The time-correlation function method

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The time-correlation function method

We define a time-correlation function as

$$C(t) \equiv\ < A(0)A(t) >$$

where the angle brackets represent an ensemble average and A is the dynamic variable of interest. If we compare the value of A(t) with its value at zero time, A(0) the two values will be correlated at sufficiently short times, but at longer times the value of A(t) will have no correlation with its value at t=0. Information on relevant dynamical processes is contained in the time decay of C(t). The starting time is arbitrary so we can also discuss the ensemble average starting at any time, t.

$$C(t) \equiv\ < A(\tau)A(t + \tau) >$$

The time-correlation function method

Normalization may also be applied by dividing by

$$< A(0)A(0) >$$

The normalized function is a decay from a value of one to some lower value (not always zero). It represents the loss of correlation with the initial value. The short time value is proportional to $<A^2>$. The asymptotic long time value is proportional to $<A>^2$ as shown in the figure below.
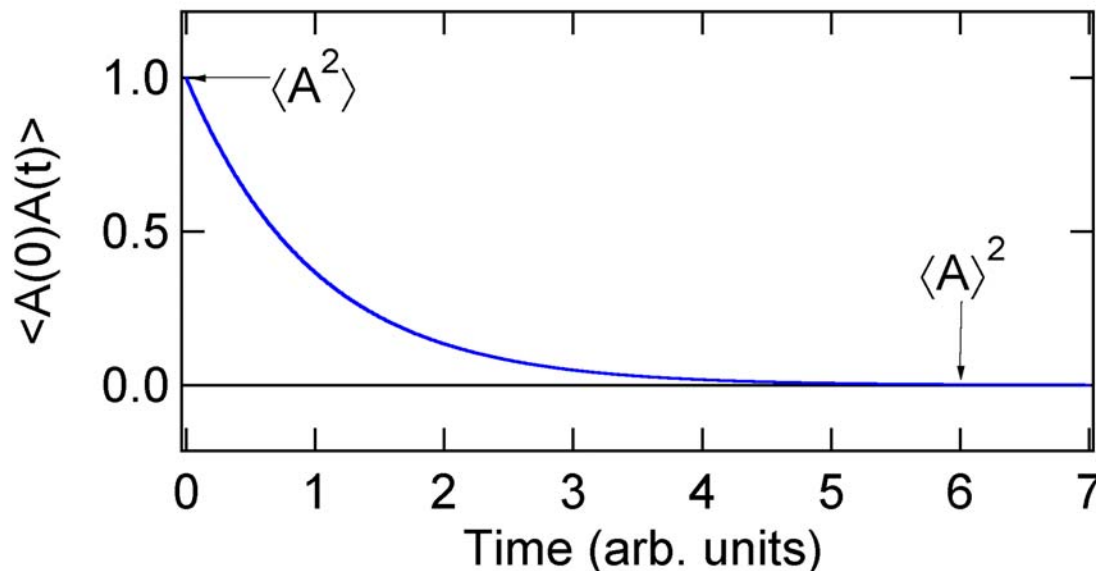
The time-correlation function method

 The decay shown in the figure is the average of a large number of trajectories. We can see that C(t) decays from <A²> to <A>².

$$<A^2> \rightarrow C(t) \rightarrow <A>^2$$

This means that initially C(0) = <A(0)A(0)>
which is clear from our definition. Note that this value is shown as 1.0 on the y-axis because of normalization. As time goes on the value of A(t) changes and becomes less correlated with its value at time zero. At long enough times A(t) has no correlation and so its average value is <A(t)>. The average value of A at time zero is <A(0)>. These averages are both average values of A and should be the same. Thus, <A(0)><A(t)> = <A(0)><A(0)> = <A(0)>². The value of zero shown in the Figure above is arbitrary. The normalized long time value is <A(0)>²/<A(0)A(0)> and is less than one, but is zero only if <A(0)> = 0.

