New approach to the x-ray-absorption problem

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We present a simple numerically stable procedure for calculating frequency-dependent response functions for a fermion system in the presence of localized perturbations over all frequency scales. In the case of the x-ray singularity problem, the asymptotic result of Nozieres and De Dominicis can be extended to excitation energies comparable to the bandwidth. The range of this extension depends on the structure of the localized perturbation.

The x-ray singularity problem was originally solved in the asymptotic limit by Nozieres and De Dominicis (ND).[1] They calculated the absorption spectrum $\mu(\omega)$ for the process in which a deep, structureless core electron is excited to the conduction band by the absorption of an x ray of frequency ω. For ω very close to the threshold frequency, ω_T, they found that

$$\mu(\omega)=\mu_0\left(\frac{D}{\omega-\omega_T}\right)^{\alpha}, \quad \omega-\omega_T \ll D \ . \tag{1}$$

In particular, they were able to calculate for a noninteracting conduction band the exponent α in terms of the phase shifts of the core-hole potential. For the case of a single phase shift δ and spinless fermions, α is given by

$$\alpha_{\rm ND}=2\left(\frac{\delta}{\pi}\right)-\left(\frac{\delta}{\pi}\right)^2 \ . \tag{2}$$

Two recently proposed numerical procedures[2-4] have renewed interest in this problem. In the first,[2,3] the conduction band is replaced by a finite set of free-electron states uniformly distributed in momentum space. Expressed in this finite basis, the Hamiltonian can be numerically diagonalized, and the absorption spectrum is subsequently evaluated. In the second procedure,[4] the integral equation derived by ND is solved numerically. Although effective for $\omega-\omega_T \simeq D$ both these techniques run into computational limitations when extended into the asymptotic region.

In this Communication, we present a simple numerical method which is uniformly accurate over the full frequency range $0<\omega-\omega_T<D$. For the case of the problem considered by ND, we find that the asymptotic form is accurate up to large $\omega-\omega_T$ (e.g., deviations of 15% for $\omega-\omega_T=0.3D$). In addition the coefficient μ_0 is evaluated (for the first time) with an estimated accuracy of 5%. Finally, we show the effect of a more structured core-hole potential on the nonasymptotic form of the absorption spectrum.

Before presenting the calculational procedure, we discuss the features of the calculated spectra. Figure 1 shows representative results for a Fermi's "golden rule" calculation of $\mu(\omega)$. The initial and final states are many-body eigenstates of

$$H_0=\sum_k \epsilon_k c_k^\dagger c_k + E_d d^\dagger d + \sum_{k,k'} G(k,k') c_k^\dagger c_{k'} dd^\dagger \ , \tag{3}$$

where the conduction-electron energy ϵ_k, measured relative to the Fermi level and lying in a band $-D$ to D, is approximated by $v_F k$ where the wave vector k is measured from the Fermi wave vector. The deep core state lies at E_d. The core–conduction-electron interaction, assumed localized [i.e., $G(k,k')=G_0$], is operative only where there is a core hole and produces a phase shift $\tan\delta=-\pi G_0/D$. The interaction with the x ray is modeled[5] by

$$H_x=w(f_0^\dagger d e^{-i\omega t}+\text{H.c.}) \ , \tag{4}$$

where $\sqrt{2}f_0=\sum_k c_k$ is a conduction-electron state localized about the core state.

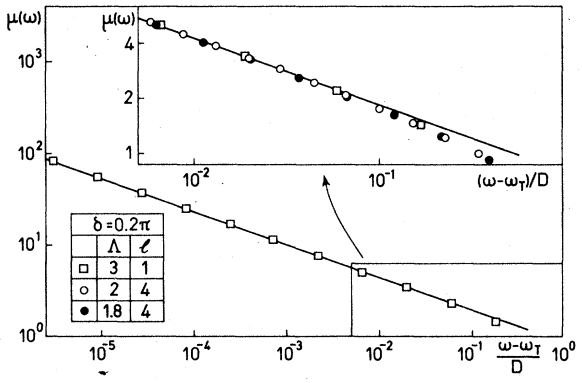

FIG. 1. Absorption spectrum for a final-state phase shift $\delta=0.2\pi$. A straight line with slope $\alpha_{\rm ND}$ is drawn through the last open square on the left-hand side and is continued into the inset. The first open square on the right-hand side was calculated with $N=5$, and the last one on the left with $N=25$. For $\Lambda=3$, $\mu_0=0.84$, and for $\Lambda=2$, $\mu_0=0.82$.

