

Time-Dependent Statistical Mechanics

14. Electromagnetic absorption by dilute gases

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1 Introduction

When the electromagnetic field couples to the electric dipole moment of the region under consideration, we see that the absorption spectrum, except for simple frequency-dependent factors, is proportional to the Fourier transform of the correlation function of the dipole moment. Using the methods we have been discussing, that correlation function can be written as

Continuation
of lecture 13
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$$\phi_{\mu_x \mu_x}(t) = \frac{1}{2} \sum_{ij} \rho_{ii} |\mu_{x,ij}|^2 (e^{-i\omega_{ij}t} + e^{i\omega_{ij}t})$$

where $\omega_{ij} = (E_i - E_j)/\hbar$. The corresponding Fourier transform is

$$\hat{\phi}_{\mu_x \mu_x}(\omega) = \pi \sum_{ij} \rho_{ii} |\mu_{x,ij}|^2 (\delta(\omega - \omega_{ij}) + \delta(\omega + \omega_{ij})) \quad (1)$$

This is the general form that we get from linear response theory. We have assumed that we can carve the system up into small regions, and that in each of them the electric field is independent of position. We have not assumed anything about the interactions between the molecules. Here i and j refer to the eigenstates of the Hamiltonian of the region.

2 Very dilute gas in the absence of collisions

If the gas is very dilute and the collisions between molecules are unimportant, we can choose our region so that it contains only one molecule (or atom).

In that case, the states i and j are eigenstates of the Hamiltonian of a single molecule. Moreover, these eigenstates are products of center of mass eigenfunctions for translational motion and internal eigenfunctions for electronic, vibrational, rotational, and spin motion. However, there are no matrix elements of the dipole moment operator connecting different translational states, so only the internal states have a significant effect on the calculation of the correlation function. We get the familiar result that the spectrum is the sum of delta functions centered at frequencies that correspond to the energy differences of internal states of the molecules. The intensity of each transition is proportional to the square of the matrix element of the dipole moment connecting the two states (as well as to the additional frequency dependent factor needed to convert the correlation function into the rate of energy absorption).

3 Simple model for the effect of collisions

A simple model for the effect of collisions is that they interrupt the periodic oscillation of the Heisenberg operators and cause the correlation function to decay in a way that reflects the frequency of collisions. We use the eigenstates for the isolated molecule but we write

$$\phi_{\mu_x \mu_x}(t) = \frac{1}{2} \sum_{ij} \rho_{ii} |\mu_{x,ij}|^2 (e^{-i\omega_{ij}t} + e^{i\omega_{ij}t}) e^{-t/\tau_c}$$

where τ_c is the mean time between collisions. We are assuming that collisions have equal effects on each of the oscillating exponentials, which is clearly a simplification.

Replacing each complex exponential by a complex exponential times a decaying real exponential is equivalent to replacing each delta function $\delta(\omega - \omega_{ij})$

by the appropriate Fourier transform, which is a Lorentzian spectrum

$$\frac{(\pi\tau_c)^{-1}}{(\omega - \omega_{ij})^2 + \tau_c^{-2}}$$

Since the change does not affect the zero time value of the correlation function, it does not change the area under this function of frequency, which is still 1. Each line is broadened, but its integrated intensity is not changed in the Fourier transform of the correlation function. The integrated intensity in the absorption spectrum will be altered slightly, depending on the frequency range in which the line is located.

It is important to note that in this discussion, the energy eigenstates we used were those for an isolated molecule.

4 Exact result for the effect of collisions

The general result should still be exact and be able to account for collisions exactly.

If we look at it naively, it looks like a sum of delta functions, whereas the simple model for the effect of collisions suggested that the spectrum should be a set of broadened lines.

In fact the exact answer gives broadened lines, but each broad line is actually a set of closely spaced delta functions. The spacing is related to the spacing of the translational center of mass energies. The spectrum of such energies is essentially continuous for systems with a large volume. Thus a set of closely spaced delta function lines leads to what looks like a broadened line.

In fact, we should in general expect that a sum such as in Eq. (1) should give a continuous spectrum because of the close spacing of the energy eigenvalues.

Thus the real problem is to understand why we get sharp lines in the absence of collisions.

We alluded to the reason for this. It has to do with the fact that the spectrum depends not only on the energy eigenvalues but also on the dipole moment matrix elements. For a very dilute gas, there are no matrix elements of the

dipole moment operator between states of different center of mass energy. The fact that the energy spectrum is essentially continuous does not lead to a continuous absorption spectrum. However, when collisions take place, the center of mass degrees of freedom interact with the internal degrees of freedom, especially the rotational motion. The net result is to give lots more nonzero matrix elements of the dipole moment between energy eigenstates, and the spectrum becomes continuous.

slides

General case of a dilute gas

Assume electric dipole interaction is most important.

