

A Summer Short Course 2016 ①

Lecture 6: Time-domain description of linear spectroscopy.

- * spectroscopy & light-matter interactions.
- * lineshape function & linear absorption spectrum.
- * spectrum of displaced harmonic oscillator model.
- * energy gap Hamiltonian \rightarrow spin-boson model.

Stationary today,
time-resolved (multiple pulses)
next two lectures.

most materials covered in this lecture can be found in Ratner's book.

So far we have focused on time evolution of density matrix \Rightarrow for experimental probe, spectroscopy methods are important \Rightarrow how we investigate condensed-phase quantum dynamics!!

timeless

* Spectroscopy

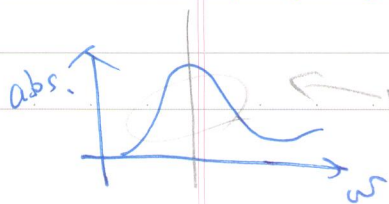
We are now ready to apply these tools to describe quantum dynamics & spectroscopy in condensed-phase systems.

First we derive a very useful description for linear spectra based on Fermi's Golden rule. We will focus on electronic spectroscopy, however, other spectra follow similar approach.

* What is spectroscopy?

* time domain vs. frequency domain.

* What are measured? observable?



not just position, the shape is also important. rate of absorption at a given frequency

timeless

* light-matter interactions,

③

So, we begin with a consideration of

light-matter interactions:

electric-dipole

Hamiltonian.

See lecture
note of 2013
Winter share
course for
the derivation
of this
"electric dipole"
Hamiltonian

$$H_{int} = -\hat{\mu} \cdot \vec{E}(t)$$

elec. field

dipole moment

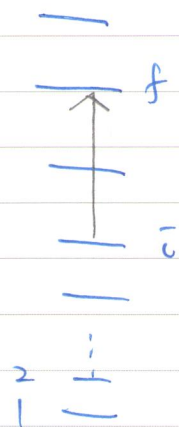
$$\approx -\hat{\mu} \cdot \vec{E}_0 \cdot \sin(\omega t)$$

frequency of light

$$= \hat{V} \cdot \sin(\omega t)$$

interaction term!!

$$\therefore H = H_0 + \hat{V} \cdot \sin(\omega t)$$



coupling to a sin-wave time-dependent field.

use this as the perturbation, FGR tells us

that the perturbation can induce transitions between

eigenstates of H_0 :

$$\hat{H}_0 |i\rangle = \epsilon_i |i\rangle$$

$$\hat{H}_0 |f\rangle = \epsilon_f |f\rangle$$

We thus consider the transition

rate from $|i\rangle \rightarrow |f\rangle$:

According to Fermi's Golden Rule.

timeless

$$|V_{fi} \cdot \vec{e}_0|^2$$

following the same procedure as derivation of FGR.

$$R_{f \leftarrow i} = \frac{2\pi}{\hbar} \cdot |V_{fi}|^2 \cdot \left\{ \delta(E_f - E_i - \hbar\omega) + \delta(E_f - E_i + \hbar\omega) \right\}$$

$E_f = E_i + \hbar\omega$, absorption. $E_f = E_i - \hbar\omega$, emission.

This is for a pair of states, Now, if the system has multiple states & we

want to calculate the rate of energy

Spectrum \Rightarrow absorption as a function of ω , then

$$\left(\frac{dE}{dt}\right)_{abs}(\omega) = \sum_f \sum_i P_i \cdot (E_f - E_i) \cdot R_{f \leftarrow i}$$

\downarrow population of $|i\rangle$ \downarrow change sign!!
 $= \frac{2\pi}{\hbar} \times \hbar\omega \times \sum_{f,i} P_i |V_{fi}|^2 \cdot \left\{ \delta(E_f - E_i - \hbar\omega) - \delta(E_f - E_i + \hbar\omega) \right\}$
 \uparrow stimulated emission.

