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Power spectrum of valence fluctuations*

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The power spectrum of the temporal fluctuations in the occupation number of an ionic shell has been evaluated using a model Hamiltonian that represents configurations hybridized with conduction-electron states. Explicit forms for the autocorrelation function and the power spectrum are derived. The results of Mössbauer and x-ray photoemission spectra experiments in intermediate-valence systems are analyzed and the connection with Kubo's stochastic theory of line shape is given. The conclusions shed light on the validity of the concept of temporal fluctuations when applied to intermediate-valence systems.

I. INTRODUCTION

In the literature on intermediate-valence systems two concepts or views are commonly used. One speaks of valence mixing when the properties are interpreted in terms of a mixed or hybridized ground state.[1-3] Alternatively, the expression "valence fluctuation" is used when the experiments are interpreted in terms of temporal fluctuations in the occupation of the ionic shells.[4]

It is interesting to study the connection between these two lines of thought and to see whether the temporal fluctuations can be explicitly shown to appear, starting from a microscopic model Hamiltonian which includes hybridization between two types of states.

The physical systems that we have in mind are rare-earth compounds, in which the mixing occurs between two $4f$ configurations like $(4f)^n$ and $(4f)^{n+1}$ In building up a solid with these rare-earth ions, the $4f$ wave functions become hybridized with conduction-electron states which form a continuum.

The ground state of the system ion plus conduction electrons is certainly stationary and should be described as a quantum admixture of the two valence states of the ion and of the band states.

Analyzing certain spectroscopic properties like x-ray photoemission spectra[5] (XPS) or Mössbauer resonance,[6] one wants to study the response of the system to a given external probe, which couples directly or indirectly to the localized $4f$ electrons. In the case of Mössbauer experiments the external probe is the radiation field of the γ rays which can excite the nucleus, whose response in turn depends directly on the number of $4f$ electrons.

Due to the hybridization previously mentioned, the number of $4f$ electrons n is not a good quantum number and its time rate of change does not vanish. The expectation value of $\dot{n}$ is zero in an equilibrium ensemble but that of $\dot{n}^2$ is nonzero and can be related to the power spectrum of equilibrium fluctuations of n.

If one were to start at $t=0$ with a state that is an eigenstate of n, and thus corresponds to an integer value of this quantity, the mean value of n will change in time. When the hybridization includes only a finite number of states this variation of $\langle n\rangle$ is an adiabatic oscillation[7] and the initial value will recur at a later time.

In the case where the localized states are hybridized with an infinite number of states, as when conduction-electron states are mixed in, there is a memory loss and the variation of $\langle n\rangle$ becomes a true stochastic fluctuation.

The problem bears certain similarities with that of the microscopic theory of Brownian motion, which can be based on a Hamiltonian describing a free particle or an oscillator coupled to a large number of other degrees of freedom[8] that play the role of a thermal bath. For a bath with a finite number N of degrees of freedom there is always the possibility of a Poincaré recurring time which however tends to infinity very rapidly with increasing N.

In order to make the description clearer we will consider a simple Hamiltonian which is exactly solvable and contains all necessary ingredients to give a mathematical description of the above given ideas.

The Hamiltonian is that of the virtual-bound-state model of Anderson and Friedel which consists of two nondegenerate localized states, a continuum of band states and a hybridization term between these two kinds of states

$$H_0 = E_0|0\rangle\langle 0| + E_1|1\rangle\langle 1| + \sum_k \epsilon_k n_k + \sum_k (V_k c_k^\dagger|0\rangle\langle 1| + V_k^\dagger|1\rangle\langle 0| c_k)\,. \tag{1}$$

Here $|0\rangle$ and $|1\rangle$ are states corresponding to the $4f^n$ and $4f^{n+1}$ configurations of the real system whose energies are E_0 and E_1, respectively. $n_k = c_k^\dagger c_k$ is the number of conduction electrons of energy ϵ_k and $c_k^\dagger$ (c_k) is the creation (annihilation) op-

erator for an electron in the state $|k\rangle$.