Spectral lineshapes

Spectral lineshapes can be calculated by determining the time-correlation function for rotational, vibrational or other motion involved. These are examples of the spectral density, which is the Fourier transform of the correlation function. The most direct route to understanding the time-correlation function is to determine an expression for the intensity of absorption or emission of a photon.
The absorption or emission intensity is defined to be:

$$I(\omega) = \sum_{i,f} p_i <f|\mu|i><i|\mu|f>\delta(\omega_{fi} - \omega)$$

where

$$p_i = \frac{e^{-\hbar\omega_i/kT}}{Q} \quad , \quad Q = \sum_{n=1}^{\infty} e^{-\hbar\omega_i/kT}$$

Spectral density

The Fourier transform of the correlation function is the spectral density. The task of calculating spectra using a correlation function involves determining the form of the Fourier transform. The delta function in the Golden Rule and intensity expressions can be represented by the integral

$$\delta(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t}dt$$

Using the Einstein relation

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

The delta function in the intensity expression is

$$\delta(\omega_{fi} - \omega) = \int_{-\infty}^{\infty} \exp\left\{i\left(\frac{E_f - E_i}{\hbar} - \omega\right)t\right\}dt$$

Spectral density

as an operator

$$\exp\left\{ i\left(\frac{E_f - E_i}{\hbar} - \omega \right) t \right\} <f|\mu|i><i|\mu|f>$$

$$= <f|f|e^{iHt/\hbar}\mu e^{-iHt/\hbar}|i|i><i|\mu|f>$$

$$= <f|\mu\left(t\right)|i><i|\mu|f>$$

The time dependent dipole operator is defined in Heisenberg representation where a time-dependent operator is related to a static operator by

$$A(t) = e^{iHt/\hbar} A(0) e^{-iHt/\hbar}$$

The above transformation is valid if i and f are eigenfunctions of the same hamiltonian. This is the case for vibrational and rotational transitions, but not electronic transitions. Using the above formalism the intensity is

$$I(\omega) = \frac{1}{2\pi} \sum_{i,f} \int_{-\infty}^{\infty} p_i <i|\mu|f><f|\mu(t)|i> e^{-i\omega t} dt$$

The closure relationship

The individual matrix elements <i|μ|f> are just numbers so the order of multiplication does not matter. Since the final states form a complete set we can use the closure relation

$$\sum_f |f><f| = 1$$

This results in

$$I(\omega) = \frac{1}{2\pi}\sum_i \int_{-\infty}^{\infty} p_i< i|\mu \cdot \mu(t)|i >e^{-i\omega t}dt$$

The sum over initial states is a weighted Boltzmann average (p_i is the Boltzmann weighting factor) so this is nothing more than an ensemble average. Thus, we can write

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} <\mu \cdot \mu(t)>_{eq}e^{-i\omega t}dt$$

The wavepacket picture

We can apply these ideas to a new concept for calculating the line shape function centered about any arbitrary frequency ω_0. We consider the decay of an excited state as a damped oscillation. This can be seen in the wave packet picture.
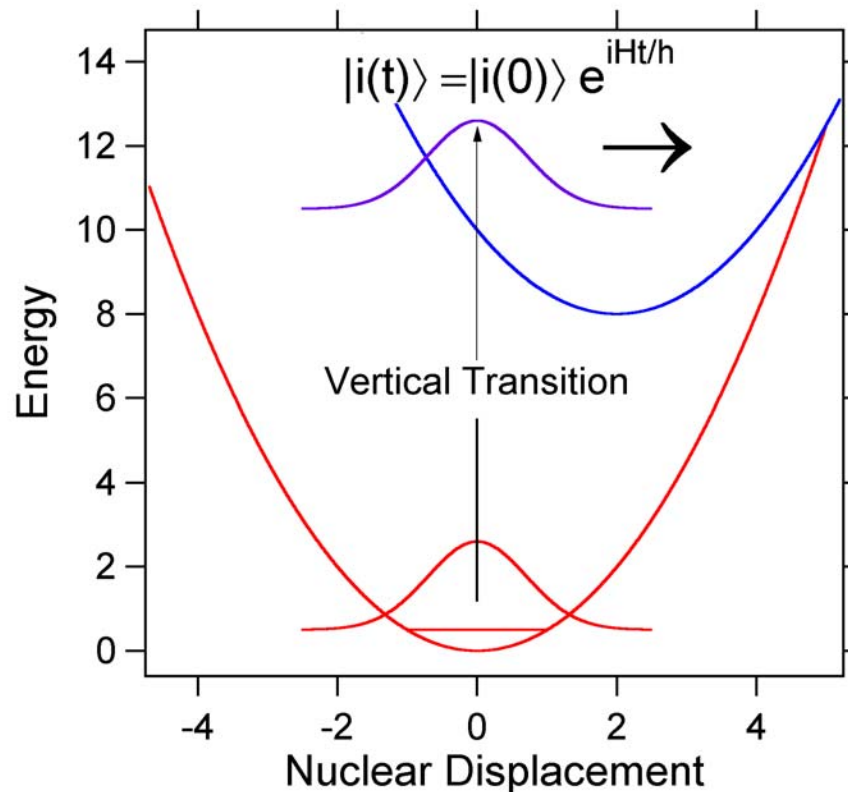
The wavepacket picture