Note: ① δ -function is even $\Rightarrow \delta(E_f - E_i + \hbar\omega) = \delta(E_i - E_f - \hbar\omega)$

② $|V_{fi}|^2 = |V_{if}|^2$

$$\sum_{f,i} P_i |V_{fi}|^2 \cdot \delta(E_f - E_i + \hbar\omega) = \sum_{f,i} P_f |V_{fi}|^2 \cdot \delta(E_i - E_f + \hbar\omega)$$

$$= \sum_{f,i} P_f |V_{fi}|^2 \cdot \delta(E_f - E_i - \hbar\omega)$$

③ when $E_f - E_i = \hbar\omega$ (enforced by the δ -function)
 then $P_f/P_i = e^{-\beta\hbar\omega}$ timeless

* absorption

①

Therefore, we can combine both terms &

yield:

$$\left(\frac{d\bar{E}}{dt}\right)_{abs}(\omega) = \underbrace{2\pi\omega_0 \cdot (1 - e^{-\hbar\omega_0})}_{\text{field property}} \cdot \underbrace{\sum_{i,f} p_{i,f} \cdot \langle f | \hat{\mu} | i \rangle^2}_{\text{material property}} \cdot \delta(\bar{E}_f - \bar{E}_i - \hbar\omega)$$

To characterize the material system without the dependence on the external field strength etc, we

define:
$$I(\omega) = \hbar \sum_{i,f} p_{i,f} \cdot \underbrace{|\langle f | \hat{\mu} | i \rangle|^2}_{\text{material property}} \cdot \delta(\bar{E}_f - \bar{E}_i - \hbar\omega)$$

This \Rightarrow the absorption lineshape of the system.

Note that this \Rightarrow an expression in the frequency domain, we can transform to time domain for easier connection to dynamics by using the F.T. representation of the δ -function.:

timeless

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$$\delta(E - \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot e^{\frac{i}{\hbar}Et}$$

$$\therefore I(\omega) = \frac{1}{\hbar} \sum_{i,f} P_i \cdot \langle f | \hat{\mu} | i \rangle \langle i | \mu | f \rangle \cdot \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot e^{\frac{i}{\hbar}(E_f - E_i)t} \cdot \frac{\hbar}{2\pi}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot \sum_{i,f} P_i \cdot \langle i | \hat{\mu} | f \rangle \cdot e^{\frac{i}{\hbar}E_f t} \cdot \langle f | \hat{\mu} | i \rangle e^{-\frac{i}{\hbar}E_i t}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot \text{Tr} \left\{ \hat{\mu} \cdot \left(\frac{1}{\hbar} H \right) \cdot e^{\frac{i}{\hbar}Ht} \cdot \hat{\mu} \cdot e^{-\frac{i}{\hbar}Ht} \cdot \rho \right\}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot \text{Tr} \left\{ \hat{\mu} \cdot e^{\frac{i}{\hbar}Ht} \cdot \hat{\mu} \cdot e^{-\frac{i}{\hbar}Ht} \cdot \rho \right\}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \cdot \langle \hat{\mu} \mu(t) \rangle$$

full Hamiltonian H_0 here, still system + bath!!
 not easy to evaluate

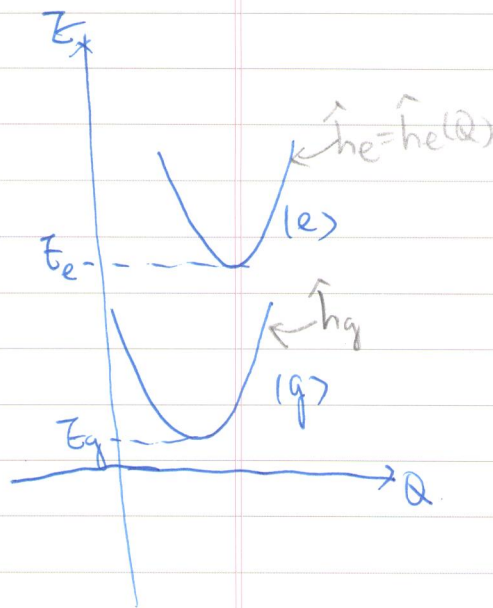
This is a very general ~~setup~~ ^{expression}, general for different setups.

