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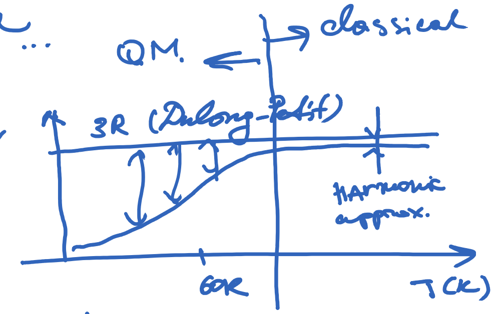
Lecture 18, Solid state physics, April 7, 2020

Quantum crystal continued...



$C_V = 3 n k_B$

if $n = N_A$, $R = N_A k_B$

$$\boxed{C_V = 3R}$$

Quantum harmonic oscillator

$[\hat{q}, \hat{p}] = i\hbar$ ← the key!!!

$$\boxed{\hat{h} = \underbrace{\frac{\hat{p}^2}{2m}}_{\text{kinetic energy}} + \frac{1}{2} m\omega^2 \hat{q}^2}$$

$\omega = \sqrt{\frac{k}{m}} \rightarrow \omega^2 m = k$

$\frac{1}{2} k x^2 \rightarrow \frac{1}{2} m\omega^2 x^2$

$\boxed{q}$ - generalized coordinate

q - classical observable

$\hat{q}$ - an operator, hermitian.

P.A.M. Dirac "The principles of Quantum Mechanics" Oxford/Clarendon press.

Introduce $\hat{a}, \hat{a}^+$:

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

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

$[\hat{q}, \hat{p}] = i\hbar$

$[a, a^+] = 1$

In these new "coordinates":

$\hat{H} = \hbar\omega\,(\underbrace{a^+ a}_{\hat{n}} + \frac{1}{2})$, $\underbrace{(n+\frac{1}{2})\hbar\omega}$, $n = 0, 1, 2 \ldots$

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

- operator identity

$|0\rangle \equiv$ ground state.

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

annihilation creation.

$a|0\rangle$?

$$\boxed{a|0\rangle = \emptyset}$$

operator identity

what is $|0\rangle$ a symbol representing a ket in some Hilbert space!

q-representation

$$\boxed{\hat{q}\, |q\rangle = q\, |q\rangle}$$

meters.

$\underset{\text{bra}}{\langle q'|}\, \hat{a}\, \underset{\text{ket}}{|0\rangle} = \sqrt{\frac{m\omega}{2\hbar}} \langle q' | \hat{q} + \frac{i\hat{p}}{m\omega} | 0\rangle = 0$

$\hat{q}\,|q\rangle = q\,|q\rangle$ ← meters.

$\int |q\rangle\langle q|\,dq = 1$

$\int \langle q|q'\rangle\,dq = \delta(q-q')$

the ket

$\langle q'|\hat{p}|\alpha\rangle = -i\hbar \frac{\partial}{\partial q'}\langle q'|\alpha\rangle$ (Sakurai)

$$\boxed{\left(q' + q_0^2 \frac{\partial}{\partial q'}\right)\underbrace{\langle q'|0\rangle}_{?} = \emptyset}$$ — a normal 1st order differential equation.

$q_0 \equiv \sqrt{\frac{\hbar}{m\omega}}$

$\langle q'|0\rangle = \psi_0(q')$ ← a regular function. It is a ground state of the SHO.

$$\boxed{\psi_0(q') = \frac{1}{\pi^{1/4}\sqrt{q_0}}\exp\left[-\frac{1}{2}\left(\frac{q'}{q_0}\right)^2\right]}$$

This all was known to us, what can we do with it?

$$\boxed{H = \frac{1}{2}\dot{u}^T \underline{\underline{M}}\,\dot{u} + \frac{1}{2}\underline{u}^T \underline{\underline{\Theta}}\,\underline{u}}$$ harmonic approximation.

$\underline{\underline{M}}$ — mass matrix; $\underline{\underline{\Theta}}$ — force-constant matrix

$(\underline{\underline{\Theta}} - \omega_f^2 \underline{\underline{M}})\chi_f = \emptyset$

$\underline{u} = \sum_f \chi_f \alpha_f$

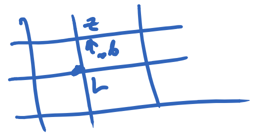
$$\boxed{\hat{H} = \frac{1}{2}\underbrace{\sum_f\left(\dot{\alpha}_f^2 + \omega_f^2\alpha_f^2\right)}_{\text{a SHO in } \alpha\text{s...}}}$$ independent SHOs!

all of this is purely classical!

