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THEORY OF SOFT X-RAY SPECTRA: NONEQUILIBRIUM DYNAMICS OF MANY ELECTRONS[1]

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Foundations of a many-body theory for the edge behavior of soft x-ray spectra of simple metals are reviewed. A way is shown how the one-electron absorption (emission) amplitude is generalized within a model of Mahan, Nozières and De Dominicis to a many-body Kubo formula with field-theoretic Green functions. Two non-perturbative methods of evaluation of a transient conduction electron – core hole susceptibility in the asymptotic limit of long times are discussed and compared: Nozières and De Dominicis solution and a solution based on the Wiener-Hopf method. It is argued that the exact solution undergoes a nonanalytic crossover from a short-time (Fredholm) to a long-time (Wiener-Hopf) regime not fully traced in the former method.

1. Introduction

It has been known for a long time that a jump of the distribution of conduction electrons at the Fermi surface must be responsible for the edge anomalies in soft x-ray absorption (emission) spectra of metals, XAS (XES). However, the actual role of many-body effects due to the instantaneous generation of a core hole and the final-state interaction for the threshold behavior of x-ray spectra had not been recognized until 1967. Anderson [1] disclosed that non-interacting electrons when scattered from a suddenly changed local potential relax to a final state orthogonal to the initial one. This effect is now known as "orthogonality catastrophe". Mahan [2] was the first to show that the final-state interaction due to the core-hole potential leads to logarithmic divergencies in perturbation theory causing a power-law decay of x-ray spectra at the threshold. Only after these theoretical predictions precise measurements using a synchrotron orbital radiation (SOR) confirmed the edge singularities experimentally [3]. Nowadays a many-body origin of the edge anomalies in soft x-ray spectra is widely accepted.

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The essence of the edge anomalies in x-ray spectra lies in peculiarities of the interaction of many itinerant electrons with a localized core hole. In pure metals it is sufficient to take into account only one core particle, since the absorption or emission of a light quantum is a linear process described by the Fermi golden rule. To describe the absorption of light we distinguish the initial and final states. We suppose that N conduction electrons and a core electron are for $t < 0$ in the ground state of an initial Hamiltonian

$$\widehat{H}_i = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a^\dagger_{\mathbf{k}} \, a_{\mathbf{k}} \; + E_c b^\dagger b \; , \tag{1}$$

where we neglected the spin of the electrons being irrelevant for the essence of the problem. The energy E_c is the ionization energy of the core electron and $\epsilon_{\mathbf{k}}$ is the dispersion relation of the band electrons. After the absorption, $t > 0$, the core electron is excited into the band and the dynamics of now $(N + 1)$ conduction electrons is governed by a new Hamiltonian with a core-hole potential

$$\widehat{H}_f = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a^\dagger_{\mathbf{k}} \, a_{\mathbf{k}} \; - \frac{1}{N} \sum_{\mathbf{k},\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}} \, a_{\mathbf{k}'} \; . \tag{2}$$

In the case of emission $\widehat{H}_i$ and $\widehat{H}_f$ interchange their roles. Since there are N ($\sim 10^{23}$) conduction electrons and only one core electron, we could assume that the excitation of the core particle does not alter the macroscopic ground state of the N band electrons. We could apply quantum mechanical, time-dependent perturbation theory to evaluate the transition amplitude for the absorption of light. The Fermi golden rule leads to

$$I_i(\omega) = \frac{2\pi}{\hbar} \int \frac{d^3k}{(2\pi)^3} |w_i(\mathbf{k})|^2 (1 - n(\epsilon_{\mathbf{k}})) \delta(\hbar\omega + E_c - \epsilon_{\mathbf{k}}) \quad , \tag{3}$$

where ω is the frequency of the incoming light, $n(\epsilon)$ is the electron density and

$$w_i(\mathbf{k}) = \int d^3r \Psi^*_{\mathbf{k}} \, (\mathbf{r}) \, \hat{\epsilon} \, . \mathbf{p} \Phi_i(\mathbf{r}) \tag{4}$$

is the dipole moment with $\Psi_{\mathbf{k}} \, (\mathbf{r})$ being the Bloch wave and $\Phi_i(\mathbf{r})$ the Wannier function of the localized core electron; $\hat{\epsilon}$ is the polarization vector of the incoming light.

Formulas (2)-(3) have served as a basis for band calculations of x-ray spectra [4]. Possible singularities can arise in such a theory only due to singularities in the density of states, i.e. due to the distribution of the conduction electrons. The one-electron theory cannot hence cope with qualitatively different threshold behavior for different inner states such as K and L spectral lines in alkali metals. The individual core states must contribute nonperturbatively to the process of absorption and emission of light and the quantum mechanical description must be replaced by a many-body theory.

