

§1. Lattice dynamics

* Quantum theory of lattice vibrations

- Review: quantum harmonic oscillator

$$\begin{aligned}
 H &= \frac{1}{2M} P^2 + \frac{1}{2} M \omega^2 X^2 \\
 &= \frac{1}{2} \hbar \omega \left(\frac{1}{M \omega \hbar} P^2 + \frac{M \omega}{\hbar} X^2 \right) \\
 &= \frac{1}{2} \hbar \omega \left(\frac{l_0^2}{\hbar^2} P^2 + \frac{1}{l_0^2} X^2 \right) \quad l_0 = \sqrt{\frac{\hbar}{M \omega}}
 \end{aligned}$$

Use a and a^\dagger to represent x and p :

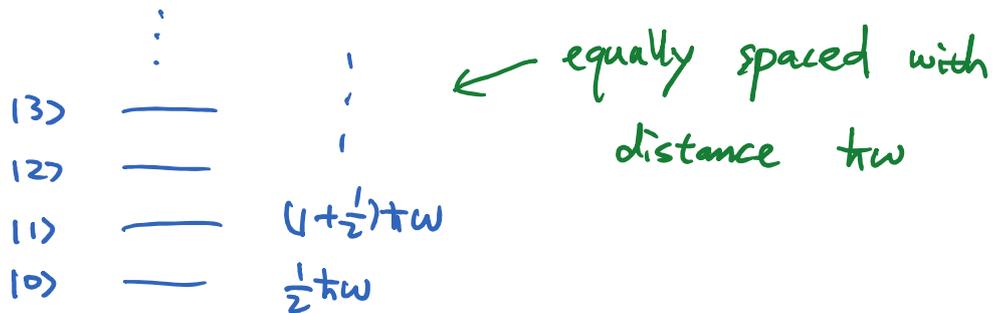
$$\begin{cases}
 x = \frac{1}{\sqrt{2}} l_0 (a + a^\dagger) \\
 p = \frac{-i}{\sqrt{2}} \frac{\hbar}{l_0} (a - a^\dagger)
 \end{cases}$$

$$\begin{aligned}
 [x, p] &= \frac{-i}{2} \hbar [a + a^\dagger, a - a^\dagger] \\
 &= \frac{-i}{2} \hbar (-1 - 1) \\
 &= i \hbar \quad \checkmark
 \end{aligned}$$

$$\begin{aligned}
 \Rightarrow H &= \frac{1}{2} \hbar \omega \left(\frac{l_0^2}{\hbar^2} P^2 + \frac{1}{l_0^2} X^2 \right) \\
 &= \frac{1}{2} \hbar \omega \left[\underbrace{-\frac{1}{2} (a - a^\dagger)^2}_{(a - a^\dagger)(a - a^\dagger)} + \frac{1}{2} \underbrace{(a + a^\dagger)^2}_{(a + a^\dagger)(a + a^\dagger)} \right] \\
 &= \frac{1}{2} \hbar \omega (a a^\dagger + a^\dagger a) \quad \begin{matrix} \text{"} \\ a^2 + (a^\dagger)^2 - a a^\dagger - a^\dagger a \end{matrix} \quad \begin{matrix} \text{"} \\ a^2 + (a^\dagger)^2 + a a^\dagger + a^\dagger a \end{matrix} \\
 &= \hbar \omega \left(a^\dagger a + \frac{1}{2} \right)
 \end{aligned}$$

Energy spectrum:

$$\begin{aligned} H |n\rangle &= \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) |n\rangle \\ &= \hbar\omega \left(n + \frac{1}{2} \right) |n\rangle \end{aligned}$$



Partition function at finite temperature T :

$$\begin{aligned} Z &= \text{Tr} e^{-\beta H} & \beta &= \frac{1}{k_B T} \\ &= \sum_{n=0}^{\infty} \langle n | e^{-\beta \hbar\omega (a^\dagger a + \frac{1}{2})} | n \rangle \\ &= \sum_{n=0}^{\infty} e^{-\beta \hbar\omega (n + \frac{1}{2})} \\ &= \frac{1}{1 - e^{-\beta \hbar\omega}} e^{-\frac{1}{2} \beta \hbar\omega} \end{aligned}$$

