

G25.2651: Statistical Mechanics

Notes for Lecture 22

I. QUANTUM TIME CORRELATION FUNCTIONS AND SPECTRA

A. The Hamiltonian

Consider a quantum system with a Hamiltonian H_0 . Suppose this system is subject to an external driving force $F_e(t)$ such that the full Hamiltonian takes the form

$$H = H_0 - BF_e(t) = H_0 + H'$$

where B is an operator through which this coupling occurs. This is the situation, for example, when the infrared spectrum is measured experimentally – the external force $F_e(t)$ is identified with an electric field $E(t)$ and B is identified with the electric dipole moment operator. If the field $F_e(t)$ is inhomogeneous, then H takes the more general form

$$H = H_0 - \int d^3x B(\mathbf{x})F_e(\mathbf{x}, t) = H_0 - \sum_{\mathbf{k}} B_{\mathbf{k}}F_{e,\mathbf{k}}(t)$$

where the sum is taken over Fourier modes. Often, B is an operator such that, if $F_e(t) = 0$, then

$$\langle B \rangle = \frac{\text{Tr}(Be^{-\beta H})}{\text{Tr}(e^{-\beta H})}$$

Suppose we take $F_e(t)$ to be a *monochromatic* field of the form

$$F_e(t) = F_\omega e^{i\omega t}$$

Generally, the external field can induce transitions between eigenstates of H_0 in the system. Consider such a transition between an initial state $|i\rangle$ and a final state $|f\rangle$, with energies E_i and E_f , respectively:

$$\begin{aligned} H_0|i\rangle &= E_i|i\rangle \\ H_0|f\rangle &= E_f|f\rangle \end{aligned}$$

(see figure below).

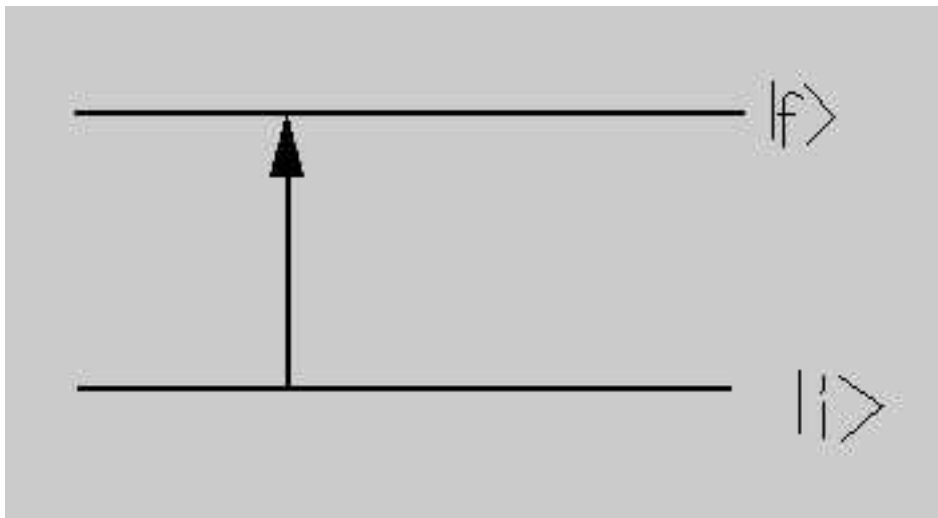


FIG. 1.

This transition can only occur if

$$E_f = E_i + \hbar\omega$$

B. The transition rate

In the next lecture, we will solve the quantum Liouville equation

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]$$

perturbatively and derive quantum linear response theory. However, the transition rate can actually be determined directly within perturbation theory using the Fermi Golden Rule approximation, which states that the probability of a transition's occurring per unit time, $R_{i \rightarrow f}$, is given by

$$R_{i \rightarrow f}(\omega) = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 |\langle f | B | i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

The δ -function expresses the fact that energy is conserved. This describes the rate of transitions between specific states $|i\rangle$ and $|f\rangle$. The transition rate between any initial and final states can be obtained by summing over both i and f and weighting the sum by the probability that the system is found in the initial state $|i\rangle$:

$$P(\omega) = \sum_{i,f} R_{i \rightarrow f}(\omega) w_i$$

where w_i is an eigenvalue of the density matrix, which we will take to be the canonical density matrix:

$$w_i = \frac{e^{-\beta E_i}}{\text{Tr}(e^{-\beta H})}$$

Using the expression for $R_{i \rightarrow f}(\omega)$, we find

$$P(\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 \sum_{i,f} w_i |\langle i | B | f \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Note that

$$P(-\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 \sum_{i,f} w_i |\langle i | B | f \rangle|^2 \delta(E_f - E_i + \hbar\omega)$$

