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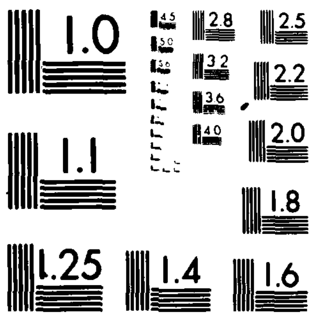

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It is shown that a rigorous mathematical theorem in the theory of Fourier transforms due to Paley and Wiener provides the bound for physically acceptable relaxation functions for long times. The exponential decay function, $\exp(-t/\tau)$, with a constant relaxation time τ, and hence also a superposition of exponential decay functions corresponding to a distribution of relaxation times, does not provide an acceptable description of relaxation phenomena. On the other hand, the assumable bound of the Paley-Wiener theorem does.

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20. ABSTRACT (Continued)

This bound turns out to have exactly the same form as a class of relaxation functions that have been successfully applied in the description of many relaxation phenomena in condensed matter. An important consequence of the Paley-Wiener theorem is the necessity for time-dependent relaxation rates which provides insight into the reason for deviation from exponential behavior for long times.

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THE PALEY-WIENER CRITERION FOR RELAXATION FUNCTIONS

It is traditional[1-5] to discuss the residual part of relaxing quantities in terms of exponential decay viz.

$$\exp(-t/\tau) \tag{1}$$

where τ is the "relaxation time" or a superposition[6-38] of exponential decay terms with a distribution of τ. In fact, deviations from this exponential behavior are usually observed in experimental measurements.[6-74] Other functional forms, namely,

$$\exp(-a(t/\tau_s)^b),\ a>0,\ 0<b<1 \tag{2a}$$

and

$$(t/\tau_s)^{-\alpha},\ \alpha>0 \tag{2b}$$

have proved to be widely applicable in the description of a large variety of relaxation phenomena in condensed matter physics.[21,39-74] Here τ_s is a characteristic time in the system. There have been many attempts[39-55] to understand the latter dependences in terms of a distribution of relaxation times. Alternatively, the functional forms (2a,b) have been viewed as fundamental in themselves and based on mechanistic origins.[56-74] The purpose of the present paper is to employ the Paley-Wiener theorem[75] on Fourier transforms together with physical requirements that have to be satisfied by any relaxation process to discriminate between the two viewpoints.

There is extensive literature[76-81] on the nature of the decay of unstable states that can be utilized in the present context. A clear exposition of this decay may be found in the papers of Khalfin[76] and Chui et al.[80] The formalism developed by Chui et al. is utilized to provide a description for relaxation processes.

Let $\mathcal{H}$ be the Hilbert space formed by the totality of the relaxing states and those which are stable. The time evolution of this total system is then described by the evolution operator $\mathcal{U}(t)=\exp(-iHt)$, where H is the self-adjoint Hamiltonian operator of the system. (Units with $\hbar=1$ are used in this paper.) For the sake of simplicity, it is assumed that there is only one relaxing state represented by the vector $|R\rangle$ of $\mathcal{H}$. The state $|R\rangle$ is associated with the

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continuous spectrum of $\mathcal{H}$ and is orthogonal to all bound stationary states of the Hamiltonian. It is assumed that the Hamiltonian H has no singular continuous spectrum. If F_ε denotes the spectral projections of H,

$$H = \int \varepsilon dF_\varepsilon = \int \varepsilon |\varepsilon\rangle\langle\varepsilon| d\varepsilon, \tag{3}$$

then the function $\langle R|F_\varepsilon|R\rangle$ is absolutely continuous, and its derivative

$$\rho(\varepsilon) = \frac{d}{d\varepsilon} \langle R|F_\varepsilon|R\rangle = \langle R|\varepsilon\rangle\langle\varepsilon|R\rangle \tag{4}$$

can be interpreted as the energy distribution of the state $|R\rangle$. In other words, the integral $\int_E^{E+\Delta E} \rho(\varepsilon)d\varepsilon$ is the probability that the energy of the state $|R\rangle$ lies in the interval $(E,E+\Delta E)$. The function $\rho(\varepsilon)$ has the following properties:

(i) $\rho(\varepsilon) \geqq 0$;

(ii) $\int \rho(\varepsilon)d\varepsilon = 1$ corresponding to the normalization condition, $\langle R|R\rangle=1$; and

(iii) $\rho(\varepsilon) = 0$ for ε outside the spectrum of H. In order that the system have a stable ground state, the spectrum of H must have a finite lower bound. Therefore $\rho(\varepsilon)$ is semibounded.

