

Separation of electrons and nuclei

- $\hat{H} = \hat{H}_e + \hat{H}_n + \hat{H}_{en}$

$\hat{\psi}(R, x) = E \psi(R, x)$

↳ electronic coordinates
↳ nuclei coordinates

$\hat{H}_e = \hat{T}_e + U_{ee}, \quad \hat{H}_n = \hat{T}_n + U_{nn}, \quad \hat{H}_{en} = U_{en}$

\downarrow \downarrow \downarrow
 $-\sum_i \frac{\hbar^2}{2m} \Delta_i$ $-\sum_A \frac{\hbar^2}{2M_A} \Delta_A$ $-\sum_i \sum_A \frac{z_A e^-}{|R_A - r_i|}$

\downarrow \downarrow
 $\frac{1}{2} \sum_{i,j} \frac{e^2}{r_{ij}}$ $\frac{1}{2} \sum_{A,B} \frac{z_A z_B e^-}{R_{AB}}$

- A way to exact solution:

$$\left[\hat{T}_e(x) + U_{ee}(x) + U_{en}(x, R) + U_{nn}(R) \right] \psi_s(x, R) = U_s(R) \psi_s(x, R)$$

R-fixed (1)

This corresponds to classical nuclei. $m(\text{electron}) \ll M(\text{nucleus})$

Quantum nuclei:

$$\psi(R, x) = \sum_s \chi_s(R) \psi_s(x, R) \Rightarrow \text{Schrödinger eq.}$$

$$\hat{T}_n(\chi_s \psi_s) = -\sum_A \frac{\hbar^2}{2M_A} \Delta_A \chi_s \psi_s = (\hat{T}_n \chi_s) \psi_s + \chi_s (\hat{T}_n \psi_s) - \sum_{A\alpha} \frac{\hbar^2}{M_A} \frac{\partial \chi_s}{\partial R_{A\alpha}} \frac{\partial \psi_s}{\partial R_{A\alpha}}$$

(2)

We obtain:

$$\sum_{\xi} \left[(\hat{T}_n \chi_{\xi}) \psi_{\xi} + (\hat{T}_n \psi_{\xi}) \chi_{\xi} - \sum_A \frac{\hbar^2}{M_A} (\nabla_A \chi_{\xi}) (\nabla_A \psi_{\xi}) + \chi_{\xi} (\hat{T}_e + U_{ee} + U_{en} + U_{nn}) \psi_{\xi} - E \chi_{\xi} \psi_{\xi} \right] = 0 \quad (3)$$

$\chi < \psi_{\xi}$
 and
 Integrate over x

$$\sum_{\xi} \left[(\hat{T}_n \chi_{\xi}) \delta_{\xi\xi} + \langle \psi_{\xi} | \hat{T}_n | \psi_{\xi} \rangle \chi_{\xi} - \sum_A \frac{\hbar^2}{M_A} (\nabla_A \chi_{\xi}) \langle \psi_{\xi} | \nabla_A | \psi_{\xi} \rangle + U_{\xi}(R) \delta_{\xi\xi} \chi_{\xi} - E \chi_{\xi} \delta_{\xi\xi} \right] = 0$$

$$\sum_{\xi} \left[\hat{T}_{\xi\xi}(R) + U_{\xi\xi}(R) \right] \chi_{\xi}(R) = E \chi_{\xi}(R) \quad (4)$$

where:

$$\hat{T}_{\xi\xi}(R) = \delta_{\xi\xi} \hat{T}_n(R) + \hat{A}_{\xi\xi}(R)$$

This is
 an operator!

$$= \sum_{A\alpha} \frac{\hbar^2}{M_A} \left[C_{\xi\xi}^{A\alpha}(R) + \frac{1}{2} D_{\xi\xi}^{A\alpha}(R) \frac{\partial}{\partial R_{A\alpha}} \right]$$

$$\langle \psi_{\xi} | \frac{\partial}{\partial R_{A\alpha}} | \psi_{\xi} \rangle \quad \langle \psi_{\xi} | \frac{\partial}{\partial R_{A\alpha}} | \psi_{\xi} \rangle$$

$$U_{\xi\xi}(R) = \delta_{\xi\xi} U_{\xi}(R)$$

These equations are exact. Note that $\hat{A}_{\xi\xi}(R)$ (diagonal) is NOT an operator, as

$$D_{\xi\xi}^{A\alpha}(R) = \langle \psi_{\xi} | \frac{\partial}{\partial R_{A\alpha}} | \psi_{\xi} \rangle = \frac{1}{2} \frac{\partial}{\partial R_{A\alpha}} \langle \psi_{\xi} | \psi_{\xi} \rangle = 0 \quad \text{if } \psi_{\xi} \text{- real} \quad \left(\text{no magnetic field} \right)$$

• $U_\xi(R)$ - adiabatic potential for the electronic state ξ

(a) Adiabatic approximation

U_{ground} is well separated from $U_{1\text{st excited}}$

$$\psi(R, x) = \psi_\xi(x, R) \chi_{\xi \geq 2}(R) \quad (5)$$

$$\left[\hat{T}_n + U_\xi(R) + \Lambda_{\xi\xi}(R) \right] \chi_{\xi \geq 2} = E_{\xi \geq 2} \chi_{\xi \geq 2} \quad (7)$$