This Hamiltonian can be diagonalized[9] and all required quantities can in principle be exactly evaluated. This is so because it is a one-particle Hamiltonian. As such it lacks the complications of the complete Anderson Hamiltonian. However, the arguments we present here refer to the non-integer occupation of the localized state, a feature already contained in (1).

II. POWER SPECTRUM OF VALENCE FLUCTUATIONS

Let us consider the quantity $u(t)=n(t)-\langle n\rangle$, where $n(t)$ is the occupation number operator of the localized state at time t and $\langle\cdots\rangle$ indicates an average over the canonical ensemble.

In order to characterize the nature of the valence fluctuations it is useful to consider the autocorrelation function

$$K(t)=\tfrac{1}{2}\langle u(t)u(0)+u(0)u(t)\rangle \tag{2}$$

and its power spectrum

$$\hat{K}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{i\omega t}K(t)\,. \tag{3}$$

Closed expressions can be given for both of these quantities. Assuming a constant density of states ρ for the conduction band we have

$$\hat{K}(\omega)=\frac{1}{2\pi}\left(\frac{1}{2}+\frac{1}{e^{\omega/T}-1}\right)\frac{2\Gamma/\pi}{\omega^2+4\Gamma^2}\times\left\{\mathrm{Im}\psi\left(\frac{1}{2}-i\,\frac{E+i\Gamma}{2\pi T}\right)+\frac{2\Gamma}{\omega}\,\mathrm{Re}\left[\psi\left(\frac{1}{2}-i\,\frac{E+i\Gamma-\omega}{2\pi T}\right)-\psi\left(\frac{1}{2}-i\,\frac{E+i\Gamma}{2\pi T}\right)\right]-(\omega\to-\omega)\right\}, \tag{4}$$

where $\Gamma=\pi\rho V^2$, $E=E_1-E_0-\epsilon_F$, ϵ_F is the chemical potential and T is the temperature. ψ indicates the diagamma function and Re and Im stand for real and imaginary parts, respectively.

The autocorrelation function is given by

$$K(t)=e^{-2\Gamma|t|}[\mathrm{Re}I(t)-|I(t)|^2]\,, \tag{5}$$

where

$$I(t)=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega\,\frac{\Gamma}{\omega^2+\Gamma^2}\,f(\omega+E)e^{i\omega t}e^{\Gamma|t|}\,. \tag{6}$$

f is the Fermi function.

It can be easily shown that in the high-temperature limit $\hat{K}(\omega)$ is simply a Lorentzian of width 2Γ or equivalently that $K(t)=\frac{1}{4}e^{-2\Gamma|t|}$ (see Fig. 1).

This exponential decay of the correlation is typical of the stochastic nature of the fluctuations.

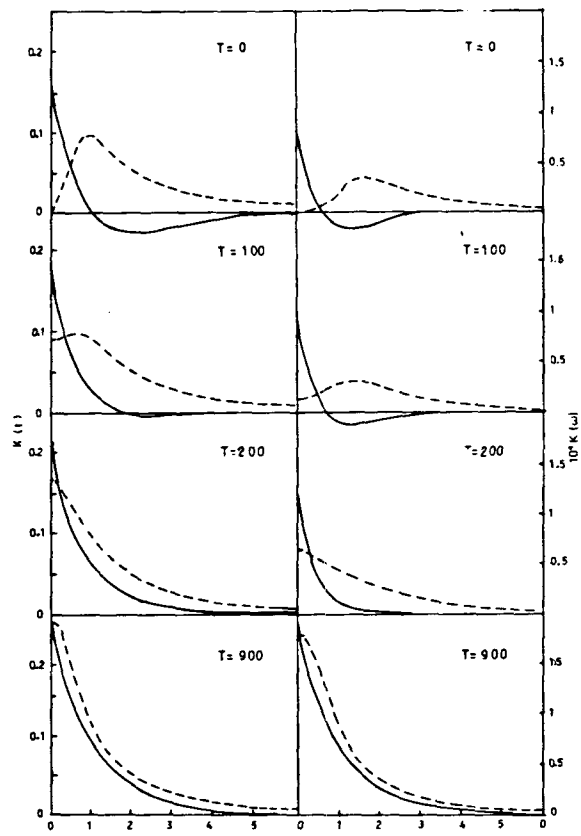

FIG. 1. Autocorrelation function $K(t)$ (full line) and the power spectrum $\hat{K}(\omega)$ (dashed line) for $\Gamma=200$ K and different temperatures. The curves to the left correspond to $E=-250$ K, those to the right to $E=-500$ K. $x=2\Gamma t$ or $x=\omega/2\Gamma$ as the case may be.