$u^T = (x^1, y^1, z^1;\ x^2, y^2, z^2;\ \ldots\ z^N)$

(f) number of the mode.

When you go to a crystal:



$u(\ell, b, \alpha)$ — small displacement from $R_0(\ell, b, \alpha)$

ℓ — cell, b — basis, α — x, y, z

$$\boxed{[\hat{u}(\ell b\alpha), \hat{p}(\ell' b' \alpha')] = i\hbar\,\delta_{\alpha\alpha'}\delta_{\ell\ell'}\delta_{bb'}}$$ ← many many variables!!!

conjugate momentum

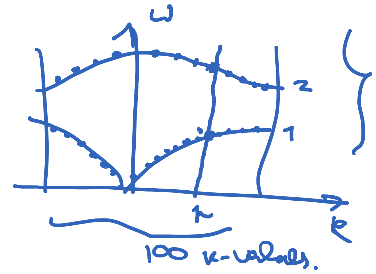
$\hat{p}(\ell b\alpha) = m_b \dot{u}(\ell b\alpha) \rightarrow -i\hbar\frac{\partial}{\partial u(\ell b\alpha)}$

$$\boxed{\hat{p} = \frac{\partial H}{\partial \dot{u}}}$$

$$\boxed{[\hat{\alpha}_f, \hat{\dot{\alpha}}_{f'}] = i\hbar\,\delta_{ff'}}$$

f — eigenmode

f: $(n, \vec{k})$



ω, k, 1, 2

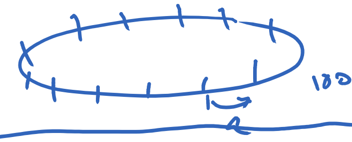
100 k-values.

$$\underset{\text{many body}}{\hat{H}} = \sum_f\left(\dot{\alpha}_f^2 + \omega_f^2\alpha_f^2\right) = \sum_f \hat{h}_f$$

$\hat{h}_f$ — single oscillator with ω_f.

single con. with ω_f.

100 k-values.



many body hamiltonian

$$|\{n_f\}\rangle = \prod_{f=1}^{3N_s} |n_f\rangle$$

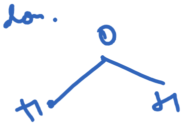
$$E = \sum_{f=1}^{3N_s} E_{nf}$$

$$\boxed{H_f|n_f\rangle = E_{n_f}|n_f\rangle, \quad E_{n_f} = \hbar\omega_f\left(n_f+\tfrac{1}{2}\right) \quad n_f = 0,1,2\ldots}$$

a state with n excitations of mode f

for a molecule of N atoms.

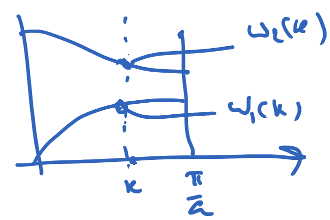
3N degrees of freedom.



9 ⇒ 3 are bondlike vibes.

$$a_f = \sqrt{\frac{1}{2\hbar\omega_f}}\left(\dot{d}_f - i\omega_f d_f\right) \qquad [a_f\, a_{f'}^\dagger] = \delta_{ff'}$$

$$d_f = i\left(\frac{\hbar}{2\omega_f}\right)^{1/2}\left(a_f - a_f^\dagger\right)$$



$a_{\omega_1 k}$, $a^\dagger_{\omega_1 k}$

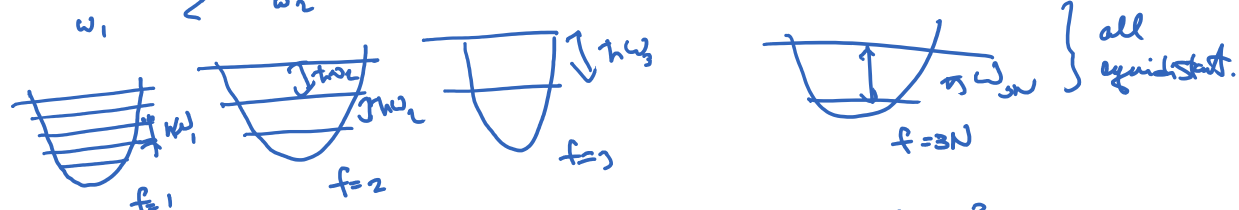
$a_{\omega_2 k}$ $a^\dagger_{\omega_2 k}$

conceptual moment

(simple but non-trivial).