Thermal average of operator A :

$$\langle A \rangle_T \equiv \frac{1}{Z} \text{Tr} (A e^{-\beta H})$$

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Example: $\langle a^\dagger a \rangle_T = \frac{1}{Z} \text{Tr}(a^\dagger a e^{-\beta H})$

$$\text{Tr}(a^\dagger a e^{-\beta H}) = \sum_{n=0}^{\infty} \langle n | a^\dagger a e^{-\beta \hbar \omega (a^\dagger a + \frac{1}{2})} | n \rangle$$

$$= \sum_{n=0}^{\infty} n e^{-\beta \hbar \omega (n + \frac{1}{2})}$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} \sum_{n=0}^{\infty} n e^{-\beta \hbar \omega n}$$

$$\frac{\partial}{\partial \omega} e^{-\beta \hbar \omega n} = -\beta \hbar n e^{-\beta \hbar \omega n}$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} \frac{-1}{\beta \hbar} \frac{\partial}{\partial \omega} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n}$$

$$= e^{-\frac{1}{2} \beta \hbar \omega} \frac{-1}{\beta \hbar} \frac{-\beta \hbar e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2}$$

$$= \frac{e^{-\frac{3}{2} \beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2}$$

$$\begin{aligned}
 \Rightarrow \langle a^\dagger a \rangle_T &= \frac{1}{Z} \text{Tr}(a^\dagger a e^{-\beta H}) \\
 &= \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \\
 &= \frac{1}{e^{\beta \hbar \omega} - 1}
 \end{aligned}$$

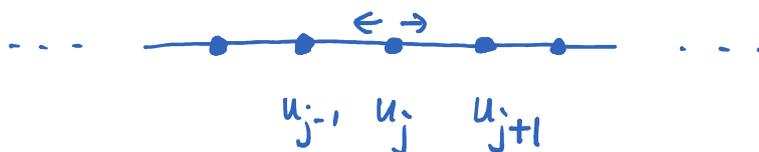
Generalization to decoupled harmonic oscillators:

$$H = \sum_{\lambda=1}^N \varepsilon_\lambda a_\lambda^\dagger a_\lambda$$

$$\Rightarrow \langle a_\lambda^\dagger a_\lambda \rangle_T = \frac{1}{e^{\beta \hbar \omega_\lambda} - 1}$$

↪ can be viewed as a demonstration
of the Bose-Einstein distribution

- Quantum dynamics of 1D monoatomic chain



$$H = \sum_{j=1}^N \frac{P_j^2}{2M} + \frac{1}{2} c \sum_{j=1}^N (u_{j+1} - u_j)^2$$

Commutation relations:

$$\begin{cases} [u_j, u_l] = [P_j, P_l] = 0 \\ [u_j, P_l] = i\hbar \delta_{jl} \end{cases}$$

Coupled harmonic oscillators!

General strategy:

$$H = \sum_{j=1}^N \frac{P_j^2}{2M} + \frac{1}{2} c \sum_{j,l=1}^N u_j D_{jl} u_l$$

$$P = \begin{pmatrix} P_1 \\ P_2 \\ \vdots \\ P_N \end{pmatrix}$$

$$= \frac{1}{2M} P^T P + \frac{1}{2} c u^T D u$$

$$u = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ u_N \end{pmatrix}$$

D: real symmetric matrix

Diagonalize D: $O^T D O = \Lambda = \begin{pmatrix} \lambda_1 & & \\ & \lambda_2 & \\ & & \ddots \\ & & & \lambda_N \end{pmatrix}$

orthogonal matrix

$$O^T O = O O^T = \mathbb{1}_{N \times N}$$

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$$\begin{aligned}
 \Rightarrow H &= \frac{1}{2M} P^T \underbrace{O^T O}_P P + \frac{1}{2} C u^T \underbrace{O^T \Lambda O}_{u'} u \\
 &= \frac{1}{2M} P'^T P' + \frac{1}{2} C u'^T \Lambda u' \\
 &= \sum_{q=1}^N \left(\frac{1}{2M} P_q'^2 + \frac{1}{2} C \lambda_q u_q'^2 \right)
 \end{aligned}$$

