Quantum description of crystal vibrations

I. 1D Harmonic oscillator: operator approach

Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2} \qquad \omega = \sqrt{\frac{K}{m}}$$

$$[\hat{x}, \hat{p}] = -i\hbar \qquad \hat{p} = -i\hbar \frac{\partial}{\partial x}$$

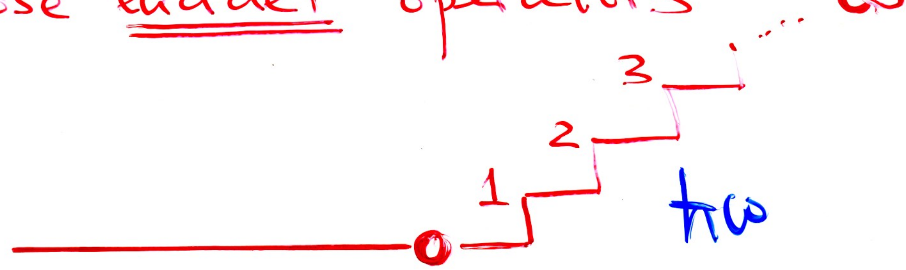
Raising and lowering operators

$$a^+ = \sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} - i\sqrt{\frac{1}{2m\omega\hbar}}\,\hat{p}$$

$$a = \sqrt{\frac{m\omega}{2\hbar}}\,\hat{x} + i\sqrt{\frac{1}{2m\omega\hbar}}\,\hat{p}$$

$$[a, a^+] \equiv a a^+ - a^+ a = 1$$

Bose ladder operators



$$H = \frac{1}{2}\hbar\omega\,(a^+a + aa^+)$$

$$aa^+ = 1 + a^+a$$

$$\boxed{H = \hbar\omega\left(a^+a + \frac{1}{2}\right)}$$

Vacuum $|0\rangle$: $\quad a|0\rangle = 0$

Coordinate representation $\quad \langle x|a|0\rangle = \phi_0(x) = A\cdot\exp\left(-\frac{x^2}{2\ell_0^2}\right)$

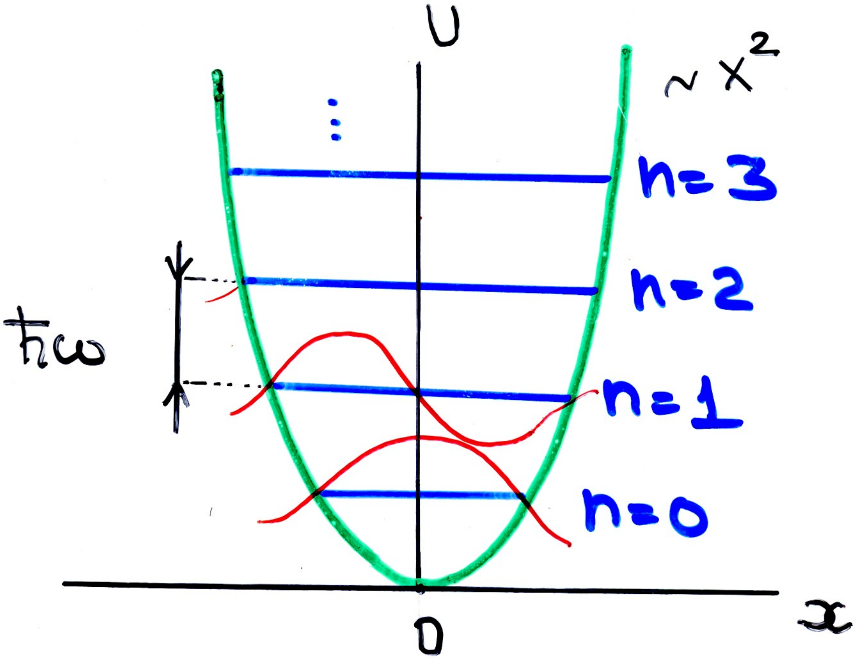
$\ell_0^2 = \frac{\hbar}{m\omega}$ characteristic length

