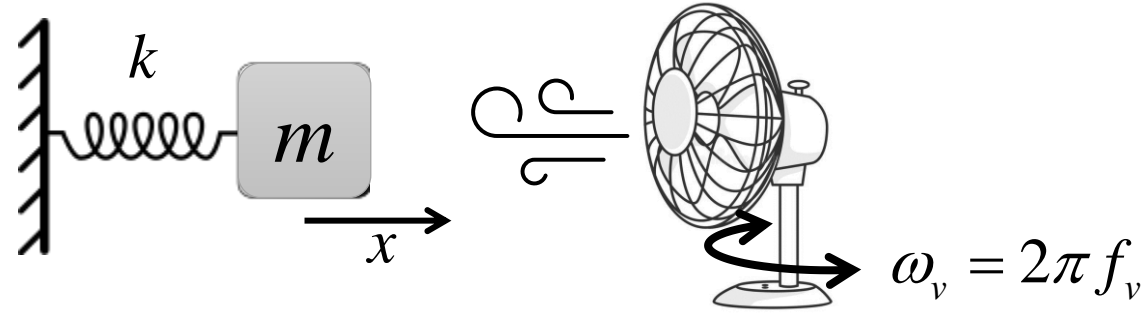
$$V(x) = \int F(x) dx = \frac{1}{2}kx^2$$

$$F(x) = -\frac{dV(x)}{dx} = -kx$$

$$V(x) = \frac{1}{2}kx^2$$



Forced (driven) harmonic oscillator



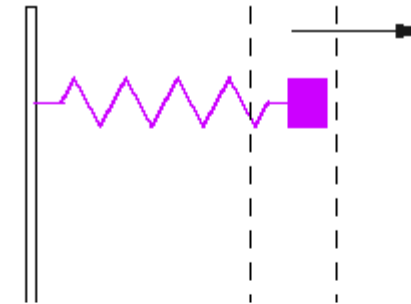
$$F = -kx + F_0 \cos(\omega_v t)$$

$$m \frac{d^2 x}{dt^2} = -kx + F_0 \cos(\omega_v t)$$

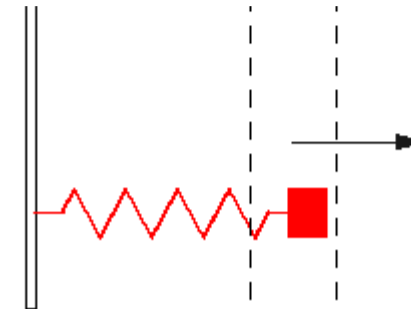
$$x(t) \rightarrow \frac{F_0}{m(\omega_0^2 - \omega_v^2)} \cos(\omega_v t + \varphi)$$

$$\omega_0 = \sqrt{\frac{k}{m}}$$

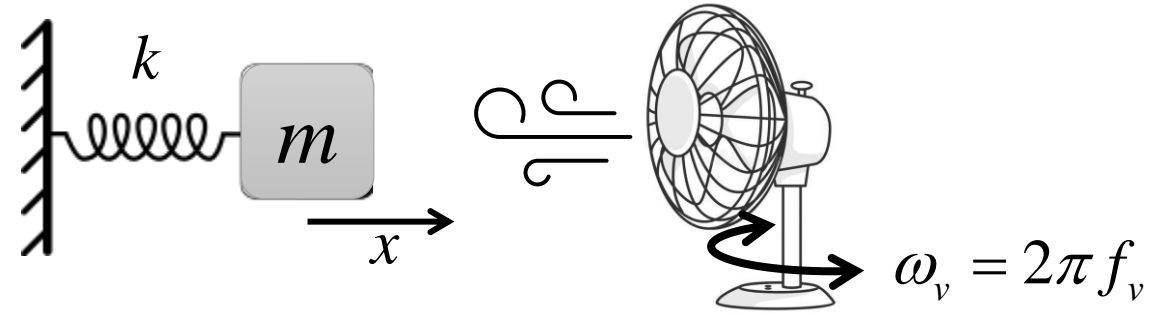
$$\omega_v < \omega_0$$



$$\omega_v > \omega_0$$



Forced (driven) harmonic oscillator



$$F = -kx + F_0 \cos(\omega_v t)$$

$$m \frac{d^2 x}{dt^2} = -kx + F_0 \cos(\omega_v t)$$

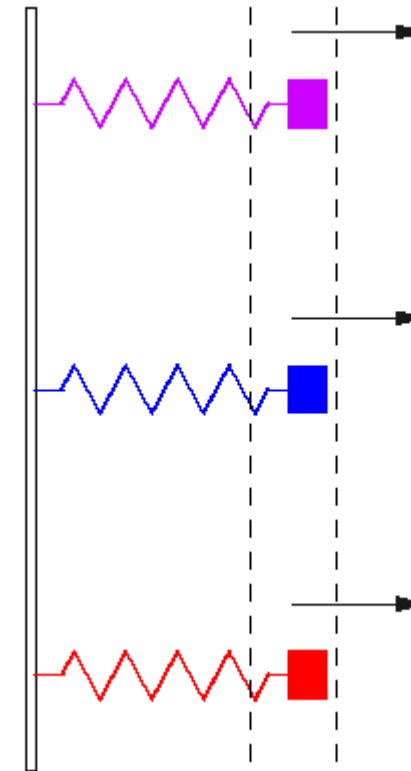
$$x(t) \rightarrow \frac{F_0}{m(\omega_0^2 - \omega_v^2)} \cos(\omega_v t + \varphi)$$

$$\omega_0 = \sqrt{\frac{k}{m}}$$

$$\omega_v < \omega_0$$

$$\omega_v = \omega_0$$

$$\omega_v > \omega_0$$



resonance



www.youtube.com/watch?v=XggxeuFDaDU

The harmonic approximation is the cornerstone of physical sciences

It's the basis for models in

- material engineering
- solid-state physics
- electrical engineering
- fluid dynamics
- electromagnetism
- molecular mechanics
- acoustics
- celestial mechanics
- statistical mechanics
- quantum mechanics
- quantum field theory
- string theory
- ...

It can be applied if the potential energy can be approximated to quadratic terms in the Taylor expansion around a minimum x_0

$$V(x - x_0) = V(x_0) + \underbrace{\frac{dV(x_0)}{dx}(x - x_0)}_{=0} + \frac{1}{2} \frac{d^2V(x_0)}{dx^2} (x - x_0)^2 + O[(x - x_0)^3]$$

Choosing $x_0 = 0$ and $V(x_0) = 0$

$$V(x) \approx \frac{1}{2} \underbrace{\frac{d^2V(0)}{dx^2}}_k x^2$$

For multidimensional systems

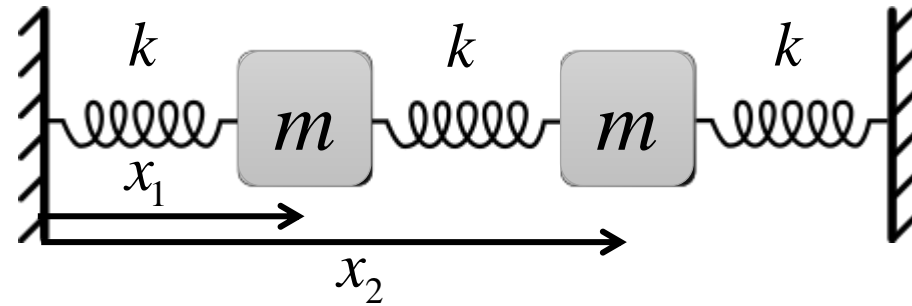
$$V(\mathbf{R}) \approx \underset{\text{choose } = 0}{V(0)} + \sum_n \underbrace{\left(\frac{\partial V(0)}{\partial R_n} \right)}_{=0} R_n + \frac{1}{2} \sum_{j,n} R_j \underbrace{\left(\frac{\partial^2 V(0)}{\partial R_j \partial R_n} \right)}_{\text{Hessian}} R_n$$
$$= \frac{1}{2} \sum_{j,n} R_j H_{jn}(0) R_n$$

Then, we search for a new set of coordinates \mathbf{Q} that decouples the system into a sum of independent simple harmonic oscillators.

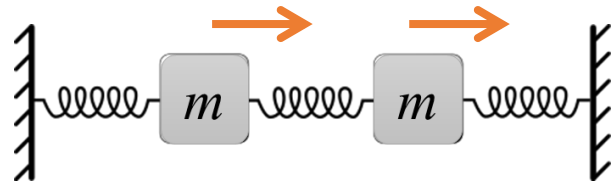
$$V(\mathbf{Q}) \approx \frac{1}{2} \sum_j \mu_j \omega_j Q_j^2$$

Normal modes in a system of particles

Coupled harmonic oscillators

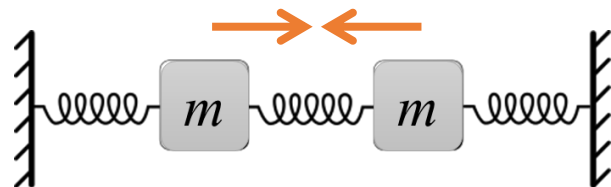


The oscillations normal to each other are



$$f_1 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$\mathbf{Q}_1 = \begin{pmatrix} x_1(t) \\ x_2(t) \end{pmatrix} = c_1 \begin{pmatrix} 1 \\ 1 \end{pmatrix} \cos(\omega_1 t + \varphi_1)$$



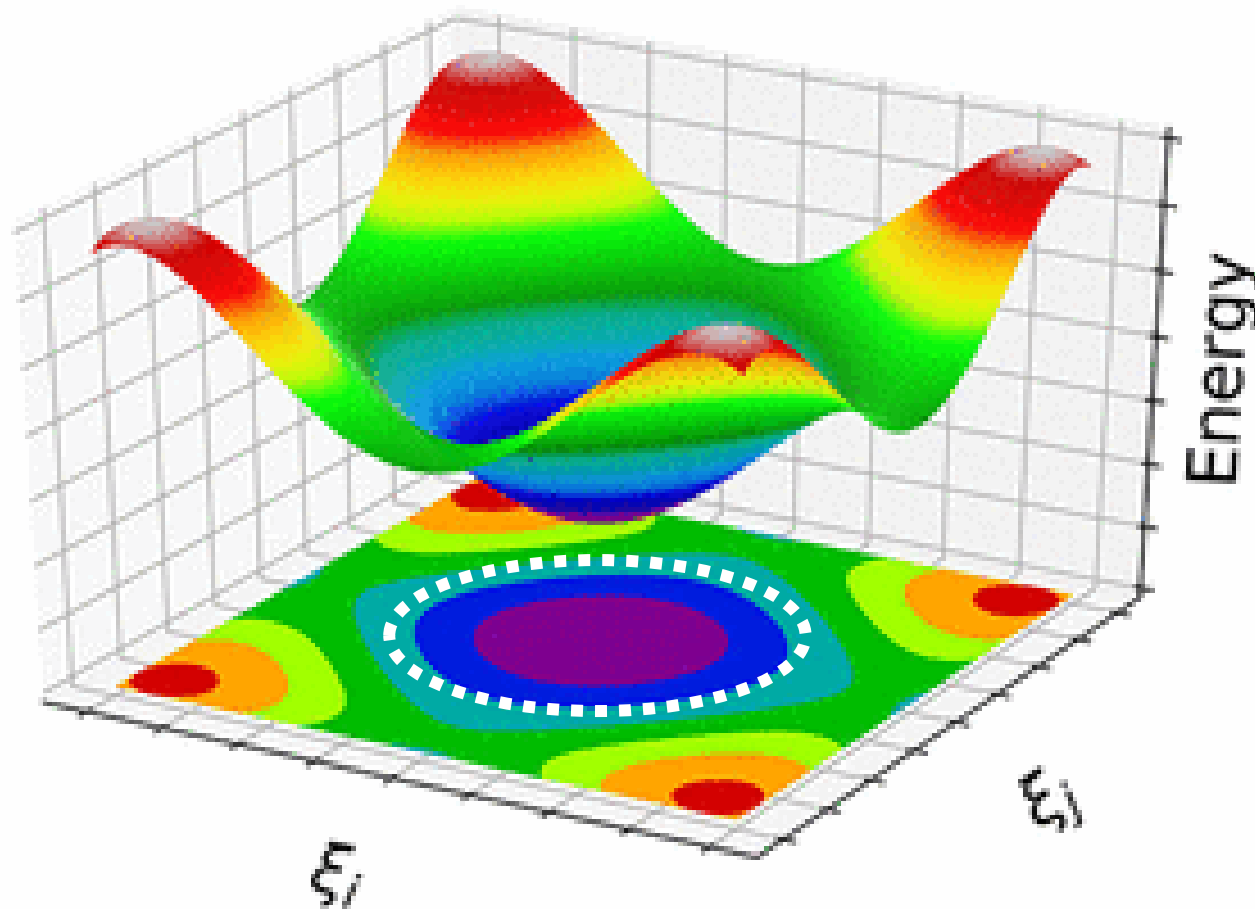
$$f_2 = \frac{1}{2\pi} \sqrt{\frac{3k}{m}}$$

$$\mathbf{Q}_2 = \begin{pmatrix} x_1(t) \\ x_2(t) \end{pmatrix} = c_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix} \cos(\omega_2 t + \varphi_2)$$

The initial conditions determine the amplitude c_i and the phase φ_i .

