

Cohesion - Recap.:

- o all consequence of the same basic e-e interaction
 - o but wide variety of bonding types
- ↔ structure in nature:

van der Waals

ionic

covalent

metallic

Hydrogen bonding

Bonds formed between small, H-containing molecules:

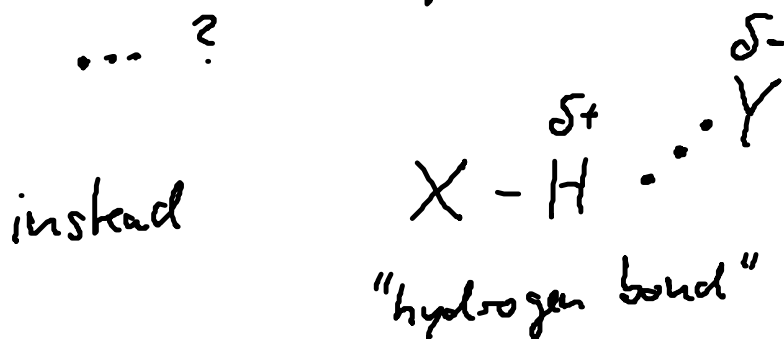
$\text{CH}_4 - \text{NH}_3$	-29 meV	} calculated high-level "quantum chemistry"
$\text{NH}_3 - \text{NH}_3$	-127 meV	
$\text{H}_2\text{O} - \text{H}_2\text{O}$	-215 meV	
$\text{H}_2\text{O} - \text{NH}_3$	-276 meV	

- o bond > vdW interaction
- o bond < ionic interaction

$$\approx kT$$

Reasons:

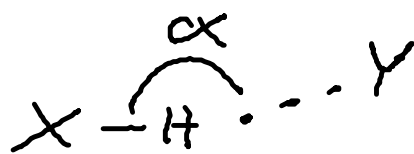
- With an electronegative partner element, H would like to "donate" its electron
- but, ionizing H is hard
(H^+ : simple proton; $E_{ion} \sim 13.6 \text{ eV}$)
- but H can form only one covalent bond
... ?



Properties:

- strongest intermolecular bond
 $\sim 0.1 - 0.5 \text{ eV}$
 $\rightarrow \approx kT$
 \rightarrow e.g. liquid water, ...
- partially electrostatic bond
but not fully:
some residual covalent interaction
quantitatively important

- Directional



$$\alpha \sim 180^\circ$$

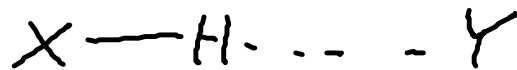
- Impact on bond lengths, vibrational frequencies:

X-H lengths increase by $\sim 0.01 - 0.05 \text{ \AA}$

ω_{vib} decrease (red-shift)

→ vibrational spectroscopy can characterize H-bonded "state" of structure

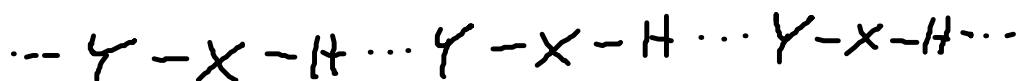
- "Quantum effects" for H^+ :



Tunneling / non-classical proton behavior may be quantitatively important.

- "Cooperativity":

H bonds can strengthen each other



chain: $E_2^{\text{H}_6} < E_3^{\text{H}_5} < \cdots < E_\infty^{\text{H}_5} \quad \sim 1.9-2$

↑
dimer

Description of H bonds:

qualitatively: "Force fields"
(classical parameterized functions
of $\{\mathbf{R}_I\}$)
→ qualitative accuracy, no
qm. predictions possible

quantitatively:

partially electrostatic: Hartree-Fock,
DFT should do.

in fact: modern DFT-GGA's work
with "chemical accuracy"

Chapter 7 Lattice vibrations

Early on (Chapter 1)

- separation ions and electrons
- ions: Born-Oppenheimer approximation
or static approximation

Born-Oppenheimer potential energy surface

Assume:

For any given configuration $\{\underline{R}_I\}$ of the nuclei, the electronic energy is equal to the ground state:

$$\min_{\Psi} E(\{\underline{R}_I\}; \Psi) =: V^{Bo}(\{\underline{R}_I\})$$

- no explicit electronic degrees of freedom
- electrons follow nuclei "instantaneously"
- no interaction of quantum-mechanical "quasiparticles" in electronic/nuclear subsystems

Hamiltonian for nuclei:

$$\underline{H} = T^{ion} + V^{Bo}(\{\underline{R}_I\})$$

Harmonic approximation

Study of vibrations:

atoms reside near minima of the PES
only small displacements from that:

$$\underline{R}_I = \underline{R}_I^{\circ} + \underline{S}_I$$

$|s_I| \ll$ NN distance in the lattice

Then (Taylor in 1D)

$$V(x) = V(x_0) + \frac{\partial}{\partial x} V \Big|_{x_0} s + \frac{1}{2} \frac{\partial^2}{\partial x^2} V \Big|_{x_0} s^2 + \dots$$