This quantity corresponds to a time-reversed analog of the absorption process. Thus, it describes an emission event $|i\rangle \rightarrow |f\rangle$ with $E_f = E_i - \hbar\omega$, i.e., emission of a photon with energy $\hbar\omega$. It can also be expressed as a process $|f\rangle \rightarrow |i\rangle$ by recognizing that

$$w_f = \frac{e^{-\beta E_f}}{\text{Tr}(e^{-\beta H})} = \frac{e^{-\beta(E_i - \hbar\omega)}}{\text{Tr}(e^{-\beta H})}$$

or

$$w_f = e^{\beta \hbar\omega} w_i \quad \Rightarrow \quad w_i = e^{-\beta \hbar\omega} w_f$$

Therefore

$$P(-\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 e^{-\beta \hbar\omega} \sum_{i,f} w_f |\langle i | B | f \rangle|^2 \delta(E_f - E_i + \hbar\omega)$$

If we now interchange the summation indices, we find

$$\begin{aligned}
P(-\omega) &= \frac{2\pi}{\hbar} |F_\omega|^2 e^{-\beta\hbar\omega} \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_i - E_f + \hbar\omega) \\
&= \frac{2\pi}{\hbar} |F_\omega|^2 \sum_{i,f} w_i |\langle i|B|f\rangle|^2 e^{-\beta\hbar\omega} \delta(E_i - E_f - \hbar\omega)
\end{aligned}$$

where the fact that $\delta(x) = \delta(-x)$ has been used. Comparing this expression for $P(-\omega)$ to that for $P(\omega)$, we find

$$P(-\omega) = e^{-\beta\hbar\omega} P(\omega)$$

which is the equation of *detailed balance*. We see from it that the probability of emission is less than that for absorption. The reason for this is that it is less likely to find the system in an excited state $|f\rangle$ initially, when it is in contact with a heat bath and hence thermally equilibrated. However, we must remember that the microscopic laws of motion (Newton's equations for classical systems and the Schrödinger equation for quantum systems) are reversible. This means that

$$R_{i \rightarrow f}(\omega) = R_{f \rightarrow i}(-\omega)$$

The conclusion is that, since $P(\omega) > P(-\omega)$, reversibility is lost when the system is placed in contact with a heat bath, i.e., the system is being driven irreversibly in time.

Define

$$\begin{aligned}
C_{>}(\omega) &= \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_f - E_i - \hbar\omega) \\
C_{<}(\omega) &= \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_f - E_i + \hbar\omega)
\end{aligned}$$

then

$$C_{<}(\omega) = e^{-\beta\hbar\omega} C_{>}(\omega)$$

Now using the fact that the δ -function can be written as

$$\delta(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-iEt}$$

$C_{>}(\omega)$ becomes

$$\begin{aligned}
C_{>}(\omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \sum_{i,f} w_i |\langle i|B|f\rangle|^2 e^{-i(E_f - E_i - \hbar\omega)t/\hbar} \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{i,f} w_i |\langle i|B|f\rangle|^2 e^{-i(E_f - E_i)t/\hbar} \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{i,f} w_i \langle i|B|f\rangle \langle f|B|i\rangle e^{-iE_f t/\hbar} e^{iE_i t/\hbar} \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{i,f} w_i \langle i|e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}|f\rangle \langle f|B|i\rangle
\end{aligned}$$

Recall that the evolution of an operator in the Heisenberg picture is given by

$$B(t) = e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}$$

if the evolution is determined solely by H_0 . Thus, the expression for $C_{>}(\omega)$ becomes

$$\begin{aligned}
C_{>}(\omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_{i,f} w_i \langle i|B(t)|f\rangle \langle f|B|i\rangle \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \sum_i w_i \langle i|B(t)B(0)|i\rangle \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \text{Tr} [\rho B(t)B(0)] \\
&= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle B(t)B(0) \rangle
\end{aligned}$$

which involves the quantum autocorrelation function $\langle B(t)B(0) \rangle$.