The analogous situation in the Brownian motion problem corresponds to the case where the velocity autocorrelation shows an exponential decay, associated with a short memory force.

As the temperature is lowered, $\hat{K}(\omega)$ developes a maximum (see Fig. 1). This fact reflects itself in an oscillating $K(t)$. At low temperatures the frequency of the oscillations is approximately given by $E+\Gamma$ as can be seen from Fig. 2.

This type of phenomenon is also shown by the velocity autocorrelation function in any microscopic model of Brownian motion, as is the case for the theory of liquids. It can be interpreted, in terms of the dynamics equations, as the force developing a memory.

A memory function can be introduced in the present context by defining it through the equation[10]

$$\frac{dK(t)}{dt}-\int_0^t dt'M(t-t')K(t')=0\,. \tag{7}$$

This memory function is related to the Green's function $\langle\langle u;u\rangle\rangle$ and can also be evaluated.[11] It

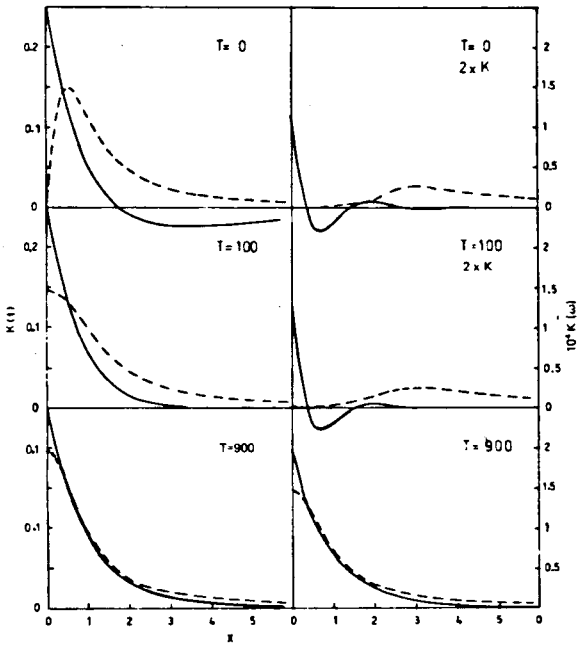

FIG. 2. $K(t)$ and $\hat{K}(\omega)$ for $\Gamma = 200$ K and different temperatures. The curves to the left correspond to $E = 0$, those to the right to $E = -1000$ K. Note that for $E = -1000$ K the two upper drawings correspond to a different scale. $x = 2\Gamma t$ or $x = \omega/2\Gamma$ as in Fig. 1.

turns out that M can be split into two parts $M(t) = M_1(t) + M_2(t)$, where $M_1(t)$ is proportional to 2Γ times a δ function. M_2 has the property of approaching zero as $T \to \infty$. This form for the memory implies that the time variation of $K(t)$ has always an exponential envelope of width $\frac{1}{2}\Gamma$.

As is apparent from Figs. 1 and 2, the power spectrum does not die out at $T = 0$, contrary to the assertion in a recent discussion of valence fluctuations.[12] This behavior which is indicative of the quantum nature of the problem at hand, can be traced to the factor $\frac{1}{2}$, in the term in the first large parentheses of expression (4) for $K(\omega)$. This factor, in turn, originates itself in the use of the symmetrized fluctuation function $K(t)$, a fact that is required by the fluctuation-dissipation theorem.

The amplitude of the fluctuations $\langle u^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2$ can be seen to decrease as $|E| = |E_1 - E_0 - \epsilon_F| \gg \Gamma$, i.e., in going to the limit of integer valence, which was to be expected. The mixing does not decrease in this case, as it is seen from the fact that the width of the level is independent of E, but fluctuations become inhibited by the Pauli principle because of the unavailability of empty conduction-electron states close to the localized level. This explains the strong temperature dependence of the fluctuations for this case, since only for $T \sim E$ there will be partially unoccupied conduction states with energies ϵ_k such that $|E_1 - E_0 - \epsilon_k| \sim \Gamma$.