Canonical commutation relations:

$$\begin{cases}
 u'_p = \sum_{j=1}^N O_{pj} u_j \\
 P'_q = \sum_{j=1}^N O_{qj} P_j
 \end{cases}$$

$$\begin{aligned}
 \Rightarrow [u'_p, P'_q] &= \sum_{j,l=1}^N O_{pj} O_{ql} \underbrace{[u_j, P_l]}_{i\hbar \delta_{jl}} \\
 &= \sum_{j=1}^N O_{pj} O_{qj} \underbrace{= O_{jq}^T}_{\text{matrix}} \\
 &= \underbrace{(OO^T)}_{Pq} \\
 &= \delta_{pq} \underbrace{I_{N \times N}}
 \end{aligned}$$

$$[u'_p, u'_q] = [P'_p, P'_q] = 0$$

N decoupled harmonic oscillators!

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In the presence of translation invariance (PBC):

Fourier modes:
$$\begin{cases} u_j = \frac{1}{\sqrt{N}} \sum_q e^{iqja} u_q \\ u_q = \frac{1}{\sqrt{N}} \sum_j e^{-iqja} u_j \end{cases} \quad \begin{array}{l} q \in \text{FBZ} \\ q = 0, \pm \frac{2\pi}{Na}, \dots \end{array}$$

$$\begin{cases} P_j = \frac{1}{\sqrt{N}} \sum_q e^{-iqja} P_q \\ P_q = \frac{1}{\sqrt{N}} \sum_j e^{iqja} P_j \end{cases}$$

$$[u_q, u_{q'}] = \frac{1}{N} \sum_{j,l} e^{-iqja - iq'la} [u_j, u_l] = 0$$

$$[P_q, P_{q'}] = \frac{1}{N} \sum_{j,l} e^{iqja} + e^{iq'la} [P_j, P_l] = 0$$

$$\begin{aligned} [u_q, P_{q'}] &= \frac{1}{N} \sum_{j,l} e^{-iqja + iq'la} [u_j, P_l] \\ &= i\hbar \frac{1}{N} \sum_j e^{i(q'-q)ja} \underbrace{[u_j, P_l]}_{= i\hbar \delta_{jl}} \\ &= i\hbar \delta_{q',q} \end{aligned}$$

Standard commutation relations!

Note that
$$\begin{cases} u_j = u_j^+ \\ P_j = P_j^+ \end{cases} \Rightarrow \begin{cases} u_{-q} = u_q^+ \\ P_{-q} = P_q^+ \end{cases}$$

$$\begin{aligned} u_q &= \frac{1}{\sqrt{N}} \sum_j e^{-iqja} u_j \\ &\Downarrow \\ u_{-q} &= \frac{1}{\sqrt{N}} \sum_j e^{iqja} u_j \\ u_q^+ &= \frac{1}{\sqrt{N}} \sum_j e^{iqja} u_j^+ \end{aligned}$$

