From Atoms to Materials: Predictive Theory and Simulations

Week 3: Dynamics of Atoms – Classical Mechanics and MD Simulations

Lecture 3.5: Normal Modes and Phonons

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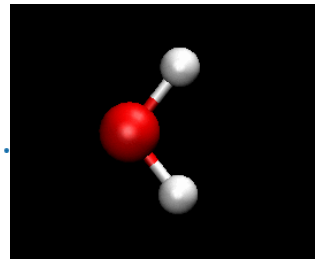
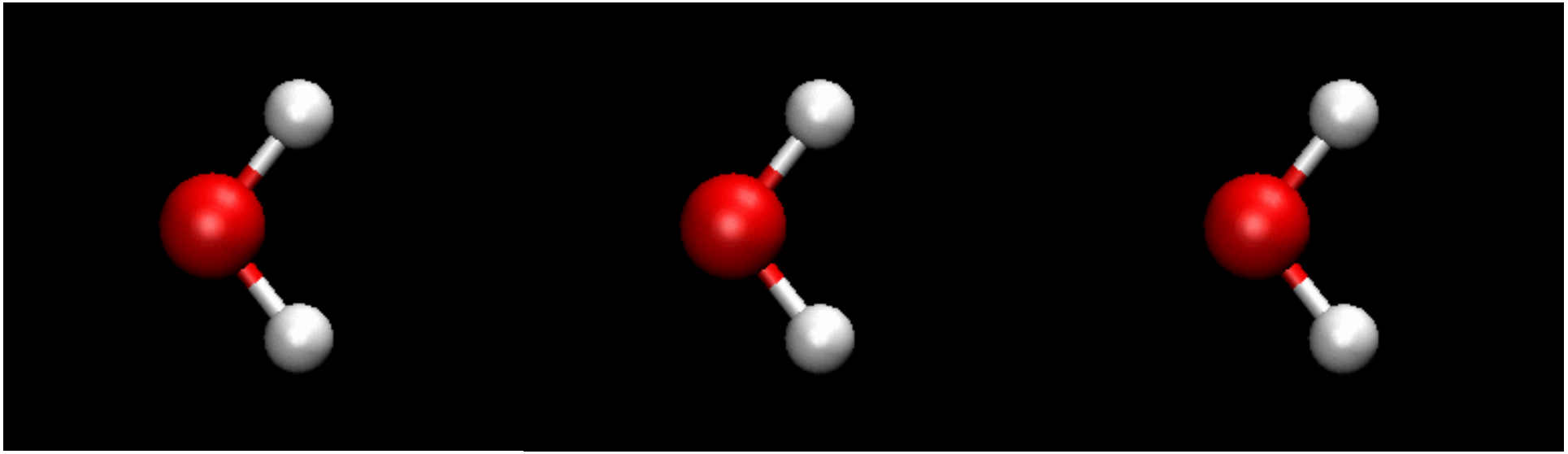
In this lecture



- Newton's equations of motion can only be solved analytically for few cases
  - Harmonic oscillator (spring and mass system)

- Ionic dynamics at low temperatures can be approximated as a set of uncoupled harmonic oscillators



Born Oppenheimer Hamiltonian for small vibrations

$$H\left(\{R_i\},\{P_i\}\right)=\sum_{i=1}^{3N}\frac{P_i^2}{2M_i}+V\left(\{R_i\}\right) \qquad i=1,2,.....3N$$

Expand H around the ground state structure $\{R_i^\circ\}$ $\Delta R_i = R_i - R_i^\circ$

$$H=\sum_{i=1}^{3N}\frac{P_i^2}{2M_i}+V\left(\{R_i^\circ\}\right)+\sum_{i}^{3N}\left.\frac{\partial V}{\partial R_i}\right|_{\{R_i^\circ\}}\Delta R_i+\frac{1}{2}\sum_{i,j}^{3N}\left.\frac{\partial^2 V}{\partial R_i \partial R_j}\right|_{\{R_i^\circ\}}\Delta R_i \Delta R_j+\ldots$$

$$\vec{P}=\begin{bmatrix}P_1\\P_2\\\vdots\\P_{3N}\end{bmatrix};\ \vec{R}=\begin{bmatrix}R_1\\R_2\\\vdots\\R_{3N}\end{bmatrix}$$