"dipole-dipole correlation function" \rightarrow linear spectra. timeless

* dephasing function,

(7)

For a general TLS Hamiltonian:



$$H = \begin{pmatrix} E_g + \hat{h}q & 0 \\ 0 & E_e + \hat{h}e \end{pmatrix}$$

depends on nuclear coordinates

dipole operator induces transition between the two states:

$$\langle g | \hat{\mu} | g \rangle = \langle e | \hat{\mu} | e \rangle = 0$$

$$\langle g | \hat{\mu} | e \rangle = \vec{\mu}_{ge}$$

$$\therefore \hat{\mu} = \begin{pmatrix} 0 & \vec{\mu}_{ge} \\ \vec{\mu}_{ge}^* & 0 \end{pmatrix} = \vec{\mu}_{ge} |g\rangle\langle e| + \vec{\mu}_{ge}^* |e\rangle\langle g|$$

Note that when $E_e - E_g \gg k_B T$, the $\rho_{eg} = |g\rangle\langle g| \times \rho_b^{eg}$
The time-correlation function:

$$\begin{aligned} \langle g | e | g \rangle &= e^{-\frac{E_e - E_g}{k_B T}} \\ \langle e | e | e \rangle &= e^{-\frac{E_e - E_g}{k_B T}} \\ S_{\mu}(t) &= \langle \mu(t) | \mu(0) \rangle = \text{Tr} \left\{ e^{-\frac{i}{\hbar} H t} \cdot \mu \cdot e^{\frac{i}{\hbar} H t} \cdot \mu \cdot \rho_{eg} \right\} \\ &= \int_{\mathcal{B}} g | e \rangle e^{-\frac{i}{\hbar} H t} \cdot (\vec{\mu}_{ge} |g\rangle\langle e| + \vec{\mu}_{ge}^* |e\rangle\langle g|) \cdot e^{\frac{i}{\hbar} H t} \cdot (\vec{\mu}_{ge} |g\rangle\langle e| + \vec{\mu}_{ge}^* |e\rangle\langle g|) \cdot \rho_b^{eg} \\ &= |\vec{\mu}_{ge}|^2 \cdot e^{-\frac{i}{\hbar} (E_e - E_g) t} \cdot \underbrace{\text{Tr}_{\mathcal{B}} \left\{ e^{-\frac{i}{\hbar} \hat{h} q t} \cdot e^{\frac{i}{\hbar} \hat{h} e t} \cdot \rho_b^{eg} \right\}}_{\text{electron}} \cdot \underbrace{F(t)}_{\text{nuclear DOFs only, timeless}} \end{aligned}$$

⑧

The last term $F(t)$ is called the dephasing function and it contains all both influence to the dipole-dipole time correlation function. Note that the electronic part gives the intensity & peak position of the spectra, whereas the dephasing function gives the "shape" of the spectrum.

The dephasing function:

Must be ≤ 1 all the time.

$$F(t) = \left\langle e^{\frac{i\hat{H}_g t}{\hbar}} \cdot e^{\frac{i\hat{H}_e t}{\hbar}} \right\rangle_0.$$

has a time-domain interpretation, i.e. Start from an equilibrium wavepacket, the overlap between propagation by \hat{H}_g & \hat{H}_e potential energy surfaces.

\Rightarrow deviates of the two PESs, nuclear dynamics on

timeless

So, the dephasing function determined the lineshape.

Then we define lineshape function:

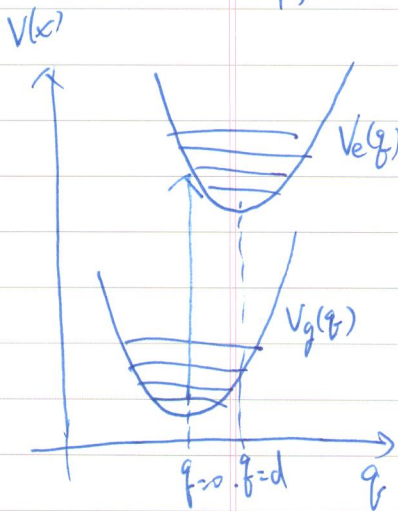
$$F(t) = e^{-g(t)}$$

← lineshape function

* displaced harmonic oscillator model.