III. DISCUSSION

As it follows from the previous sections there seems to exist a sound mathematical basis for the idea of temporal fluctuations, when the intermediate valence system is described through a pair of ionic configurations which are hybridized with a continuum of conduction-electron states.

Let us see what these fluctuations would imply for the experiments in Mössbauer spectroscopy and XPS. It has recently been shown[13] that these experiments can be accounted for by using a Hamiltonian similar to the one considered here to which a term H' is added describing the coupling of the f states population to the nucleus,

$$H = H_0 + H' ,$$
$$H' = \omega_A(1-n)a^\dagger a + \omega_B n a^\dagger a . \tag{8}$$

Here $a^\dagger$ is the operator that creates a nuclear excitation, which has energy ω_A or ω_B depending on whether the localized state is in the configuration $|0\rangle$ or $|1\rangle$, respectively. In Ref. 13 the response of the system to an external electromagnetic field was evaluated by using a Green's-functions technique. In this way it was possible to derive the Kubo[14] equations for the response of a system subjected to stochastic modulation.

We will see below that the quantum-dynamic equations that follow from the Hamiltonian (8) are exactly of the type discussed by Kubo[14] in his theory of motional narrowing.

The Hamiltonian H' can be written

$$H' = (\bar{\omega} + \omega_1)a^\dagger a , \tag{9}$$

where $\bar{\omega} = \omega_A(1-\langle n \rangle) + \omega_B\langle n \rangle$ and $\omega_1 = (\omega_B - \omega_A)u$. The equation of motion for a reads

$$\dot{a}(t) = i[\bar{\omega} + \omega_1(t)]a(t) . \tag{10}$$

This is the equation for an oscillator with a random frequency $\omega_1(t)$ of the same type as those discussed in Ref. 14.

As shown by Kubo the important parameters that determine the type of response of the system, in the Markovian approximation, are the amplitude of modulation and the correlation time of the fluctuations. The first is given by

$$\Delta^2 = \langle \omega_1^2 \rangle = (\omega_B - \omega_A)^2(\langle n^2 \rangle - \langle n \rangle^2) . \tag{11}$$

The correlation time of modulation is defined by Kubo through

$$\tau_c = \frac{1}{\Delta^2}\int_0^\infty d\tau \langle \omega_1(t+\tau)\omega_1(\tau) \rangle . \tag{12}$$

In our case due to the oscillating character of the correlation function this definition does not seem to be the most adequate. As we saw earlier, the correlation function has an exponential envelope

of width $\frac{1}{2}\Gamma^{-1}$ so it seems more adequate to take simply $\tau_c \cong \frac{1}{2}\Gamma^{-1}$.

The two possible regimes are distinguished by the magnitude of

$$\Delta\tau_c = [(\omega_B - \omega_A)/2\Gamma](\langle n^2\rangle - \langle n\rangle^2)^{1/2}. \quad (13)$$

For the Mössbauer experiments $\omega_B - \omega_A \approx 10^{-7}$ K and since we expect $\Gamma \sim 10^2$ K, we see that $\Delta\tau_c \ll 1$, which defines the fast-modulation regime. Kubo has shown that in this case a single narrow line of width $\Delta^2\tau_c$ is expected. Since this can be smaller than the nuclear widths, only the latter would be found in experiments.[6]

In order to discuss the XPS experiments a Hamiltonian like (1) is not enough since it is necessary to include three different valence states in order to have the possibility of observing two absorption lines.