In this paper we discuss the foundations of the simplest many-body theory for the edge anomalies in x-ray spectra due to Mahan, Nozières and De Dominicis (MND) and concentrate on two different nonperturbative ways to obtain an asymptotic solution at the edge. The first one is a solution in the time representation due to Nozières and De Dominicis [5] and the second one is a solution in the frequency representation based on the Wiener-Hopf method [6]. The assumptions and results of these solutions are compared and discussed. We show that the latter approach has a broader range of applicability and enables to track down the crossover from short to long time asymptotics and to put down general, mathematical criteria for the existence of the edge singularity in the Green function of the core hole.

2. Many-body theory for x-ray spectra

It is inevitable to abandon the quantum mechanical, one-particle description to win a more realistic picture of the physical mechanism of absorption and emission of light in metals. We must treat the effects of the transient core hole *nonperturbatively*. The first effect due to the excitation of a core electron is the instantaneous generation of a local core-hole potential. It causes that the ground state of the conduction electrons evolves in time towards a state orthogonal to the initial one (orthogonality catastrophe). A time-dependent potential

$$\widehat{V} = -\theta(t) \exp\{-\eta t\} \frac{1}{N} \sum_{\mathbf{k},\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}} \, a_{\mathbf{k}'} \; , \tag{5}$$

where η is an infinitesimal damping factor, influences the time evolution of the initial state and the new state at time t can be represented as ($\hbar = 1$)

$$|\Psi_N(t)> = \widehat{S}(t,0)|FS(N)> \equiv e^{-i\widehat{H}_i t} e^{i\widehat{H}_f t} |FS(N)> =$$
$$T\left[\exp\left\{-i\int_0^t dt' \widehat{V}^I_\eta(t')\right\}\right] |FS(N)>, \tag{6}$$

where $\widehat{V}^I_\eta(t)$ is the potential in the interaction picture with the unperturbed Hamiltonian $\widehat{H}_i$ and $|FS(N)>$ is a Fermi sea of N free electrons. The overlap amplitude between the final and initial state is

$$A_N(t) = < \Psi_N(t)|FS(N)> = < FS(N)|\widehat{S}(t,-\infty)|FS(N)> \; . \tag{7}$$

In the long-time limit this overlap goes to zero, however, not exponentially as used to be the case in decay processes of excited states in nuclear physics, but rather with some power of t. For a contact potential ($V_{\mathbf{k}\mathbf{k}'} = V$) we obtain for $N \to \infty$ [1],[7],[8]:

$$A_N(\infty) \sim C N^{-\sigma} \quad , \quad \sigma = \frac{\delta^2}{2\pi^2} \quad , \quad \delta \equiv Im \ln(1 + VG(i\eta)) \; . \tag{8}$$

(8) is an important result, since it tells us that the adiabatic theorem is not valid for this problem. If the adiabatic theorem were valid, then $|A_N(\infty)|$ should approach 1 in the thermodynamic limit.

We have two distinct Hamiltonians $\widehat{H}_i$ and $\widehat{H}_f$ controlling the dynamics of the conduction electrons for $t < 0$ and $t > 0$, respectively. The problem we are facing now is

to decide which Hamiltonian should be used in the actual calculations of the absorption and emission amplitudes. Although the electron dipole interaction with light is linear, i.e. perturbative, the creation of a transient electron-hole pair nonperturbatively changes the evolution operator of the conduction electrons. The initial state is no longer an eigenstate of the final Hamiltonian. To evaluate the absorption amplitude we have to generalize the golden rule so that the initial state is the ground state of $\widehat{H}_i$ and the final states are eigenstates of $\widehat{H}_f$. Then a many-body generalization of (3) is [9]

$$I(\omega) = 2Re \sum_f \int_0^\infty dt e^{-i(E_f - E_c - \omega_+)t} | < \Psi_f(N+1) | \widehat{W} | \Psi_i(N) > |^2 \quad , \tag{9}$$

where $|\Psi_i(N)>= b^\dagger |FS(N)>$, $\widehat{W} = \sum_{\mathbf{k}} (w(\mathbf{k}) a^\dagger_{\mathbf{k}} b + c.c.)$ and E_f is an eigenenergy of the Hamiltonian $\widehat{H}_f$ with an eigenstate $|\Psi_f(N+1)>$. It is not evident how are the matrix elements in (9) related to many-body Green functions. Only linear response theory and Kubo formula provide such an information. They are, however, not directly applicable here because of a nonperturbative, abrupt change in the dynamics of the electron system caused by the absorption (emission) of light. It was Nozières and co-workers [10], [5] who proposed a new many-body Hamiltonian containing appropriately $\widehat{H}_i$ and $\widehat{H}_f$, now called Mahan-Nozières-De Dominicis (MND) Hamiltonian

$$\widehat{H}_{MND} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a^\dagger_{\mathbf{k}} \, a_{\mathbf{k}} \, + E_c b^\dagger b - \frac{1}{N} \sum_{\mathbf{k},\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}} \, a_{\mathbf{k}'} b b^\dagger \, . \tag{10}$$