A simple model used often in spectroscopy

is the displaced oscillator model:



$$\hat{H}_g = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

← displacement

$$\hat{H}_e = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 (q-d)^2$$

Note that $\hat{H}_e = e^{-\frac{i}{\hbar}d\hat{p}} \cdot \hat{H}_g \cdot e^{\frac{i}{\hbar}d\hat{p}}$,

which is easily proved by using

the Baker-Hausdorff identity: $e^{A} B e^{-A} = B + [A, B] + \dots$

~~Baker~~

Therefore :

$$F(t) = \text{Tr} \left\{ e^{\frac{i\hat{H}t}{\hbar}} \cdot e^{\frac{i\hat{H}t}{\hbar}} \rho_b^{eq} \right\}$$

assume $\hbar\omega_0 \gg k_B T$,
so $\rho_b^{eq} = |v=0\rangle\langle v=0|$

$$= \langle v=0 | e^{\frac{i\hat{H}t}{\hbar}} \cdot e^{\frac{i\hat{H}t}{\hbar}} | v=0 \rangle$$

$$= \langle 0 | e^{\frac{i\hat{H}t}{\hbar}} \cdot e^{\frac{-i\hat{d} \cdot \hat{p}}{\hbar}} \cdot e^{\frac{i\hat{H}t}{\hbar}} \cdot e^{\frac{i\hat{d} \cdot \hat{p}}{\hbar}} | 0 \rangle$$

$$F(t) = e^{\frac{i\hat{H}t}{\hbar}} \cdot \rho_b^{eq} \cdot e^{\frac{i\hat{H}t}{\hbar}}$$

$$= \langle 0 | e^{\frac{-i\hat{d} \cdot \hat{p}(t)}{\hbar}} \cdot e^{\frac{i\hat{d} \cdot \hat{p}}{\hbar}} | 0 \rangle$$

see next
page or
use cumulant
expansion !!

$$= e^{D \cdot (e^{-i\omega_0 t} - 1)}$$

$$D = \frac{m\omega_0}{2\hbar} \cdot d^2$$

D: Huang-Rhys factor, measures the strength of vibronical couplings.

$$\text{So, } I(\omega) \approx \int_{-\infty}^{\infty} dt \cdot e^{i\omega t} \cdot S_{\mu\mu}(t)$$

$$= |M_{eg}|^2 \cdot \int_{-\infty}^{\infty} dt \cdot e^{i(\omega - \omega_{eg})t} \cdot e^{D(e^{-i\omega_0 t} - 1)}$$

$$= |M_{eg}|^2 \cdot \int_{-\infty}^{\infty} dt \cdot e^{i(\omega - \omega_{eg})t} \cdot \sum_{n=0}^{\infty} \frac{1}{n!} \cdot D^n \cdot [e^{-i\omega_0 t}]^n$$

$$\omega_{eg} = \frac{E_e - E_g}{\hbar}$$

* Useful identities for Harmonic oscillators.

$$\frac{d}{dt} a = \frac{i}{\hbar} [H, a] = -i\omega_0 \cdot a \rightarrow a(t) = a \cdot e^{-i\omega_0 t}$$

$$\frac{d}{dt} a^\dagger = \frac{i}{\hbar} [H, a^\dagger] = i\omega_0 a^\dagger \rightarrow a^\dagger(t) = a^\dagger \cdot e^{i\omega_0 t}$$

$$x = \sqrt{\frac{\hbar}{2m\omega_0}} \cdot (a^\dagger + a)$$

$$p = i\sqrt{\frac{m\hbar\omega_0}{2}} \cdot (a^\dagger - a)$$

For operators \hat{A} linear in the coordinates or momenta:

\leftarrow n^{th} -order cumulant expansion

$$\langle e^{\hat{A}} \rangle = e^{\frac{1}{2}\langle \hat{A}^2 \rangle}$$

\leftarrow Exact for H.O.

prove this one!!

Thus we can derive:

$$\langle e^{\alpha_1 a + \beta_1 a^\dagger} e^{\alpha_2 a + \beta_2 a^\dagger} \rangle = e^{(\alpha_1 + \alpha_2)(\beta_1 + \beta_2) \cdot (n + \frac{1}{2}) + \frac{1}{2}(\alpha_1 \beta_2 - \beta_1 \alpha_2)}$$

Vacuum state, which easily leads to.