Hamiltonian expansion in matrix form

$$H = \sum_{i=1}^{3N} \frac{P_i^2}{2M_i} + V\left(\left\{R_i^\circ\right\}\right) + \sum_i^{3N} \left.\frac{\partial V}{\partial R_i}\right|_{\left\{R_i^\circ\right\}} \Delta R_i + \frac{1}{2}\sum_{i,j}^{3N} \left.\frac{\partial^2 V}{\partial R_i \partial R_j}\right|_{\left\{R_i^\circ\right\}} \Delta R_i \Delta R_j$$

$$H = V_0 + \frac{1}{2}\begin{bmatrix} P_1, P_2 \ldots P_{3N} \end{bmatrix} \begin{bmatrix} \frac{1}{M_1} & 0 & \cdots & 0 \\ 0 & \frac{1}{M_2} & & \\ \vdots & & \ddots & \\ 0 & & & \frac{1}{M_{3N}} \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \\ \vdots \\ P_{3N} \end{bmatrix} +$$

$$+\frac{1}{2}\begin{bmatrix} \Delta R_1, \Delta R_2 \ldots \Delta R_{3N} \end{bmatrix} \begin{bmatrix} K_{1,1} & K_{2,1} & \cdots & K_{3,N1} \\ K_{1,2} & K_{2,2} & & \\ \vdots & & \ddots & \\ K_{1,3N} & & & K_{3N,3N} \end{bmatrix} \begin{bmatrix} \Delta R_1 \\ \Delta R_2 \\ \vdots \\ \Delta R_{3N} \end{bmatrix}$$

The Hessian matrix

This system is equivalent to a set of unit mass particles:

With positions: $R'_i = \sqrt{M_i} R_i$

And momentum is: $P'_i = \dot{R}'_i = \sqrt{M_i}\dot{R}_i = \frac{P_i}{\sqrt{M_i}}$

$$H\left(\{R'_i\},\{P'_i\}\right) = \frac{1}{2}\left[P'_1, P'_2, \ldots, P'_{3N}\right]\begin{bmatrix} P'_1 \\ P'_2 \\ \vdots \\ P'_{3N} \end{bmatrix} + \frac{1}{2}\left[\Delta R'_1, \Delta R'_2, \ldots, \Delta R'_{3N}\right]\begin{bmatrix} K_{ij}/\sqrt{M_i M_j} \end{bmatrix}\begin{bmatrix} \Delta R'_1 \\ \Delta R'_2 \\ \vdots \\ \Delta R'_{3N} \end{bmatrix}$$

Hessian matrix
Symmetric by construction

Normal modes of vibrations

Diagonalize Hessian matrix: $\left[K_{ij} / \sqrt{M_i M_j} \right]$

Eigenvalues: ω_α^2

Eigenvectors: ρ_α

Using the eigenvectors as a basis, instead of the original variables

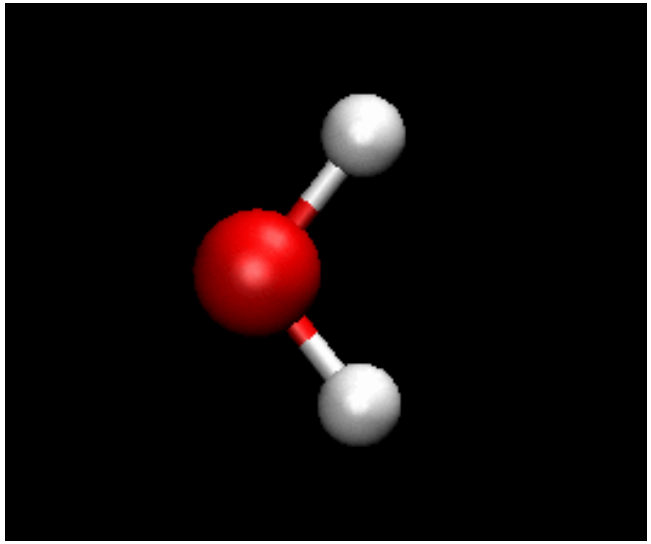
$$H = \frac{1}{2}\left[\pi_1, \pi_2, \ldots, \pi_{3N}\right] \begin{bmatrix} \pi_1 \\ \pi_2 \\ \vdots \\ \pi_{3N} \end{bmatrix} + \frac{1}{2}\left[\rho_1, \rho_2, \ldots, \rho_{3N}\right] \begin{bmatrix} \omega_1^2 & & & 0 \\ & \omega_2^2 & & \\ & & \ddots & \\ 0 & & & \omega_{3N}^2 \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \vdots \\ \rho_{3N} \end{bmatrix}$$

$$\sum_{\alpha=1}^{3N} \left(\frac{\pi_\alpha^2}{2} + \frac{1}{2}\omega_\alpha^2 \rho_\alpha^2 \right)$$

A set of uncoupled harmonic oscillators!