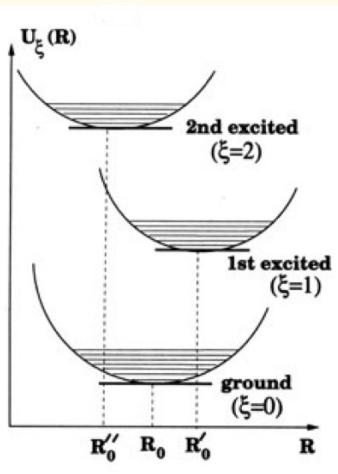
$$\left(\frac{m}{M}\right)^{3/4}$$

small parameter

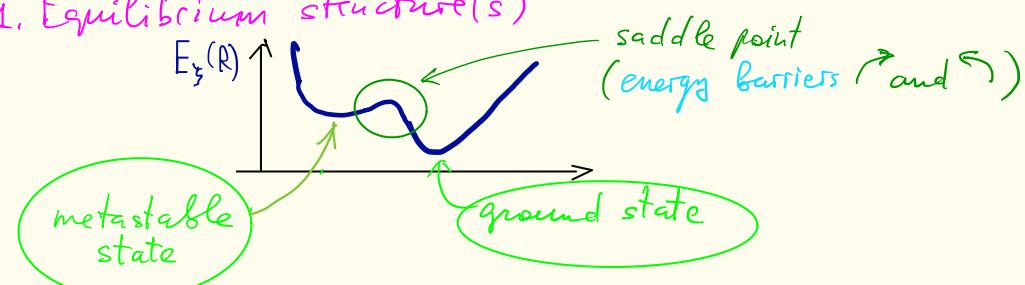
$$(6) \quad \hbar\omega / |E_0(R) - E_1(R)| \ll 1$$

In many cases the R -dependence is defined by $U_\xi(R)$, $\Lambda_{\xi\xi}(R)$ can be treated as a constant.

$$(8) \quad E_\xi(R) = U_\xi + \Lambda_{\xi\xi} \quad \text{- potential energy of electrons and nuclei, when the latter are fixed at } R \text{ and are "classical" (PES)}$$



1. Equilibrium structure(s)



2. Vibrations \Rightarrow Thermal properties

3. Stability

Elections follow the nuclei adiabatically

Vibrations (introduction of the idea only)

$$E_\xi(R) = U_\xi + \Lambda_{\xi\xi} \quad \leftarrow \text{PES around } R_0 \text{ (minimum)}$$

Expand this to the 2nd order in atomic displacements $U_A = R_A - R_A^0$ around equilibrium positions (the minimum of the PES):

$$= \sum_{A\alpha} \underbrace{\left(\frac{\partial E_\xi}{\partial R} \right)^0}_{\text{Ad}} U_{A\alpha} + \frac{1}{2} \sum_{A\alpha, A'\alpha'} \underbrace{\left(\frac{\partial^2 E_\xi}{\partial R_{A\alpha} \partial R_{A'\alpha'}} \right)^0}_{\Phi_{A\alpha, A'\alpha'}} U_{A\alpha} U_{A'\alpha'} + \dots \quad (9)$$

↑
- atomic forces
↑
vibrations

Force constant matrix

$$\left[T_h + \frac{1}{2} \sum_{A\alpha, A'\alpha'} \Phi_{A\alpha, A'\alpha'} U_{A\alpha} U_{A'\alpha'} \right] X_{\xi\alpha} = E_{\xi\alpha} X_{\xi\alpha}$$

quantum equations of atomic vibrations.

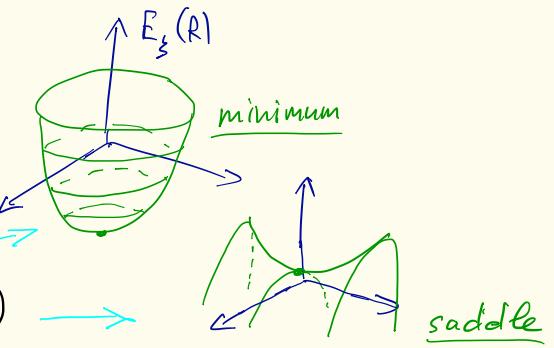
(=0 at the minimum)

Stability

The matrix $\Phi = \|\Phi_{A\alpha, A'\alpha'}\|$ is positively defined

Eigenvalues of Φ are ω_x^2 . If all $\omega_x^2 > 0$.

If $\omega_x^2 < 0 \Rightarrow$ purely imaginary (unstable)



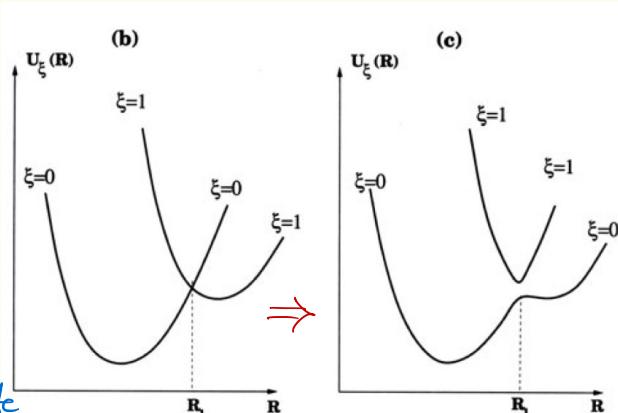
(b) non-adiabaticity ($U_{\xi_1}(R), U_{\xi_2}(R)$ cross)

$$\Psi(R, x) = \psi_{\xi_1}(x, R)\chi_{\xi_1}(R) + \psi_{\xi_2}(x, R)\chi_{\xi_2}(R) \quad (11)$$

near the crossing. \Rightarrow vibronic coupling

$\hat{N}_{\xi_1 \xi_2}$ - operator of non-adiabaticity

\hookrightarrow crossing is avoided (e.g. perturbation
(degeneracy lifted) theory for degenerate
states)



• Diabatic expansion

$$\Psi(R, x) = \sum_{\xi} \underbrace{\psi_{\xi}(x, R_0)}_{\text{in the minimum of the PES } U_{\xi}(R)} \chi_{\xi}(R) \quad (12)$$

Born-Oppenheimer
1927

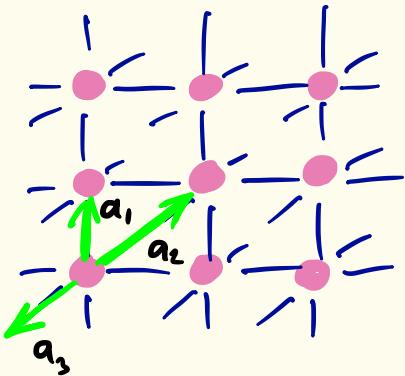
Here $U_{\xi_1 \xi_2}(R)$ is not diagonal; $\hat{T}_{\xi_1 \xi_2}(R)$ is diagonal.