Figure 1 has several striking features. The overall agreement between the numerically evaluated spectrum and the ND power law is remarkable. In the extreme asymptotic limit, $\omega-\omega_T<10^{-9}D$, the exponent α agrees with α_{ND} to 5–7 decimal places. For $\omega-\omega_T\lesssim D$, there are deviations from the ND law, but they are small.

The deviations from the universal behavior (1) depend on specific features of the model. To illustrate this, we consider in Fig. 2 a weakly momentum-dependent core-hole potential $G(k,k')=G_0+(k+k')G_1$. For $\omega-\omega_T<10^{-3}D$ the absorption spectrum cannot be visually distinguished from the asymptotic form (the horizontal dashed-dot line). For larger $\omega-\omega_T$ the deviations from ND law are a function of the momentum dependence of the core hole potential.

Finally, we turn to a description of the method which we believe should be useful for any problem where the conduction electrons feel a spatially localized perturbation. Central to the method is a reorganization of the conduction-electron energy term in (3). This two-step procedure has been described extensively elsewhere.[6] Briefly put, in the first step the conduction band is divided on a logarithmic scale defined by a parameter $\Lambda>1$. For all the conduction states that could be constructed in any interval $\Lambda^{-m-1}<|\epsilon_k|<\Lambda^{-m}$, only the one most localized on the core state is kept.[7] In the second step, a basis transformation converts the conduction-band term into $\sum_{n=0}^{\infty}\epsilon_n(f_n^\dagger f_{n+1}+\text{H.c.})(1+\Lambda^{-1})/2$, where the f_n are fermion operators, f_0 being the same operator as defined after (4). For large n, $\epsilon_n\cong D\Lambda^{-n/2}$; it follows that keeping the first N terms in the conduction-band Hamiltonian will ensure an absolute accuracy of $D\Lambda^{-(N-1)/2}$ for the single-particle eigenvalues of H_0. Accordingly we define a truncated Hamiltonian

$$H_N=\left(\frac{1+\Lambda^{-1}}{2}\right)\sum_{n=0}^{N-1}\epsilon_n(f_n^\dagger f_{n+1}+\text{H.c.})+E_d d^\dagger d+2G_0 f_0^\dagger f_0 dd^\dagger\ . \tag{5}$$

The numerical diagonalization of H_N leads to the following results: (a) If there is *no* core hole ($dd^\dagger\equiv 0$) then the single-particle levels E_{Nl}^l for both particles and holes are given by

$$\frac{2E_{Nl}^l\Lambda^{(N-1)/2}}{D(1+\Lambda^{-1})}=|\eta_{l+1}^*|\simeq\Lambda^l\ . \tag{6}$$

(b) If there is a core hole ($dd^\dagger\equiv 1$) then the single-particle levels E_{NF}^l are

$$\frac{2E_{NF}^l\Lambda^{(N-1)/2}}{D(1+\Lambda^{-1})}=\begin{cases}\eta_{l+1}^+\simeq\Lambda^{l-\delta/\pi}, & \text{electrons}\\ \eta_{l+1}^-\simeq\Lambda^{l+\delta/\pi}, & \text{holes}\end{cases}\ . \tag{7}$$

The quoted approximate forms for the η's are accurate to three decimal places for all l, except $l=0$.

The absorption spectrum is then calculated by "smoothing" the Fermi's "golden rule" result,

$$\mu(\omega-\omega_T)=2\pi w^2\sum|\langle F|f_0^\dagger d|I\rangle|^2\delta(\omega-\omega_T-\omega_{FN}^*)\ . \tag{8}$$

Here $|I\rangle$ and $|F\rangle$ are many-particle states constructed from the single-particle levels as described in Fig. 3.