This Hamiltonian reduces to $\widehat{H}_i$ if there is no core hole and to $\widehat{H}_f$ in states with a core hole. The advantage of Hamiltonian (10) is that it allows to rewrite the absorption (emission) amplitude using the standard field-theoretic Green functions. Since the initial state may not eventually be the ground state of $\widehat{H}_{MND}$, we generalize $I(\omega)$ in (9) to finite temperatures as

$$I_\beta(\omega) = \frac{2\pi}{\mathcal{Z}} \sum_{n,m} e^{-\beta E_m} | < \Psi_m | \widehat{W} | \Psi_n > |^2 \delta(E_n - E_m - \omega) \, , \tag{11}$$

where E_n are eigenenergies of $\widehat{H}_{MND}$ with eigenvectors $|\Psi_n>$. It is a standard way to derive from (11) a Kubo-like representation using field-theoretic Green functions [11]

$$I_\beta(\omega) = \frac{1}{\mathcal{Z}} 2Re \int_0^\infty dt \, e^{i\omega_+ t} Tr \left[e^{-\beta \widehat{H}_{MND}} \widehat{W}(t) \widehat{W}(0) \right] \, , \tag{12}$$

where $\widehat{W}(t) = e^{it\widehat{H}_{MND}} \widehat{W} e^{-it\widehat{H}_{MND}}$. There is no difference in the MND description between the initial and final states as well as between the emission and absorption. There is hence no abrupt change in the Hamiltonian and the adiabatic theorem and linear response theory may be regained. Switching from the Heisenberg to the interaction picture we obtain a final formula for the absorption amplitude

$$I_\beta(\omega) = 2Re \frac{1}{N} \sum_{\mathbf{k},\mathbf{k}'} w(\mathbf{k}) w(\mathbf{k}')^* \int_0^\infty dt e^{i\omega_+ t} < T \left[b^\dagger(t) a_{\mathbf{k}'}(t) a^\dagger_{\mathbf{k}}(0) b(0) \right] >_\beta \, , \tag{13}$$

where $< ... >_\beta$ denotes thermal averaging with $\beta = k_B T$ and $\widehat{H}_{MND}$. In the emission case we simply change the integration interval to $(-\infty, 0)$ and replace $\omega + i\eta$ with $\omega - i\eta$.

3. Solution of the MND problem due to Nozières and De Dominicis

The MND problem now consists in finding an explicit expression for the absorption (emission) amplitude (13). Let us remind that the MND problem can be approached without referring to the MND Hamiltonian (10). The spectral function $I(\omega)$ is then calculated directly from (11) using the state vectors of the conduction electrons (Slater determinants) and Hamiltonians $\widehat{H}_i$ and $\widehat{H}_f$. Such approaches to the MND problem are reviewed in [9].

In our paper we concentrate exclusively on nonperturbative methods for solving the MND problem starting with (13), in particular on the effective one-body schemes aiming at the exact asymptotic solution in the vicinity of the x-ray edge. It means either to evaluate a conduction electron-core hole susceptibility

$$\chi_{\mathbf{k},\mathbf{k}'}(t) = < T \left[b^\dagger(t) a_{\mathbf{k}'}(t) a^\dagger_{\mathbf{k}}(0) b(0) \right] >_\beta \tag{14}$$

in the long-time limit, or to derive the asymptotics of $I(\omega)$ in the limit $|\omega - \omega_T| \to 0$, where ω_T is a threshold frequency.

A manageable way to reach the asymptotic solution proved to be the time representation and the evaluation of $\chi_{\mathbf{k},\mathbf{k}'}(t)$ in the long-time limit. Such an approach to the MND problem was launched by Nozières and De Dominicis (ND) [5]. A similar in spirit, but different in the method of solution is the Wiener-Hopf trick introduced to the MND problem in [7],[8],[6]. In this and the following sections we briefly analyze and compare these two methods and their results.