In general, a quantum time correlation function in the canonical ensemble is defined by

$$C_{AB}(t) = \frac{\text{Tr} [A(t)B(0)e^{-\beta H}]}{\text{Tr} [e^{-\beta H}]}$$

In a similar manner, we can show that

$$C_{<}(\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle B(0)B(t) \rangle \neq C_{>}(\omega)$$

since

$$[B(0), B(t)] \neq 0$$

in general. Also, the product $B(0)B(t)$ is not Hermitian. However, a hermitian combination occurs if we consider the energy difference between absorption and emission. The energy absorbed per unit of time by the system is $P(\omega)\hbar\omega$, while the emitted into the bath by the system per unit of time is $P(-\omega)\hbar\omega$. The energy difference $Q(\omega)$ is just

$$\begin{aligned} Q(\omega) &= [P(\omega) - P(-\omega)]\hbar\omega \\ &= P(\omega)[1 - e^{-\beta\hbar\omega}]\hbar\omega \\ &= 2\pi\omega|F_\omega|^2 C_{>}(\omega)[1 - e^{-\beta\hbar\omega}] \end{aligned}$$

But since

$$C_{<}(\omega) = e^{-\beta\hbar\omega} C_{>}(\omega)$$

it follows that

$$C_{>}(\omega) + C_{<}(\omega) = (1 + e^{-\beta\hbar\omega}) C_{>}(\omega)$$

or

$$C_{>}(\omega) = \frac{C_{>}(\omega) + C_{<}(\omega)}{1 + e^{-\beta\hbar\omega}}$$

Note, however, that

$$\begin{aligned} C_{>}(\omega) + C_{<}(\omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle B(t)B(0) + B(0)B(t) \rangle \\ &= \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \frac{1}{2}[B(0), B(t)]_+ \rangle \end{aligned}$$

where $[\dots]_+$ is known as the anticommutator: $[A, B]_+ = AB + BA$. The anticommutator between two operators is, itself, hermitian. Therefore, the energy difference is

$$\begin{aligned} Q(\omega) &= \frac{2\omega}{\hbar} |F_\omega|^2 \frac{1 - e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [B(0), B(t)]_+ \rangle \\ &= \frac{2\omega}{\hbar} |F_\omega|^2 \tanh(\beta\hbar\omega/2) \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [B(0), B(t)]_+ \rangle \end{aligned}$$

The quantity $\langle [B(0), B(t)]_+ \rangle$ is the symmetrized quantum autocorrelation function. The classical limit is now manifest ($\tanh(\beta\hbar\omega/2) \rightarrow \beta\hbar\omega/2$):

$$Q(\omega) \rightarrow |F_\omega|^2 \int_{-\infty}^{\infty} dt e^{i\omega t} \langle B(0)B(t) \rangle$$

The classically, the energy spectrum $Q(\omega)$ is directly related to the Fourier transform of a time correlation function.

C. Examples

Define

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \frac{1}{2} [B(0), B(t)]_+ \rangle$$

which is just the frequency spectrum corresponding to the autocorrelation function of B . For different choices of B , $G(\omega)$ corresponds to different experimental measurements.

Consider the example of a molecule with a transition dipole moment vector μ . If an electric field $\mathbf{E}(t)$ is applied, then the Hamiltonian H' becomes

$$H' = -\mu \cdot \mathbf{E}(t)$$

If we take $\mathbf{E}(t) = E(t)\hat{\mathbf{z}}$, then

$$H' = -\mu_z E(t)$$

Identifying $B = \mu_z$, the spectrum becomes

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \frac{1}{2} [\mu_z(0), \mu_z(t)]_+ \rangle$$

or for a general electric field, the result becomes

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \frac{1}{2} (\mu(0) \cdot \mu(t) + \mu(t) \cdot \mu(0)) \rangle$$

These spectra are the *infrared* spectra.

As another example, consider a block of material placed in a magnetic field $\mathcal{H}(t)$ in the z direction. The spin S_z of each particle will couple to the magnetic field giving a Hamiltonian H'

$$H' = - \sum_{i=1}^N S_{i,z} \mathcal{H}(t)$$

The net magnetization created by the field m_z is given by

$$m_z = \frac{1}{N} \sum_{i=1}^N S_{i,z}$$

so that

$$H' = -N m_z \mathcal{H}(t)$$

Identify $B = m_z$ (the extra factor of N just expresses the fact that H' is extensive). Then the spectrum is

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \frac{1}{2} [m_z(0), m_z(t)]_+ \rangle$$

which is just the NMR spectrum. In general for each correlation function there is a corresponding experiment that measures its frequency spectrum.