The most basic approximation used to describe the nuclear motion is to treat the Born-Oppenheimer potential energy surface in a **harmonic approximation** around the minimum.

Then, we look for a set of coordinates where the vibrations are **independent** of each other (they are **normal** to each other).



We start from the usual Cartesian coordinates \mathbf{R} and approximate the PES to second order

$$E^{(H)}(\mathbf{R}) \approx \underbrace{E(\mathbf{R}_{\min})}_{\text{choose} = 0} + \sum_n \underbrace{\left(\frac{\partial E(\mathbf{R}_{\min})}{\partial R_n} \right)}_{=0} R_k + \frac{1}{2} \sum_{j,n} R_j \underbrace{\left(\frac{\partial^2 E(\mathbf{R}_{\min})}{\partial R_j \partial R_n} \right)}_{\text{Hessian}} R_n$$
$$= \frac{1}{2} \sum_{j,n} R_j H_{jn}^{(\text{Cart})} R_n$$

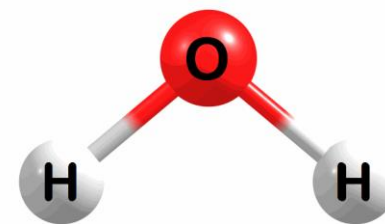
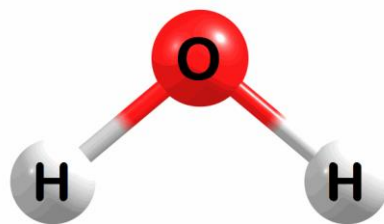
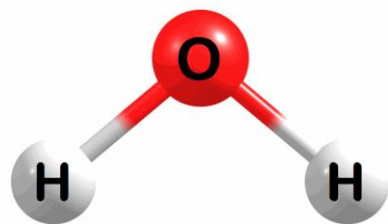
Then we search for normal coordinates (or modes) \mathbf{Q} where

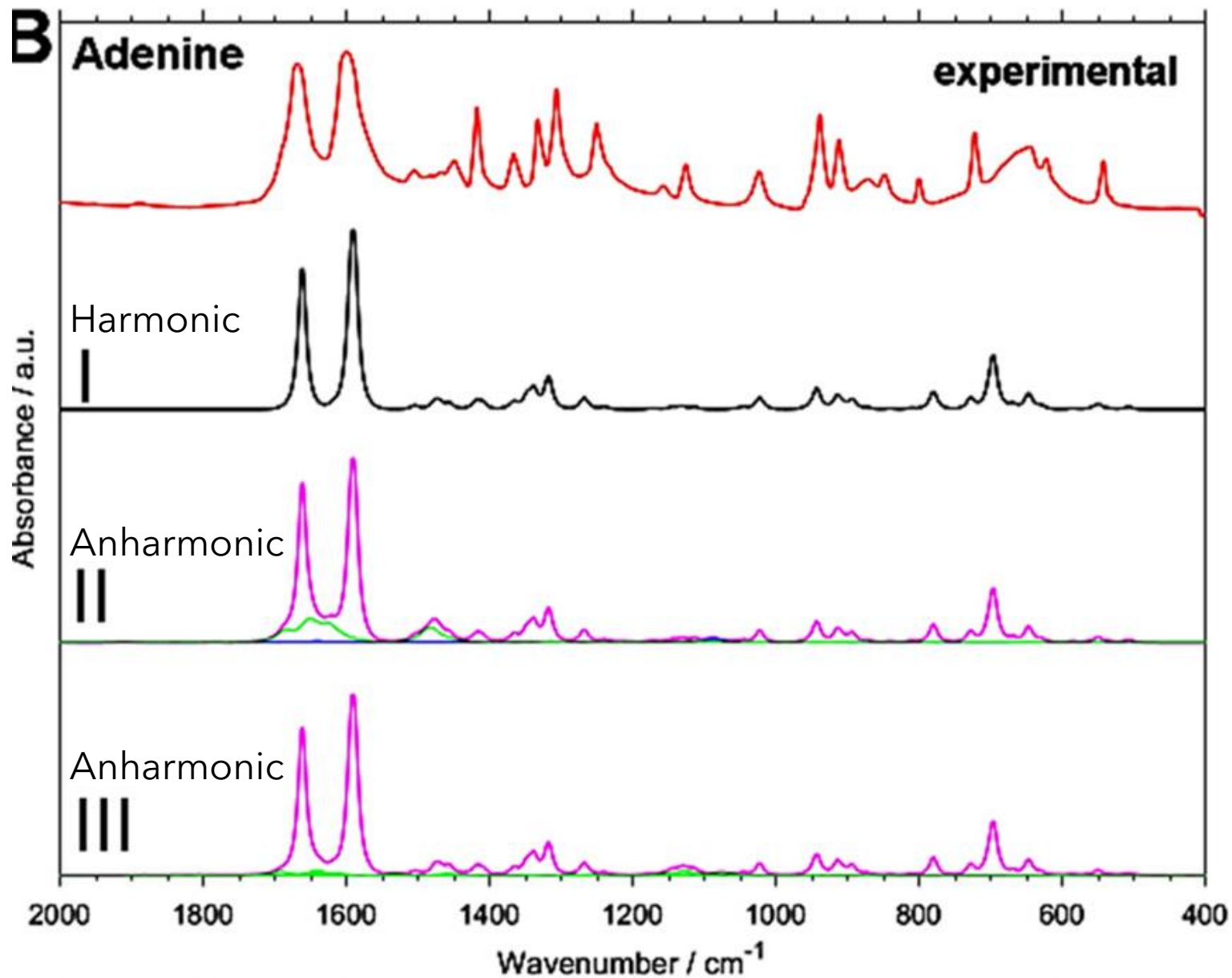
$$E^{(H)}(\mathbf{Q}) \approx \frac{1}{2} \sum_j \mu_j \omega_j Q_j^2$$

The molecule is approximated as a collection of independent $3N-6$ vibrations with frequencies

$$f_i = \frac{\omega_j}{2\pi}$$

of a mass μ_i along Q_i .





Molecules behave as independent harmonic oscillators, as IR spectra reveal.

How are molecular normal modes and frequencies computed?

To compute normal modes and its frequencies, we start from

$$E(\mathbf{R}) \approx \frac{1}{2} \sum_{j,n} R_j H_{jn}^{(Cart)} R_n$$

Cartesian Hessian matrix

$$\mathbf{H}^{(Cart)} = \begin{pmatrix} \frac{\partial^2 E}{\partial X_1 \partial X_1} & \frac{\partial^2 E}{\partial X_1 \partial Y_1} & \dots & \frac{\partial^2 E}{\partial X_1 \partial Z_{Nat}} \\ \frac{\partial^2 E}{\partial Y_1 \partial X_1} & \frac{\partial^2 E}{\partial Y_1 \partial Y_1} & \dots & \frac{\partial^2 E}{\partial Y_1 \partial Z_{Nat}} \\ \vdots & \vdots & \dots & \vdots \\ \frac{\partial^2 E}{\partial Z_{Nat} \partial X_1} & \frac{\partial^2 E}{\partial Z_{Nat} \partial Y_1} & \dots & \frac{\partial^2 E}{\partial Z_{Nat} \partial Z_{Nat}} \end{pmatrix}$$

Compute mass-weighted Hessian matrix

$$H_{\alpha\beta}^{(MWC)} = \frac{H_{\alpha\beta}^{(Cart)}}{\sqrt{M_{\alpha}M_{\beta}}}$$

Compute mass-weighted coordinates

$$\mathbf{q}^{(MWC)} = \sqrt{M_{\alpha}} \mathbf{R}_{\alpha}$$

Determine center of mass

$$\mathbf{R}_{CM} = \frac{1}{M} \sum_{\alpha} M_{\alpha} \mathbf{R}_{\alpha}$$

Displace to CM reference

$$\mathbf{r}_{\alpha} = \mathbf{R}_{\alpha} - \mathbf{R}_{CM}$$

Compute the **moment of inertia tensor**

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} = \begin{pmatrix} \sum_{\alpha} M_{\alpha} (y_{\alpha}^2 + z_{\alpha}^2) & -\sum_{\alpha} M_{\alpha} x_{\alpha} y_{\alpha} & -\sum_{\alpha} M_{\alpha} x_{\alpha} z_{\alpha} \\ -\sum_{\alpha} M_{\alpha} y_{\alpha} x_{\alpha} & \sum_{\alpha} M_{\alpha} (x_{\alpha}^2 + z_{\alpha}^2) & -\sum_{\alpha} M_{\alpha} y_{\alpha} z_{\alpha} \\ -\sum_{\alpha} M_{\alpha} z_{\alpha} x_{\alpha} & -\sum_{\alpha} M_{\alpha} z_{\alpha} y_{\alpha} & \sum_{\alpha} M_{\alpha} (x_{\alpha}^2 + y_{\alpha}^2) \end{pmatrix}$$

Diagonalize it

$$\mathbf{I}' = \mathbf{X}^{\dagger} \mathbf{I} \mathbf{X}$$

Create a mass-weighted Cartesian to internal coordinates transformation matrix **D**

- Generate 3 translation vectors
- Generate 3 global rotation vectors
- Generate other $3N - 6$ vectors with Schmidt orthogonalization

Transform mass-weighted Cartesian coordinates to internal coordinates

$$\mathbf{Q}^{(Int)} = \mathbf{D}\mathbf{q}^{(MWC)}$$

Transform Hessian to internal coordinates

$$\mathbf{H}^{(Int)} = \mathbf{D}^\dagger \mathbf{H}^{(MWC)} \mathbf{D}$$

Diagonalize it

$$\mathbf{\Lambda} = \mathbf{L}^\dagger \mathbf{H}^{(Int)} \mathbf{L}$$

Frequencies and normal modes

Frequencies

$$f_i = \sqrt{\frac{\lambda_i}{4\pi^2 c^2}}$$

Force constants

$$k_i = 4\pi^2 f_i^2 c^2 \mu_i$$

Cartesian displacements

$$Q_{ni}^{(Cart)} = \sum_{j=1}^{3N} \left(\frac{D_{nj} L_{ji}}{\sqrt{M_n}} \right)$$

Reduced masses

$$\mu_i = \left(\sum_n \left(Q_{ni}^{(Cart)} \right)^2 \right)^{-1}$$

Try it yourself:

envision.entos.ai

(If you still don't have an account, you must sign up with your AMU email.)