Equations are much simpler as $\nabla_A \psi_{\xi} = 0$.

This method is also exact in principle.

$\left(\frac{m}{M}\right)^{1/4}$
small parameter

A note on crystals



Atoms inside UC:

- $\vec{a}_1, \vec{a}_2, \vec{a}_3$ - basic primitive translations
 $\vec{L} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$ - Lattice vector
integers

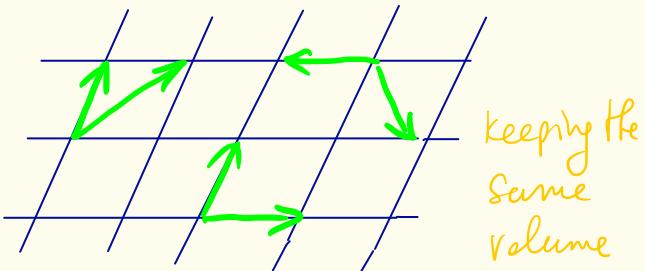
This forms the Bravais lattice. $\Rightarrow 1$ atom in the unit cell.

- If more than 1 atom are in the UC, then the BL's are shifted with respect to each other.

$$\vec{R}_s = s_1 \vec{a}_1 + s_2 \vec{a}_2 + s_3 \vec{a}_3 \quad [0 \leq s_i < 1]$$

$$V_c = (\vec{a}_1 \cdot [\vec{a}_2 \times \vec{a}_3]) - \text{UC volume}$$

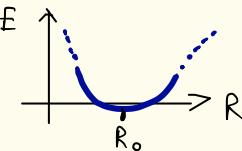
- Different choice of basic translations:



$$\vec{a}'_i = \sum_{j=1}^3 T_{ij} \vec{a}_j$$

The new cell is $|T|$ times larger than the old one.

Atomic vibrations

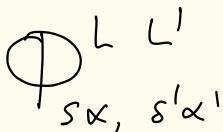


- We consider a single PES, e.g. the ground state.

$$E = E_0 + \frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j \quad j, i \in (A, \alpha) \quad \leftarrow \text{harmonic approximation}$$

quadratic form $\Phi_{ij} = \Phi_{ji}$ (Φ - symmetric matrix)

(26)



- Translational symmetry: $\vec{u}_A = \vec{v}$ for $\forall i$

$$\text{The force } F_{A\alpha} = -\frac{\partial E}{\partial u_{A\alpha}} = -\sum_{A'\alpha'} \Phi_{A\alpha, A'\alpha'} u_{A'\alpha'} = -\sum_{\alpha'} \vec{v}_{\alpha'} \left(\sum_{A'} \Phi_{A\alpha, A'\alpha'} \right) = 0 \Rightarrow \boxed{\sum_{A'} \Phi_{A\alpha, A'\alpha'} = 0} \quad (27)$$

- Periodic systems (crystals) $i, j \Rightarrow (\vec{L} s \alpha)$ \vec{L} - unit cell; $\alpha - x_1 y_1 z$
s - atom within the cell

$$(a) \text{ displace 1 atom } u_{ls\alpha} \neq 0 \Rightarrow \Delta E = \frac{1}{2} \Phi_{s\alpha, s\alpha}^{LL} u_{ls\alpha}^2 \Rightarrow \Phi_{s\alpha, s\alpha}^{LL} \text{ does not depend on } L \quad (28)$$

$$(b) \text{ displace 2 atoms } u_{ls\alpha}, u_{l's'\alpha'} \neq 0 \Rightarrow \Delta E = \frac{1}{2} \left(\Phi_{s\alpha, s\alpha}^{LL} u_{ls\alpha}^2 + \Phi_{s\alpha', s\alpha'}^{LL'} u_{l's'\alpha'}^2 \right) + \Phi_{s\alpha, s\alpha'}^{LL'} u_{ls\alpha} u_{l's'\alpha'} \quad (28)$$

$$\Rightarrow \Phi^{LL'} \text{ can only depend on the difference } L-L' \Rightarrow \boxed{\Phi^{LL'} = \Phi^{L-L'}} \quad (30)$$

• Equations of motion (classical) $H = \sum_i \frac{p_i^2}{2M_i} + \frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j$ (31) $i \equiv (A\alpha)$

$$m_k \ddot{u}_k$$

$$(32) \quad \dot{p}_k = f_k, \quad f_k = -\frac{\partial}{\partial u_k} \left[\frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j \right] = -\sum_i \Phi_{ki} u_i \quad (33) \quad \Rightarrow M_k \ddot{u}_k = -\sum_i \Phi_{ki} u_i \quad (34)$$

Change to matrix notations: $M \ddot{u} = -\Phi u$ (35)

$$M = \begin{pmatrix} M_1 & & \\ & M_2 & \\ & & \ddots \end{pmatrix} \quad u = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \end{pmatrix} \quad \Phi = \begin{pmatrix} \Phi_{11} & \Phi_{12} & \dots \\ \Phi_{21} & \Phi_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (36)$$

