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Theory of ac Conductivity Based on Random Walks

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It is shown that a simple random-walk formalism is not sufficient to derive ac conductivities when the influence of the first–waiting-time distribution is considered.

The continuous-time random walk of Montroll and Weiss[1] has been employed by Sher and Lax[2] and subsequently by Moore[3] to derive ac conductivity in situations where the conduction is primarily by hopping. The treatment ostensibly has applications to amorphous materials where at moderate frequencies the conductivity is frequently proportional to ω^{ν}, where ω is the angular frequency and ν is a constant of the order of unity. Sher and Lax are able to fit theoretical curves to experimental data quite successfully through a frequency-dependent term of the form

$$i\omega\psi(\omega)[1-\psi(\omega)]^{-1}, \qquad (1)$$

where $\psi(\omega)$ is the Fourier transform of the probability density of the waiting time between hops in a random walk.

Firstly I shall derive a formula for the ac conductivity in a much simpler fashion than Sher and Lax and secondly show that expression (1) is incorrect.

Suppose a potential gradient is suddenly applied to a material in which the carriers perform a Montroll-Weiss type of random walk. In this walk, independent electrons (say) are trapped at sites which may be distributed at random. Hopping takes place between sites; the transitions themselves are virtually instantaneous with a waiting time between hops with probability density $f(t)$. The potential gradient naturally causes the probability of a hop in the forward direction to be greater than that in the reverse direction so that a steady component of current is produced.

With the use of a type of argument employed by Feller,[4] the probability that a transition takes place in interval dt at time t after application of

the field is equal to

$$[\boldsymbol{h}(t)+\boldsymbol{h}(t)*f(t)+\boldsymbol{h}(t)*f(t)*f(t)+\boldsymbol{h}(t)*f(t)*f(t)*f(t)+\ldots]dt, \tag{2}$$

where $\boldsymbol{h}(t)$ is the probability density of the first-jump waiting interval. If the carrier moves a mean distance λ in the direction of the field, e is the electronic charge, and l is the circuit length, the mean charge transported around the circuit in dt is

$$\langle\Delta Q\rangle = (e\lambda/l)[\boldsymbol{h}+\boldsymbol{h}*f+\boldsymbol{h}*f*f+\boldsymbol{h}*f*f*f+\ldots]dt, \tag{3}$$

which is equivalent to a mean current

$$\langle I(t)\rangle = (e\lambda/l)[h+h*f+h*f*f+h*f*f*f+\ldots]. \tag{4}$$

Taking the Fourier transform in such a way as to be consistent with electric circuit theory ($\partial/\partial t \rightarrow i\omega$) and performing a geometric sum yields for the Fourier transform of the mean indicial reponse

$$\langle I(\omega)\rangle = (e\lambda/l)\frac{\boldsymbol{h}(\omega)}{[1-\psi(\omega)]}, \tag{5}$$

where

$$\begin{aligned}\boldsymbol{h}(\omega) &= \int_{-\infty}^{\infty}\boldsymbol{h}(t)e^{-i\omega t}\,dt,\\ \psi(\omega) &= \int_{-\infty}^{\infty}f(t)e^{-i\omega t}\,dt.\end{aligned} \tag{6}$$

The impulsive response can be obtained from the indicial response by multiplying Eq. (5) by $i\omega$; summing over all electrons gives for the impulsive response in terms of the current density

$$\langle j(\omega)\rangle = ne\lambda i\omega h(\omega)/[1-\psi(\omega)], \tag{7}$$

where n is the electron density. This is proportional to the complex ac conductivity $\rho(\omega)$.

We may cast this equation into the form given by Sher and Lax by introducing the ordinary mobility and diffusion coefficients K and D, respectively. The drift velocity v of a carrier is related to the quantity λ by

$$v = \lambda/\mu, \tag{8}$$

where μ is the mean time between hops, so that

$$KeE = \lambda/\mu, \tag{9}$$

where $\boldsymbol{E}$ is the applied electric field. Employing the Einstein relation

$$D = kTK, \tag{10}$$

where k is Boltzmann's constant and T is the temperature, we have

$$\langle j(\omega)\rangle = i\omega\boldsymbol{h}ne^2D\mu E/kT(1-\psi).$$

We may now express D in terms of the variance of the jump distance σ^2 for a three-dimensional random walk[5] in the absence of an applied field,

$$D = \sigma^2/6\mu, \tag{11}$$

which results in

$$\langle j(\omega)\rangle = \frac{ne^2\sigma^2E}{6kT}\frac{i\omega\boldsymbol{h}}{1-\psi}. \tag{12}$$

If we put $\boldsymbol{h}=\psi$ this result is virtually identical to that of Sher and Lax: They introduce a generalized variance which is a function of frequency. Nevertheless, in comparisons with experimental data σ^2 is treated as a constant.