1. The mode picture.

$\omega_1 < \omega_2 < \omega_3 \ldots\ldots < \omega_{3N}$



$n_1 = 2 \qquad n_2 = 0 \qquad n_3 = 0 \quad \ldots \quad n_{3N} = 3$

forget about the zero point energy $\underline{E_{ZP} = \frac{1}{2}\hbar\omega_1 + \frac{1}{2}\hbar\omega_2 \ldots\ldots \frac{1}{2}\hbar\omega_{3N}}$, $\forall n = 0$

$$\underline{E = 2\hbar\omega_1 + 0 \ldots\ldots + 3\hbar\omega_{3N}}$$ above the g.s. (excluding ZPE).

This way counts excitations of the f normal modes!

2. phonon way

spectrum of the system.

$\hbar\omega_{3N}$

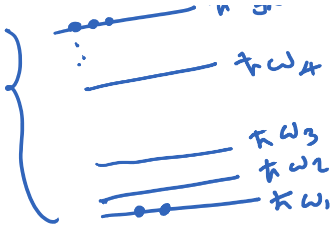
⋮

$\hbar\omega_4$

} this is not an equidistant

level evals.

Allowed energy levels.

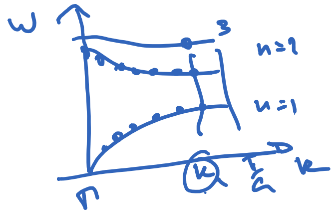


this is not an equidistant spectrum!!!

$|2000\ldots3\rangle$ – the ket describing this state of the molecule.

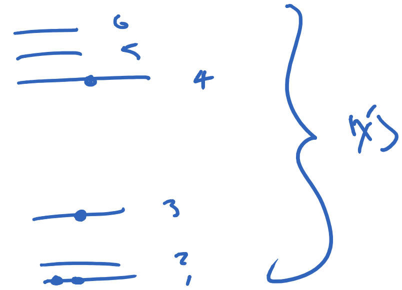
2 phonons of type 1, and 3 phonons of type 3N.

In a solid.



phonon $3, \vec{k}_2$

$$\boxed{\begin{gathered} H = \sum_{\substack{f \\ (n,k)}} \hat{H}_f \\ H_f = (a_f^\dagger a_f + \tfrac{1}{2})\hbar\omega_f \qquad E_{n_f} = \hbar\omega_f(n_f + \tfrac{1}{2}) \\ |\chi\rangle = \prod_1^{3N} |n_f\rangle \quad , \quad \mathcal{E} = \sum_1^{3N} E_{n_f} \end{gathered}}$$



$$|\chi'\rangle = |n_1=2\rangle\,|n_2=0\rangle\,|n_3=1\rangle\,|n_4=1\rangle\,|n_5=0\rangle\,|n_6=0\rangle$$

$$\hat{H}|\chi'\rangle = E'|\chi'\rangle \qquad E' = \hbar\omega_1(2+\tfrac{1}{2}) + \hbar\omega_2(0+\tfrac{1}{2}) + \ldots$$

you can agree to neglect ZP energy.

often you do this wrt the center of mass:

$$u(\begin{smallmatrix} n \\ \alpha \end{smallmatrix}) = R_\alpha^{CM} + i\sum_f \chi(\begin{smallmatrix} n \\ \alpha \end{smallmatrix}|f)\left(\frac{\hbar}{2\omega_f}\right)^{1/2}(a_f - a_f^\dagger)$$

$$H = \frac{1}{2M_{TOT}}\sum P_\alpha^2 + \sum_f \hbar\omega_f(a_f^\dagger a_f + \tfrac{1}{2}).$$

$$\hat{u}\begin{pmatrix} \ell \\ b \\ \alpha \end{pmatrix} = R_\alpha^{cm} + i\sum_{kj}\left[\frac{\hbar}{2Nm_b\,\omega(\begin{smallmatrix} k \\ j \end{smallmatrix})}\right]^{1/2}\left[\hat{e}\left(\begin{smallmatrix} \ell \\ b \end{smallmatrix}\Big|\begin{smallmatrix} k \\ j \end{smallmatrix}\right)e^{i\vec{k}\cdot\vec{R}(\begin{smallmatrix} \ell \\ b \end{smallmatrix})}\,\hat{a}\left(\begin{smallmatrix} k \\ j \end{smallmatrix}\right) + \text{h.c.}\right]$$

momentum branch

kills an excitation of the oscillator with $\omega(k, j)$.

static description

What about time?

What about time?