Excited states $\quad |n\rangle = (a^+)^n|0\rangle$

$a^+a = \hat{n}$: $\quad \hat{n}|n\rangle = n|n\rangle$

$n = 0, 1, \ldots \infty$

$$\hat{H} \rightarrow \hbar\omega\,(\hat{n} + 1/2)$$



Normalized states $\langle n' | n \rangle = \delta_{n,n'}$
orthogonal

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^+)^n |0\rangle$$

$$|n\rangle = \frac{a^+}{\sqrt{n}} |n-1\rangle$$

$$a^+ |n\rangle = \sqrt{n+1}\, |n+1\rangle$$ raising operator

$$a|n\rangle = \begin{cases} \sqrt{n}\, |n-1\rangle & n \geq 1 \\ \emptyset & n = \emptyset \end{cases}$$ lowering operator

$$\hat{n} = a^+ a \qquad \hat{n}|n\rangle = n|n\rangle$$

occupation #

Lattice vibrations in harmonic approx:

$$H^{harm} = \sum_{\vec{R}} \frac{\vec{P}^2(\vec{R})}{2M} + \frac{1}{2}\sum_{\vec{R}}\sum_{\vec{R}'} D_{\mu\nu}(\vec{R}-\vec{R}')\, u_\mu(\vec{R})\, u_\nu(\vec{R}')$$

Quantum description:

$$[\hat{u}_\mu(\vec{R}), \hat{P}_\nu(\vec{R}')] = -i\hbar\, \delta_{\mu\nu}\, \delta_{\vec{R},\vec{R}'}$$

$$\Downarrow$$

phonons : $\omega_s(\vec{k})$ $\vec{\epsilon}_s(\vec{k})$

?

Classical description $\Rightarrow$ N normal modes

$$a_{\vec{k}s} = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{-i\vec{k}\cdot\vec{R}}\, \vec{\epsilon}_s(\vec{k}) \cdot$$

$$\cdot \left[\sqrt{\frac{M\omega_s(\vec{k})}{2\hbar}}\, \vec{u}(\vec{R}) + i \sqrt{\frac{1}{2\hbar M \omega_s(\vec{k})}}\, \vec{P}(\vec{R}) \right]$$

$a^+_{\vec{k}s}$ = Hermitian conjugate $(a_{\vec{k}s})$: ① $i \rightarrow -i$ ②

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Commutation relations

$$\left[a_{\vec{k}s}, a^{+}_{\vec{k}'s'}\right] = \delta_{\vec{k}\vec{k}'} \cdot \delta_{ss'}$$

$$\left[a_{\vec{k}s}, a_{\vec{k}'s'}\right] = \left[a^{+}_{\vec{k}s}, a^{+}_{\vec{k}'s'}\right] = 0$$

To establish use $\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = \begin{cases} N & \vec{k} \in RL \\ \phi & \vec{k} \notin RL \end{cases}$

$\vec{u}(\vec{R})$ in terms of phonon creation and destruction operators

$$\vec{u}(\vec{R}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}=1}^{N} \sum_{s=1}^{3} \sqrt{\frac{\hbar}{2M\omega_s(\vec{k})}} \left(a_{\vec{k}s} + a^{+}_{-\vec{k}s}\right) \cdot$$

$$\cdot \vec{\epsilon}_s(\vec{k}) \exp(i\vec{k}\cdot\vec{R})$$

used

$$\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}} = \begin{cases} N, & \vec{R} = \phi \\ \phi, & \vec{R} \neq 0 \end{cases}$$

$$\vec{P}(\vec{R}) = \frac{-i}{\sqrt{N}} \sum_{\vec{k}=1}^{N} \sum_{s=1}^{3} \sqrt{\frac{\hbar M \omega_s(\vec{k})}{2}} \left(a_{\vec{k}s} - a^{+}_{-\vec{k}s} \right) \cdot$$

$$\cdot \, \vec{\epsilon}_s(\vec{k}) \, e^{i\vec{k}\cdot\vec{R}}$$

$$\hat{H} = \sum_{\vec{k}s} \hbar\omega_{\vec{k}s} \left(a^{+}_{\vec{k}s} a_{\vec{k}s} + 1/2 \right)$$

3N independent quantum harmonic oscillators

$$\hat{n}_{\vec{k}s} = a^{+}_{\vec{k}s} a_{\vec{k}s}$$ occupation number operator

Vacuum $$|0\rangle \equiv \underbrace{|0_1\rangle |0_2\rangle \ldots |0_N\rangle}_{3N \text{ modes}}$$

$$a_{\vec{k}s}|0\rangle = 0 \quad \forall \, \vec{k}s$$

$$\hat{n}_{\vec{k}s}|0\rangle = 0$$

$\{n_{\vec{k}s}\}$ a set of phonon occupation numbers: $n_{\vec{k}s} = 0, 1, 2, \ldots +\infty$

$$E = \sum_{\vec{k}s} \hbar\omega_s(\vec{k})\left(n_{\vec{k}s} + 1/2\right)$$ energy

Quantum states

$$|n_{\vec{k}_1 s_1}, \ldots, n_{\vec{k}_2 s_2}, \ldots, n_{\vec{k}_N s_3}\rangle$$

In the harmonic approximation

$n_{\vec{k}s}$ are integrals of the motion:

once fixed, they do not change in time

$E = E\{n_{\vec{k}s}\}$ is an integral of the motion

energy

Momentum of phonons $\sum_{\vec{k}s} \vec{k}_s \cdot n_{\vec{k}s} = \vec{k}$?