The only hope to solve a many-body problem nonperturbatively is to transform it to an effective one-body problem and to solve the resultant Dyson equations. ND succeeded in the former step completely and in the latter one only conditionally. They made use of an important observation that the dynamics of the core particles separates from that of the conduction electrons. It is because of no energy transfer between the local and mobile degrees of freedom in the many-body perturbation theory for the MND Hamiltonian [12]. We can hence decouple the two Green functions of the conduction and the core electrons contributing to the susceptibility χ, i.e.

$$\chi_{\mathbf{k},\mathbf{k}'}(t) = < T \left[b^\dagger(t) b(0) \right] >_\beta \left\{ < T \left[a_{\mathbf{k}'}(t) a^\dagger_{\mathbf{k}}(0) \right] >_\beta \right\}_t \, . \tag{15}$$

However, we paid a price for this decoupling. We had to introduce a new symbol $\{...\}_t$ to the thermal averaging for the conduction electrons. This symbol says that we have to use a *nonequilibrium*, transient Green function evaluated with a time-dependent Hamiltonian. It is the MND Hamiltonian (10), where the core-hole potential is acting only on the time interval $[0, t]$, i.e. $V_{\mathbf{k},\mathbf{k}'} \to V_{\mathbf{k},\mathbf{k}'} [\theta(t') - \theta(t'-t)]$. The core-hole Green function in (15) consists of all closed loops of conduction electrons in the many-body perturbation expansion to the susceptibility χ. It represents a "vacuum" amplitude

and reflects a reaction of the conduction electrons to the transient core-hole potential V. It is nothing else than the amplitude $A(t)$ for the orthogonality catastrophe. The transient Green function of the band electrons in (15) then comprises connected "potential-scattering" contributions to χ free of loops of conduction electrons. It is hence effectively a one-body Green function of noninteracting electrons scattered by a deep hole. However, this function must be evaluated out of equilibrium where neither momentum nor energy is conserved. The only many-body effect in the Green function of the condution electrons due to a core particle is then the dynamical cutoff $\{...\}_t$.

To evaluate the susceptibility $\chi_{\mathbf{k},\mathbf{k}'}(t)$ now means to construct and solve Dyson equations for the core-hole and the transient, conduction electron Green functions separately. Since the Green function of a core hole is a sum of all closed loops, it can be represented as an exponential

$$\mathcal{G}^h(t) = i < T\left[b^\dagger(t)b(0)\right] >= ie^{C(-t)^*} , \tag{16}$$

where $C(t)$ is a sum of connected closed loops. To derive a Dyson equation for a corresponding Green function, we must open one internal propagator by cutting a line in $C(t)$. It can be done by a variation with respect to the interaction strength. The resultant Dyson equation for a contact potential has a form [5],[6]:

$$\Gamma_t(t_1,t_2;\lambda) = G(t_1-t_2) - \lambda\int_0^t dt' G(t_1-t')\Gamma_t(t',t_2;\lambda) , \tag{17}$$

where at $T=0$, $G(t) = N^{-1}\sum_{\mathbf{k}} G(t,\mathbf{k}) = N^{-1}\sum_{\mathbf{k}}(2\pi)^{-1}\int d\omega e^{-i\omega t}\times\left[\omega-\epsilon_{\mathbf{k}}-i\eta sgn\omega\right]^{-1}$ is the diagonal (local) element of the Green function of the conduction electrons, λ is an intermediate interaction ($\lambda\in[0,V]$). The function $C(t)$ is then constructed from Γ_t as

$$C(t) = \ln i\mathcal{G}_0(t) - \int_0^t dt'\int_0^V d\lambda\Gamma_t(t',t'_+;\lambda) . \tag{18}$$

The Dyson equation for the nonequilibrium Green function of the conduction electrons has a structure analogous to (17). We use a representation

$$-i\left\{< T\left[a_{\mathbf{k}'}(t)a^\dagger_{\mathbf{k}}(0)\right] >_\beta\right\}_t = G(t,\mathbf{k})\delta(\mathbf{k}-\mathbf{k}') - V\int_0^t dt' G(t-t',\mathbf{k}')\Gamma_t(t',0;\mathbf{k}) , \tag{19}$$

where the function $\Gamma_t(t_1,t_2;\mathbf{k})$ fulfills an equation

$$\Gamma_t(t_1,t_2;\mathbf{k}) = G(t_1-t_2,\mathbf{k}) - V\int_0^t dt' G(t_1-t')\Gamma_t(t',t_2;\mathbf{k}) . \tag{20}$$

Equations (17) and (20) are the desired Dyson equations to be solved. The kernel of these integral equations is the diagonal element of the Green function of noninteracting conduction electrons and is explicitly known contrary to other many-body problems. It is due to a separation of the dynamics of the conduction and the core electrons in the MND problem. The only evidence of many-body effects here are the closed loops in the core-hole Green function and the transient form of the band-electron propagator.