To see what some specific lineshapes look like, consider as an ansatz a pure exponential decay for the correlation function $C_{BB}(t)$:

$$C_{BB}(t) = \langle B^2 \rangle e^{-\Gamma|t|}$$

The spectrum corresponding to this time correlation function is

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} C_{BB}(t)$$

and doing the integral gives

$$G(\omega) = \frac{\langle B^2 \rangle}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}$$

which is shown in the figure below:

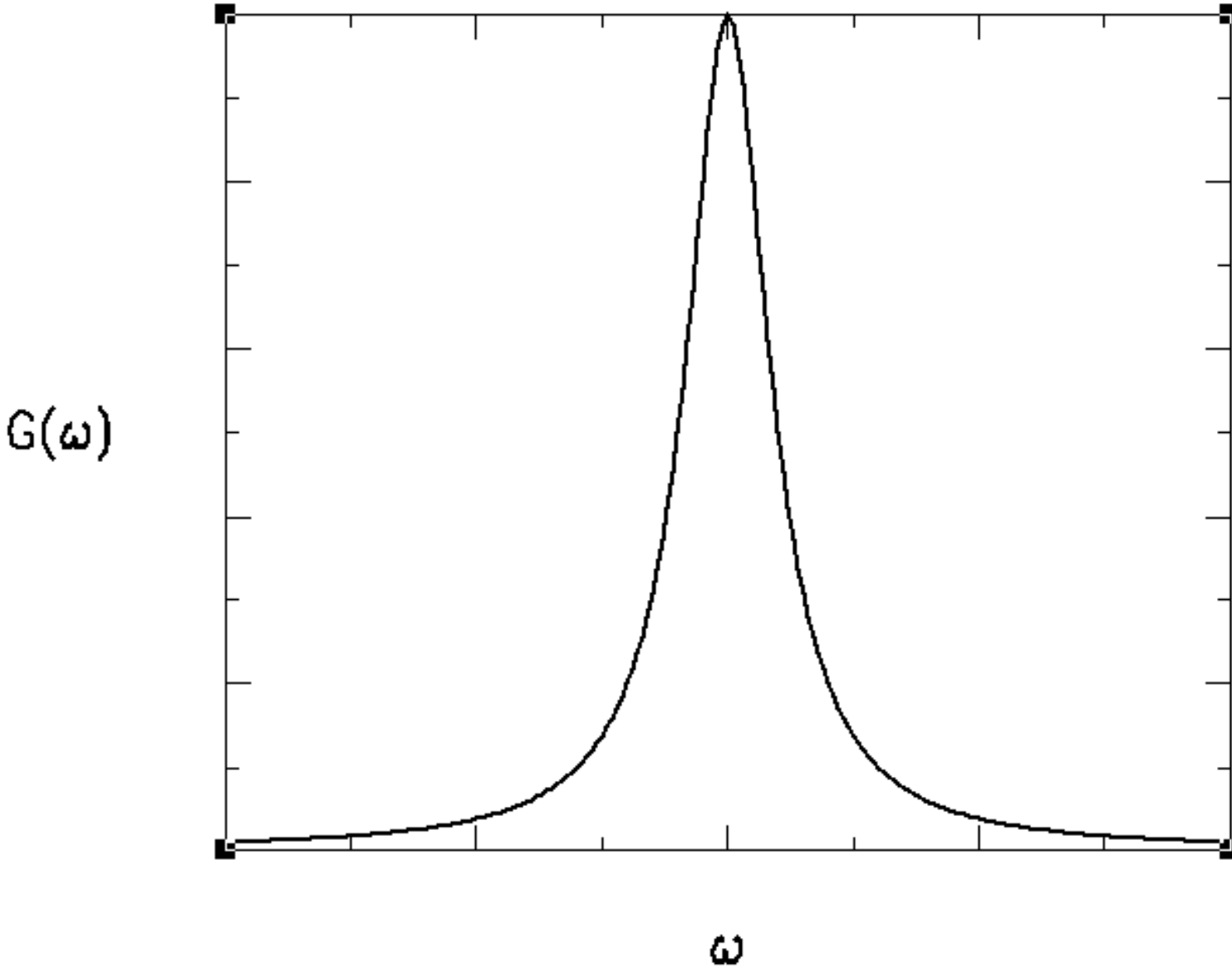


FIG. 2.

We see that the lineshape is a Lorentzian with a width Γ .