So $n=0$.
(or we $T=0K$).

$$\langle 0 | e^{\frac{i}{\hbar} d \cdot p(t)} e^{\frac{i}{\hbar} d p} | 0 \rangle = e^{\frac{m\omega_0}{2\hbar} \cdot d^2 \cdot (e^{-i\omega_0 t} - 1)}$$

(cont. from p.10)

(1)

$$= |\mu_{eg}|^2 \cdot \sum_{n=0}^{\infty} e^{-D} \cdot \frac{D^n}{n!} \cdot \int_{-\infty}^{\infty} dt \cdot e^{i(\omega - \omega_{eg} - n\omega_0)t}$$

$$= |\mu_{eg}|^2 \cdot \sum_{n=0}^{\infty} \boxed{e^{-D} \cdot \frac{D^n}{n!}} \cdot \underline{\delta(\omega - \omega_{eg} - n\omega_0)}$$

\parallel
 $F(\omega)$

\uparrow δ -function peaks

\uparrow
Franck-Condon factor!!

\Rightarrow the spectrum is a series of δ -functions; each represents a transition to a different vibrational excited state.

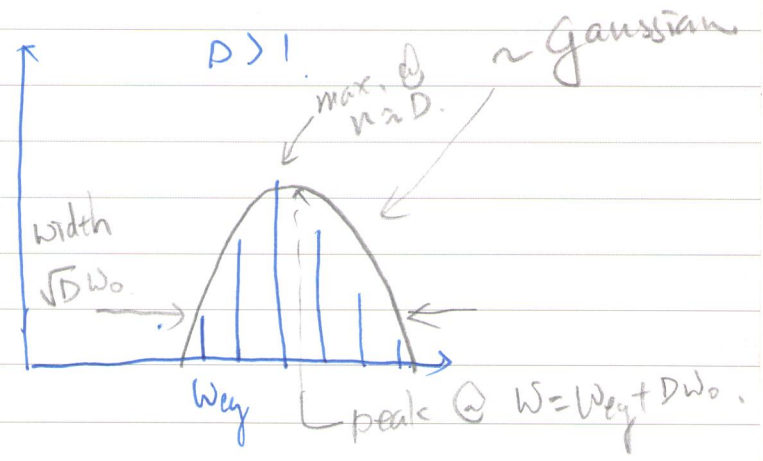
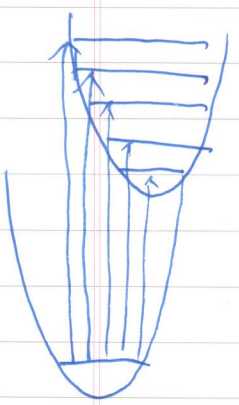
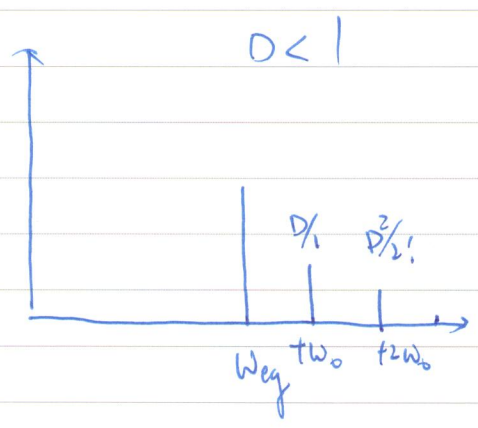
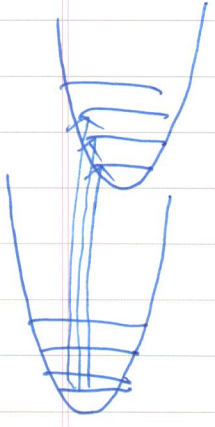
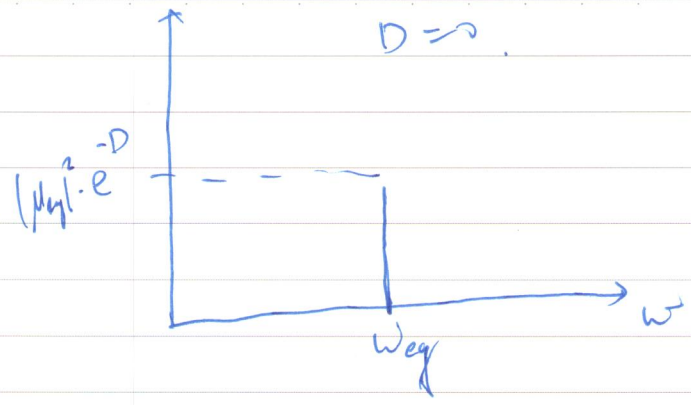
picture,
or
next
page.