The red curve represents the ground state and the blue curve represents the excited state. The wavepacket is shown as a Gaussian function. It represents the probability amplitude of the nuclei. If electromagnetic radiation in the optical region of the electromagnetic spectrum is absorbed then a vertical electronic transition occurs in a molecule. This takes the molecule from its ground state potential energy surface (red) to its excited state surface (blue). However, the nuclei do not have time to change position during this process so their probability distribution remains the same. Note that this distribution is not the equilibrium distribution in the excited state and so the nuclei begin to oscillate back and forth as indicated by the arrow.

The wavepacket picture

The oscillation is a time-dependent phenomenon and therefore the operator that governs the change in the nuclear position is

$$|i(t)> = e^{iH't/\hbar}|i(0)>$$

where H is the excited state hamiltonian. Since $H'|i\rangle = E_0|i\rangle$ we can also write this as:

$$|i(t)> = e^{iE_0 t/\hbar}|i(0)> = e^{i\omega_0 t}|i(0)>$$

The oscillations described above are due to nuclear motion. The function that represents the line shape for this process will be the Fourier transform of

$$L(\omega) = \int_0^\infty e^{i\omega_0 t} e^{-t/T_2} e^{-i\omega t} dt = \int_0^\infty \exp\left\{-\left(\frac{1}{T_2} + i\omega - i\omega_0\right)t\right\}dt$$

The wavepacket picture

In the preceding derivation we have left out the constants for clarity and we have considered explicitly the excited population change represented by the dephasing time T_2. The functional form $e^{-i\omega_0 t}$ implies that oscillations occur without dephasing. We would need to incorporate an additional term to represent pure dephasing due to a loss of coherence between the ground and excited state wavefunctions.

The Fourier transform leads to

$$ \Lambda(\omega) = \frac{1/T_2}{\pi\left(\left(1/T_2\right)^2 + \left(\omega - \omega_0\right)^2\right)} $$

for the real part of the Lorentzian. We often use the definition $\Gamma = 1/T_2$.

The wavepacket picture

Note that this is a normalized function so that the integral of $\Lambda(\omega)$ from $-\infty$ to ∞ is equal to one. Notice that the analogy with NMR is evident in the fact that our excited state decay function is a sinusoid times an exponential. The real and imaginary parts have the appearance

$$\Lambda(\omega) = \frac{\Gamma}{\pi\left(\Gamma^2 + \left(\omega - \omega_0\right)^2\right)}$$

Note the similarity in appearance between this function and a free-induction decay in NMR spectroscopy.
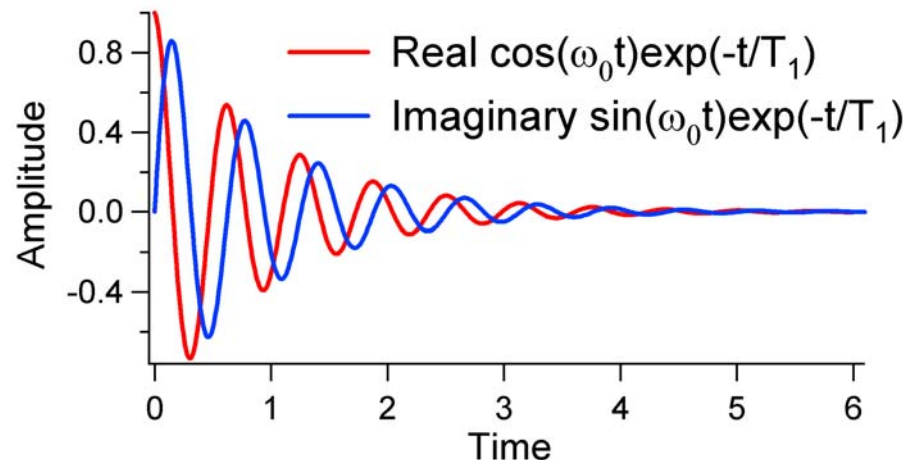
# Similarities and differences of optical and NMR spectroscopies