The residual part of a relaxing quantity, Q(t), at an instant t for the relaxing state $|R\rangle$ is

$$Q(t) \propto |\langle R|\exp(-itH)|R\rangle|^2 . \tag{5}$$

The residual relaxing amplitude

$$c(t) = \langle R|\exp(-itH)|R\rangle \tag{6}$$

may be seen to be the Fourier transform of the energy distribution function $\rho(\varepsilon)$,

$$c(t) = \int \exp(-i\varepsilon t)\ \rho(\varepsilon)\ d\varepsilon \quad . \tag{7}$$

The Paley-Wiener theorem[75] turns out to be the touchstone for the determination of the bounds on the long time behavior of relaxation processes. This theorem, stated in the present context is: the necessary and sufficient conditions that $\rho(\varepsilon)$, the Fourier transform of c(t) given by Eqn. (6) defined in $-\infty<t<\infty$, vanishes below some value of ε, say zero (i.e. $\rho(\varepsilon)$ is semibounded in the ε-variable) are

$$\text{(i)} \int_{-\infty}^{\infty} |c(t)|^2 dt < \infty \text{ (square integrability of } c(t)\text{)} \tag{8a}$$

and

$$\text{(ii)} \int_{-\infty}^{\infty} \frac{|\ln|c(t)||}{1+t^2} dt < \infty \quad . \tag{8b}$$

These conditions imply that for $(t/\tau_s) \to +\infty$,

$$|c(t)|^2 \leqq \exp(-a(t/\tau_s)^b), \ a>0, \ 0<b<1 \ . \tag{9}$$

Here τ_s is a characteristic time so as to make a dimensionless. It should be noted that both the forms (2a,b) satisfy this inequality whereas the exponential form (1) does not. Thus the two cases, Eqn. (1) and (2), are mutually exclusive. The case b=1 corresponds to a physically unrealistic, unbounded $\rho(\varepsilon) \propto a\tau_s^{-1}((a/\tau_s)^2+\varepsilon^2)^{-1}$, and therefore violates the conditions of the Paley-Wiener theorem. Since a single exponential form is unphysical, a superposition of them is also unphysical. Hence the idea of superposition of exponentially decaying functions must also be ruled out as a viable description of relaxation phenomena.

The exclusion of b=0 in Eq. (2a) follows from the fact that the corresponding c(t) would violate the condition of square integrability, Eqn (8a), which is also physically untenable since, then Q(t) cannot then be proportional to $|c(t)|^2$. However when

$$|c(t)|^2 \leqq (t/\tau_s)^{-\alpha} \text{ with } \alpha>1 \text{ for } t/\tau_s \to \infty \ , \tag{10}$$

the requirements of the Paley-Wiener theorem are again met. It is remarkable that both the Paley-Wiener limiting form, Eqn (2a), and the simple inverse power decay, Eqn (2b) have been repeatedly found to govern many different relaxation processes in condensed matter physics. Both of these have also been predicted from microscopic models.[55-74]

Since $|c(t)|^2$ is monotonic for large t/τ_s, it follows from Eqs. (5) and (9) that,

$$-\frac{dQ}{dt} \propto -\frac{d|c(t)|^2}{dt} \leqq a\ (b/\tau_s)\ (t/\tau_s)^{b-1}\ |c(t)|^2, \ t/\tau_s \to \infty \ (0<b<1) \tag{11}$$

The effective transition rate W(t) has a bound

$$W(t) \leqq a\ (b/\tau_s)\ (t/\tau_s)^{b-1} \ , \ (0<b<1) \ . \tag{12}$$

Thus W(t) has an essential dependence on t. The impact of time dependent transition rates in relaxation processes has recently been discussed elsewhere.[82]

The limit of b=1 would have led to a constant transition rate, as is the familiar result for an exponential decay. As noted above this case was ruled out so that the transition rate must be a function of time and must have the bound given by Eqn. (12).

Eqn. (12) may be extended to include the case where b=0 by the following straightforward procedure wherein $ab \to \alpha$ as $b \to 0$ such that α is nonzero. Then

$$W(t) \leqq \alpha t^{-1}. \tag{13}$$

This corresponds to the case described by Eqn. (10). It is interesting to note that Eqs. (9,12,13) provide a hierarchy of bounds for a relaxing quantity and their corresponding transition rates.

The fact that the effective transition rate has an essential dependence on time shows that it is not compatible with the traditional derivation of constant transition rates by means of the Fermi golden rule.[83] In fact the breakdown of the Fermi golden rule has been very often noted in the literature.[84-88] The familiar expression for the transition rate[83] is a good approximation for long times $t \gg (\Delta E)^{-1}$ where ΔE is the energy difference between the two states between which the transition is taking place. The explicit examples of the breakdown of this are in Bremstrahlung in Quantum Electrodynamics and the X-ray edge problem in solid state physics. In the relaxation regime, such characteristic energy differences may approach zero. This indicates the breakdown of the approximation in the derivation of the constant transition rate. In this situation, one must carry out a more careful calculation which leads to a time dependent transition rate as discussed above.

The occurrence of apparent constant transition rates for the "Elementary Excitations"[89] commonly observed spectroscopically in condensed matter viz. neutron, Raman, microwave, far infrared, infrared, visible, ultraviolet, X-ray etc., may be understood to be consistent with the Paley-Wiener theorem if b is taken to approach unity but never quite attain it. Such cases probe either the discrete states or continuum states of the many particle Hamiltonian H with typical energies in the range $\gtrsim 10^{10}$ Hz such as electrons, phonons, magnons, etc., and the approximation $t\Delta E \gg 1$ holds good. For relaxation phenomena, b rarely approaches unity. What are involved in the low frequency relaxation processes are low frequency excitations of the system below, say 10^{10} Hz. It is clear that an experimental effort should be made to observe these excitations directly. In fact they may have already been observed in recent experiments.[90] In general, the effect of these excitations should occur in any of a number of long tail transient spectroscopic observations made possible by modern electronic advances.

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