The Montroll-Weiss formalism employed by Sher and Lax makes no distinction between $h(t)$ and $f(t)$ so that expression (1) is naturally obtained by them. However the inclusion of $h(\omega)$ makes a very important difference except when $\omega \sim 0$ [if $\boldsymbol{h}(t)$ and $f(t)$ correspond to proper distributions $\boldsymbol{h}(\omega)=\psi(\omega)=1$]. The density $\boldsymbol{h}(t)$ can easily be obtained in terms of $f(t)$ in the limit when the hopping has been taking place for an infinite time before application of the field. The theory is given by Feller[4] and the result is

$$h(t) = \mu^{-1}[1-F(t)], \tag{13}$$

where $F(t)$ is the distribution corresponding to $f(t)$. Thus

$$\boldsymbol{h}(\omega) = [1-\psi(\omega)]/i\omega\mu$$

and we see on inserting this in Eq. (12) that $\rho(\omega)$ is independent of ω. It is worthwhile emphasizing that this conclusion is not a consequence of the derivation presented here but is equally true for the Sher and Lax treatment if $\boldsymbol{h}(t)$ is properly included in their random-walk formalism.

The lack of any frequency dependence is of course due to the nature of the model: The assumption that the wave functions are completely localized results in a model which is essentially classical in character where the hops occur instantaneously.

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Excited-State Exchange Broadening of Optical Transitions in $PrCl_3$

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We have observed an anomalous broadening of two fluorescence lines in $PrCl_3$. The new effect is observed only when the terminal state is a magnetic doublet and only at low temperatures ($T < 100$ K). However, the effect is seen far above any transition or ordering temperature. The broadening can be, at least partially, suppressed by application of a large magnetic field. The effect is almost certainly a cooperative phenomenon arising from an interaction between ground- and excited-state ions.

In previous papers[1,2] we have investigated the properties of $PrCl_3$ and $Pr_{0.01}La_{0.99}Cl_3$. In the course of this work we observed an unexpected behavior of the fluorescent linewidths which we report in this Letter.

The experimental setup is the same as described in Refs. 1 and 2 except that a superconducting magnet was used to obtain the magnetic field data. The $^3P_0(\mu = 0)$ level was pumped with the pulsed dye laser (4 nsec pulse width) from the $^3H_4$ ground state (excitation ~488 nm). Fluorescence of the $^3P_0$ to the $^3F_2$ and $^3H_6$ manifolds was observed[3,4] (Fig. 1). In hexagonal $PrCl_3$ and $LaCl_3$ (site symmetry C_{3h} or $\bar{3}$) the levels with $\mu = 1, 2$ are doublets while those with $\mu = 0, 3$ are nondegenerate.

The anomaly that attracted our interest is displayed in the upper (solid) curve in Fig. 2 which is a plot of linewidth versus temperature of the $^3P_0$-$^3F_2$ emission (645 nm) in $PrCl_3$. Theories based on ion-phonon interactions predict a monotonic decrease in linewidth with decreasing temperature.[5] Indeed, the data (curve 2) for $Pr_{0.01}La_{0.99}Cl_3$ are monotonic. If a large magnetic field splits the Zeeman components, the linewidth as a function of temperature of these components changes as seen in curve 3. The maximum reduction of width occurs when the two components are fairly well separated[6] and further increase of the field to 90 kG has no effect.

In Fig. 3 we show the linewidth as a function of temperature for transitions to $^3H_6$ in $PrCl_3$.[7] The 619-nm transition in zero field (curve 1) does not display the dramatic increase of linewidth at lower temperatures. Note, however, that at 20 K its width is more than double that in dilute crystals (curve 2). In the latter, we see that there is significant phonon broadening even at 50 K so that a minimum, such as observed in the 645-nm line, would be effectively masked. In a magnetic field the linewidth of the 619-nm emission in $PrCl_3$ becomes about as narrow as it is in the

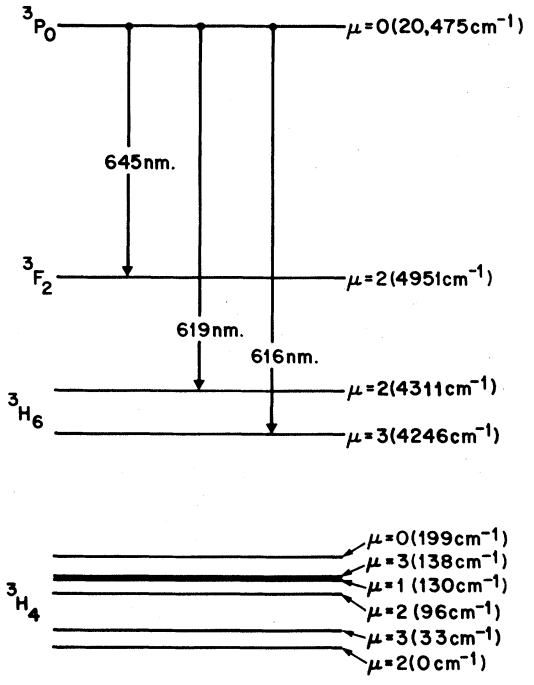

FIG. 1. Partial energy-level diagram of $Pr_{0.01}La_{0.99}Cl_3$. We display only those levels of interest. The energy of each level is shown at the right. (The energies and hence transition wavelengths change slightly in $PrCl_3$.)