The application of the time correlator is similar is NMR and Optical spectroscopy.   However, the form of the correlation function is different. In NMR spectroscopy the spins are rotated by a 90o pulse and they rotate in the x,y plane.
The resulting FID (correlation function in this case) is collection of sine and cosine functions that represent in-phase and out-of-phase components.
Optical spectroscopy consists of several different cases, electronic, vibrational, rotational and even dielectric spectroscopy. We will first treat electronic spectroscopy.
In optical spectroscopy a wave packet refers to the distribution Of nuclear positions at equilibrium. This packet is transferred To the excited state potential energy surface by absorption.

Evolution of the wavepacket in optical spectroscopy
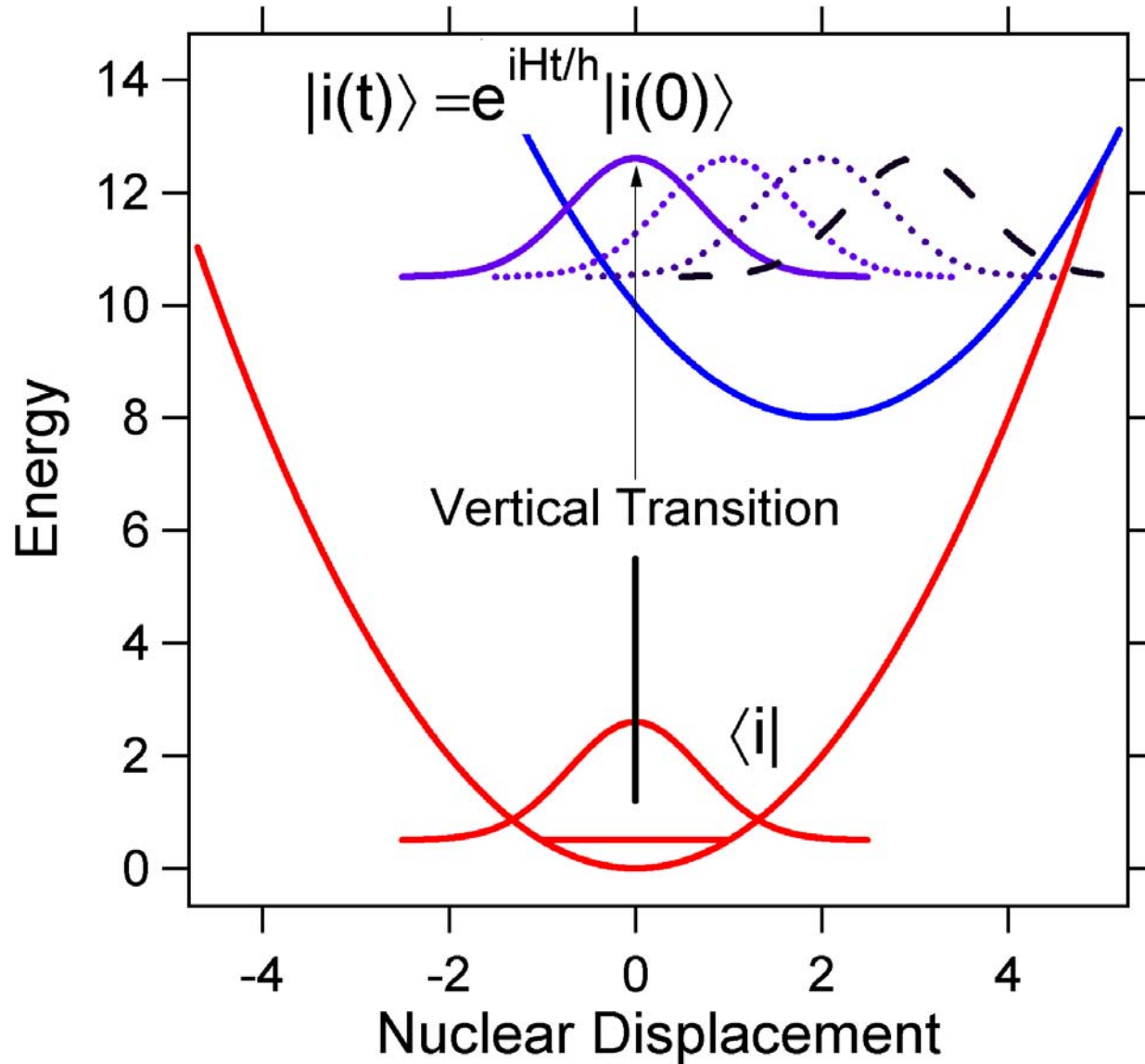
The time correlator

$$\left\langle i | i(t) \right\rangle = \exp\left\{ S\left(\left(\nu + 1 \right) e^{i\omega t} + \nu e^{-i\omega t} - \left(2\nu + 1 \right) \right) \right\}$$