Heisenberg Picture

$$\hat{A}(t) = e^{\frac{i\hat{H}t}{\hbar}} A \, e^{-\frac{i\hat{H}t}{\hbar}}$$

Schrödinger operator.

$$\boxed{\begin{aligned} i\hbar \dot{A}_H &= [A_H, H] \\ A_H(0) &= A_S \end{aligned}}$$

what about $\hat{a}\binom{k}{j}$?

$(k\,j) = f$

$$i\hbar \, \dot{a}\binom{k}{j} = \left[a\binom{k}{j}, H\right] = \hbar\,\omega\binom{k}{j}\left[a\binom{k}{j}, a^{+}\binom{k}{j} a\binom{k}{j}\right] = \hbar\,\omega\binom{k}{j} a\binom{k}{j}.$$

$$\boxed{a_H\binom{k}{j} = e^{-i\omega\binom{k}{j}t} a_S\binom{k}{j}}$$

go back to stat. Mech.

why? Because, we started all that to fix Dulong-Petit!

I am going to compute the specific heat, but will now use Q.M.

$$Z \equiv \sum_i e^{-\beta E_i}$$ (in the space of $|i\rangle$: $\hat{H}|i\rangle = E_i|i\rangle$) – partition function.

$\beta = 1/kT$

$$F = -kT \ln Z, \qquad S = -\frac{\partial F}{\partial T} \qquad \boxed{E = -\frac{\partial}{\partial \beta}\ln Z} \; *$$

$$E = F + TS = \frac{1}{Z}\sum_i E_i e^{-\beta E_i}$$

If you have 2 independent systems, described by Z_1, Z_2.

The combined system: $Z_{12} = Z_1 \cdot Z_2$

We decided to describe vibrations of the crystal as 3N independent harmonic oscillators. (only true if you neglect $\frac{\partial^3 V}{\partial u \partial u \partial u}, \frac{\partial^4 V}{\partial u \partial u \partial u \partial u} \ldots$)

$$H = \sum_{1}^{3N} H_f$$ – 3N independent SHO.

$$Z = \prod_{1}^{3N} \sum_{n_f=0}^{\infty} e^{-\beta\hbar\omega_f\left(n_f + \frac{1}{2}\right)} = \prod_f e^{-\frac{\beta\hbar\omega_f}{2}} \underbrace{\sum_{n_f=0}^{\infty}\left(e^{-\beta\hbar\omega_f}\right)^{n_f}}_{\text{geometric series}}$$

$-\beta\hbar\omega_f$

$Z = \prod_f \sum_{n_f=0} \quad + \quad \underbrace{\sum_{n_f=0}}_{\text{geometric series}}$

$$\boxed{Z = \prod_f \frac{e^{-\frac{\beta \hbar \omega_f}{2}}}{1 - e^{-\beta \hbar \omega_f}}} \leftarrow \text{a triumph!!!}$$

Now use (*)

$$E = \underbrace{E_0}_{\substack{\text{zero point energy} \\ \infty}} + \sum_f \frac{\hbar \omega_f}{e^{\beta \hbar \omega_f} - 1} = E_0 + \sum_f \hbar \omega_f \langle n_f \rangle$$

$$\langle n_f \rangle = \frac{1}{e^{\beta \hbar \omega_f} - 1}$$

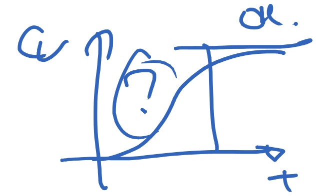
Planck's formula.

$$\left(\langle E \rangle = \sum_f \hbar \omega_f \left(\langle n \rangle + \frac{1}{2} \right) \right)$$

Specific heat

1. high temperature

$$\boxed{C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \sum_f \hbar \omega_f \langle n_f \rangle}$$



$$\langle n_f \rangle = \frac{1}{\underbrace{e^{\beta \hbar \omega_f}}_{\text{Taylor}} - 1} \xrightarrow[T \to \infty]{} \frac{1}{\frac{\hbar \omega_f}{kT}}$$

$\beta = 1/kT \Rightarrow 0$

$kT \gg \hbar \omega_f$

$1\text{eV} \approx 11{,}000\,\text{K}$

$\hbar \omega_f \sim 100\,\text{meV}$

$$C_V = \frac{\partial}{\partial T} \sum_f \cancel{\hbar \omega_f} \frac{kT}{\cancel{\hbar \omega_f}} = \frac{\partial}{\partial T} kT \sum_{f=0}^{3N} 1 = k\,3N \leftarrow \text{Dulong-Petit.}$$

we have got our classical result back!!!