Derivation of Linear Response Function

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In order to derive the response function — also called frequency-dependent polarizability — we must first partition the Hamiltonian into two parts: the time-independent Hamiltonian, and the time dependent response:

$$H = H_0 + H'(t) \tag{1}$$

Furthermore, the time-dependent Schrödinger equation is given as:

$$H\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{2}$$

In the interaction picture, $\Psi_0'(t) = \Psi_0' e^{-iE_0t/\hbar}$. Thus we can partition the time-dependent wavefunction (expanding over basis of complete eigenstates) as

$$\begin{aligned}\Psi_0'(t) &= \sum_n c_n(t)\Psi_n \\ \Psi_0' e^{-iE_0t/\hbar} &= \sum_n c_n(t)e^{-iE_nt/\hbar}\Psi_n \\ \Psi_0' &= \Psi_0 + \sum_{n\neq 0} c_n(t)e^{-i\omega_{0n}t}\Psi_n \end{aligned} \tag{3}$$

Where

$$\omega_{0n} = (E_n - E_0)/\hbar \tag{4}$$

are real, positive, *exact* excitation frequencies of unperturbed system. Note that $c_0(t) = 1$. We are assuming that $H'(t)$ is turned on slowly at time $t \to -\infty$. Substitute 1 and 3 into 2, separate the orders, and impose the boundary conditions that $c_0 = 1$ and $c_m = 0$ $(n \neq 0)$ at $t \to -\infty$. This gives

$$i\hbar\dot{c}_n = \langle n|H'(t)|0\rangle e^{i\omega_{0n}t} \tag{5}$$

If we let

$$H'(t) = F(t)A \tag{6}$$

Where we a 'fixed' Hermitian operator A determines the 'shape' of the perturbation, while time dependence is confined to the (real) 'strength' factor $F(t)$.

For a perturbation beginning at time $t \to -\infty$ up to time t,

$$c_n(t) = (i\hbar)^{-1} \int_{-\infty}^{t} \langle n|A|0\rangle F(t') e^{i\omega_{0n}t'} dt' \tag{7}$$

Which, to first order, determines the perturbed wavefunction. Now we are interested not in the perturbed wavefunction *per se*, but rather in the response of an observable O to the perturbation.

$$\delta\langle O\rangle = \langle O\rangle - \langle O\rangle_0 = \int_{-\infty}^{t} K(OA|t-t')F(t')dt' \tag{8}$$

where

$$K(OA|t-t') = (i\hbar)^{-1} \sum_{n\neq 0} [\langle 0|O|n\rangle\langle n|A|0\rangle e^{-i\omega_{0n}(t-t')} - \langle 0|A|n\rangle\langle n|O|0\rangle e^{i\omega_{0n}(t-t')}] \tag{9}$$

This is a time correlation function, relating fluctuation of $\langle O\rangle$ at time t to the strength of the perturbation A at some earlier time t'. $K(OA|t-t')$ is defined only for $t' < t$, in accordance with the principle of causality. Thus, it is a function only of the difference $\tau = t - t'$. Recalling the definitions of the Fourier transform $f(\omega)$:

$$f(\omega) = \int_{-\infty}^{\infty} F(t) e^{i\omega t} dt \qquad F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) e^{-i\omega t} d\omega \tag{10}$$

Then instead of 6, we have:

$$H'(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) A_\omega e^{-i\omega t} d\omega \tag{11}$$

Requiring $H'(t)$ to be Hermitian,

$$H'(t) = H'(t)^\dagger$$
$$\frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) A_\omega e^{-i\omega t} d\omega = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(-\omega) A_\omega^\dagger e^{i\omega t} d\omega \tag{12}$$

Now,

$$A_{-\omega} = A_\omega^\dagger \qquad f(-\omega) = f(\omega) \tag{13}$$

Which, upon combining the expressions for $H'(t)$ so as to 'Hermitize' the expression:

$$2H'(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} (f(\omega)A_\omega e^{-i\omega t} + f(\omega)A_{-\omega} e^{i\omega t}) d\omega$$

$$H'(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega) \frac{1}{2} (A_\omega e^{-i\omega t} + A_{-\omega} e^{i\omega t}) d\omega \tag{14}$$

$$\tag{15}$$

Thus

$$A = \frac{1}{2}(A_\omega + A_{-\omega}) \tag{16}$$

with $F(t)$ real. Instead of working in the time domain, we may also consider the response in terms of a single oscillatory perturbation. This means that

$$H'(\omega) = \frac{1}{2}(A_\omega e^{-i\omega t} + A_{-\omega} e^{i\omega t}) \tag{17}$$

To ensure $H'(\omega)$ builds smoothly from zero at $t \to -\infty$, we can introduce a convergence factor $e^{\eta t}$ with the initial condition $c_0 = 1$ and $c_n = 0$, which gives:

$$c_n(t) = \lim_{\eta \to 0} \left(-\frac{1}{2\hbar} \right) \left\{ \frac{\langle n|A_\omega|0\rangle}{\omega_{0n} - \omega - i\eta} e^{i(\omega_{0n} - \omega - i\eta)t} + \frac{\langle n|A_{-\omega}|0\rangle}{\omega_{0n} + \omega - i\eta} e^{i(\omega_{0n} + \omega - i\eta)t} \right\} \tag{18}$$

Then, collecting terms of $\pm\omega$:

$$\delta\langle O\rangle = \frac{1}{2} \left[\Pi(OA_\omega|\omega) e^{-i\omega t} + \Pi(OA_{-\omega}|-\omega) e^{i\omega t} \right] \tag{19}$$

Finally:

$$\Pi(OA_\omega|\omega) = \lim_{\eta \to 0} \left(\frac{1}{\hbar} \right) \sum_{n \neq 0} \left\{ \frac{\langle 0|O|n\rangle\langle n|A_\omega|0\rangle}{\omega + i\eta - \omega_{0n}} - \frac{\langle 0|A_\omega|n\rangle\langle n|O|0\rangle}{\omega + i\eta + \omega_{0n}} \right\} \tag{20}$$

Which is the response function, or frequency-dependent polarizability.