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$$\begin{aligned}
H &= \sum_j \frac{P_j^2}{2M} + \frac{1}{2} c \sum_j (u_{j+1} - u_j)^2 \\
&= \sum_j \frac{P_j^2}{2M} + \frac{1}{2} c \sum_j (2u_j^2 - u_{j+1}u_j - u_{j-1}u_j) \\
&= \frac{1}{N} \sum_j \sum_{q, q'} \frac{1}{2M} P_q P_{q'} e^{-i(q+q')ja} \leftarrow \frac{1}{N} \sum_j e^{i(q+q')ja} = \delta_{q', -q} \\
&\quad + \frac{1}{2} c \sum_j \sum_{q, q'} u_q u_{q'} \left[2e^{i(q+q')ja} - e^{iq(j+1)a + iq'ja} \right. \\
&\quad \quad \quad \left. - e^{iq(j-1)a + iq'ja} \right] \\
&= \sum_q \frac{1}{2M} P_q P_{-q} + \frac{1}{2} \sum_q u_q u_{-q} (2 - e^{iqa} - e^{-iqa}) \\
&= \sum_q \left(\frac{1}{2M} P_q P_{-q} + 2C \sin^2 \frac{qa}{2} u_q u_{-q} \right) \\
&= \sum_q \left(\frac{1}{2M} P_q P_{-q} + \frac{1}{2} M \omega_q^2 u_q u_{-q} \right)
\end{aligned}$$

$$\omega_q = \sqrt{\frac{4C}{M}} \left| \sin \frac{qa}{2} \right| \leftarrow \text{frequency from classical E.O.M!}$$

$$H = \sum_q H(q), \quad \text{where } [H(q), H(q')] = 0$$

\Rightarrow Diagonalize each $H(q)$ separately!

Each $H(q)$ describes a harmonic oscillator.

$q \in \text{FBZ} \rightarrow N$ independent harmonic oscillators

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Define bosonic creation and annihilation operators:

$$\left\{ \begin{aligned} a_q &= \sqrt{\frac{m\omega_q}{2\hbar}} u_q + i \sqrt{\frac{1}{2M\hbar\omega_q}} P_{-q} \\ a_q^+ &= \sqrt{\frac{m\omega_q}{2\hbar}} u_{-q} - i \sqrt{\frac{1}{2M\hbar\omega_q}} P_q \end{aligned} \right.$$

Subtlety: Rigorously speaking, $q=0$ has to be treated separately.

Zero mode, $\omega_q = 0$ for $q=0$

Note that $H(q=0) = \frac{P_{q=0}^2}{2M}$ "center-of-mass momentum"

We will not deal with this issue here.

Check: $[a_q, a_{q'}] = [a_q^+, a_{q'}^+] = 0$

$$[a_q, a_{q'}^+] = \delta_{qq'}$$

$$\begin{aligned} [a_q, a_{q'}] &= -i \frac{1}{2\hbar} [u_q, P_{q'}] - i \frac{1}{2\hbar} [P_{-q}, u_{-q'}] \\ &= -i \frac{1}{2\hbar} i\hbar \delta_{qq'} - i \frac{1}{2\hbar} (-i\hbar \delta_{qq'}) \\ &= 0 \end{aligned}$$

$$\begin{aligned} [a_q, a_{q'}^+] &= -i \frac{1}{2\hbar} [u_q, P_{q'}] + i \frac{1}{2\hbar} [P_{-q}, u_{-q'}] \\ &= -i \frac{1}{2\hbar} i\hbar \delta_{qq'} + i \frac{1}{2\hbar} (-i\hbar \delta_{qq'}) \\ &= \delta_{qq'} \quad \checkmark \end{aligned}$$

Inverse transformation:

$$\begin{cases} u_q = \sqrt{\frac{\hbar}{2M\omega_q}} (a_q + a_{-q}^\dagger) \\ p_q = (-i) \sqrt{\frac{M\hbar\omega_q}{2}} (a_{-q} - a_q^\dagger) \end{cases}$$

$$\begin{cases} u_j = \frac{1}{\sqrt{N}} \sum_q u_q e^{i\mathbf{q}\cdot\mathbf{j}a} = \frac{1}{\sqrt{N}} \sum_q e^{i\mathbf{q}\cdot\mathbf{j}a} \sqrt{\frac{\hbar}{2M\omega_q}} (a_q + a_{-q}^\dagger) \\ p_j = \frac{1}{\sqrt{N}} \sum_q p_q e^{-i\mathbf{q}\cdot\mathbf{j}a} = \frac{1}{\sqrt{N}} \sum_q e^{-i\mathbf{q}\cdot\mathbf{j}a} (-i) \sqrt{\frac{M\hbar\omega_q}{2}} (a_{-q} - a_q^\dagger) \end{cases}$$