ND succeeded only partly in solving Dyson equations (17) and (20). There is no substantial problem in solving these equations on finite intervals, i.e. $t<\infty$. These equations are Fredholm integral equations whenever the local propagator $G(t)$ is a bounded function [13]. A solution can be obtained using Fredholm determinants (e.g. by time discretization). There are no singularities in the solution for finite times, at least at weak coupling where perturbation theory applies. Problems arise only if we want to approach the long-time limit $t\to\infty$.Then the Hilbert-Schmidt norm of the integral kernel

$$\| G \|^2_{2,t} = \int_0^t dt_1 dt_2 |G(t_1-t_2)|^2 = \frac{t}{2}\int_{-t}^t dt' |G(t')|^2$$

diverges at least linearly with t. Eqs. (17) and (20) are then no longer of Fredholm type. There is no simple tool to solve these equations in the long-time limit. Note that the long-time limit is troublesome at any temperature, although the edge singularity is expected to exist only at zero temperature.

ND concentrated only on the case $T=0$, where the existence of the edge singularity is known from perturbation theory to be a consequence of a jump of $ImG(\omega)$ at the Fermi level. From this fact they correctly deduced that only the long-time asymptotics of $G(t)$ matters. They proposed an asymptotic transformation of an infinite interval so that the integral $\int_0^t dt'|G(t')|$ develops the same logarithmic singularity on a fixed, finite interval. They replaced the actual integral kernel $G(t)$ on an infinite interval by an asymptotic expression

$$G^a(t) = -i\nu_0\left[P\frac{1}{t} + A\delta(t)\right] \tag{21}$$

acting on a finite interval. There ν_0 is the DOS at the Fermi energy and A is a global weight for the short-time contribution to $G(t)$. Integral equations (17) and (20) with the asymptotic kernel $G^a(t)$ become singular and are exactly solvable using the Riemann-Hilbert boundary problem [13]. A solution for Γ_t matching the noninteracting case ($V\to 0$) then is

$$\Gamma_t(t_1,t_2;\lambda) = G^a(t_1-t_2)\left[\frac{t_1(t-t_2)}{t_2(t-t_1)}\right]^{\delta/\pi} , \tag{22}$$

where $\delta = Im\ln(1+\lambda\tilde{G}(i\eta))$ is the phase shift due to the core-hole potential at the Fermi energy. Analogously for the function $\Gamma_t(t_1,t_2;\mathbf{k})$, where only we have do decompose the Green function into partial waves. From solution (22) we then obtain the full asymptotics of the core-hole Green function

$$|< T\left[b^\dagger(t)b(0)\right] >| \sim t^{-\sum_l (2l+1)\delta_l^2/\pi^2} \tag{23}$$

and of the nonequilibrium Green function of the conduction electrons

$$|\left\{< T\left[a_{\mathbf{k}'}(t)a^\dagger_{\mathbf{k}}(0)\right] >\right\}_t| \sim t^{-1+2\delta_l/\pi} \tag{24}$$

with δ_l being the phase shift of the $l-$th partial wave due to the potential V. The resultant asymptotics of the susceptibility $\chi_l(t)$ then is

$$|\chi_l(t)| \sim \frac{1}{t}(\xi t)^{2\delta_l/\pi - \sum_{l'}(2l'+1)\delta_{l'}^2/\pi^2} \quad \text{or} \quad |\chi_l(\Delta\omega)| \sim \left(\frac{\xi}{\Delta\omega}\right)^{2\delta_l/\pi - \sum_{l'}(2l'+1)\delta_{l'}^2/\pi^2} \tag{25}$$

with $\Delta\omega = |\omega - \omega_T|$. This is the famous ND result for the threshold behavior of soft x-ray spectra. It is important to note that the critical exponent in (25) when expanded in the interaction strength V coincides with the result of perturbation theory in leading order.

4. Solution of the MND problem with the Wiener-Hopf method

The ND solution can be accepted from the mathematical point of view only conditionally, since it is based on an asymptotic representation (21). This representation, though intuitively reasonable, has no rigorous foundation. It is supported by physical arguments and by other approaches [9] confirming the result (25). There is, however, no proof that (25) is exact. A natural question arises if there is another approach avoiding the asymptotic transformation (21) and producing the exact long-time asymptotics of the susceptibility $\chi_{\mathbf{k},\mathbf{k}'}(t)$ directly. An answer to this question offers a method of Wiener and Hopf developed in the thirties by solving classical radiation processes [14]. It appears that the MND problem is another physical situation where the elegant method of Wiener and Hopf finds application [6].