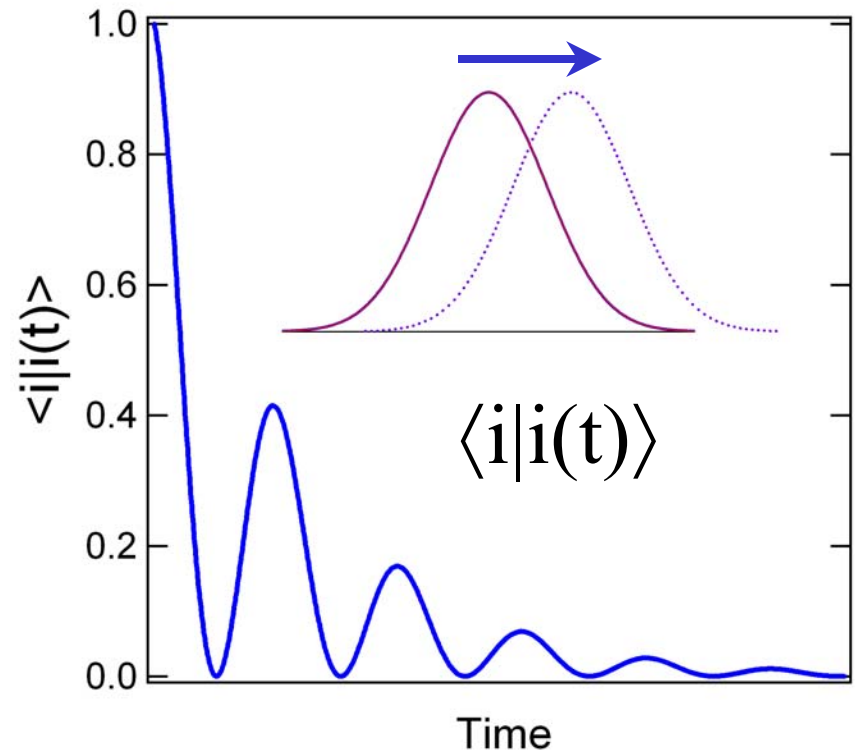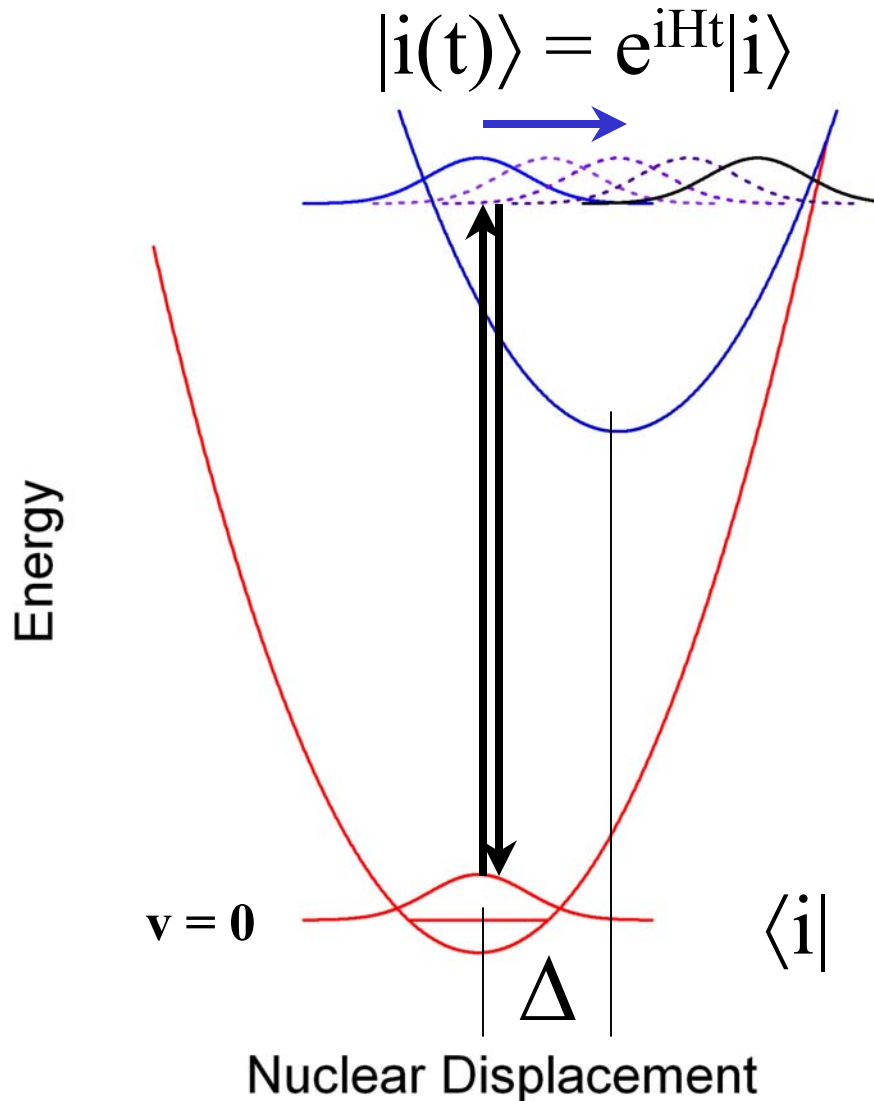S is the electron-vibration coupling constant
S = $\Delta^2/2$.
ν is the vibration partition function. We have
also called this Q (or z). All of these
nomenclatures are in standard use.