¿ is conserved ?

Anharmonic terms

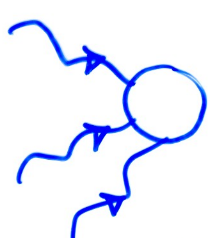
$$u^3 \sim \sum_{\vec{k}_i s_i} \Gamma \, (a_{\vec{k}_1 s_1} + a^+_{-\vec{k}_1 s_1})(a_{\vec{k}_2 s_2} + a^+_{-\vec{k}_2 s_2}) \cdot$$

$$\cdot (a_{\vec{k}_3 s_3} + a^+_{-\vec{k}_3 s_3})$$

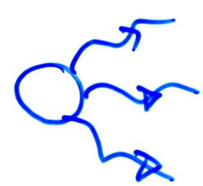
$$H^{(3)} \sim a^3_{..}, \; a^{+3}_{..}, \; a^+_{..} a^2_{..}, \; (a^+_{..})^2 a_{..}$$

$$\langle \{ n'_{\vec{k}s} \} | \, H^{(3)} \, | \{ n_{\vec{k}s} \} \rangle$$

produces change in occupation #'s

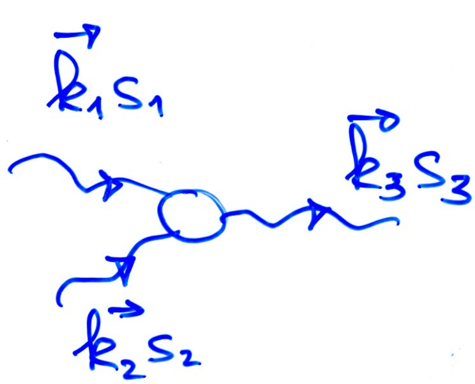


a^3



a^{+3}

do not conserve energy $\Rightarrow$ only virtual processes possible
(corrections to the ground state energy)



$$a^+_{\vec{k}_3 s_3} a_{\vec{k}_2 s_2} a_{\vec{k}_1 s_1}$$

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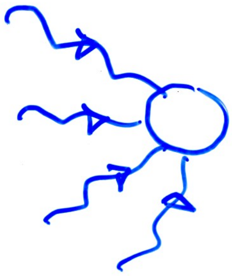
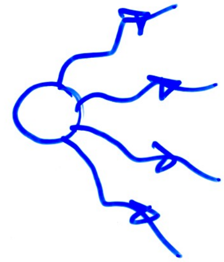
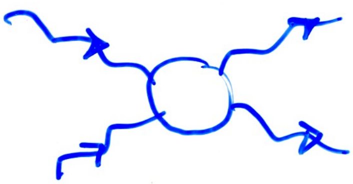
Quartic anharmonicity $\sim u^4$