If we put the upper limit of integration in (17) $t = \infty$ we obtain

$$\Gamma_\infty(t_1,t_2;\lambda) = G(t_1-t_2) - \lambda\int_0^\infty dt' G(t_1-t')\Gamma_\infty(t',t_2;\lambda) \quad . \tag{26}$$

This is a Wiener-Hopf integral equation supposed the integral kernel $G(t)$ is a square integrable function on the interval $(-\infty,\infty)$ [15]. If this is the case we can find an exact solution to (26) without further assumptions or restrictions on the long-time asymptotics of the function $G(t)$. Since $G(t) \in L_2(-\infty,\infty)$, it must, however, be bounded in the long-time limit as

$$t \to \infty \qquad |G(t)| < Ct^{-\alpha} \quad , \quad \alpha > \frac{1}{2} \quad . \tag{27}$$

No singularity of $G(t)$ at finite times is assumed.

To solve (26) with the Wiener-Hopf trick we apply a Fourier transform on (26) in both time variables

$$\widetilde{\Gamma}_\infty(\omega_1,\omega_2;\lambda) = 2\pi\delta(\omega_1-\omega_2)\widetilde{G}(\omega_1) - \lambda\widetilde{G}(\omega_1)\widetilde{\Gamma}_+(\omega_1,\omega_2;\lambda) \quad , \tag{28}$$

where $\Gamma_+(t_1,t_2;\lambda) = \theta(t_1)\,\Gamma_\infty(t_1,t_2;\lambda)$ is a projection of Γ_∞ onto the positive half-axis, i.e. $\Gamma_+ \in L_2^+ := L_2(0,\infty)$ in the first variable. To resolve (28) we use the following two

properties [15]: a) $L_2(-\infty,\infty) = L_2^- \oplus L_2^+ := L_2(-\infty,0)\oplus L_2(0,\infty)$, b) if $f,g \in L_2^+(L_2^-)$ then $(f*g)(t) = \int dt' f(t-t')g(t') \in L_2^+(L_2^-)$; and a Wiener-Hopf representation

$$1+\lambda\widetilde{G}(\omega) = \frac{E^+(\omega)}{E^-(\omega)} \quad , \quad E^\pm(\omega) = \exp\left\{\frac{1}{2\pi i}\int_{-\infty}^\infty \frac{e^{\mp i x\eta}dx}{x-\omega\mp i\eta}\ln(1+\lambda\widetilde{G}(x+i\eta sgn x))\right\} \tag{29}$$

where $E^\pm$ are analytic functions on upper (lower) complex half planes, i.e. belong to $L_2^\pm$. We are now in a position to separate (orthogonal) functions from $L_2^\pm$ and to obtain an explicit form for $\widetilde{\Gamma}_+(\omega_1,\omega_2;\lambda)$:

$$\widetilde{\Gamma}_+(\omega_1,\omega_2;\lambda) = \frac{1}{i(\omega_2-\omega_1-i\eta)}\frac{\widetilde{G}(\omega_2-i\eta sgn\omega_2)}{1+\lambda\widetilde{G}(\omega_2-i\eta sgn\omega_2)}\frac{E^+(\omega_2)}{E^+(\omega_1)} \tag{30}$$

(30) is an exact solution to (28). To complete the solution for the Green function of the core electrons we insert (30) into (18) and obtain an integral representation for the exponent

$$C(t) = C_0(t) - it\int_0^V d\lambda\int_{-\infty}^\infty \frac{d\omega d\omega'}{4\pi^2}\frac{1-e^{-i(\omega-\omega')t}}{(\omega-\omega'+i\eta)^2}\frac{\widetilde{G}(\omega'-i\eta sgn\omega')}{1+\lambda\widetilde{G}(\omega'-i\eta sgn\omega')}\frac{E^+(\omega')}{E^+(\omega)} \tag{31}$$

The integral in (31) diverges linearly with $t\to\infty$. We hence have to use a regularization. The best way to do it is to solve (26) in leading order of $1/t$ for large but finite time intervals $(0,t)$. The leading contribution to the solution is again provided by the Wiener-Hopf method as will be discussed in the next section. On a finite interval we are able to control the divergent terms when limiting $t\to\infty$ and obtain the following regular expression [6]

$$C(t) = C_0(t) - it\int_0^V \frac{d\lambda}{2\pi i}\left\{\int_{-\infty}^\infty d\omega\frac{e^{i\omega\eta}\widetilde{G}(\omega-i\eta sgn\omega)}{1+\lambda\widetilde{G}(\omega-i\eta sgn\omega)} + \frac{1}{t}P\int_{-\infty}^\infty\frac{d\omega}{\omega^2}I_+(\omega)\right\} \quad , \tag{32}$$