Most quantum chemical programs allow to compute molecular normal modes.

Hessian matrices can be computed analytically (fast) or numerically (slow).

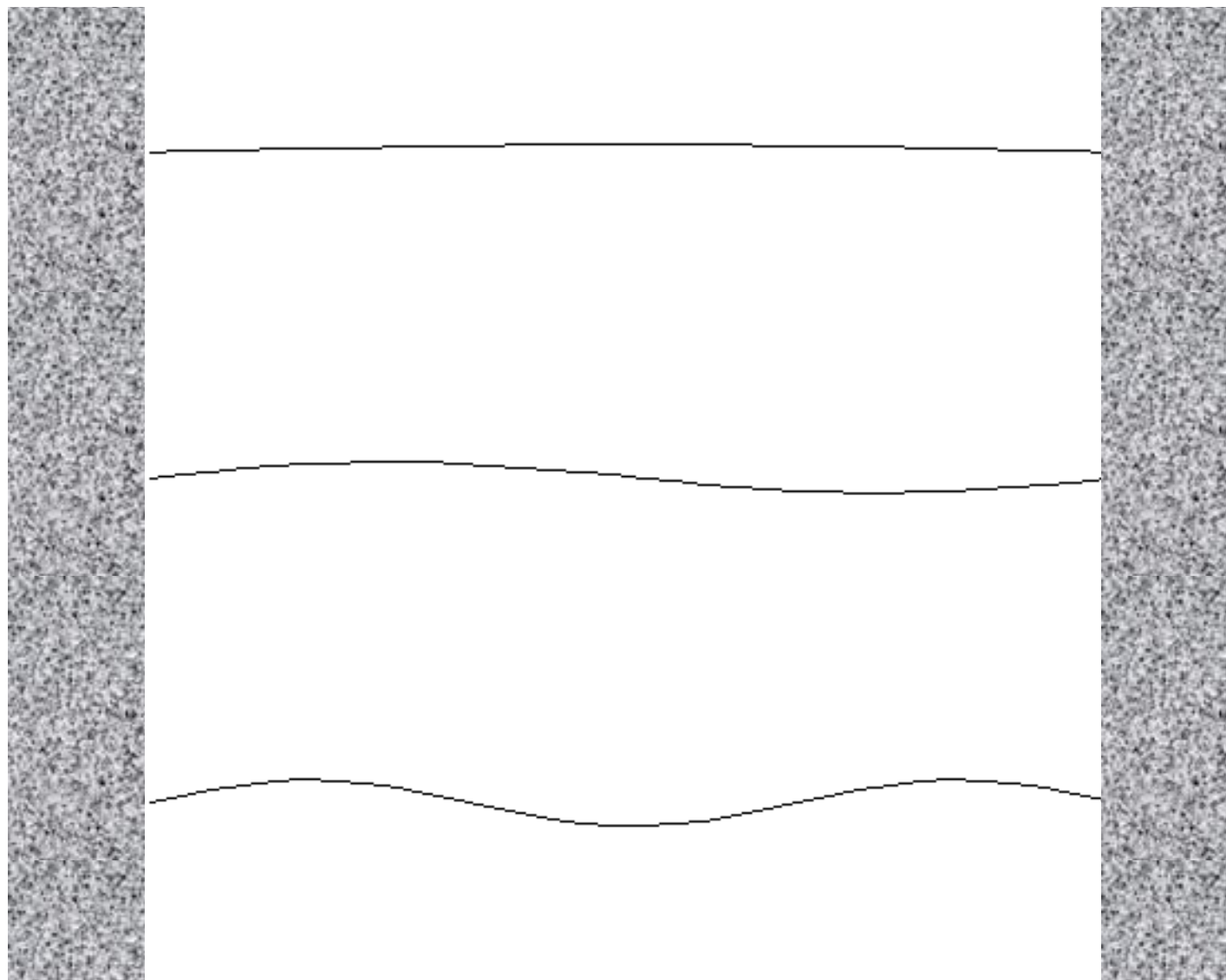
Gamess software contains VSCF method for anharmonic corrections.

Normal modes in a continuous medium

We may replace the atomistic for a continuous description if the material is large enough.

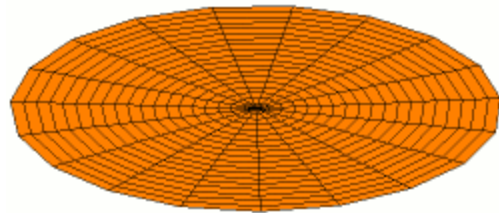
Then, this continuum's vibrational modes form the basis for describing wave and phonon propagation.

A few vibrational modes of a string with fixed ends.

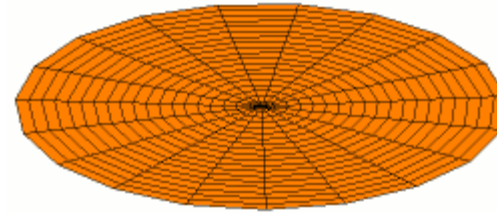


A few vibrational modes of a circular membrane with fixed perimeter

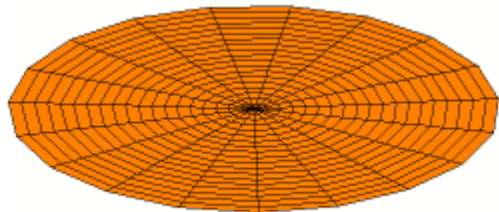
(0,1) mode (1s)



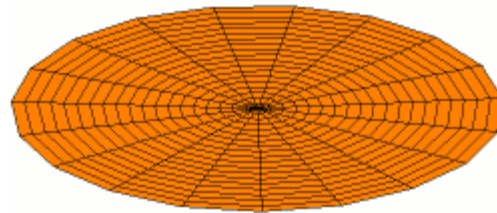
(0,2) mode (2s)



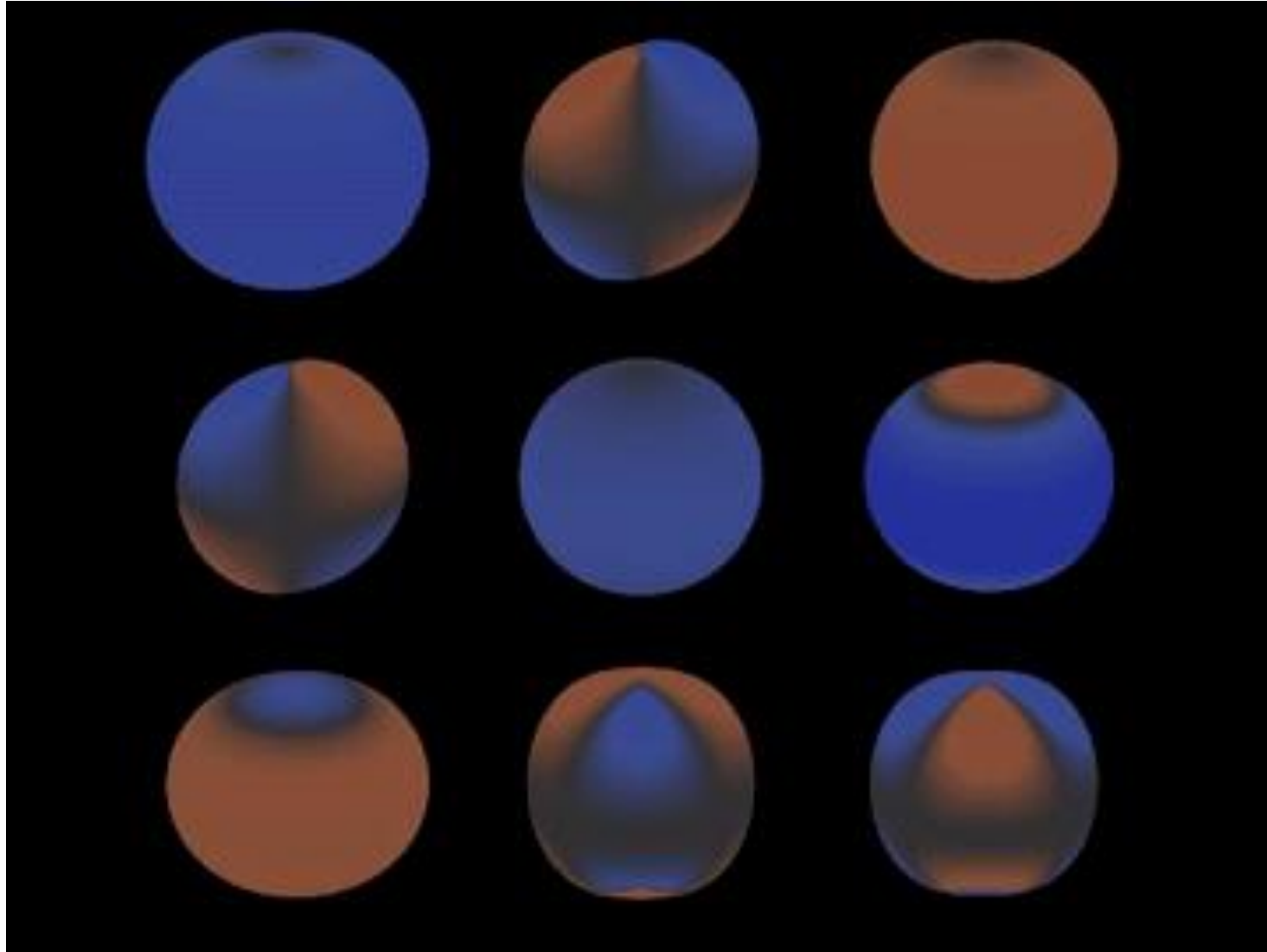
(1,1) mode (2p)




(2,1) mode (3d)



A few vibrational modes of a sphere



youtu.be/rQkciLCmnPk

A large, semi-transparent red sphere is centered on a black background. Inside the sphere, the text "Heat & Sound" is written in white, sans-serif font. A thin white horizontal line is positioned below "Heat & Sound", and the word "Phonon" is written in a larger, bold, white, sans-serif font below the line.