The simplest Hamiltonian including three different valence states is the Anderson Hamiltonian with spin degeneracy H_A, including the intraatomic Coulomb repulsion U. We should include a term like

$$H' = \sum_{q\sigma} E_q b^{\dagger}_{q\sigma} b_{q\sigma}, \quad (14)$$

where $b^{\dagger}_{q\sigma}(b_{q\sigma})$ creates (annihilates) a free electron of energy E_q, which is the one to be detected. The x-ray electromagnetic field couples to an operator $A_{q\sigma} = b^{\dagger}_{q\sigma} d_\sigma$ corresponding to the excitation of a localized electron to a free running state. The coupling to the conduction electron states is given by terms like $A_{kq\sigma} = b^{\dagger}_{q\sigma} c_{k\sigma}$, which only give a background counting and will not be considered here. Defining $A_q = \sum_\sigma A_{q\sigma}$, the equations of motion are given by

$$\dot{A}_q = i[\bar{\omega} + \omega_1(t)]A_q + i\sum_{k\sigma} V_k A_{kq\sigma}, \quad (15)$$

where

$$\bar{\omega} = 2(E_q - E_0) - U\langle n\rangle,$$

$$\bar{\omega}_1(t) = -U(n - \langle n\rangle) = -Uu,$$

$$n = n_\uparrow + n_\downarrow,$$

and E_0 is the energy of the localized electron state.

Except for the last term in (15), we would have the same situation as before.

A complete solution of the problem is in this case not possible, and the autocorrelation function of the fluctuating variable u cannot be exactly evaluated. The memory function corresponding to Eq. (7) can be approximately evaluated by a Green's-function technique. Although the details of the behavior of $K(t)$ will depend on the approximation scheme used, a second-order expansion of $M(t)$ shows that at high temperatures the correlations die exponentially with a width $\frac{1}{2}\Gamma^{-1}$ and that the fluctuations persist at low temperatures with an oscillatory character, as before.

Equation (15) contains the effect of the fluctuations in the form analyzed by Kubo, through the term $\omega_1(t)$, and the extra term that comes from the hybridization. It can be shown that this extra term gives rise to the "natural" linewidth for this case.[15]

The relevant parameters are now $\tau_c \cong \frac{1}{2}\Gamma^{-1}$ and $\Delta^2 = U^2(\langle n^2\rangle - \langle n\rangle^2)$. The product $\Delta\tau_c = (U/2\Gamma) \times (\langle n^2\rangle - \langle n\rangle^2)$ for $U \sim 10^4$ K is now much greater than one, for an intermediate valence case. One expects thus to observe two lines at a distance U apart, and with a width never smaller than the "natural" width Γ.

Starting from an exactly solvable model Hamiltonian we have thus clarified which are the implications and which the limitations of the concept of temporal fluctuations in understanding the measurements on intermediate valence systems.

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[1]L. L. Hirst, J. Phys. Chem. Solids 35, 1285 (1974).
[2]B. Alascio, Solid State Commun. 16, 717 (1975).
[3]C. E. T. Goncalves da Silva and L. M. Falicov, Phys. Rev. B 13, 3948 (1976).
[4]D. Wohlleben and B. Coles, *Magnetism*, edited by H. Suhl (Academic, New York (1973), Vol. V; C. M. Varma, Rev. Mod. Phys. 48, 219 (1976).
[5]M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanan, and L. D. Longinotti, Phys. Rev. Lett. 32, 885 (1974).
[6]E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. 30, 1053 (1973).
[7]See any textbook on quantum chemistry.
[8]G. W. Ford, M. Kac, and P. Mazur, J. Math. Phys. 6, 504 (1965); C. George, Physica (Utr.) 26, 453 (1960); A. López, Z. Phys. 192, 63 (1966).
[9]D. R. Hamann, Phys. Rev. B 2, 1376 (1970). P. W. Anderson, Phys. Rev. 124, 41 (1961).
[10]K. S. Singwi, *Atomic Motions in Liquid and Neutron*

Scattering, in Theory of Condensed Matter (IAEA, Vienna, 1968).
[11]W. Götze (unpublished lecture notes, Helsinski, 1973).
[12]L. L. Hirst, Phys. Rev. B 15, 1 (1977).
[13]C. Balseiro and B. Alascio, Solid State Commun. (to be published).
[14]R. Kubo, *A Stochastic Theory of Line Shape and Relaxation in Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, Edinburgh and London, 1961).
[15]M. E. Foglio and B. Alascio (unpublished).