where $I_+(\omega) = \theta(\omega)\,[I(\omega)-I(0^+)] + \theta(-\omega)\,[I(\omega)-I(0^-)]$ and

$$I(\omega) = \frac{1}{\pi}\int_{-\infty}^\infty d\omega' e^{i\omega'\eta}$$

$$\times\left[\frac{E^+(\omega')}{E^+(\omega+\omega')}\frac{\widetilde{G}(\omega'-i\eta sgn\omega')}{1+\lambda\widetilde{G}(\omega'-i\eta sgn\omega')} + \frac{E^+(\omega+\omega')}{E^+(\omega')}\frac{\widetilde{G}(\omega+\omega'-i\eta sgn(\omega+\omega'))}{1+\lambda\widetilde{G}(\omega+\omega'-i\eta sgn(\omega+\omega'))}\right] . \tag{33}$$

Formulas (31)-(33) are valid asymptotically for $t\to\infty$ at any temperature and for arbitrary function $G(t)\in L_2(-\infty,\infty)$. The second integral in (32) becomes logarithmically divergent at $T=0$ and can be evaluated explicitly. The asymptotic expression for $C(t)$ then is

$$C(t) = -it\left(E_c + \frac{1}{\pi}\int_{-\infty}^0 d\omega Im\ln(1+V\widetilde{G}_c(\omega)) + \frac{\delta^2}{2\pi^2}\frac{1}{it}\ln\xi|t|\right) \tag{34}$$

with a regularization factor ξ. From (34) we can obtain the long-time asymptotics of the core-hole Green function at $T = 0$:

$$| < T\left[b^\dagger(t)b(0)\right] > | \sim t^{-\sum_l (2l+1)\delta_l^2/2\pi^2} \tag{35}$$

The critical exponent is then 1/2 of the ND result (23).

An analogous Wiener-Hopf integral equation to (20) can be constructed also for the transient Green function of the conduction electrons. It is, however, not so easy to extract from it the dominant asymptotic behavior of the function $\left\{< T\left[a_{\mathbf{k}'}(t)a^\dagger_{\mathbf{k}}(0)\right] >\right\}$ at long times. The result seems to be sensitive to an inevitable finite-time regularization. A deeper analysis is necessary to obtain the definite long-time asymptotics of the full susceptibility $\chi_{\mathbf{k},\mathbf{k}'}(t)$ within the Wiener-Hopf method.

5. Discussion

After the asymptotic result of Nozières and De Dominicis for the threshold behavior of x-ray spectra had been confirmed by other approaches, the MND problem seemed to be solved and understood completely. However, the solution based on the Wiener-Hopf method erodes our certainty about the *rigorous* long-time asymptotics of the relevant Green functions. A few questions arise from comparison of the ND result with that from the Wiener-Hopf method. Which is the exact edge exponent? What are the necessary and sufficient conditions for the existence of the edge singularity? What is actually going on at long but finite times?

To answer these questions we must compare the assumptions of the two asymptotic methods. The Wiener-Hopf solution is strictly exact only at $t = \infty$. This alone is insufficient for the dominant asymptotics at long times. To obtain the exact asymptotic solution at long times, it is necessary to solve (17) on large but finite time intervals $[0, t]$. The Wiener-Hopf method is not, however, applicable on finite intervals. To use the Fourier representation we have to extend the functions from the interval $[-t, t)$ periodically onto $(-\infty, \infty)$. The spaces $L_2^\pm(-t, t)$ are not closed with respect to convolution for such periodic functions. E.g. for $f, g \in L_2^+ = L_2[0, t)$ we have

$$\begin{aligned}(f * g)(t_1) = \int_{-t}^{t} dt' f(t_1 - t')g(t') = \theta(t_1)\int_0^{t_1} dt' f(t_1 - t')g(t') \\ +\theta(-t_1)\int_0^{-t_1} dt' f(t - t')g(t' + t + t_1)\end{aligned} \tag{36}$$