Look at the Hamiltonian terms:

$$\begin{aligned} \frac{1}{2M} p_q p_{-q} &= \frac{1}{2M} (-i) \frac{M\hbar\omega_q}{2} (a_{-q} - a_q^\dagger)(a_q - a_{-q}^\dagger) \\ &= -\frac{1}{4} \hbar\omega_q (\underbrace{a_{-q} a_q + a_q^\dagger a_{-q}^\dagger}_{\text{red}} - \underbrace{a_q^\dagger a_q - a_{-q} a_{-q}^\dagger}_{\text{green}}) \end{aligned}$$

$$\begin{aligned} \frac{1}{2} M\omega_q^2 u_q u_{-q} &= \frac{1}{2} M\omega_q^2 \frac{\hbar}{2M\omega_q} (a_q + a_{-q}^\dagger)(a_{-q} + a_q^\dagger) \\ &= \frac{1}{4} \hbar\omega_q (\underbrace{a_q a_{-q} + a_{-q}^\dagger a_q^\dagger}_{\text{red}} + \underbrace{a_{-q}^\dagger a_{-q} + a_q a_q^\dagger}_{\text{green}}) \end{aligned}$$

$$\begin{aligned} \Rightarrow H &= \sum_q \left[\frac{1}{2M} p_q p_{-q} + \frac{1}{2} M\omega_q^2 u_q u_{-q} \right] \\ &= \sum_q \hbar\omega_q \left(\underbrace{a_q^\dagger a_q + \frac{1}{2}}_{\text{red}} \right) \end{aligned}$$

$$\begin{aligned} \downarrow \\ a a^\dagger &= [a, a^\dagger] + a^\dagger a \\ &= a^\dagger a + 1 \end{aligned}$$

Eigenstates:

$$|n_{q=0}, n_{q=\frac{2\pi}{Na}}, n_{q=-\frac{2\pi}{Na}}, \dots, n_{q=\frac{\pi}{a}}\rangle$$

$$= \frac{1}{\sqrt{n_{q=0}! \dots n_{q=\frac{\pi}{a}}!}} (a_{q=0}^+)^{n_{q=0}} (a_{q=\frac{2\pi}{Na}}^+)^{n_{q=\frac{2\pi}{Na}}} \dots (a_{q=\frac{\pi}{a}}^+)^{n_{q=\frac{\pi}{a}}} |0\rangle$$

$$n_q = 0, 1, \dots, \infty$$

Eigenenergies:

$$H |n_{q=0}, \dots, n_{q=\frac{\pi}{a}}\rangle = \sum_q \hbar \omega_q (n_q + \frac{1}{2}) |n_{q=0}, \dots, n_{q=\frac{\pi}{a}}\rangle$$

$$E = \sum_q \hbar \omega_q (n_q + \frac{1}{2})$$

Generalization to 1D diatomic chain and 3D crystal
is straightforward:

$$H_{1D \text{ diatomic}} = \sum_q \hbar \omega_q^- (a_q^+ a_q + \frac{1}{2}) \quad \text{acoustic}$$

$$+ \sum_q \hbar \omega_q^+ (b_q^+ b_q + \frac{1}{2}) \quad \text{optical}$$

$$H_{3D} = \sum_{q, \nu=1,2,3} \hbar \omega_{q,\nu}^+ (a_{q,\nu}^+ a_{q,\nu} + \frac{1}{2}) \quad 3 \text{ acoustic}$$

$$+ \sum_{q, \nu=4, \dots, 3r} \hbar \omega_{q,\nu}^+ (a_{q,\nu}^+ a_{q,\nu} + \frac{1}{2}) \quad 3r-3 \text{ optical}$$