$\rho_\alpha(t) = A \cdot e^{i\omega_\alpha t} = A[\cos(\omega t) + i \sin(\omega t)]$

Normal modes example: water

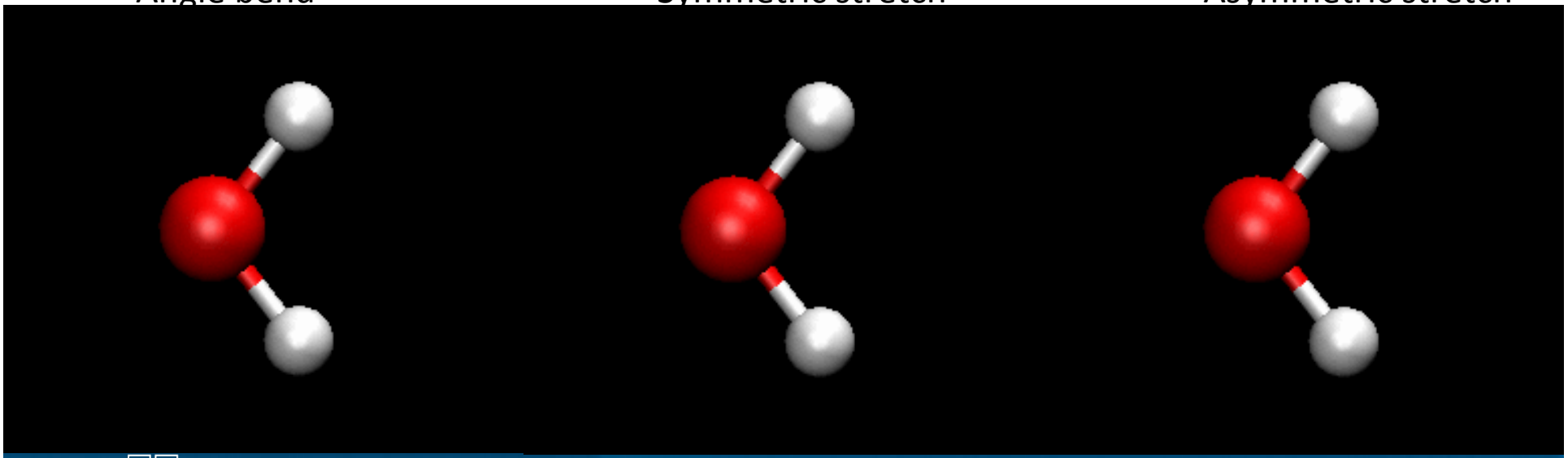


Full dynamics (harmonic)

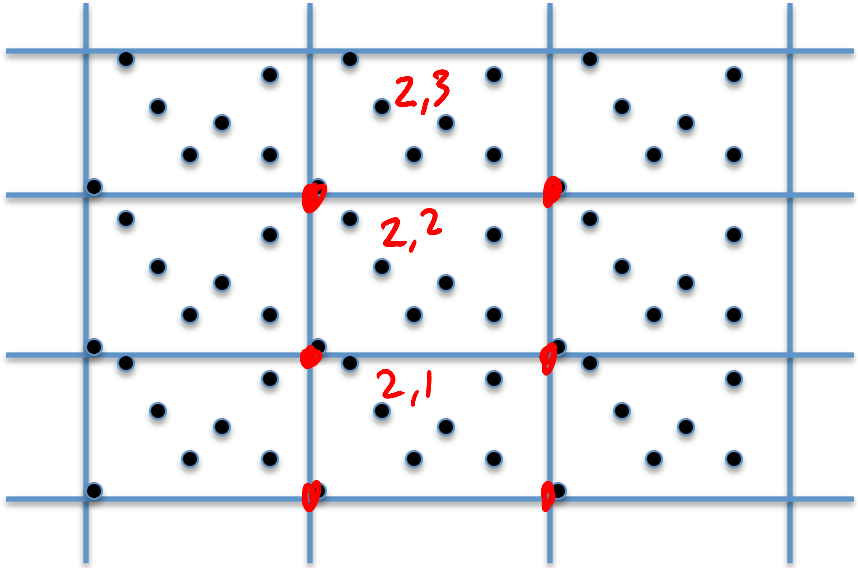
Angle bend

Symmetric stretch

Asymmetric stretch



Atomic vibrations crystals



- N atoms per cell: i=1, 2, … N
- N_{cell} cells: I=1,2,…N_{cell}

$R_{i,I}$: position of i^{th} atom in I^{th} cell

R_I: Bravais lattice site of cell I

Expand B-O Hamiltonian around equilibrium to second order:

$$H = \sum_{i,I}^{3N,N_{cell}} \frac{P_{i,I}^2}{2M_i} + V\left(\left\{R^{\circ}_{i,I}\right\}\right) + \sum_{i,I}^{3N,N_{cell}} \left.\frac{\partial V}{\partial R_{i,I}}\right|_{\left\{R^{\circ}_{i,I}\right\}} \Delta R_{i,I} + \frac{1}{2}\sum_{i,I,j,J}^{3N,N_{cell}} \left.\frac{\partial^2 V}{\partial R_{i,I}\partial R_{j,J}}\right|_{\left\{R^{\circ}_{i,I}\right\}} \Delta R_{i,I}\Delta R_{j,J}$$