Dynamical matrix

$$V = M^{1/2} u \Rightarrow M^{1/2} \ddot{v} = -\Phi M^{1/2} V \Rightarrow \ddot{v} = -D V, \quad D = M^{-1/2} \Phi M^{-1/2}$$

Trial solution: $V(t) = Y e^{i\omega t}$, $-\omega^2 Y = -D Y$ or $DY = \omega^2 Y$ (37) Eigenproblem

\Rightarrow normal modes are $Y^{(\lambda)} = M^{-1/2} Y_\lambda e^{i\omega_\lambda t}$ (38)

The vibrational frequencies: $|D - \omega^2 E| = 0$ E - identity matrix

Eigenvectors Y_λ can be all chosen orthonormal: $Y_\lambda^+ Y_{\lambda'} = \delta_{\lambda\lambda'}$ orthogonality

$$e^{i\alpha D} = \sum_\lambda e^{i\alpha\omega_\lambda^2} Y_\lambda Y_\lambda^+ \Rightarrow \text{at } \alpha=0 \quad E = \sum_\lambda Y_\lambda Y_\lambda^+ \quad \Leftarrow \text{completeness}$$

Stability

$$\bullet \text{PE} = \frac{1}{2} U^T \Phi U = \frac{1}{2} U^T (M^{1/2} \mathcal{D} M^{1/2}) U = \frac{1}{2} (M^{1/2} U)^T \mathcal{D} (M^{1/2} U)$$

$$\mathcal{D} = \sum_{\lambda} \omega_{\lambda}^2 Y_{\lambda} Y_{\lambda}^T \quad (\text{spectral theorem})$$

$$\text{PE} = \frac{1}{2} (M^{1/2} U)^T \sum_{\lambda} \omega_{\lambda}^2 Y_{\lambda} Y_{\lambda}^T (M^{1/2} U) = \frac{1}{2} \sum_{\lambda} \omega_{\lambda}^2 \underbrace{(M^{1/2} Y_{\lambda}^T U)}_{\text{scalar}} \underbrace{(M^{1/2} Y_{\lambda}^T U)}_{Y_{\lambda}} = \sum_{\lambda} \frac{\omega_{\lambda}^2 y_{\lambda}^2}{2}$$

• $D^T = D \Rightarrow \omega_{\lambda}^2 \in \mathbb{R} \text{ (real)}$

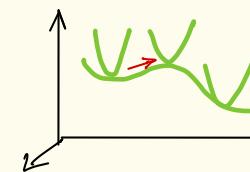
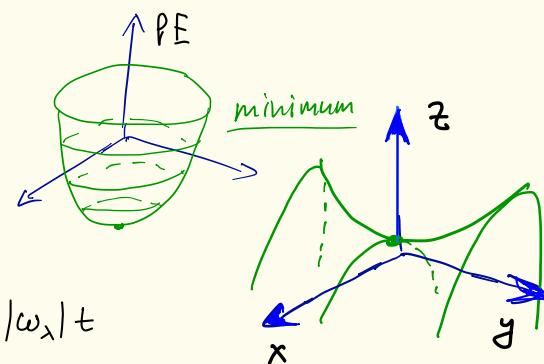
(a) $\omega_{\lambda}^2 > 0$ for $\forall \lambda \Rightarrow \text{stable}$

(b) $\exists \omega_{\lambda}^2 < 0 \Rightarrow \text{unstable}$

$$e^{\pm i \omega_{\lambda} t} \Rightarrow e^{\pm i (i |\omega_{\lambda}|) t} = e^{\mp |\omega_{\lambda}| t}$$

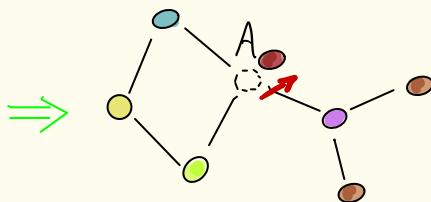
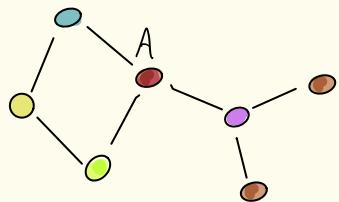
dissociative solution

(c) $\exists \omega_{\lambda} - \text{small} \Rightarrow \text{soft mode}$



Frozen phonon approximation

$U_{\xi}(R)$ - ground state property, can differentiate numerically



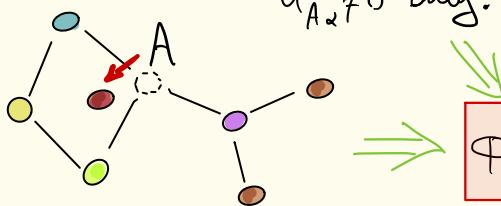
$$F_{B\beta}^{(+)} = - \sum_{A'\alpha'} \Phi_{B\beta, A'\alpha'} U_{A'\alpha'} \quad (40)$$

$$= - \Phi_{B\beta, A\alpha} U_{A\alpha}$$

$$\Phi_{B\beta, A\alpha} = - F_{B\beta}^{(+)} / U_{A\alpha} \quad (41)$$

Better precision:

- $U_{A\alpha}$ as well

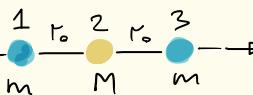
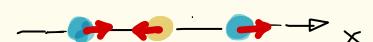
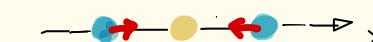


$$\Phi_{B\beta, A\alpha} \approx - (F_{B\beta}^{(+)} - F_{B\beta}^{(-)}) / 2 U_{A\alpha} \quad (42)$$

$$\Phi_{B\beta, A\alpha} = \begin{pmatrix} & & & \\ & & & \\ & & \ddots & \\ & \vdots & & \\ & & & \\ & & & \end{pmatrix}_{B\beta}^{A\alpha}$$

It won't be symmetric. Need to **impose** the symmetrisation posteriori by either accepting Δ , ∇ or averaging over two.