\Rightarrow at $D=0$, single peak $|0_g\rangle \rightarrow |0_e\rangle$.

\Rightarrow at $D < 1$, small displacement,

\Rightarrow at $D > 1$, large displacement,

D corresponds roughly to the mean number of vibrational quanta excited in vertical absorption.



* Fluorescence : ~~different~~ con

In FL, we assume the vibrational relaxation is rapid, thus the emission is from a quasi-equilibrium population on the excited-state potential energy surface.

Thus : $\rho_0 = |e; 0_e\rangle\langle e; 0_e|$

and $I_{FL}(\omega) = \int_{-\infty}^{\infty} dt \cdot e^{i(\omega - \omega_{eg} - \lambda)t} \times e^{-g^*(t)}$

FL & abs lineshape are related to each other :



* Energy gap Hamiltonian :

Now, what if a real bath of harmonic modes is coupled to the electronic excitation? In this case, it is easier to use a "energy-gap" hamiltonian.

$$\begin{pmatrix} \epsilon_g + \hbar g & 0 \\ 0 & \epsilon_e + \hbar e \end{pmatrix} \Rightarrow \begin{pmatrix} 0 & 0 \\ 0 & \epsilon_e - \epsilon_g + \lambda \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & m\omega_0^2 \cdot d \cdot \hat{x} \end{pmatrix} + \hbar g \otimes I_s.$$

$$H = \underbrace{(\epsilon_e - \epsilon_g + \lambda) \cdot |e\rangle\langle e|}_{H_s} + \underbrace{\hbar g}_{H_b} + \underbrace{m\omega_0^2 \cdot d \cdot |e\rangle\langle e| \cdot \hat{x}}_{H_{sb}}$$

$$= H_s + H_b + g \cdot \omega_0 \cdot |e\rangle\langle e| \cdot (b^\dagger + b).$$

generalize to collective modes \uparrow coupling constant.

$$H = H_s + H_b + \sum_i g_i \cdot \omega_i \cdot |e\rangle\langle e| \cdot (b_i^\dagger + b_i).$$

define $\delta\omega = m\omega_0 \cdot d \cdot |e\rangle\langle e| \cdot \hat{x}.$

timeless

then

(15)

$$F(t) = \left\langle \exp \left[-i \int_0^t dt_1 \delta W(t_1) \right] \right\rangle$$

$$\approx e^{-\int_0^t dt_2 \int_0^{t_2} dt_1 \langle \delta W(t_2 - t_1) \delta W(t_1) \rangle}$$

$\leftarrow m^2 \omega_0^2 d^2 \langle X(t) X(t) \rangle$

$$\therefore g(t) = \int_0^t dt_2 \int_0^{t_2} dt_1 C_{\delta W \delta W}(t_2 - t_1)$$

single collective mode

$$= D_1 \omega_0^2 \int_0^t dt_2 \int_0^{t_2} dt_1 \left[\coth\left(\frac{\beta \hbar \omega}{2}\right) \cos(\omega t) + i \sin(\omega t) \right]$$

Note that for a continuous bath described by the spectral density

$$J(\omega) = \sum_i g_i^2 \omega_i^2 \delta(\omega - \omega_i)$$

$$\text{then } C_{\delta W \delta W}(t) = \int_0^\infty d\omega \left[\coth\left(\frac{\beta \hbar \omega}{2}\right) \cos(\omega t) J(\omega) + i \sin(\omega t) J(\omega) \right]$$

#

As we have unnormalized !!