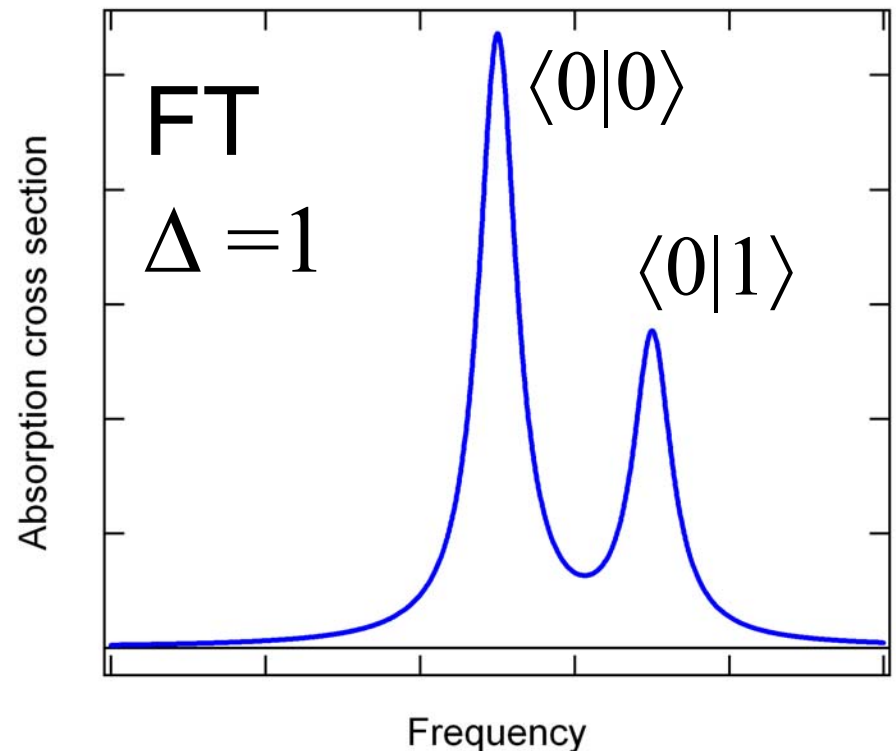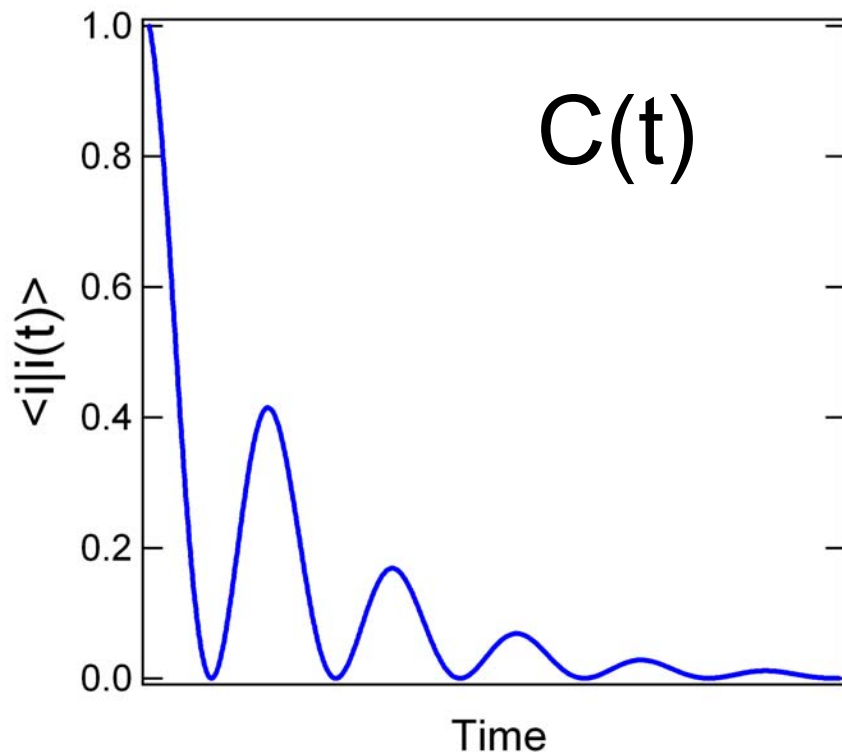$$\nu = \frac{1}{e^{\hbar\omega/kT} - 1}$$