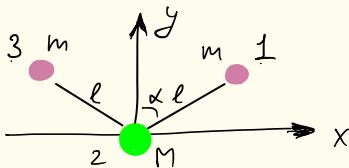
- For crystals with PBC this method would only give vibrations for certain $\vec{k} \in \Gamma$. Larger UC are needed to have more \vec{k} points reproduced. Perturbation theory enables one to consider any \vec{k} using even the primitive unit cell.

- For finite systems (e.g. molecules):
- (a) translational invariance: momentum $\vec{P} = \sum_A m_A \dot{\vec{u}_A} = 0 \Rightarrow \sum_A m_A u_{A\alpha} = 0$ (43)
- (b) rotational invariance: angular momentum $\vec{M} = \sum_A m_A [\vec{r}_A \times \dot{\vec{u}}_A] = 0$
- Small vibrations: $\vec{M} = \sum_A m_A [(\vec{r}_A^0 + \vec{u}_A) \times \dot{\vec{u}}_A] \approx \sum_A m_A [\vec{r}_A^0 \times \dot{\vec{u}}_A] = \frac{d}{dt} \sum_A m_A [\vec{r}_A^0 \times \vec{u}_A] \equiv 0$
- $\Rightarrow \sum_A m_A [\vec{r}_A^0 \times \vec{u}_A] = 0$ (44)
- 3 Dof less
- Total # of Dof = $3N - 6$ (non-linear molecules)
- Linear molecules: $3N - 5$ (one rotation less)
- 3 Dof less as well
- Example 1  $U = \frac{1}{2} k(x_3 - x_2)^2 + \frac{1}{2} k(x_1 - x_2)^2$ (45)
- New variables:
- $Q_a = x_1 + x_3$
- $Q_b = x_1 - x_3$ (46)
- Condition: $m(x_1 + x_3) + Mx_2 = 0 \Rightarrow x_2$ can be eliminated.
- $KE = \frac{1}{2} m(\dot{x}_1^2 + \dot{x}_3^2) + \frac{1}{2} M\dot{x}_2^2 = \frac{mM}{4M} \dot{Q}_a^2 + \frac{m}{4} \dot{Q}_b^2$, $J = M+2m$ (47)
- $PE = U = \frac{kJ^2}{4M^2} Q_a^2 + \frac{k}{4} Q_b^2$ (48)
- $\left\{ \begin{array}{l} x_1 = \frac{1}{2}(Q_a + Q_b) \\ x_3 = \frac{1}{2}(Q_a - Q_b) \\ x_2 = -\frac{m}{M} Q_a \end{array} \right.$ (50)
- The Hamiltonian: $H = H_a + H_b$, $H_a = \frac{mJ}{4M} \dot{Q}_a^2 + \frac{kJ^2}{4M^2} Q_a^2$, $H_b = \frac{m}{4} \dot{Q}_b^2 + \frac{k}{4} Q_b^2$ (51)
- Q_a, Q_b - normal coordinates with frequencies:
- $\omega_a^2 = \frac{kM}{mM}$ and $\omega_b^2 = \sqrt{\frac{k}{m}}$ (52)
- Q_a -mode: 
- Q_b -mode: 

Example 2

Translational invariance:

$$m(x_1 + x_3) + Mx_2 = 0, \quad m(y_1 + y_3) + My_2 = 0 \quad (53)$$



Rotational invariance:

$$m[\vec{r}_1 \times (x_1)] + m[\vec{r}_3 \times (x_3)] + M[\vec{r}_2 \times (x_2)] = 0$$

$$\left(\begin{array}{c} l \sin \alpha \\ l \cos \alpha \end{array} \right) \quad \left(\begin{array}{c} -l \sin \alpha \\ l \cos \alpha \end{array} \right) \quad \left(\begin{array}{c} 0 \\ 0 \end{array} \right)$$

$$\sin(x_1 - x_3) - \cos(x_1 + x_3) = 0 \quad (54)$$

Instead of 6 variables, we have only 3.

- Introduce new variables:

$$(55) \quad \begin{aligned} Q_a &= x_1 + x_3 \\ Q_{s2} &= y_1 + y_3 \\ Q_{s1} &= x_1 - x_3 \end{aligned} \quad \Rightarrow \quad \begin{cases} x_1 = \frac{1}{2}(Q_a + Q_{s1}) \\ y_1 = \frac{1}{2}(Q_{s2} + Q_a \operatorname{ctg} \alpha) \end{cases} \quad \begin{cases} x_2 = -\frac{m}{M}Q_a \\ y_2 = -\frac{m}{M}Q_{s2} \end{cases} \quad \begin{cases} x_3 = \frac{1}{2}(Q_a - Q_{s1}) \\ y_3 = \frac{1}{2}(Q_{s2} - Q_a \operatorname{ctg} \alpha) \end{cases} \quad (56)$$

- Considering \vec{r}_{12} and \vec{r}_{32} in the 1st order with respect to displacements x_1, y_1, x_2, y_2 and x_3, y_3 :

$$\delta l_{12} = (x_1 - x_2) \sin \alpha + (y_1 - y_2) \cos \alpha \quad \delta l_{32} = -(x_3 - x_2) \sin \alpha + (y_3 - y_2) \cos \alpha \quad (57)$$