a^4

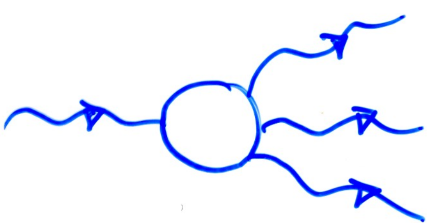


a^{+4}

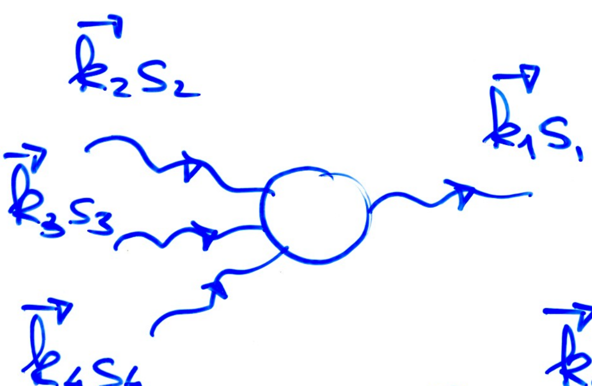


scattering of two phonons

$(a^+)^2 a^2$



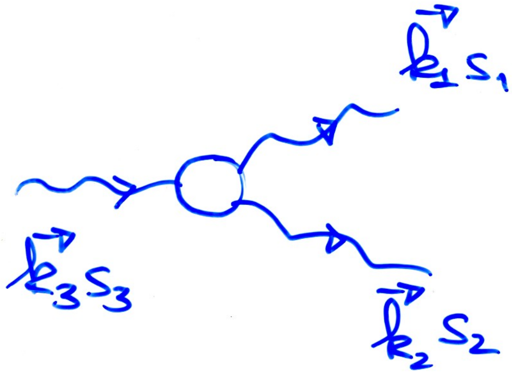
$(a^+)^3 a$



$a^+ a^3$

$$\vec{k}_2 + \vec{k}_3 + \vec{k}_4 = \vec{k}_1 + \vec{K}$$

$$\sum_{i=2}^{3} \hbar\omega_{s_i}(\vec{k}_i) = \hbar\omega_{s_1}(\vec{k}_1)$$



$$a^{+}_{\vec{k}_1 s_1} a^{+}_{\vec{k}_2 s_2} a_{\vec{k}_3 s_3}$$

① Energy conservation

$$\hbar\omega_{s_3}(\vec{k}_3) = \hbar\omega_{s_1}(\vec{k}_1) + \hbar\omega_{s_2}(\vec{k}_2)$$

② (Crystal) momentum conservation

$$\vec{k}_3 = (\vec{k}_1 + \vec{k}_2) + \underset{\in RL}{\vec{K}}$$

$\vec{K} = 0$

Normal processes

$\vec{K} \in RL$, $\vec{K} \neq 0$

Umklapp processes

$$\sum_i \vec{k}_i = \sum_f \vec{k}'_f + \vec{K}$$

for arbitrary number of phonons

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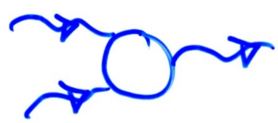
In thermal equilibrium

$$n_s(\vec{k}) = \frac{1}{\exp\left(\frac{\hbar\omega_s(\vec{k})}{k_B T}\right) - 1}$$

① At $T \ll \Theta_D$

only phonons with $\hbar\omega_s(\vec{k}) \ll \Theta_D$ present

② $\vec{k}_2 + \vec{k}_3 = \vec{k}_1 + \vec{k}$



for $\vec{k} \neq 0$ at least one of phonons should have $|\vec{k}_i| \sim k_D$

$\Downarrow$

exp small $n_s(k_D)$

- Umklapp processes are frozen out at $T \ll \Theta_D$

- Umklapp processes lead to non-conservation of initial momentum

$$\sum_i \vec{k}_i$$

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The notion of crystal momentum

$$H_i = \sum_{\vec{R}} \frac{\vec{P}^2(\vec{R})}{2M} + \frac{1}{2}\sum_{\vec{R},\vec{R}'} \phi\left(\vec{R} + \vec{u}(\vec{R}) - \vec{R}' - \vec{u}(\vec{R}')\right)$$

total Hamiltonian $\Longleftrightarrow$ total Momentum

$$H_e = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} v_{ij}(\vec{r}_i - \vec{r}_j)$$

$$H_{i-e} = \sum_{i,e} w_i\left(\vec{r}_i - \vec{R} - \vec{u}(\vec{R})\right)$$

$$H = H_i + H_e + H_{i-e}$$

Translational symmetry of H

$$\vec{r}_i \to \vec{r}_i + \vec{r}_0$$

$$\boxed{\vec{R} \to \vec{R} + \vec{r}_0}$$

$$\vec{u}(\vec{R}) \to \vec{u}(\vec{R}) + \vec{r}_0$$

$\Rightarrow$ total momentum is conserved

(ions + electrons)

Crystal Momentum

crystal symmetry ...... Bravais lattice ...

... all crystal points $\vec{R}$ are equivalent ...

A special transformation

$$\vec{r}_i \to \vec{r}_i + \vec{R}_0 \qquad \text{electrons}$$

$$\vec{u}(\vec{R}) \to \vec{u}(\vec{R}-\vec{R}_0)$$

ions

$$\vec{P}(\vec{R}) \to \vec{P}(\vec{R}-\vec{R}_0)$$

Hamiltonian is invariant: we perform $\sum_{\vec{R}}$

quantity that is conserved

$\shortparallel$

CRYSTAL momentum

Symmetry breaking:

① $\frac{1}{2}K\sum_{\vec{R}}\left[\vec{u}(\vec{R})\right]^2$

pinning ions

② $\sum_{\vec{R}} \frac{\vec{P}^2(\vec{R})}{2M(\vec{R})}$

Breaking crystal symmetry

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