At T = 0, ν = 0.

Wavepacket dynamics: Absorption

$$|i(t)\rangle = e^{iHt}|i\rangle$$

Energy

$v = 0$

Δ

$\langle i|$

Nuclear Displacement

$\langle i|i(t)\rangle$

Time

Notice that the loss of overlap
of |i(t)> with the original distribution
starts at 1 and although it oscillates
it never becomes negative.

Fourier transform of exponentially damped sinusoid is a Lorentzian

$$\sigma_A = \frac{2\pi\omega_0 M_{if}^2}{3\hbar c} \int_{-\infty}^{\infty} \langle i|i(t)\rangle \exp\left\{i(\omega_i + \omega_0)t - \Gamma t\right\} dt$$

C(t)

FT

$\Delta = 1$

$\langle 0|0\rangle$

$\langle 0|1\rangle$

Application of the time correlator to absorption

M is the electronic transition moment. This can be calculated from the overlap of wave functions in the ground and excited state.

The ground and excited state potential energy surfaces can be calculated. The practical application of quantum chemistry to the calculation of potential energy surfaces will be described shortly.

It must be kept in mind that the hamiltonian in the ground state and excited state are not the same. The correlation function can be applied to electronic and nuclear motion together or following the Condon approximation it can be applied to the nuclear motion alone treating the electronic part as a constant.

Definitions of the transition moment

Since we have considered the intensity of absorbed radiation we can use the following definitions for m to relate explicitly to spectra.

1. Microwave or far infrared: $\mu_{fi} = \mu_0$, the permanent dipole moment of the molecule.

2. Infrared
$$\mu_{fi} = \left(\frac{\partial \mu}{\partial Q}\right) Q$$

where Q is a normal coordinate of vibration

3. Rayleigh scattering:
$$\mu_{fi} = \mu_{ind} \propto e_f \cdot \alpha \cdot e_i$$

where α is the ground state polarizability and e_i and e_s are the direction of incident and scattered radiation, respectively.

4. Raman scattering:
$$\mu_{fi} = \mu_{ind} \propto e_f \cdot \frac{\partial \alpha}{\partial Q} \cdot e_i$$

where the polarizability derivative is taken with respect to the normal coordinate Q.

Definitions of the transition moment

We can also apply the formalism to the following phenomena.
5.   Solvent dynamics: the correlation function is
$$C(t) = <\delta\omega(0)\delta\omega(t)>.$$
The energy fluctuations due to electrostatic interactions of solvent molecules is described.
6.   Dielectric relaxation: The time-dependent response of a medium to an applied electric field can be described using a relaxation function, which is an auto-correlation function of the dielectric response.