The angle's <321 change can be obtained e.g. from $\cos(2\alpha + \delta\alpha) = \vec{r}_{12} \cdot \vec{r}_{32} / r_{12} r_{32}$:

$$\delta\alpha = \frac{1}{l} \left\{ [-(x_3 - x_2) + (x_1 - x_2)] \cos \alpha - [(y_3 - y_2) + (y_1 - y_2)] \sin \alpha \right\} \quad (58)$$

$$PE = \frac{k_1}{2} (\delta l_{12}^2 + \delta l_{22}^2) + \frac{k_2}{2} (\ell \delta \alpha)^2 = \frac{k_1}{4} \left(\frac{2m}{M} + \frac{1}{s^2} \right) \left(1 + \frac{2m}{M} s^2 \right) Q_a^2 + \frac{Q_{S1}^2}{4} (k_1 s^2 + 2k_2 c^2) + \left(\frac{m}{2M} \right)^2 Q_{S2}^2 (k_1 c^2 + 2k_2 s^2) + \frac{m}{2M} (k_1 - 2k_2) \cos Q_{S1} Q_{S2}, \text{ where } \begin{array}{l} c = \cos \alpha \\ s = \sin \alpha \end{array} \quad (58)$$

$$\bullet KE = \frac{m}{2} (\dot{q}_1^2 + \dot{q}_3^2) + \frac{M}{2} \dot{\ell}^2 = \dot{Q}_a^2 \frac{m}{4} \left(\frac{2m}{M} + \frac{1}{s^2} \right) + \frac{m}{4} \dot{Q}_{S1}^2 + \frac{m}{4M} \dot{Q}_{S2}^2 \quad (60)$$

$$\bullet EoM \quad \ddot{\mathcal{L}} = KE - PE, \quad \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}} = \frac{\partial \mathcal{L}}{\partial q} \quad (q \rightarrow Q_a, Q_{S1}, Q_{S2}) \quad (61) \quad (62)$$

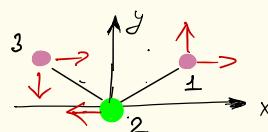
Q_a coordinate is already separated,
normal mode 1 $\Rightarrow \omega_a^2 = \frac{k_1}{m} \left(1 + \frac{2m}{M} s^2 \right)$ (63)

Q_{S1} and Q_{S2} are still coupled:

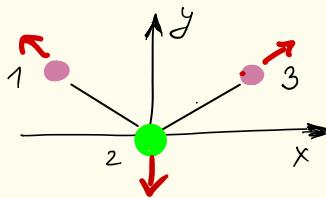
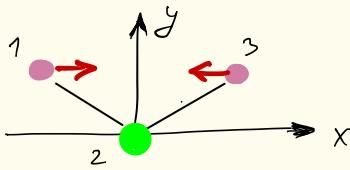
$$\frac{d^2}{dt^2} \begin{pmatrix} Q_{S1} \\ Q_{S2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{m} (k_1 s^2 + 2k_2 c^2) & -\frac{m}{Mm} (k_1 - 2k_2) sc \\ -\frac{1}{m} (k_1 - 2k_2) cs & -\frac{m}{mM} (k_1 c^2 + 2k_2 s^2) \end{pmatrix} \begin{pmatrix} Q_{S1} \\ Q_{S2} \end{pmatrix} = -A \begin{pmatrix} Q_{S1} \\ Q_{S2} \end{pmatrix} \quad (64)$$

Vibrations $\begin{pmatrix} Q_{S1} \\ Q_{S2} \end{pmatrix} = Y e^{i\omega t}$ are obtained from $A Y = \omega^2 Y$, yielding

$$\omega^4 - \left[\frac{k_1}{m} \left(1 + \frac{2m}{M} c^2 \right) + \frac{2k_2}{m} \left(1 + \frac{2m}{M} s^2 \right) \right] \omega^2 + \frac{2mk_1 k_2}{Mm^2} = 0 \quad (65)$$



$Q_{S1} = Q_{S2} = 0$
$x_1 = x_3, y_1 = -y_3$
$y_2 = 0, x_2 = -x_1$



$$\Phi_a = 0 \Rightarrow \begin{cases} x_1 = \frac{1}{2} Q_{S1} \\ y_1 = \frac{1}{2} Q_{S2} \end{cases} \quad \begin{cases} x_2 = 0 \\ y_2 = -\frac{m}{M} Q_{S2} \end{cases} \quad \begin{cases} x_3 = -\frac{1}{2} Q_{S1} \\ y_3 = \frac{1}{2} Q_{S2} \end{cases} \quad \begin{matrix} Q_{S1} \sim Q_{S2} \\ (\text{from eigen vectors of } 2 \times 2) \end{matrix}$$

- A realistic force field model for H_2O :

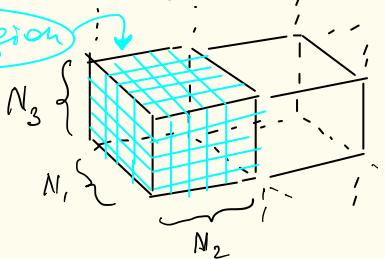
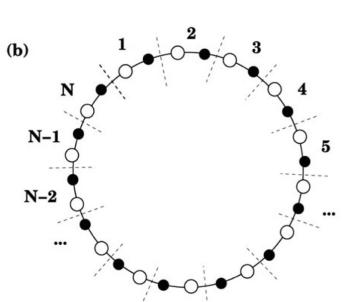
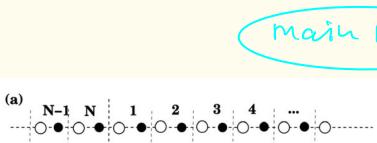
$$U(x_1, x_2, \theta) \approx U_0 + \frac{1}{2} K_r (\delta \ell_{12}^2 + \delta \ell_{32}^2) + \frac{1}{2} K_\theta \ell^2 \delta \alpha^2 + K'_r \delta \ell_{12} \delta \ell_{32} + K_{r\theta} \ell (\delta \ell_{12} + \delta \ell_{32}) \delta \alpha \quad (67)$$

$$K_r \approx 52.76; \quad K_\theta = 4.75; \quad K'_r = -0.63; \quad K_{r\theta} = 1.42 \quad (\text{eV}/\text{\AA}^2); \quad \ell = 0.9576 \text{ \AA}$$