Then: $\frac{\partial}{\partial x} V \Big|_{x_0} = 0$ if x_0 is a minimum

$$V(s) = V(x_0) + \frac{1}{2} \frac{\partial^2}{\partial x^2} V \Big|_{x_0} s^2$$

$$F = - \frac{\partial}{\partial s} V(s) = -c s$$

$$c = \frac{\partial^2}{\partial x^2} V(x) \Big|_{x=x_0}$$

Harmonic oscillator in 1D

We will see:

works for vibrations, heat capacities, ...

but not lattice expansion
transport
phase transitions

3D Harmonic approximation.

$$V^{Bo}(\{\underline{R}_I\}) = V^{Bo}(\{\underline{R}_I^0\})$$

$$+ \frac{1}{2} \sum_{\substack{IJ \\ \text{ions}}}^{MM} \sum_{\substack{\mu, \nu \\ \text{coordinates}}}^{3,3} s_{I,\mu} \bar{\Phi}_{\mu\nu}(\underline{R}_I, \underline{R}_J) s_{J,\nu}$$

where

$$\bar{\Phi}_{\mu\nu}(\underline{R}_I, \underline{R}_J) = \frac{\partial^2}{\partial s_{I,\mu} \partial s_{J,\nu}} V^{Bo}(\{\underline{R}_I\}) \Big|_{\{\underline{R}_I^0\}}$$

Each pair of ions I, J

gets its own 3×3 matrix $\Phi_{\mu\nu}$

→ in real space: $3M \times 3M$ entries

$$M \sim 10^{23}$$

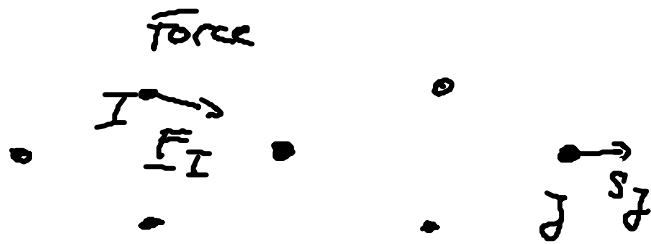
Simplification:

- Periodicity: reduce to r atoms $\alpha = 1, \dots, r$ in the unit cell

- Local properties of $\bar{\Phi}$:

Second derivative by finite difference

$$\bar{\Phi}_{\mu\nu}(\underline{R}_I, \underline{R}_J) = F_{I,\mu}(\underline{R}_1^0, \dots, \underline{R}_J^0 + s_{J,\nu}, \dots, \underline{R}_M^0) / s_{J,\nu}$$



$$\bar{\Phi}(\underline{R}_I, \underline{R}_J) \rightarrow 0 \quad \text{for large } |\underline{R}_I, -\underline{R}_J|$$

in practice: 3-5 · a e.g. in /a

Classical Equations of Motion

[very useful for many questions]

Hamiltonian function:

$$E = \sum_{I=1}^M \frac{M_I}{2} \dot{\underline{s}}_I^2 + V^{BO}(\{\underline{R}_I^0\}) + \frac{1}{2} \sum_{I,J}^{M,M} \underline{s}_I \cdot \bar{\Phi}(\underline{R}_I, \underline{R}_J) \cdot \underline{s}_J$$

EOM:

$$M_I \ddot{s}_I = - \sum_J^M \underline{\underline{\Phi}}(\underline{R}_I, \underline{R}_J) s_J$$

coupled harmonic oscillators

Separate off time: $s_{I,\mu}(t) = u_{I,\mu} e^{i\omega t}$

$$\rightarrow M_I \omega^2 u_{I,\mu} = \sum_{J,\nu} \underline{\underline{\Phi}}_{\mu\nu}(\underline{R}_I, \underline{R}_J) u_{J,\nu}$$

still coupled; still 10^{23} DOF

use periodicity:

$$\underline{R}_I = \underline{R}_n + \underline{R}_\alpha$$

↑
origin of unit
cell n

↑
atom in given
cell; $\alpha = 1, \dots, r$

Relabel $\underline{\underline{\Phi}}_{\mu\nu}(\underline{R}_I, \underline{R}_J) \rightarrow \underline{\underline{\Phi}}_{\alpha\mu}^{\beta\nu}(n, n')$

$$\doteq \underline{\underline{\Phi}}_{\alpha\mu}^{\beta\nu}(n - n')$$

Ansatz: wave of displacements u_I in discrete lattice I .

$$u_{\alpha\mu}(\underline{R}_n) = \frac{1}{\sqrt{M_\alpha}} c_{\alpha\mu} e^{i\mathbf{k} \cdot \underline{R}_n}$$

