Core-hole Green's function: Dispersion theory

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The core-hole Green's function in the x-ray edge problem is calculated exactly for some model electron-hole interactions: these include contact and separable potentials. Using the theory of determinants, it is shown that the Green's function may be expressed exactly as a series of terms, where the nth term has n electron-hole pairs excited. Exact expressions are given for the nth term in the series. The series is then resummed using a cumulant expansion. The results show that the electron-hole interaction is renormalized by dispersion integrals.

I. INTRODUCTION

In a metal, the electrons in the core levels of the ion can be removed by excitation to the continuum states using synchrotron radiation or electron scattering. The vacant core orbital is called a core hole. Here we wish to derive some exact results for the core hole Green's function. These exact results are obtained using a simple model of the interaction between the core hole and the conduction electrons: We use contact or separable potentials. These potentials are very approximate when compared to the realistic interactions in actual metals. However, we use them in the present case because we are able to obtain some exact results.

The core-hole Green's function, and its spectral function, play an important role in MND (Mahan,[1] Nozières, and de Dominicis[2]) theory of the x-ray edge singularity. The spectral function can also be inferred from an x-ray photoelectron spectroscopy XPS measurement.[3–5] There have been many theoretical treatments of the core-hole Green's function by both analytical[6–11] and computational techniques.[12–15] The computer studies have usually employed the contact model, so that our exact results are directly comparable to them.

A full study of the core-hole Green's function would include the interaction between the hole and phonons, and other excitations.[16] Our present model omits most of these, and includes the hole interactions with the electron-hole pair spectra of the conduction electrons. These excitations are responsible for an infrared divergence in the spectral function,[16] which is well documented experimentally.[4–5] In any analytical approach, such as ours, the usual method of handling the infrared divergence is to use a cumulant or linked cluster expansion as a resummation of the divergent terms.[17] Thus the statement of the many-body problem is that we have an initial state Hamiltonian H_i before the core hole is created. The final state Hamiltonian H_f describes the additional interaction between the conduction electrons and the core hole,[1]

$$H_i=\sum_k \epsilon_k c_k^\dagger c_k \ ,$$
$$H_f=H_i+\sum_{kk'} V_{kk'} c_k^\dagger c_{k'} \ . \tag{1}$$

The core-hole Green's function at zero temperature can be written exactly in the form[1]

$$G(t)=G_0(t)e^{-\phi(t)-i\Delta t} \ ,$$
$$G_0(t)=-i\Theta(t)\exp(-it\epsilon_h) \ ,$$
$$\phi(t)=\int_0^\infty \frac{du}{u}\rho(u)(1-e^{-iut}) \ , \tag{2}$$
$$\Delta=\frac{2}{\pi}\int_0^{E_F} d\epsilon\,\delta(\epsilon) \ .$$

The exponential function $\phi(t)$ is obtained by the resummation of the cumulant expansion. The theoretical problem is to determine how its kernal $\rho(u)$ depends functionally upon the electron-hole interaction $V_{kk'}$. Several previous theoretical results will be described below. The self-energy Δ is given exactly according to Fumi's theorem.[18]

Table I shows some previously derived results for the kernel $\rho(u)$ in the exponential function $\phi(t)$. Langreth[7] obtained a result which is only valid to second order in the electron-hole interaction, but includes all electron-electron interactions to this order. This formula has been evaluated by Minnhagen, who has shown that the frequency depen-

TABLE I. Kernel of linked cluster expansion.

$\rho(u)$	Asymptotic	Authors
$\frac{1}{u}\sum_q V_0(q)^2 \mathrm{Im}\left[\frac{1}{\epsilon(q,u)}\right] q^2/4\pi e^2$	$\frac{m^2}{2\pi}\sum_q \left\lvert\frac{V_0(q)}{\epsilon_1(q)}\right\rvert^2 \frac{1}{q}$	Langreth[a]
$\frac{1}{u\pi^2}\int_{E_F}^{E_F+u} d\epsilon \sin^2\delta(\epsilon)$	$\frac{\sin^2\delta_F}{\pi^2}$	Combescot and Nozières[b]
$\frac{1}{u}\int_{k_1<k_F}\frac{d^3k_1}{(2\pi)^3}\int_{k_2>k_F}\frac{d^3k_1}{(2\pi)^3}\lvert T_{k_1k_2}\rvert^2\delta(u+\epsilon_1-\epsilon_2)$	$\frac{\sin^2\delta_F}{\pi^2}$	Mahan[c]

[a]Reference 7.
[b]Reference 8.
[c]Reference 9.

dence of the screening is very important.[10–11] Most other theories have ignored electron-electron interactions in solving simplified model Hamiltonians—we shall also ignore it here. Next in Table I is the suggestion of Combescot and Nozières[8] that the kernel is related to a function of the phase shift. Their phase-shift result was obtained by summing sets of diagrams in the linked cluster expansion, and thus goes well beyond the second Born approximation of Langreth. However, the Combescot-Nozières (CN) result is not the exact kernel. They point out that their asymptotic form ($t\to\infty$) for

$$\phi(t)\to(\sin^2\delta_F/\pi^2)\ln(t)$$

whereas Nozières and de Dominicis[2] showed that the exact asymptotic expression should be

$$\phi(t)\to(\delta_F^2/\pi^2)\ln(t).$$

The CN results were based upon a separable potential model. The CN result for $\rho(u)$ was recently derived for nonseparable potentials by Hänsch and Ekardt.[19] Last in Table I is the formula of Mahan,[9] who showed that $\sin^2\delta(\epsilon)$ is better approximated by an off-diagonal T matrix. He also presented the next term in the series for $\rho(u)$, which is proportional to the cube of the T matrix.