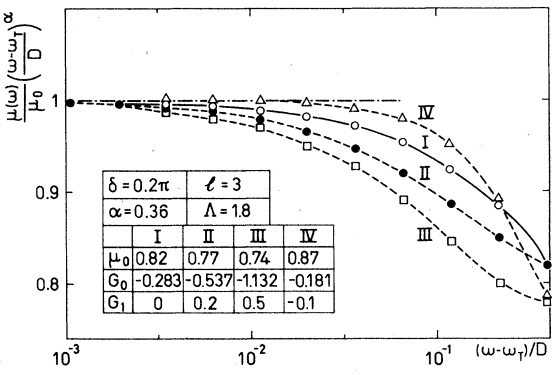

FIG. 2. Absorption spectrum normalized by the ND form (1) for four values of the parameter G_1 in the momentum-dependent core-hole potential. In each case G_0 was adjusted to give the same final-state phase shift. The parameter μ_0, which depends on G_1, was obtained by calculating the absorption rate for $\omega-\omega_T<10^{-6}D$ and fitting the result to (1) with $\alpha=\alpha_{ND}$.

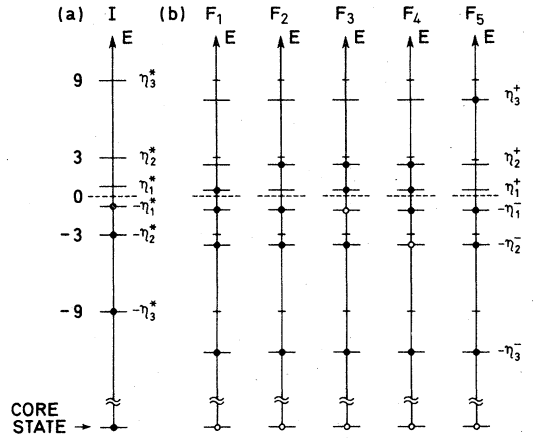

FIG. 3. Initial (a) and five lowest-energy final (b) states that are constructed from the single-particle energy levels given in (6) and (7). The vertical energy axis is scaled by $2\Lambda^{(N-1)/2}/(1+\Lambda^{-1})$. The core state, filled (empty) in the initial (final) state, is also shown as a level far below the conduction band. In the initial state, only the levels below the Fermi level (at 0) are filled. In the final state, *at least* one of the levels above the Fermi level must be filled. However, particle-hole excitations are allowed, as in F_3 and F_4.

In particular, the excitation energy ω_{FN}^{*} (equal to the final-state energy minus the threshold energy ω_T) is the sum of the energies of the filled levels above the Fermi level plus the sum of the hole energies. For example, the configuration F_3 has an excitation energy proportional to $\eta_1^+ + \eta_2^+ + \eta_1^-$. The matrix element in (8) is a determinant involving single-particle matrix elements amongst the eigenstates of the single-particle energy levels (6) and (7) comprising the many-particle initial and final states.

The absorption spectrum calculated through (8) is a series of δ functions at all $\omega - \omega_T = \omega_{FN}^{*}$ as illustrated in Fig. 4. The magnitude of each δ function is proportional to $|\langle F|H_x|I\rangle|^2$ and varies considerably with ω_{FN}^{*}, depending on the number of particle-hole excitations in the final configuration.

To convert these discrete lines into a smooth absorption spectrum $\bar{\mu}(\omega - \omega_T)$, we use a numerically stable smoothing procedure defined by

$$\bar{\mu}(\omega_{Nl} - \omega_T) = \int_{-\infty}^{\infty} \mu(\xi) f(\xi, \omega_{Nl} - \omega_T)\, d\ln\xi \ , \qquad (9)$$

where the convolution function $f(\xi, \omega)$ is a box

$$f(\xi, \omega) = \begin{cases} l/\ln\Lambda, & |\ln\xi - \ln\omega| < \frac{1}{2}\ln\Lambda \\ 0, & \text{otherwise} \end{cases} \qquad (10)$$