As a further example, suppose $C_{BB}(t)$ is a decaying oscillatory function:

$$C_{BB}(t) = \langle B^2 \rangle e^{-\Gamma|t|} \cos \omega_0 t$$

which describes well the behavior of a harmonic diatomic coupled to a bath. The spectrum can be shown to be

$$G(\omega) = \frac{\langle B^2 \rangle \Gamma}{\pi} \left[\frac{\Gamma^2 + \omega^2 + \omega_0^2}{(\Gamma^2 + (\omega - \omega_0)^2) (\Gamma^2 + (\omega + \omega_0)^2)} \right]$$

which contains two peaks at $\omega = \pm \sqrt{\omega_0^2 - \Gamma^2}$ as shown in the figure below:

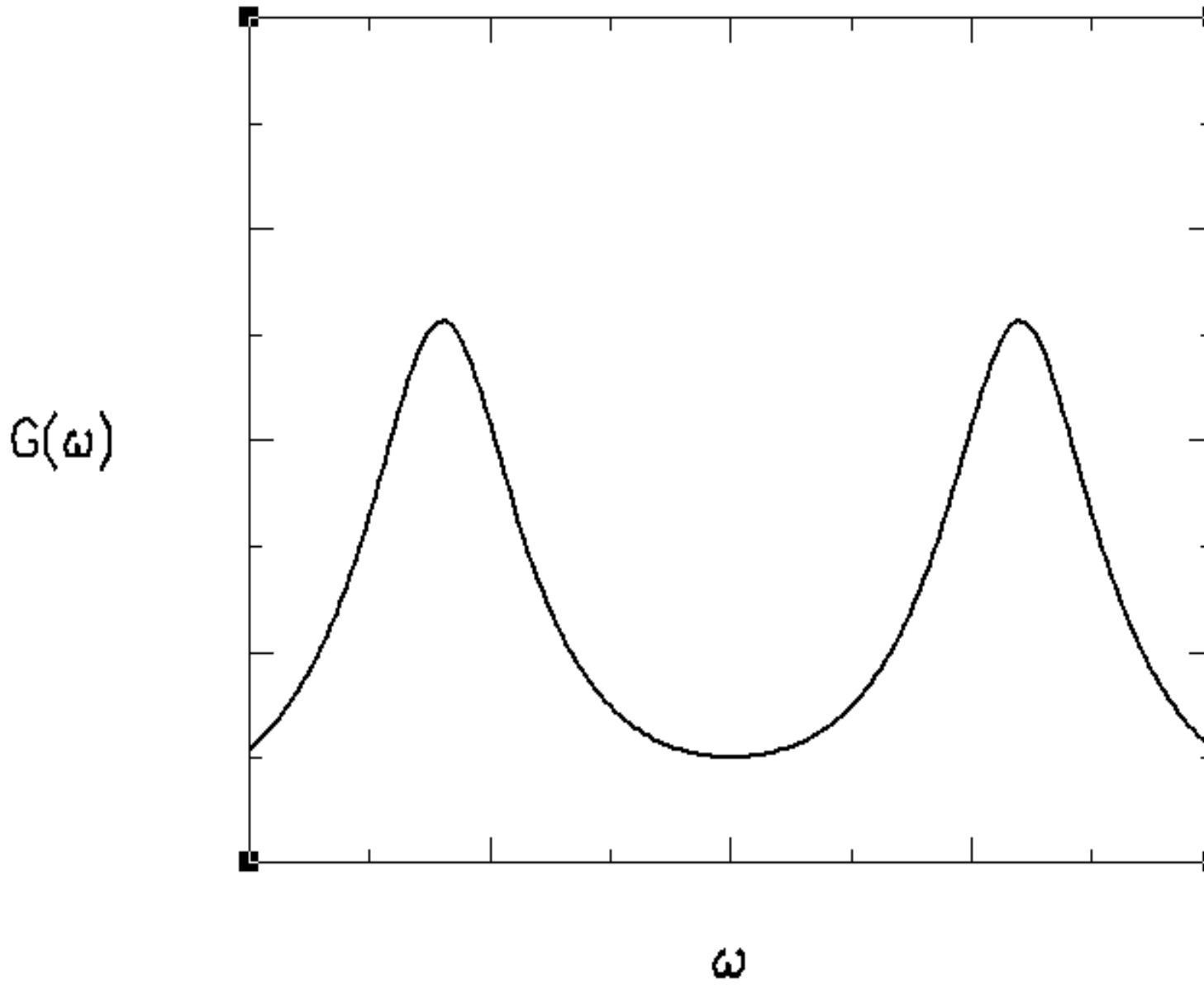


FIG. 3.