This yields:

$$M_{\alpha} \omega^2 \frac{1}{\sqrt{M_{\alpha}}} c_{\alpha\mu} e^{i\mathbf{k}\cdot\mathbf{R}_n}$$

$$= \sum_{n', \beta, \nu} \overline{\Phi}_{\alpha\mu}^{\beta\nu}(n-n') \frac{1}{\sqrt{M_{\beta}}} c_{\beta\nu} e^{i\mathbf{k}\cdot\mathbf{R}_{n'}}$$

Rearrange:

$$\omega^2 c_{\alpha\mu} = \sum_{\beta\nu} D_{\alpha\mu}^{\beta\nu}(\mathbf{k}) c_{\beta\nu}$$

$$D_{\alpha\mu}^{\beta\nu}(\mathbf{k}) = \frac{1}{\sqrt{M_{\alpha}M_{\beta}}} \sum_{n'} \overline{\Phi}_{\alpha\mu}^{\beta\nu}(n-n') e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_{n'})}$$

"dynamical matrix"

contains all lattice terms as one sum!

We have

$3r \cdot M$ original equations \rightarrow $3r$ equations
for each \mathbf{k} !

for each \mathbf{k} :

$$\det(\hat{D}(\mathbf{k}) - \omega^2 \mathbb{1}) = 0$$

3r solutions:

$$\omega_i(\underline{k}) \quad \& \quad \underset{\substack{\uparrow \\ \text{orthornal}}}{e_{\alpha n}^{(i)}(\underline{k})} \quad i=1, \dots, 3r$$

$$\underline{s}_{\alpha n}^{(i, \underline{k})}(t) = \frac{1}{\sqrt{M_{\alpha}}} \underline{e}_{\alpha}^{(i)}(\underline{k}) \cdot e^{i(\underline{k} \cdot \underline{R}_{\alpha} - \omega_i(\underline{k}) \cdot t)}$$

positions associated with 3M
decoupled oscillators ("normal modes")

Any arbitrary time-dependent displacement
can be written as a linear combination
of $\underline{s}_{\alpha n}^{(i, \underline{k})}(t)$.

Properties of \underline{k} :

- $\omega_i(\underline{k})$ "dispersion relation of phonons"
is periodic in \underline{k} space, periodicity \underline{G}
like $E_n(\underline{k})$
- has the same symmetry as $E_n(\underline{k})$

space group + time reversal

$$\omega_i(\underline{k}) = \omega_i(-\underline{k})$$

- Due to periodic boundary conditions (over M ions): number of allowed \underline{k} -values is finite

$$\frac{M}{r} \text{ unit cells} \Leftrightarrow \frac{M}{r} \underline{k} \text{ values in the BZ}$$

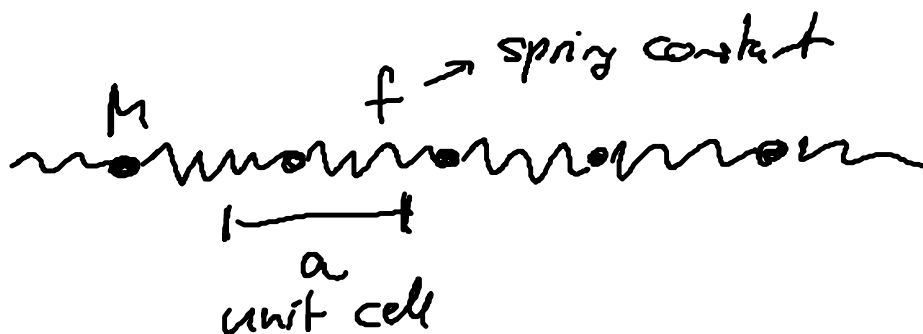
- as $M \rightarrow \infty$, $\omega_i(\underline{k})$ is an analytic function but $i = 1, \dots, 3r$ restricted unlike $\epsilon_n(\underline{k})$

Classical vibrations: Example

$$i, \underline{k}, \alpha, n, \mu, \beta, \nu, \nu$$

→ lots of book-keeping

"Toy model": Linear chain of id. atoms



Equilibrium: $x_{n+1}^0 - x_n^0 = a$

Displacements $x_n \rightarrow x_n^0 + s_n$

$$M \ddot{s}_n = -f (s_n - s_{n+1}) + f (s_{n-1} - s_n)$$

use $s_n = \frac{1}{\sqrt{M}} e \cdot e^{i(k \cdot a n - \omega t)}$

$$\omega^2 M = f (2 - e^{ika} - e^{-ika})$$

$$= f (2 - 2 \cos ka)$$

$$= 4 \cdot f \cdot \sin^2 \frac{ka}{2}$$

$$\omega(k) = 2 \sqrt{\frac{f}{M}} \left| \sin \frac{ka}{2} \right|$$

