On the Equivalence of Moment Method and Fourier Transform Method in the Theory of Spectral Line Shape

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The method of moment, due to Van Vleck\(^1\), which offers a very powerful means to analyse the magnetic resonance absorption spectra, can be shown to be equivalent to the method of Fourier transform which is often used in the theory of pressure broadening of spectral lines.\(^2\),\(^3\),\(^4\)

Let \( g(\omega) \) be the shape function of a spectral line normalized so that
\[
\int_{-\infty}^{\infty} g(\omega) d\omega = 0. \tag{1}
\]

If we denote the Fourier transform of the shape function by \( f(\tau) \), we can easily find that
\[
f(\tau) = \sum_{n=0}^{\infty} \frac{(i\tau)^n}{n!} \langle \omega^n \rangle_{Af}. \tag{2}
\]

If we are concerned with electric or magnetic dipole radiation linearly polarized parallel to the \( x \)-axis, the intensity of radiation, emitted or absorbed, accompanied by the transition \( a \rightarrow b \) is proportional to \( |\mu_x, ab|^2 \), \( \mu_x \) being the \( x \)-component of the electric or magnetic dipole moment of the system which we are interested in. Thus we have for \( \langle \omega^n \rangle_{Af} \)
\[
\langle \omega^n \rangle_{Af} = \sum_{a,b} \frac{\omega_{a,b}^n |\mu_x, ab|^2}{\sum_{a,b} |\mu_x, ab|^2}. \tag{3}
\]

where \( \omega_{a,b} \) is the circular frequency corresponding to the transition \( a \rightarrow b \). This expression is just the starting point of Van Vleck's method of moment.

Now, we take the Heisenberg representation for the matrix \( \mu_x \). Then it is easy to see that
\[
\langle \omega^n \rangle_{Af} = \frac{i^{-n} T_e[\mu_x(t) \mu_x(t)]}{T_e[\mu_x(t)]}. \tag{4}
\]

Inserting this into Eq. (2), we have a very simple expression for the Fourier transform \( f(\tau) \):
\[
f(\tau) = T_e[\mu_x(t+\tau) \mu_x(t)]/T_e[\mu_x(t)]. \tag{5}
\]

As the trace of the matrix for an observable is proportional to the mean value of it, we see that the Fourier transform of the shape function is nothing other than the auto-correlation function of the dipole moment, as it is the case in the classical theory.\(^5\)

The matrix \( \mu_x(t+\tau) \) can be derived from the matrix \( \mu_x(t) \) by the unitary transformation
\[
\mu_x(t+\tau) = \exp(iH_\tau/\hbar) \mu_x(t) \exp(-iH_\tau/\hbar), \tag{6}
\]

where \( H \) is the Hamiltonian of the system. We now divide the Hamiltonian \( H \) into the two constituents \( H_0 \) and \( H_1 \):
\[
H = H_0 + H_1,
\]

where \( H_0 \) is the part of the Hamiltonian, with the transition between the eigenstates of which we identify the spectral line, and \( H_1 \) is the interaction between dipoles which gives rise to the line width.

If we take the representation in which \( H_0 \) is diagonal, then the matrix element \( \langle j | \mu_x(t+\tau) | k \rangle \) corresponding to the transition from the eigenstate \( j \) of \( H_0 \) with energy \( E_0, j \) to the eigenstate \( k \) with energy \( E_0, k \) becomes
\[
\langle j | \mu_x(t+\tau) | k \rangle = \exp(i\omega_{0,jk}\tau)
\cdot \langle j | \exp(iH_\tau/\hbar) \mu_x(t) \exp(-iH_\tau/\hbar) | k \rangle,
\]

where
\[
\omega_{0,jk} = (E_0, j - E_0, k)/\hbar. \tag{7}
\]

Inserting this expression into Eq. (5) and inversely transforming from \( f(\tau) \) to \( g(\omega) \), we obtain as the shape function \( g_{jk}(\omega) \) corresponding to the transition \( j \rightarrow k \)
\[
g_{jk}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[-i(\omega - \omega_{0,jk})\tau] \times \langle j | \exp(iH_\tau/\hbar) \mu_x(t) \exp(-iH_\tau/\hbar) | k \rangle
\times \langle k | \mu_x(t) | j \rangle d\tau/|\langle j | \mu_x(t) | k \rangle|^2. \tag{8}
\]
Eq. (6) is valid, in the adiabatic approximation, even when \( H_t \) contains the time explicitly, as in the theory of pressure broadening, if we substitute the product \( H_t \tau \) by the integral \( \int_t^{t + \tau} H_t(t') \, dt' \). When this substitution is made, Eq. (8) is just the standard form of the line shape function in the Fourier transform theory of the pressure broadening. In any case, we see that the problem of line shape can be reduced to the Fourier analysis of the interaction representation for the dipole moment.

2) H. M. Foley, Phys. Rev. 69 (1946), 616.  
4) M. Mizushima, Phys. Rev. 83 (1951), 94.  