Heat & Sound

Phonon

fb.watch/IXg8-6oTAn/

Spin-boson PES

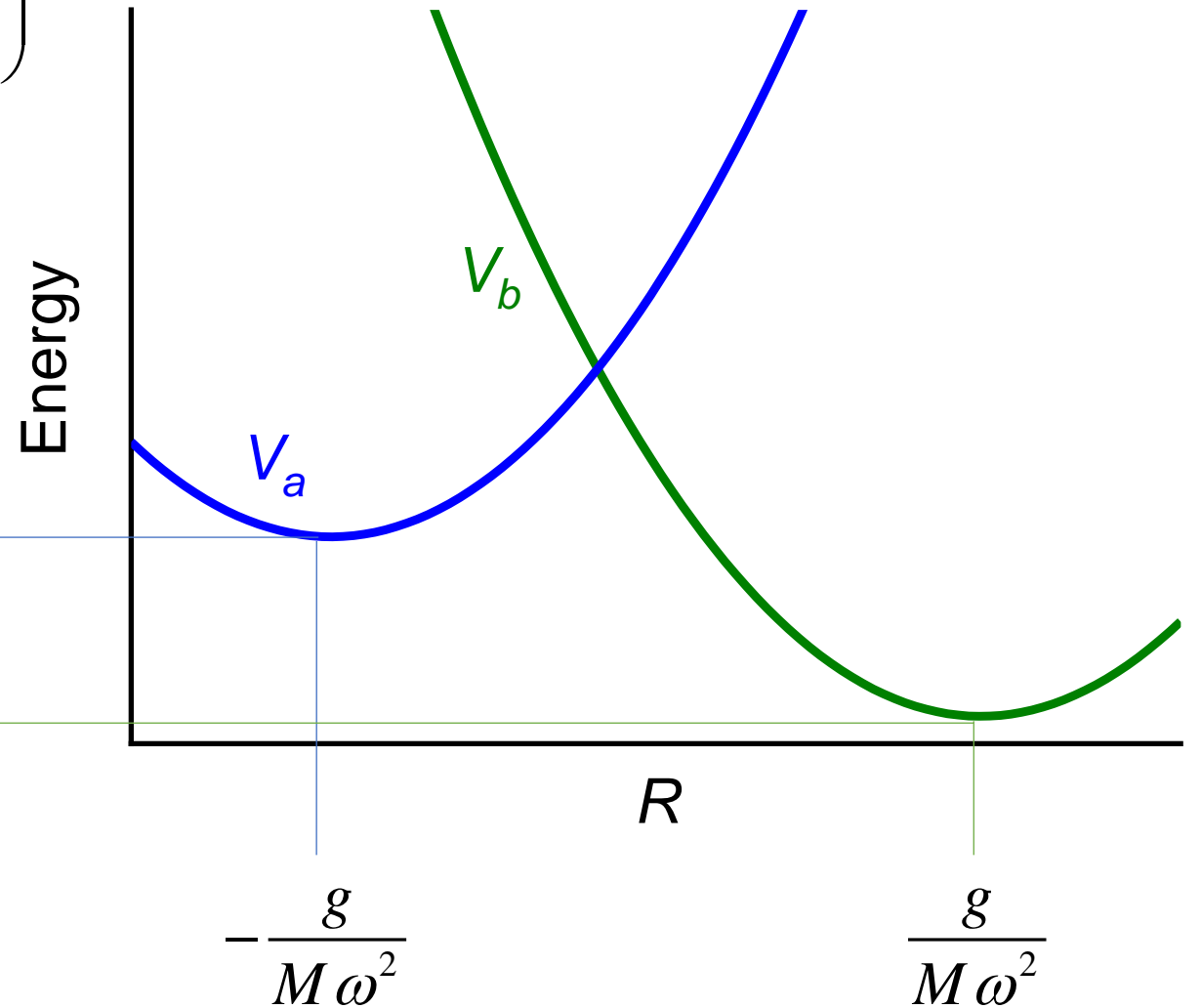
$$V_a(R) = \left(\varepsilon_0 - \frac{1}{2} \frac{g^2}{M \omega^2} \right) + \frac{1}{2} M \omega^2 \left(R + \frac{g}{M \omega^2} \right)^2$$

$$V_b(R) = \left(-\varepsilon_0 - \frac{1}{2} \frac{g^2}{M \omega^2} \right) + \frac{1}{2} M \omega^2 \left(R - \frac{g}{M \omega^2} \right)^2$$

$$V_{ab} = -v_0$$

$$\left(\varepsilon_0 - \frac{1}{2} \frac{g^2}{M \omega^2} \right)$$

$$\left(-\varepsilon_0 - \frac{1}{2} \frac{g^2}{M \omega^2} \right)$$



N -dimensional model of a two-state system coupled to a harmonic bath.

$$V_a(\mathbf{R}) = \sum_{j=1}^N \left[\left(\varepsilon_0 - \frac{1}{2} \frac{g_j^2}{M_j \omega_j^2} \right) + \frac{1}{2} M_j \omega_j^2 \left(R_j + \frac{g_j}{M_j \omega_j^2} \right)^2 \right]$$

$$V_b(\mathbf{R}) = \sum_{j=1}^N \left[\left(-\varepsilon_0 - \frac{1}{2} \frac{g_j^2}{M_j \omega_j^2} \right) + \frac{1}{2} M_j \omega_j^2 \left(R_j - \frac{g_j}{M_j \omega_j^2} \right)^2 \right]$$

$$V_{ab} = -v_0$$

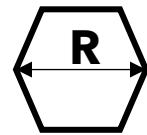
Leggett et al. *Rev Mod Phys* **1987**, 59, 1

Chen; Reichman. *J Chem Phys* **2016**, 144, 094104

\mathbf{V} is a diabatic representation of the potential energy surface.

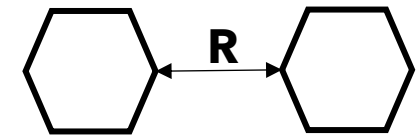
$$\mathbf{V}(\mathbf{R}) = \begin{bmatrix} V_a(\mathbf{R}) & -V_0 \\ -V_0 & V_b(\mathbf{R}) \end{bmatrix}$$

It is useful to build models because \mathbf{V} is written by coupling independent parts.