Vibrations in crystals: equations of motion

$$H = \sum_{i,I}^{3N,N_{cell}} \frac{P_i^2}{2M_i} + V\left(\left\{R^{\circ}_{i,I}\right\}\right) + \sum_{i,I}^{3N,N_{cell}} \left.\frac{\partial V}{\partial R_{i,I}}\right|_{\left\{R^{\circ}_{i,I}\right\}} \Delta R_{i,I} + \frac{1}{2}\sum_{i,I,j,J}^{3N,N_{cell}} \left.\frac{\partial^2 V}{\partial R_{i,I}\partial R_{j,J}}\right|_{\left\{R^{\circ}_{i,I}\right\}} \Delta R_{i,I}\Delta R_{j,J}$$

Equations of motion:

$$\dot{P}_{i,I} = M_i \Delta\ddot{R}_{i,I} = -\frac{\partial H}{\partial R_{i,I}} = \sum_{j,J}^{3N,N_{cell}} \left.\frac{\partial^2 V}{\partial R_{i,I}\partial R_{j,J}}\right|_{\left\{R^{\circ}_{i,I}\right\}} \Delta R_{j,J}$$

Ansatz:

$$\Delta R_{i,I} = \frac{\rho_{i,I}}{\sqrt{M_i}} e^{i\omega t} \qquad \Delta\ddot{R}_{i,I} = \omega^2 \frac{\rho_{i,I}}{\sqrt{M_i}} e^{i\omega t}$$

$$\omega^2 \sqrt{M_i}\,\rho_{i,I} e^{i\omega t} = \sum_{j,J}^{3N,N_{cell}} \frac{K_{iI,jJ}}{\sqrt{M_j}} \rho_{j,J} e^{i\omega t}$$

$$\omega^2 \rho_{i,I} = \sum_{j,J}^{3N,N_{cell}} \frac{K_{iI,jJ}}{\sqrt{M_j M_i}} \rho_{j,J}$$

Same eigenvalue problem as before (Hessian matrix)

Vibrations crystals: dynamical matrix

Eigenvalue problem involves a $(3NxN_{cell})^2$ matrix

$$\omega^2 \rho_{i,I} = \sum_{j,J}^{3N,N_{cell}} \frac{K_{iI,jJ}}{\sqrt{M_j M_i}} \rho_{j,J}$$

with: $\Delta R_{i,I} = \frac{\rho_{i,I}}{\sqrt{M_i}} e^{i\omega t}$

Ansatz II: $\rho_{i,I} = u_i e^{ikR_I}$

$$\omega^2 u_i e^{ikR_I} = \sum_{j,J}^{3N,N_{cell}} \frac{K_{iI,jJ}}{\sqrt{M_j M_i}} u_j e^{ikR_j}$$

Bravais lattice appears the same when viewed from any lattice site (I can pick *I* to be the origin)

$$\omega^2 u_i = \sum_{j}^{3N} u_j \sum_{J}^{N_{cell}} \frac{K_{iI,jJ}}{\sqrt{M_j M_i}} e^{ik\left(R_J - R_I\right)}$$

Dynamical matrix $H_{ij}(k)$ is only NxN but needs to be solved all k-points in the First Brillouin Zone

Summary: small vibrations

- Molecules
  - Eigenvalues of the Hessian matrix: vibrational frequencies
  - Eigenvectors of the Hessian matrix: normal modes

$$\begin{bmatrix} & K_{ij} / \sqrt{M_i M_j} & \end{bmatrix} \qquad \omega_\alpha^2 \qquad \rho_\alpha \qquad \Delta R_{\alpha,i} = \frac{\rho_{\alpha,i}}{\sqrt{M_i}} e^{i\omega_\alpha t}$$

- Crystals
  - Eigenvalues of the Dynamical matrix: vibrational frequencies
  - Eigenvectors of the Dynamical matrix: normal modes

$$H_{ij}(k) = \sum_J^{N_{cell}} \frac{K_{i0,jJ}}{\sqrt{M_j M_i}} e^{ikR_J} \qquad \omega_\alpha^2(k) \qquad u_\alpha(k) \qquad \Delta R_{\alpha,i,I}(k) = \frac{u_{\alpha,i}}{\sqrt{M_i}} e^{i\left(kR_I + \omega_\alpha(k)t\right)}$$