• Crystals $i \equiv (Ls\alpha)$ $D\gamma = \omega^2 \gamma \Rightarrow \sum_{L's'\alpha'} D_{s\alpha, s'\alpha'}^{L-L'} \gamma_{s'\alpha'}^{L'} = \omega^2 \gamma_s^L$ (68)

Born-von Karman boundary conditions:

main region



$N = N_1 N_2 N_3$ primitive cells

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ - primitive lattice vectors

BvK conditions:

$$U_{\vec{L} + N_1 \vec{a}_1} = U_{\vec{L}}$$

$$U_{\vec{L} + N_2 \vec{a}_2} = U_{\vec{L}}$$

$$U_{\vec{L} + N_3 \vec{a}_3} = U_{\vec{L}}$$

Reciprocal space: $\vec{a}_i \cdot \vec{B}_j = 2\pi \delta_{ij}$ (70)

\vec{B}_j - primitive reciprocal lattice vectors

Brillouin zone (BZ): $\vec{k} \in BZ$

Let us take some \vec{k} and apply $\sum_L e^{i\vec{k}\vec{L}}$ to both sides of (68):

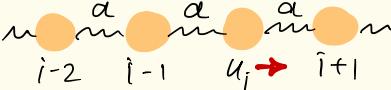
$$\sum_{L,L'} D^{L-L'} \gamma^{L'} e^{-i\vec{k}\vec{L}} = \omega \left[\sum_L e^{-i\vec{k}\vec{L}} \gamma^L \right] \stackrel{L}{\Rightarrow} \left(\sum_{L''} D^{L''} e^{-i\vec{k}\vec{L}''} \right) \left(\sum_{L'} e^{i\vec{k}\vec{L}'} \gamma^{L'} \right) = \omega^2 \left(\sum_L e^{-i\vec{k}\vec{L}} \gamma^L \right) \quad (71)$$

$$\sum_{s'\alpha'} D_{s\alpha, s'\alpha'}^{\vec{k}} \gamma_{s'\alpha'}^{\vec{k}} = \omega_k^2 \gamma_s^{\vec{k}}, \quad D^{\vec{k}} = \sum_L D^L e^{-i\vec{k}\vec{L}} \quad (72) \quad \gamma^{\vec{k}} = \sum_L e^{-i\vec{k}\vec{L}} \gamma^L \quad (73)$$

$D^{\vec{k}} \gamma^{\vec{k}} = \omega_k^2 \gamma^{\vec{k}}$ normal modes and their frequencies are characterised by the wave vector \vec{k} .
Finite size!

Translational symmetry!

● Crystalline systems

Example 3  Monoatomic lattice

$$\mathcal{L} = \sum_{n=-\infty}^{\infty} \left\{ \frac{1}{2} m \ddot{u}_n^2 - \frac{1}{2} \mathfrak{R} (u_{n+1} - u_n)^2 \right\}, \quad \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{u}_n} = \frac{\partial \mathcal{L}}{\partial u_n} \quad (74)$$

$$\frac{\partial \mathcal{L}}{\partial \dot{u}_n} = m \ddot{u}_n; \quad f_n = -\frac{\partial \mathcal{L}}{\partial u_n} = +\mathfrak{R} (u_{n+1} - u_n) - \mathfrak{R} (u_n - u_{n-1}) \Rightarrow m \ddot{u}_n = \mathfrak{R} (u_{n+1} - 2u_n + u_{n-1}) \quad (75)$$

Use $u_n(t) = A_n e^{-ik_0 t}$ with $A_n = A e^{ikan}$ $\Rightarrow -A \omega^2 = k (e^{ika} - 2 + e^{-ika}) A$

$$\omega^2 = \frac{2\mathfrak{R}}{m} (1 - \cos ka) \quad (76)$$

$$u_n^{(k)}(t) = A e^{-ikt} e^{ikan}$$

In the classical limit $a \rightarrow 0$
we have $u^{(k)}(t) \sim \exp[i(kx - \omega t)]$
a wave-like solution.

Here $\omega(k)$ - dispersion relation. (77)

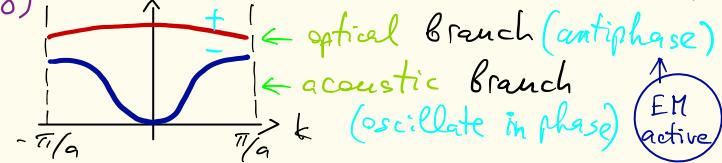
$-\frac{\pi}{a} < k \leq \frac{\pi}{a}$ as otherwise solutions repeat themselves \Rightarrow BZ in 1D.