Molecular model

- Energies of specific states
- Couplings



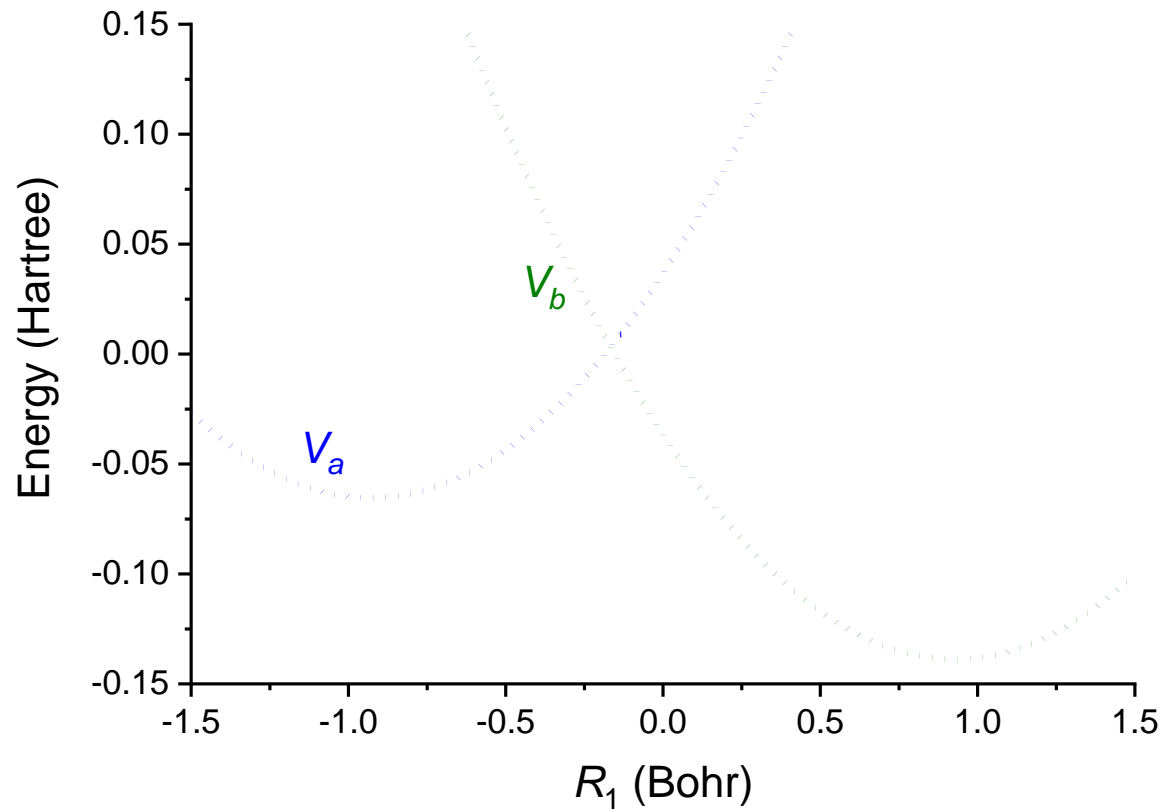
Supramolecular model

- Site energies
- Couplings

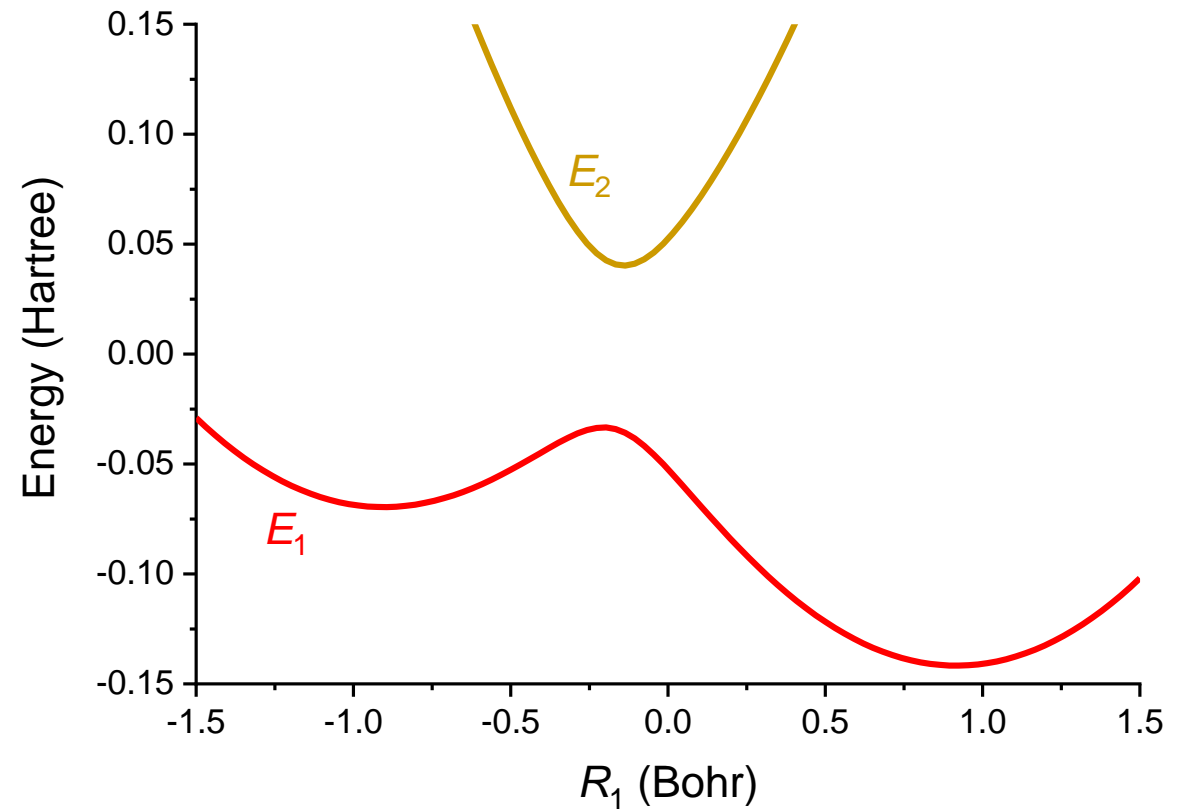
Diagonal terms

Off-diagonal terms

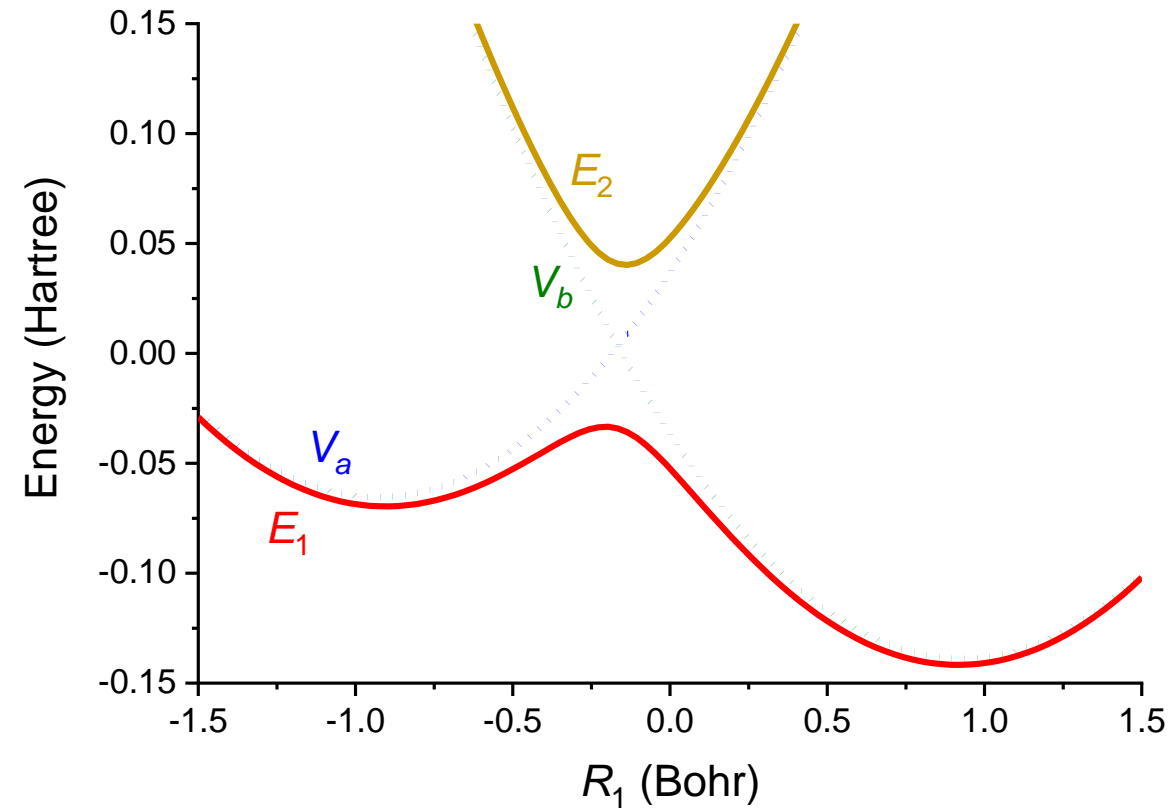
Diabatic representation \mathbf{V} is not a solution of the electronic Schrödinger equation



A solution of the electronic Schrödinger equation is the adiabatic representation \mathbf{E}



The two representations are related



The adiabatic representation \mathbf{E} is obtained by searching the eigenvalues of the diabatic representation \mathbf{V}

$$\mathbf{E}(\mathbf{R}) = \mathbf{D}^{-1} \mathbf{V}(\mathbf{R}) \mathbf{D}$$

$$\mathbf{V}(\mathbf{R}) = \begin{bmatrix} V_a(\mathbf{R}) & -\nu_0 \\ -\nu_0 & V_b(\mathbf{R}) \end{bmatrix} \longrightarrow \mathbf{E}(\mathbf{R}) = \begin{bmatrix} E_1(\mathbf{R}) & 0 \\ 0 & E_2(\mathbf{R}) \end{bmatrix}$$

For details, see the appendix at the end of this presentation

Diabatic SBH

$$V_a(\mathbf{R}) = \sum_{j=1}^N \left[\left(\varepsilon_0 - \frac{1}{2} \frac{g_j^2}{M_j \omega_j^2} \right) + \frac{1}{2} M_j \omega_j^2 \left(R_j + \frac{g_j}{M_j \omega_j^2} \right)^2 \right]$$

$$V_b(\mathbf{R}) = \sum_{j=1}^N \left[\left(-\varepsilon_0 - \frac{1}{2} \frac{g_j^2}{M_j \omega_j^2} \right) + \frac{1}{2} M_j \omega_j^2 \left(R_j - \frac{g_j}{M_j \omega_j^2} \right)^2 \right]$$

$$V_{ab} = -v_0$$

Adiabatic SBH

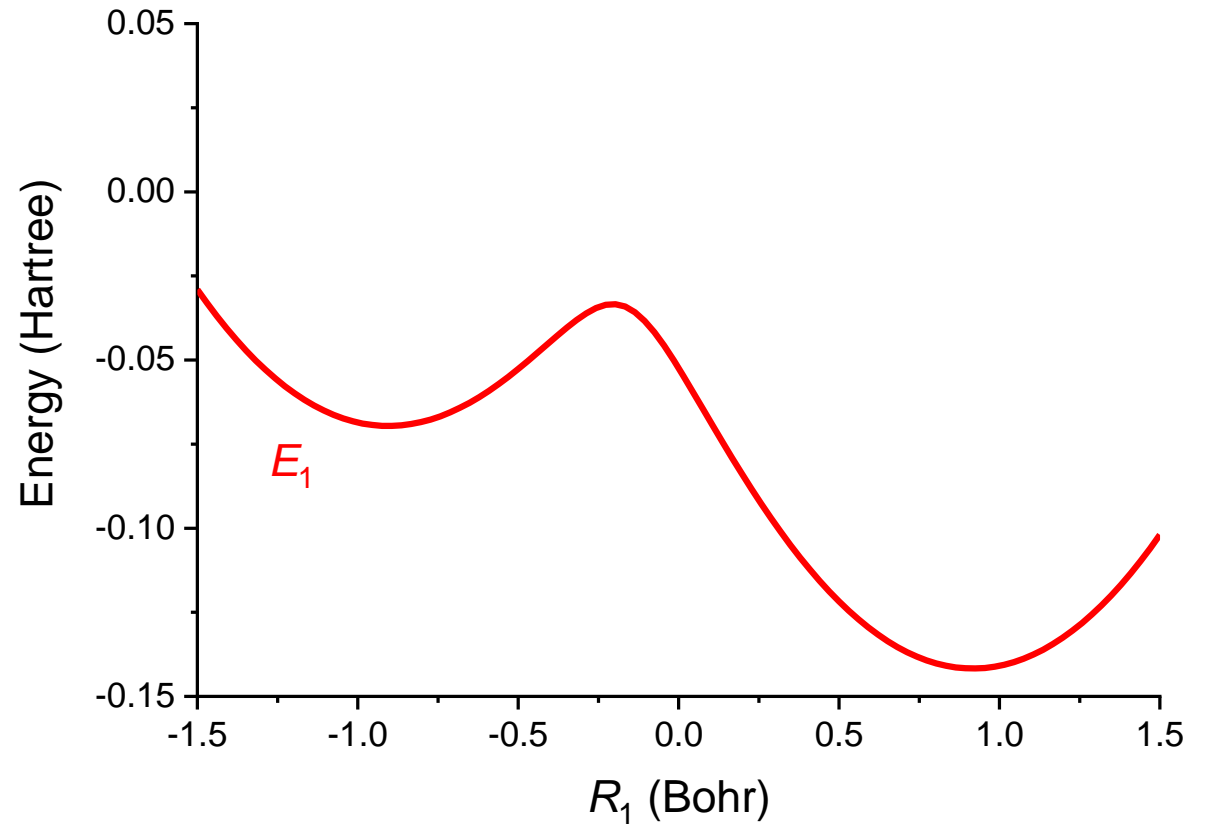
$$E_1(\mathbf{R}) = \frac{1}{2} \sum_{j=1}^N M_j \omega_j^2 R_j^2 - \left[\left(\sum_{j=1}^N g_j R_j + \varepsilon_0 \right)^2 + v_0^2 \right]^{1/2}$$

$$E_2(\mathbf{R}) = \frac{1}{2} \sum_{j=1}^N M_j \omega_j^2 R_j^2 + \left[\left(\sum_{j=1}^N g_j R_j + \varepsilon_0 \right)^2 + v_0^2 \right]^{1/2}$$

$$E_{10} = 0$$

In Practical Work 3, we will implement a Python function to compute the energy and gradient of the lowest state of 1-dimensional SBH

$$E_1(R_1) = \frac{1}{2} M \omega^2 R_1^2 - \left[(gR_1 + \varepsilon_0)^2 + v_0^2 \right]^{1/2}$$

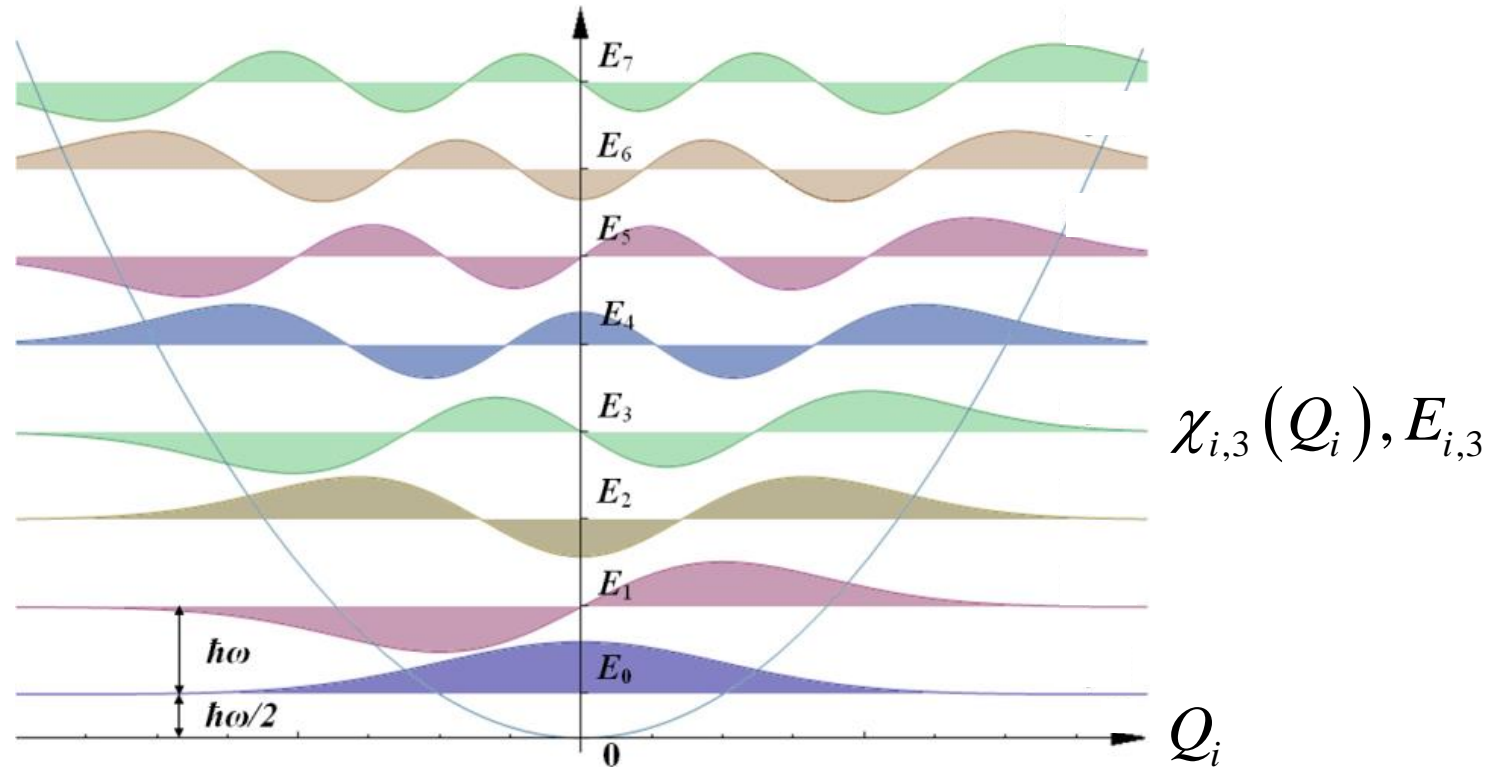


QM of normal modes

Because each normal mode is driven by a harmonic potential

$$E_i(Q_i) = \frac{1}{2} \mu_i \omega_i Q_i^2$$

the independent mode of mass μ_i can be described as a quantum harmonic oscillator with wave function $\chi_{i,n}$ and energy $E_{i,n}$ in level n .