Assume electric field is polarized in the x direction.

Divide the space into regions small compared with the wavelength of light.

The relevant correlation function is

$$\phi_{\mu_x \mu_x}(t) = \frac{1}{2} \sum_{ij} \rho_{ii} |\mu_{x,ij}|^2 (e^{-i\omega_{ij}t} + e^{i\omega_{ij}t})$$

where $\omega_{ij} = (E_i - E_j)/\hbar$. The corresponding Fourier transform is

$$\hat{\phi}_{\mu_x \mu_x}(\omega) = \pi \sum_{ij} \rho_{ii} |\mu_{x,ij}|^2 (\delta(\omega - \omega_{ij}) + \delta(\omega + \omega_{ij}))$$

The rate of energy absorption is

$$R(\omega) = \frac{g_0^2}{2} \omega \chi''_{BB}(\omega) = \frac{g_0^2}{2\hbar} \omega \tanh(\hbar\omega/2k_B T) \hat{\phi}_{BB}(\omega)$$

Very dilute gas in the absence of collisions

Choose each region so that it contains no more than one molecule.

The states i and j are eigenstates of the Hamiltonian of a single molecule.

Each eigenstate is a product of a center of mass eigenfunction and an internal eigenfunction.

There are no matrix elements of the dipole moment operator connecting states with different center of mass quantum numbers.

Only internal states have an effect on the calculation of the correlation function.

We get the familiar result:

- the spectrum is the sum of delta functions centered at frequencies that correspond to the energy differences of internal states of the molecules.
- the intensity of each transition is proportional to the square of the matrix element of the dipole moment connecting the two states

Doppler broadening

High resolution experiments at very low density show that the lines are not true delta functions but they are slightly broadened.

To describe this we must take into account the fact that the interaction between the electric field and a molecule depends on the position of the molecule.

Simple model for the effect of collisions in a dilute gas

Choose each region to be large enough to have more than one molecule.

Collisions interrupt the periodic oscillation of the Heisenberg operators.

They cause the correlation function to decay in a way that reflects the frequency of collisions.

We use the eigenstates for the isolated molecules but we write

$$\phi_{\mu_x \mu_x}(t) = n \left[\frac{1}{2} \sum_{ij} \rho_{ii} |\mu_{x,ij}|^2 (e^{-i\omega_{ij}t} + e^{i\omega_{ij}t}) \right] e^{-|t|/\tau_c}$$

where

- N is the number of molecules in a region
- τ_c is the mean time between collisions.

We are assuming that collisions have equal effects on each of the oscillating exponentials, which is clearly a simplification.

Replacing each

$$e^{-i\omega_{ij}t} \quad \text{by} \quad e^{-i\omega_{ij}t} e^{-|t|/\tau_c}$$

is equivalent to replacing each

$$\delta(\omega - \omega_{ij}) \quad \text{by} \quad \frac{(\pi\tau_c)^{-1}}{(\omega - \omega_{ij})^2 + \tau_c^{-2}}$$

Each line is broadened, but its integrated intensity is not changed in the Fourier transform of the correlation function.

The integrated intensity in the absorption spectrum will be altered slightly, depending on the frequency range in which the line is located.

The energy eigenstates we used were those for an isolated molecule, even though the molecules are not isolated. This is intrinsic to this way of modeling the effect of collisions.

Exact result for the effect of collisions

The general result should be exact and account for collisions exactly.

The general result is a sum of delta functions, whereas the simple model for the effect of collisions predicts a set of broadened lines.

In fact the general result when there are collisions gives broadened lines, but each broad line is actually a set of closely spaced delta functions.

The spacing is related to the spacing of the translational center of mass energies.

The spectrum of such energies is essentially continuous for systems with a large volume.

Thus a set of closely spaced delta function lines can lead to what looks like a broadened line.

We should in general expect that a sum such as in the general result should give a continuous spectrum because of the close spacing of the energy eigenvalues.

Thus the real problem is to understand why we get sharp lines in the absence of collisions.

For a very dilute gas, there are no matrix elements of the dipole moment operator between states of different center of mass quantum numbers.

Hence, the essentially continuous energy spectrum does not lead to a continuous absorption spectrum.

When collisions take place, the center of mass degrees of freedom interact with the internal degrees of freedom, especially the rotational motion.

The result is to give lots more nonzero matrix elements of the dipole moment between energy eigenstates, and the spectrum becomes continuous.

end of slides