Example 4  Two atoms in the basis $\bullet V_h \bullet U_h$

$$\begin{cases} m_1 \ddot{u}_n = k (v_n - 2u_n + u_{n-1}) \\ m_2 \ddot{v}_n = k (u_n - 2v_n + v_{n+1}) \end{cases} \Rightarrow \begin{pmatrix} u_n(t) \\ v_n(t) \end{pmatrix} = \begin{pmatrix} (l_1) \\ (l_2) \end{pmatrix} e^{ikt} e^{ikan} \quad (78)$$

$$\begin{pmatrix} 2k - m_1 \omega^2 & -k(1 + e^{-ika}) \\ -k(1 + e^{ika}) & 2k - m_2 \omega^2 \end{pmatrix} \begin{pmatrix} l_1 \\ l_2 \end{pmatrix} = 0 \quad (79)$$

Yields two solutions: $\omega_{\pm}(k)$, $-\frac{\pi}{a} < k \leq \frac{\pi}{a}$



Example 5 Central forces

$$PE = \frac{1}{2} \sum_{AB} \int \phi(R_{AB}) \quad (80)$$

nearest neighbours only (between unlike atoms)

Expand the pairwise interaction:

$$\vec{R}_A = \vec{R}_A^0 + \vec{u}_A, \quad \vec{R}_{AB} = \vec{R}_{AB}^0 + (\vec{u}_A - \vec{u}_B) \quad (81)$$

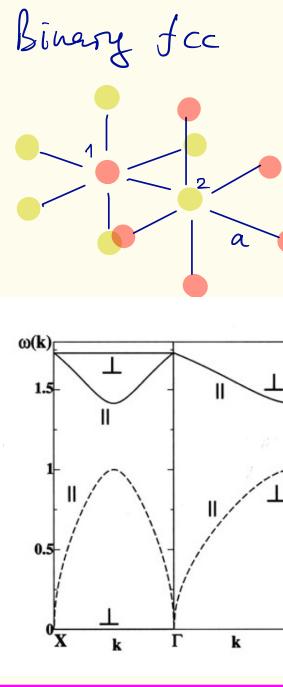
$$\phi(R) = \phi(|\vec{R} + \vec{u}|) = \phi(R^0) + \sum_{\alpha} \left(\frac{\partial \phi}{\partial R_{\alpha}} \right)^0 u_{\alpha} + \frac{1}{2} \sum_{\alpha \alpha'} \left(\frac{\partial^2 \phi}{\partial R_{\alpha} \partial R_{\alpha'}} \right)^0 u_{\alpha} u_{\alpha'} + \dots \quad (82)$$

$$\text{where } \vec{u} = \vec{u}_i - \vec{u}_j \text{ and } \frac{\partial \phi}{\partial R_{\alpha}} = \phi'(R) \frac{\partial R}{\partial R_{\alpha}} = \phi'(R) \frac{R_{\alpha}}{R} \quad \text{and} \quad (83)$$

$$(84) \quad \frac{\partial^2 \phi}{\partial R_{\alpha} \partial R_{\alpha'}} = \frac{\partial}{\partial R_{\alpha}} \left(\phi'(R) \frac{R_{\alpha}}{R} \right) = \phi'(R) \frac{\delta_{\alpha \alpha'}}{R} + \frac{R_{\alpha} R_{\alpha'}}{R} \left(\frac{1}{R} \phi''(R) \right) = \phi''_{\alpha \alpha'}(R)$$

$$PE = \frac{1}{4} \sum_{AB} \int \phi_{\alpha \alpha'}(\vec{R}_{AB}^0) (\vec{u}_A - \vec{u}_B) (\vec{u}_A - \vec{u}_B) = \frac{1}{2} \sum_A \left(\sum_B \int \phi_{\alpha \alpha'}(\vec{R}_{AB}^0) \right) U_{A\alpha} U_{A\alpha'} - \frac{1}{2} \sum_{AB} \int \phi_{\alpha \alpha'}(\vec{R}_{AB}^0) U_{A\alpha} U_{B\alpha'} \quad (85)$$

$$\Rightarrow \boxed{\Phi_{S\alpha S'\alpha'}^{\vec{L}-\vec{L}'}} = \delta_{LL'} \delta_{SS'} \sum_{L''S''} \int \phi_{\alpha \alpha'}(\vec{L}_S - \vec{L}_{S''}) - \phi_{\alpha \alpha'}(\vec{L}_S - \vec{L}'_{S'}) \quad (86)$$



Classical force field

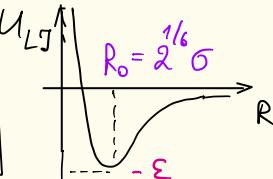
- $U_s(R)$ - fitted by a certain function of R to the DFT total energies,

- Pair-wise approximation

$$U_{LJ}(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

Lennard-Jones potential

Pauli repulsion vDW attraction

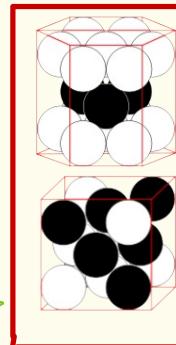


Many atoms:

$$U = \frac{1}{2} \sum_{ij} U_{ij}(|\vec{R}_i - \vec{R}_j|)$$

Many atoms:

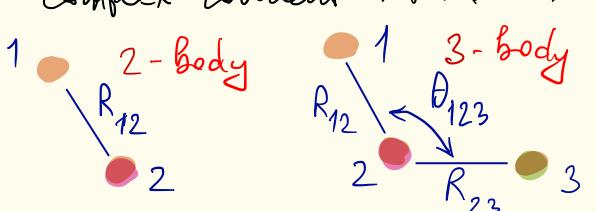
Interactions between nn and nnn are the most important ones. In crystals close packing is dominated as the number of nn is optimised.



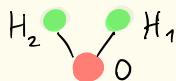
hexagonal close packed (hcp)
[Al, Au, Ag, ...] 3D

face-centered close-packed (fcc)
[Co, Zn, Ti, Ru, ...]

- Biological molecules Here many-body terms are essential as more complex covalent interactions take place.



Example



More complex interactions are also possible.

+ long range pairwise interactions can be added