The total nuclear wave function can be approximated as the product of the normal mode wave functions

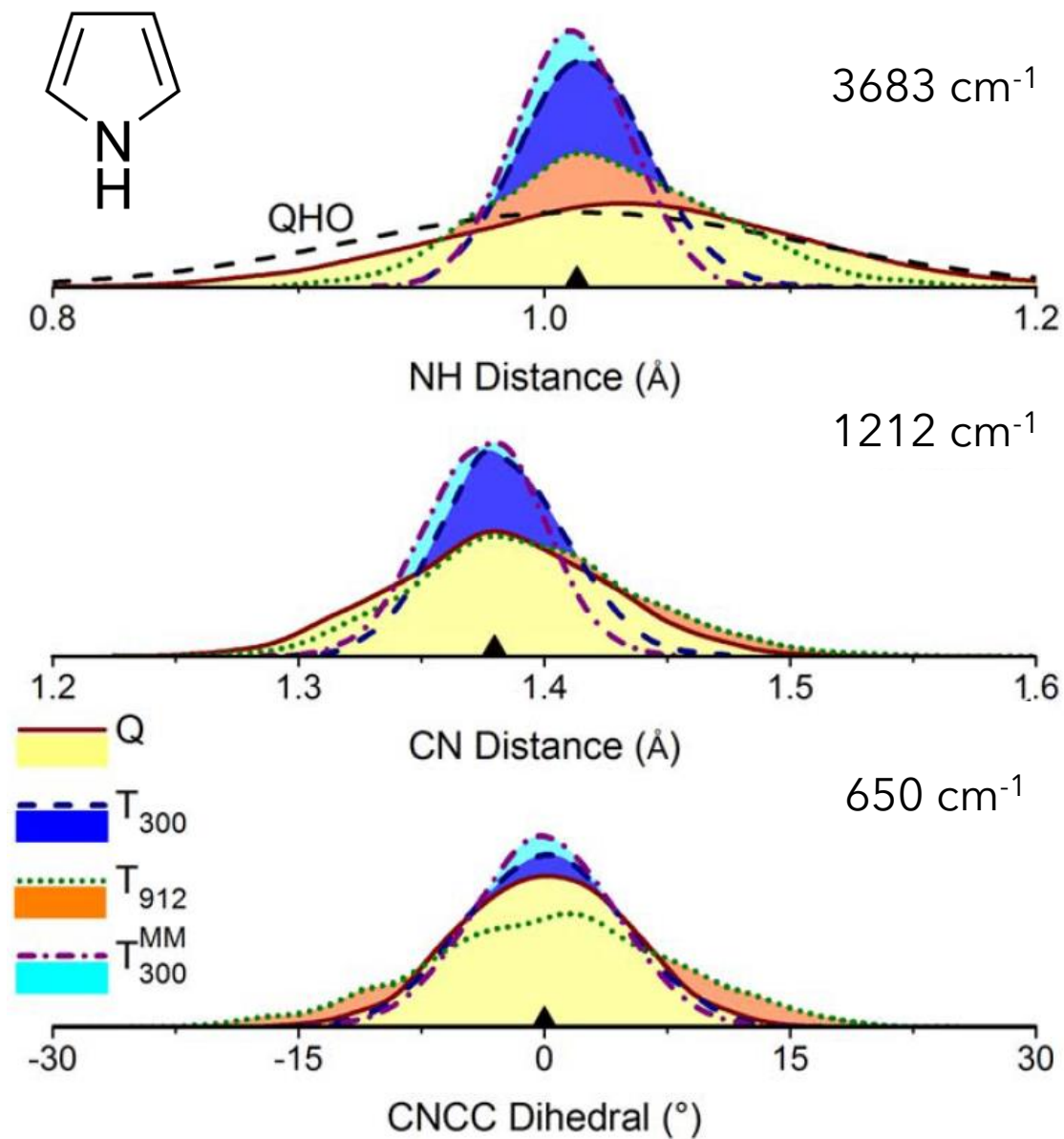
$$\chi(\mathbf{Q}) = \prod_{j=1}^{3N-6} \chi_{j,n(j)}(Q_j)$$

The vibrational energy is the sum of the normal mode energies

$$\begin{aligned} E_{vib} &= \sum_{j=1}^{3N-6} E_{j,n(j)} \\ &= \sum_{j=1}^{3N-6} \left(n(j) + \frac{1}{2} \right) \hbar \omega_j \end{aligned}$$

The zero-point energy is

$$E_{zp} = \sum_{j=1}^{3N-6} E_{j,0} = \frac{1}{2} \sum_{j=1}^{3N-6} \hbar \omega_j$$



The nuclear distribution coming from quantum mechanics and classical molecular dynamics are usually different.

Using the normal modes

Infrared spectrum and dynamics

We can indirectly obtain the IR spectrum from MD simulations too.

Suppose we run molecular dynamics and compute the total dipole moment $\mu(t)$ as a function of time t .

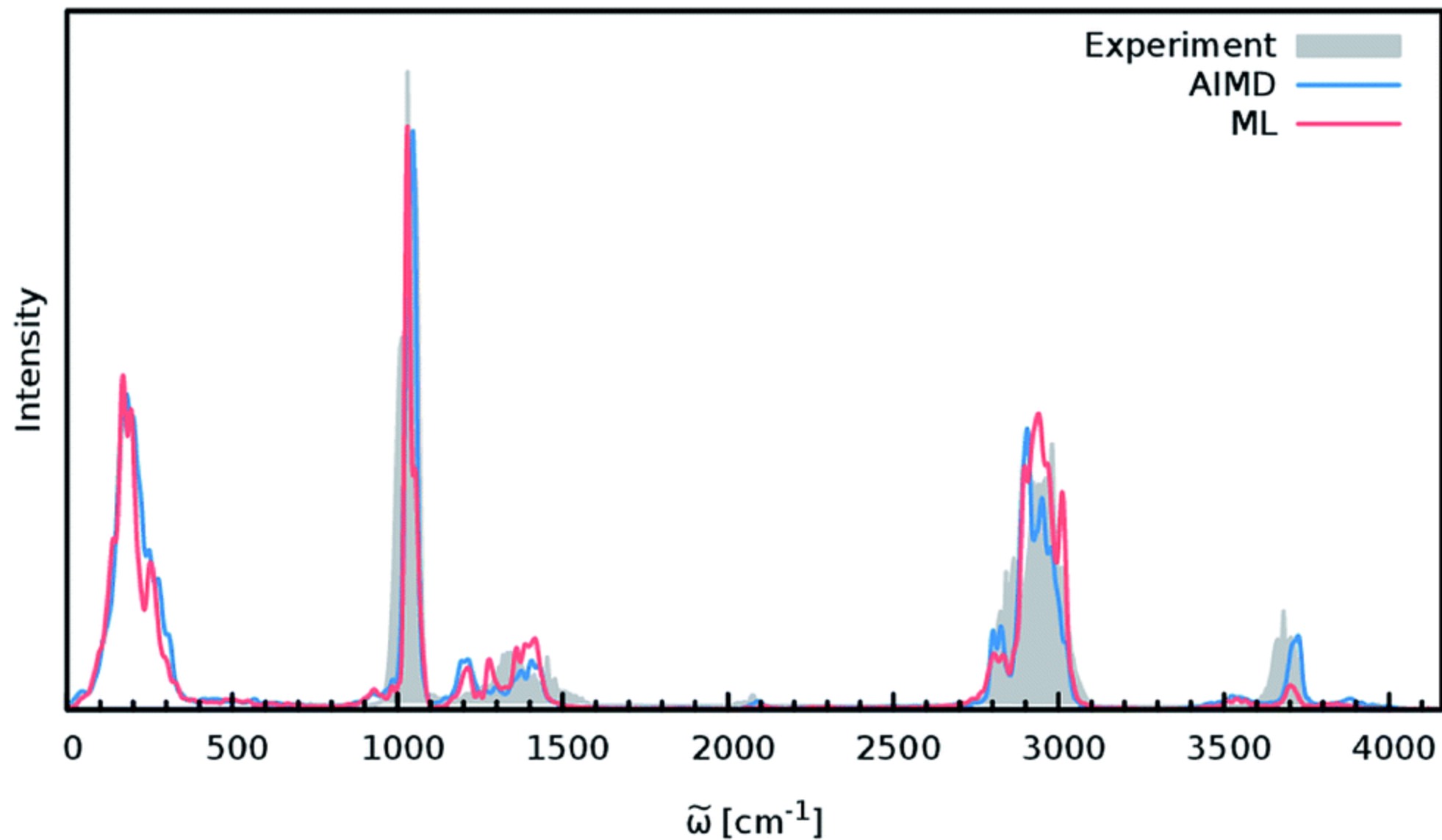
The IR line shape is

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mu(t) \cdot \mu(t) \rangle e^{-i\omega t}$$

This is the Fourier transform of the time correlation of the dipole moment.

We will discuss this type of procedure later in the course.