and the energies ω_{Nl} are given by

$$\omega_{Nl} - \omega_T = \left(\frac{1+\Lambda^{-1}}{2}\right)\Lambda^{-(N-1)/2+l-(\delta/\pi)} \ , \qquad (11)$$

namely, at the positive final-state single-particle levels. In Fig. 4 we show what configurations are included inside the convolution funtion for three sets of (N,l) chosen so that $(N-1)/2 - l$ is a constant (viz., 1). For $l = 0, 1, 2$ the convoluted absorption rate is 4.86, 1.45, 1.43, and hence converges rapidly for increasing l. Generally $l = 1$ provides μ_0 values within 5% of the $l \to \infty$ limit, as is further evidenced by the inset of Fig. 1 where the $l = 1$ (for $\Lambda = 3$) and the $l = 4$ (for $\Lambda = 2$ and 1.8) points fall on the same line.

Perhaps the most surprising aspect of the smoothing procedure is that the width of convolution function is comparable to the single-particle spacing. Intuitively one might expect that a much broader convolution function would be required. Two arguments can be offered in support of the smoothing procedure. (1) For the phase shift $\delta = 0$, we can analytically calculate (9) and show that it is identical for any Λ to a spectrum resulting from the convolution with a much broader smoothing function. Further, the identical spectra converge rapidly to the continuum limit at $\Lambda \to 1$. (2) For finite δ, no analytic calculation exists which would allow the $\Lambda \to 1$ limit to be taken. However, a numerical study in which various absorption spectra were calculated for $\Lambda = 2, 3, 5$, and 9 showed a rapid convergence to a limiting curve for Λ going from 9 to 2. This convergence suggests that the convoluted absorption rates calculated with $\Lambda = 2$ or 3 represent approximations accurate to within a few percent to the rates in the continuum spectrum.

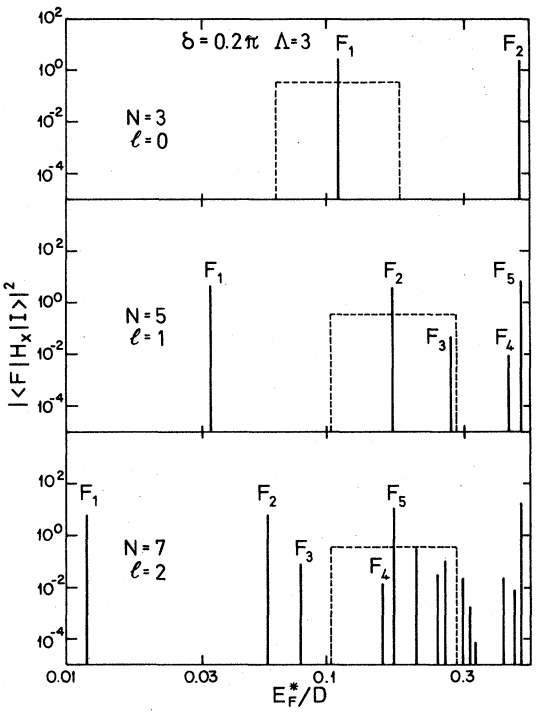

FIG. 4. Procedure for calculating the convoluted absorption for three different $l = 0, 1, 2$. $|\langle F|H_x|I\rangle|^2$ is the matrix element entering the calculation of μ in (8). From (11) it follows that to calculate the absorption rate for any energy in the range $0.047D < \omega - \omega_T < 0.222D$ we have to use one of the (N,l) pairs: (3,0), (5,1), and (7,2). We show the absorption lines calculated from (8) for $N = 3, 5$, and 7 and in each case the convolution function $f(\xi, \omega)$, shown as a dashed line, is centered about the appropriate excitation energy $(\eta_1^+, \eta_2^+, \eta_3^+)$ in units of $(1/2)(1+\Lambda^{-1})\Lambda^{-(N-1)/2}$.

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[5]In the actual numerical calculation G_0 is divided by A_Λ in calculating the phase shift and $w=\sqrt{A_\Lambda/\pi}$. $A_\Lambda=[(\Lambda+1)/(\Lambda-1)]\ln\Lambda/2$ and goes to unity as $\Lambda\to 1$.

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