and the convolution does not vanish for negative times t_1. Property (36) violates one of the necessary conditions, (b), for the application of the Wiener-Hopf trick. It is, however, important that the second term in (36) is proportional to $Af(t) + Bg(t)$ in the asymptotic limit $t \to \infty$. Since the functions f and g are square integrable, they must fall off at long times according to (27). We can expand around the solution at $t = \infty$ with a small parameter proportional to $t^{-\alpha}$ and the Wiener-Hopf solution can be applied and remains valid in leading order of t^{-1} also on large, finite intervals. The critical exponent at the edge singularity (35) calculated within the Wiener-Hopf method must be exact! The reason why the ND solution misses the exact exponent by a factor of 2 is the following. The asymptotic substitution (21) for the actual local propagator of the conduction electrons $G(t)$ can be understood as a "compactification" of an infinite interval. Thereby the infrared divergency due to the length of the integration interval is transformed to an ultraviolet divergency of the new asymptotic propagator acting on a finite interval. Long-time distances are transformed to short distances (around the interval edges) and vice versa. There is only one singular region at long times ($t \to \infty$) in the original equation with no singularity at the lower edge ($t = 0$). However, in the ND solution both the interval limits of the transformed equation are singular. Each end of the interval contributes to the edge exponent with the Wiener-Hopf result, hence the difference by a factor of 2. The only possible interpretation of the ND result is that, because of the symmetric treatment of the interval ends, the asymptotic transformation (21) corresponds to a compactification of the full infinite interval $(-\infty, \infty)$. The ND transformation is inappropriate for half-infinite intervals with asymmetric end points such as $(0, \infty)$.

The Wiener-Hopf method also proves more useful to decide under which circumstances the edge singularity arises. The ND approach can only be used if the local propagator of the conduction electrons has the long-time asymptotics t^{-1}. This need not always be the case [16]. Within the Wiener-Hopf method we are able to put down precise mathematical conditions for the existence of the edge singularity. The Wiener-Hopf technique is applicable to square integrable integral kernels $G(t)$ ($G \in L_2(-\infty, \infty)$). If there is no singularity at finite times then $L_1(-\infty, \infty) \subset L_2(-\infty, \infty)$. The edge singularity appears *if and only if* $G \in L_2(-\infty, \infty) \cap G \notin L_1(-\infty, \infty)$. Since only the long-time asymptotics matters, the edge singularity exists for the propagators $G(t)$ with the following asymptotics

$$t \to \infty \quad , \quad G(t) \sim t^{-\alpha} \quad , \quad \frac{1}{2} < \alpha \leq 1 \quad . \tag{37}$$

The form of the singularity remains the same, i.e. (34). However for the asymptotics other than the usual one, i.e. $\alpha = 1$, the phase shift is either saturated ($\delta = \pi/2$) or has effectively infinite interaction strength.

The solution of the MND problem on a finite but large time interval has two different regimes. The first one is perturbative regime governed by a Fredholm solution and the other one is a nonperturbative regime where the Wiener-Hopf method is applicable. The Fredholm method of solving integral equations [13] is applicable in situations where the Neumann perturbation series in the integral kernel converges. This imposes a bound onto the interaction strength V and the integral kernel $G(t)$. The latter must be a Hilbert-Schmidt operator fulfilling an inequality

$$V^2 \int_0^t dt_1 \int_0^t dt_2 \, |G(t_1 - t_2)|^2 = V^2 \frac{t}{2} \int_{-t}^{t} dt' \, |G(t')|^2 = V^2 t \|G\|_{2,t}^2 < 1 \quad . \tag{38}$$

It essentially tells us that $(V/w)^2 wt < C$, where w is the band width of the conduction electrons and C is a dimensionless constant. In this regime perturbation theory and the ND asymptotics are appropriate. However, if we approach the real long-time limit, then $(V/w)^2 wt \gg 1$, perturbation expansion in the interaction strength breaks down.

A crossover to the Wiener-Hopf nonperturbative solution must occur. This crossover is present at any temperature independently of the edge singularity. It is an intrinsic feature of the Wiener-Hopf solution that expanding in the interaction strength and then taking the limit $t \to \infty$ does not commute with taking the long-time limit first and then expanding in the interaction strength [?].

In summary, we discussed foundations of a many-body theory for the edge behavior of soft x-ray spectra of metals. We reviewed the way how the one-electron, golden-rule absorption (emission) amplitude can be extended within the MND model to a many-body Kubo formula using field-theoretic Green functions. We then concentrated on two effective one-body formulations of the MND problem producing a nonperturbative asymtotic solution of the transient conduction electron-core hole susceptibility at long times. The former method due to Nozières and De Dominicis, using an intuitive asymptotic transformation, was shown to lead to a different long-time limit fromthe mathematically exact solution based on the Wiener-Hopf method. Not only misses the ND solution the critical edge exponent by a factor of 2, it also seems to be less versatile in applications than the latter approach. Particularly at finite temperatures and in situations with more intricate long-time asymptotics of the local propagator of the conduction electrons. The presented analysis and comparison of the two solutions showed that the way in which a transient excitation in the MND model approaches equilibrium is a delicate, nontrivial process explicitly demonstrating breakdown of perturbation theory and the existence of a nonanalytic crossover from a short-time to a long-time regime. Ignoring this fact may lead to an incorrect continuation of short-time (perturbative) results to the long-time critical region.

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