Methanol, 30 ps



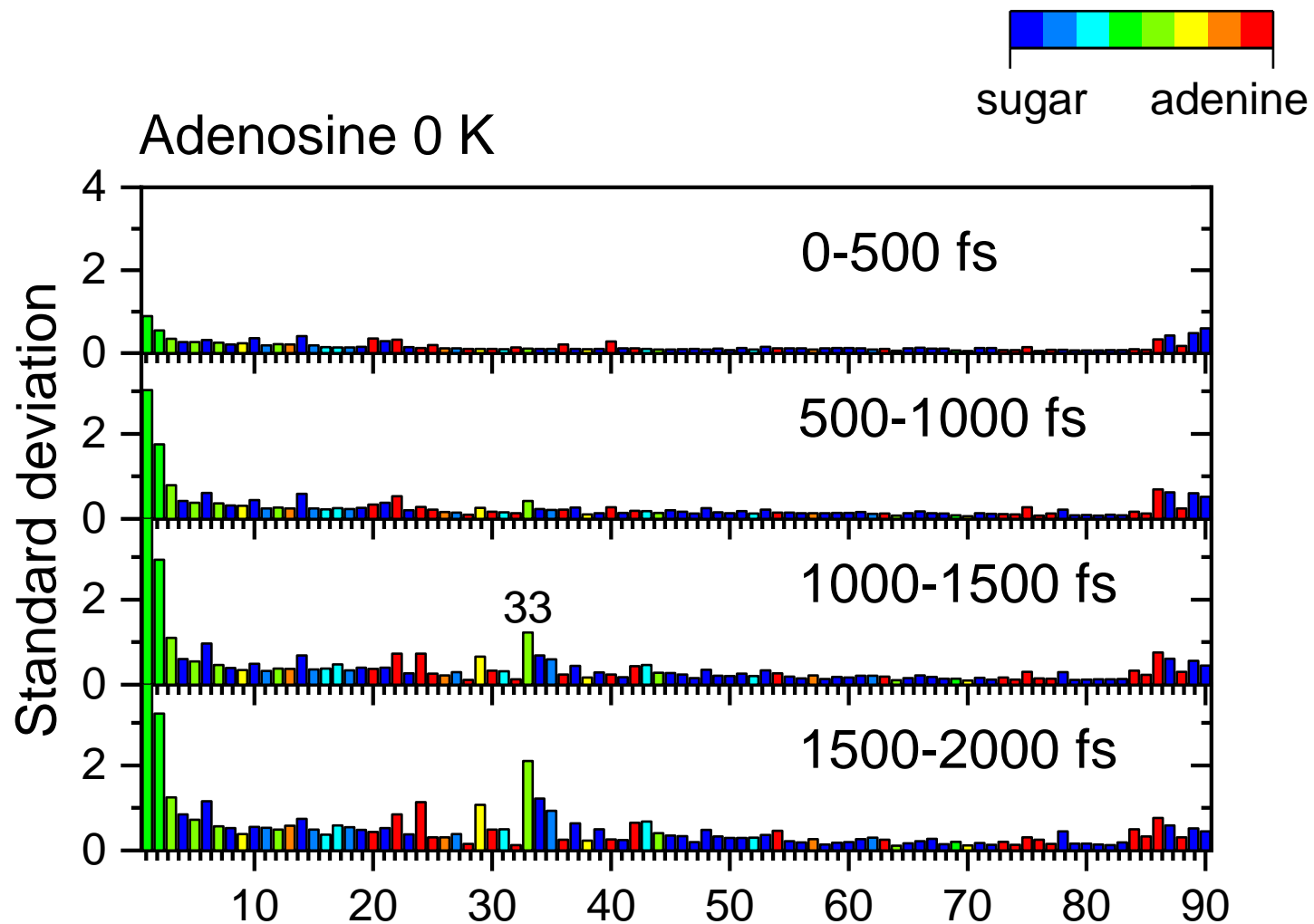
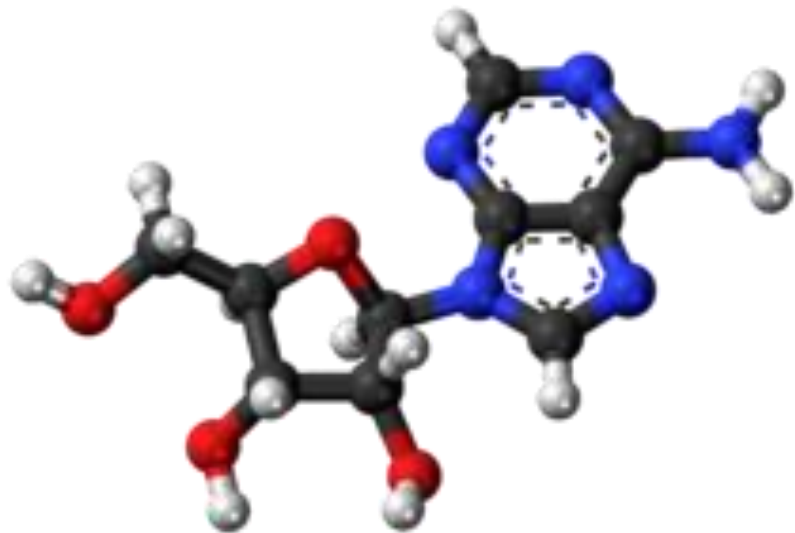
Normal mode analysis

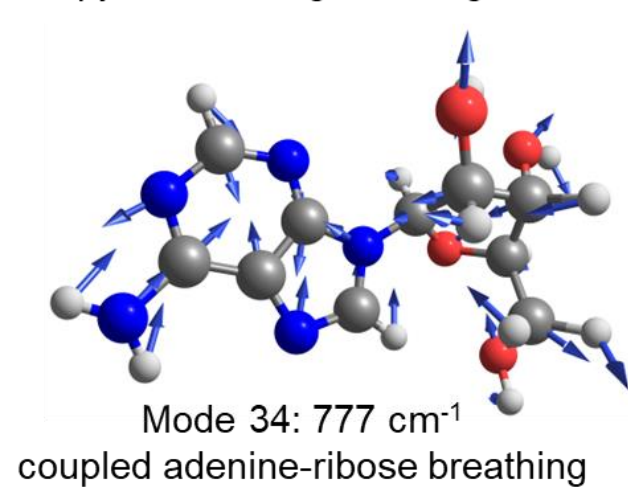
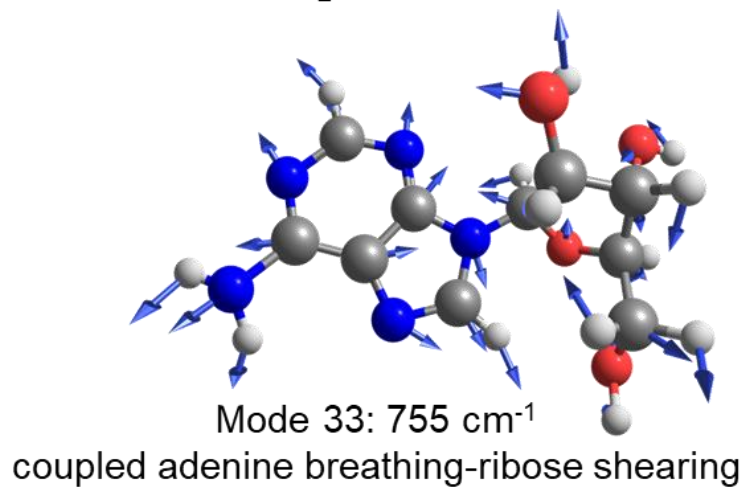
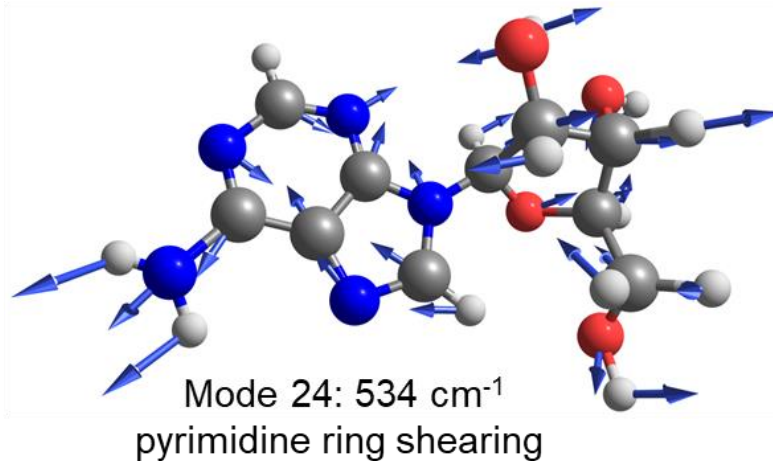
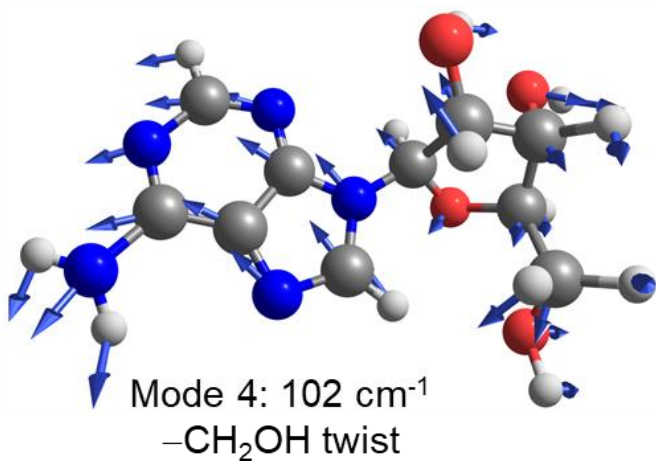
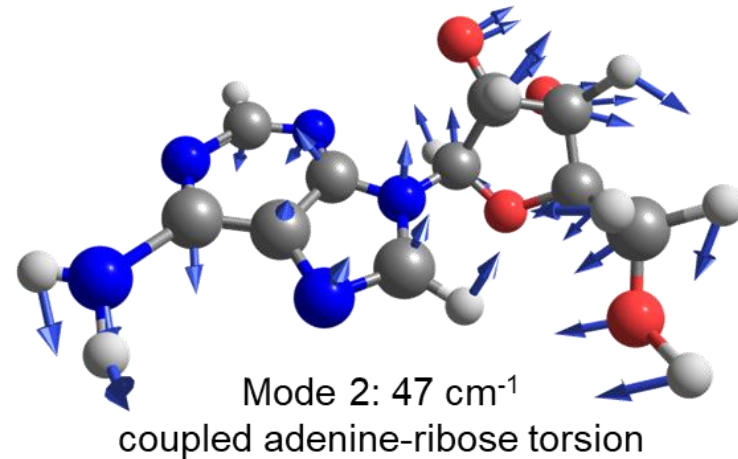
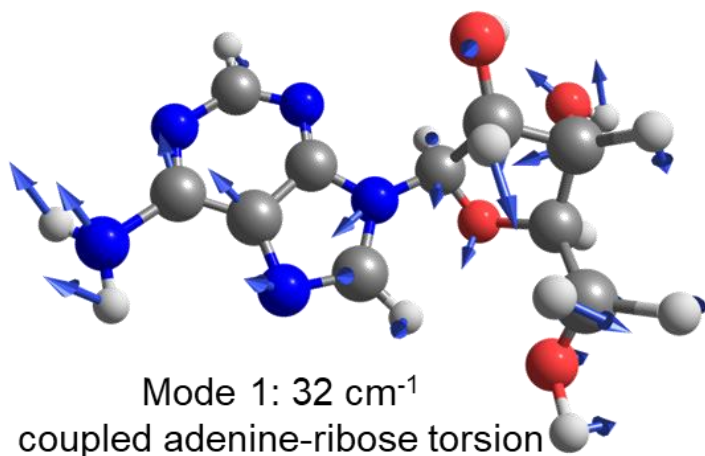
Normal modes can serve as a basis for decomposing molecular dynamics.

The MD results are projected on pre-computed normal modes.

The contribution of each mode tells which molecular groups contribute the most.

Normal mode analysis of excited-state adenosine's dynamics





$n = 10$



$n = 50$



$n = 250$



Drawn with circles

To know more:

Normal modes

- gaussian.com/wp-content/uploads/dl/vib.pdf

Manipulating matrices

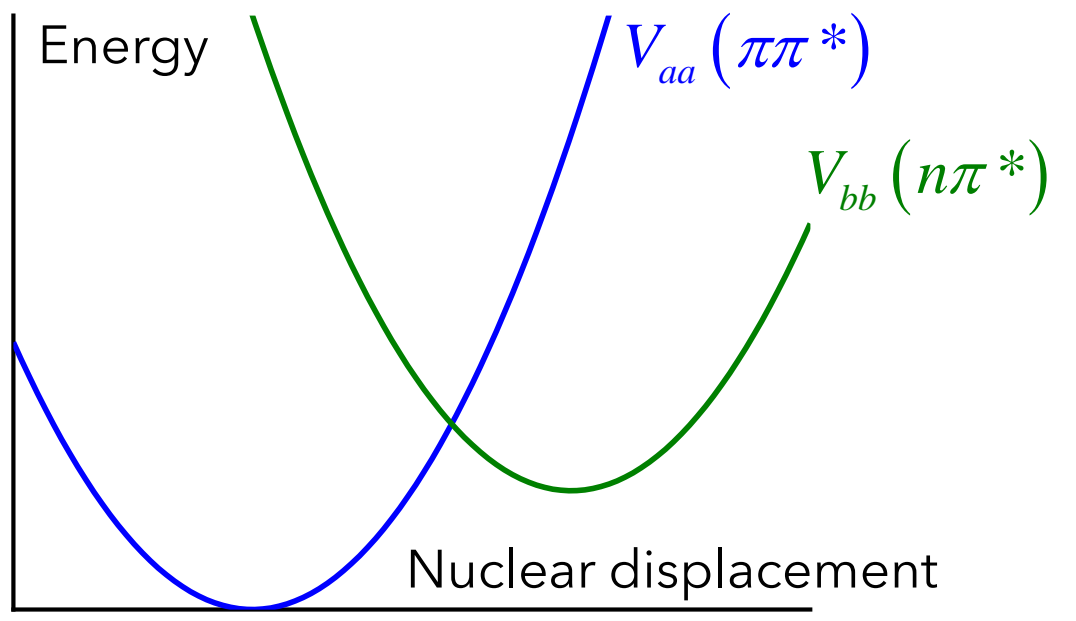
- Petersen; Pedersen. The Matrix Cookbook, **2012**

Appendix

Adiabatic x diabatic PES

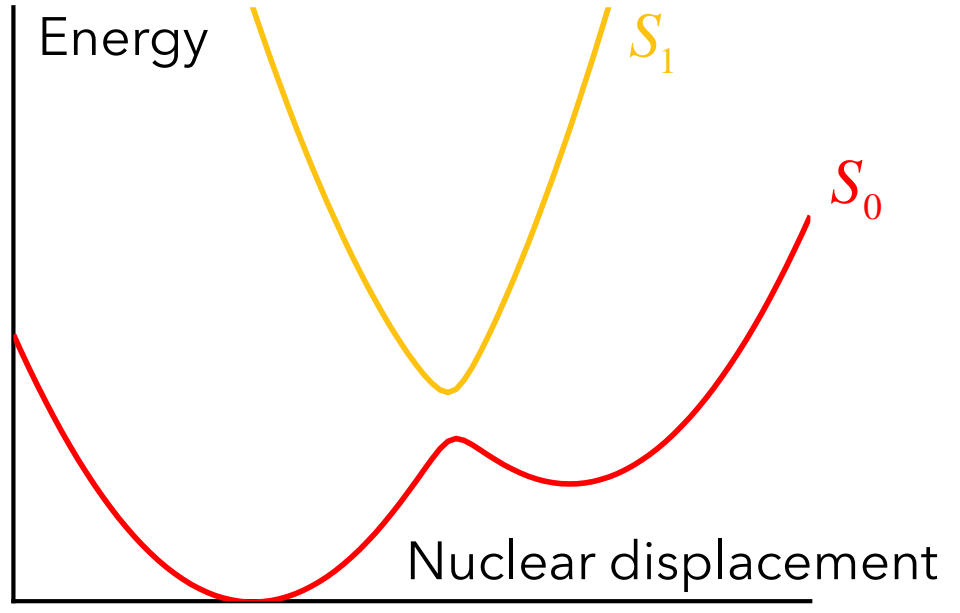
Diabatic representation

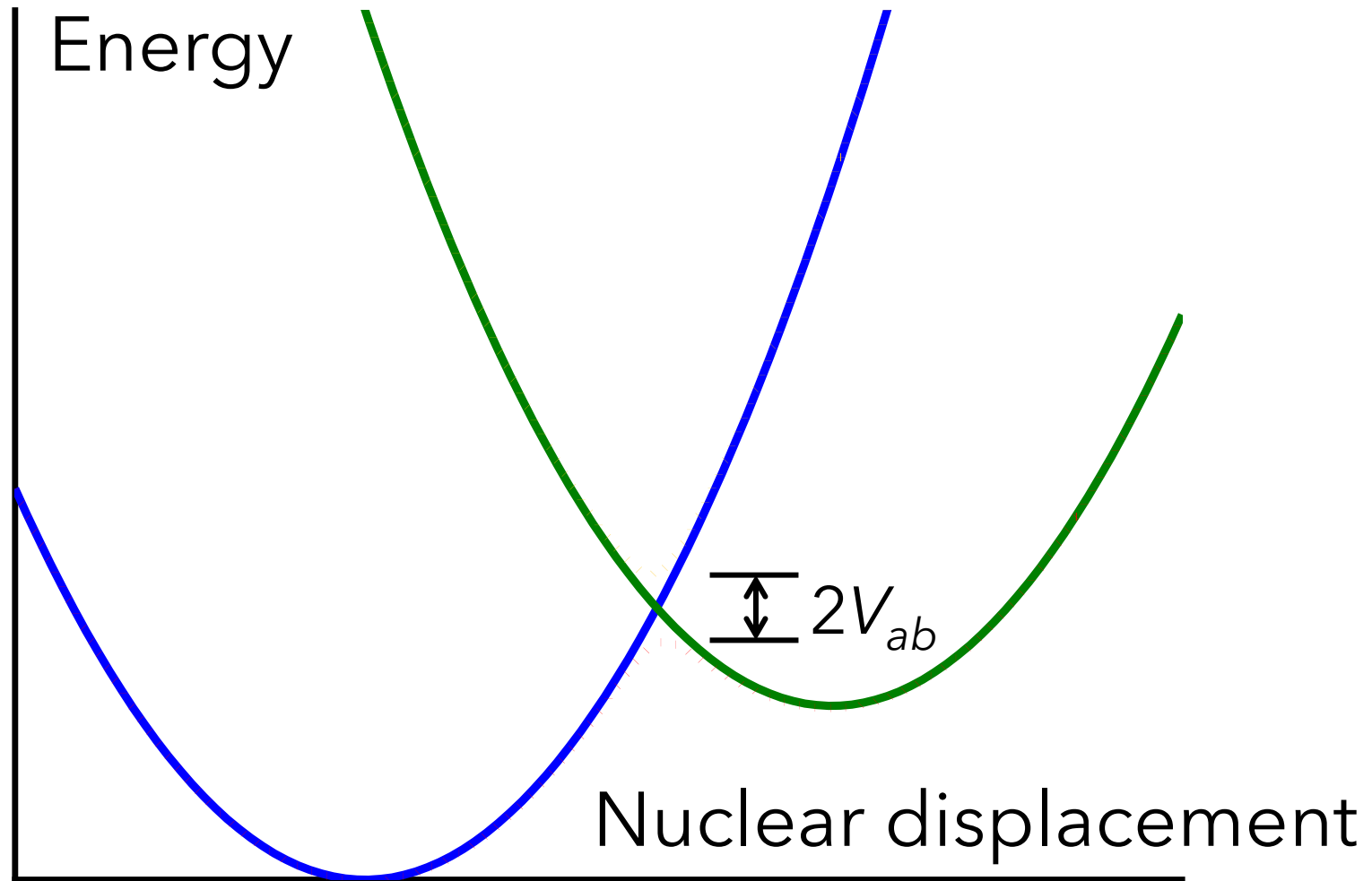
$$H^{(diabatic)} = \begin{bmatrix} V_{aa} & V_{ab} \\ V_{ab} & V_{bb} \end{bmatrix}$$



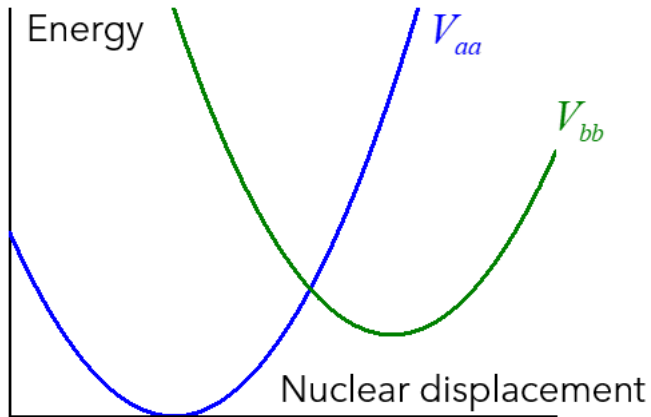
Adiabatic representation

$$H^{(adiabatic)} = \begin{bmatrix} E_0 & 0 \\ 0 & E_1 \end{bmatrix}$$





Diabatic



PES follows electronic character

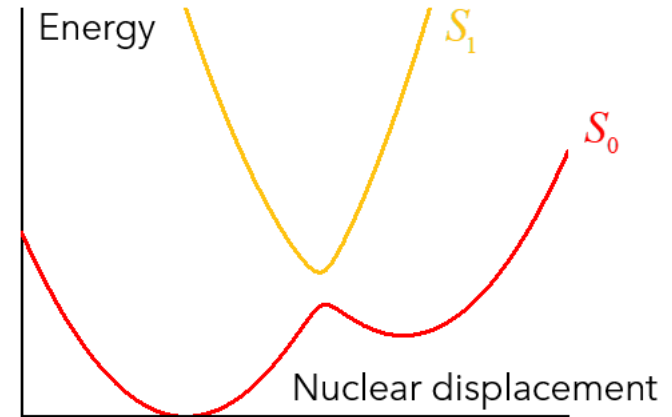
Model PES are usually diabatic

Good for quantum dynamics (PES differentiable everywhere)

Bad for BO dynamics (what to do at the crossing?)

Experimental observables depending on transition probabilities (like oscillator strength) are diabatic

Adiabatic



PES follows state order

Quantum chemical calculations (eg DFT) are normally adiabatic

Bad for quantum dynamics (PES non-differentiable at conical intersections)

Good for BO dynamics (always single surfaces)

Experimental observables depending on transition energies are adiabatic

Transforming diabatic into adiabatic PES

$$\det\left(H^{(diabatic)} - \mathbf{I}E\right) = \det\begin{pmatrix} V_{aa} - E & V_{ab} & V_{ac} & \cdots \\ V_{ab} & V_{bb} - E & V_{bc} & \cdots \\ V_{ac} & V_{bc} & V_{cc} - E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} = 0$$

Solve this equation for E .

For 2 diabatic states, analytical solution:

$$\det \begin{pmatrix} V_{aa} - E & V_{ab} \\ V_{ab} & V_{bb} - E \end{pmatrix} = 0$$

$$(V_{aa} - E)(V_{bb} - E) - V_{ab}^2 = 0$$

$$E_0 = \frac{V_{aa} + V_{bb}}{2} - \sqrt{\left(\frac{V_{aa} - V_{bb}}{2}\right)^2 + V_{ab}^2}$$

$$E_1 = \frac{V_{aa} + V_{bb}}{2} + \sqrt{\left(\frac{V_{aa} - V_{bb}}{2}\right)^2 + V_{ab}^2}$$

The adiabatic energy gradient is obtained by direct differentiation:

$$\frac{\partial E_0}{\partial R_i} = \frac{1}{2} \left(\frac{\partial V_{aa}}{\partial R_i} + \frac{\partial V_{bb}}{\partial R_i} \right) + \left(\frac{1}{4} (V_{bb} - V_{aa}) \left(\frac{\partial V_{bb}}{\partial R_i} - \frac{\partial V_{aa}}{\partial R_i} \right) + V_{ab} \frac{\partial V_{ab}}{\partial R_i} \right) \left(\frac{1}{4} (V_{bb} - V_{aa})^2 + V_{ab}^2 \right)^{-1/2}$$

$$\frac{\partial E_1}{\partial R_i} = \frac{1}{2} \left(\frac{\partial V_{aa}}{\partial R_i} + \frac{\partial V_{bb}}{\partial R_i} \right) - \left(\frac{1}{4} (V_{bb} - V_{aa}) \left(\frac{\partial V_{bb}}{\partial R_i} - \frac{\partial V_{aa}}{\partial R_i} \right) + V_{ab} \frac{\partial V_{ab}}{\partial R_i} \right) \left(\frac{1}{4} (V_{bb} - V_{aa})^2 + V_{ab}^2 \right)^{-1/2}$$

The nonadiabatic coupling vector is:

$$\left\langle \phi_0 \left| \frac{\partial \phi_1}{\partial R_i} \right. \right\rangle = \frac{1}{1 + \left(\frac{2V_{ab}}{V_{bb} - V_{aa}} \right)^2} \left(\frac{1}{(V_{bb} - V_{aa})} \frac{\partial V_{ab}}{\partial R_i} - \frac{V_{ab}}{(V_{bb} - V_{aa})^2} \left(\frac{\partial V_{bb}}{\partial R_i} - \frac{\partial V_{aa}}{\partial R_i} \right) \right)$$

More than 2 diabatic states requires numerical solutions
(eigenvalue search)