The goal of the present work is to add another item to the list in Table I. More importantly, we shall give results whose physical meaning can be precisely stated. Our term represents the exact amplitude for making an electron-hole pair. The previous items do not represent the exact one-pair intensity.

We assert that the Langreth result does not represent the exact one-pair amplitude. This statement is perhaps surprising, since we have long regarded it as the exact pair result. However, the Langreth result is the exact one-pair intensity for a different problem. It is exact for a system of electrons whose Hamiltonian remains H_i for all time, i.e., the core hole can only scatter the electrons without changing their eigenvalues. However, in the x-ray edge problem, the Hamiltonian is changing from H_i to H_f. Significant recent work[20–23] has shown that the matrix element, and hence intensity, for the creation of pairs undergoes changes when the central potential changes. We present here a new result for the exact intensity for one and two pairs.

In the present approach, we will give an exact cumulant expansion, which is the linked cluster expansion of Brout and Carruthers.[17] First, we show that the core-hole Green's function for the model Hamiltonian (1) is given by a series which represents the excitation of multiple electron-hole pairs: The nth term in the series is the exact term for n pairs. We provide an exact expression for the nth term, and thus, formally, an exact expression for the Green's function. This series is then resummed into a cumulant expression. This resummation produces a kernel which is itself a series of terms

$$\rho(u)=\sum_j \rho^{(j)}(u)\ . \tag{3}$$

There is a well-defined meaning to each term $\rho^{(j)}(u)$ in this series[17]: $\rho^{(1)}(u)$ is found from the exact probability of a single electron-hole pair. It is constructed by summing all solutions which have a single electron above the Fermi sea, and a single empty level below. The use of $\rho^{(1)}(u)$ alone in the cumulant expansion means that one-pair probabili-

ties are given exactly, while multipair probabilities are given approximately: $\rho^{(2)}(u)$ is derived from the one- and two-pair intensities. The inclusion of this term in the cumulant expansion means that one- and two-pair probabilities are given exactly. Also, in multipair terms, $\rho^{(2)}(u)$ introduces correlation between emission of pairs, whereas using $\rho^{(1)}(u)$ alone has all pairs uncorrelated: $\rho^{(3)}(u)$ provides the exact three-pair intensity, while providing further correlations for multipair events.

The expansion of the core-hole Green's function allows the procedure introduced earlier for the exciton singularity.[24] We formulate the problem in a system of finite size, with a finite set of eigenstates. Some theorems in the theory of determinants are used to find the exact multipair probabilities.[25] Then we carefully take the limit of an infinite system to obtain the final results.

II. SEPARABLE POTENTIAL

The present calculation employs a separable potential out of necessity. The theoretical approach employs the theory of determinants. As we shall see, it only works for a separable potential. Here we quickly review the properties of such potentials. These properties are well known, and have, for example, been given by CN.

We take the Friedel model for the system. The core hole is at the center of a large sphere of radius R. Later we take the limit $R\to\infty$. The conduction-electron wave functions vanish on the surface of the sphere.

Let $V(r)$ be the interaction potential between the immovable core hole and the conduction electron. The potential can scatter the electron from k to k'. For the separable potential, this matrix element factors into the product of a function of k and k':

$$\langle k\,|\,V\,|\,k'\rangle=\frac{1}{R}g_k g_{k'}\ .$$

The factor of R^{-1} in front is from wave-function normalization in the sphere of radius R. The wave function $|\,k\,\rangle$ is the eigenstate of H_i. The eigenstates of H_f are denoted by an overbar $|\,\bar{k}\,\rangle$. The T matrix can also be shown to be separable:

$$\langle k\,|\,V\,|\,\bar{\lambda}\rangle=\frac{1}{R}g_k\bar{g}_\lambda\ ,$$

$$\bar{g}_\lambda=g_\lambda/[1-\Sigma(\epsilon_\lambda)]\ ,$$

$$\Sigma(\epsilon)=\frac{1}{R}\sum_k\frac{g_k^2}{\epsilon_k-\epsilon}\ .$$

The phase shift δ_k results from the scattering of the electron by the core hole, and is defined as

$$\tan\delta(\epsilon)=\frac{\mathrm{Im}\Sigma(\epsilon)}{1-\mathrm{Re}\Sigma(\epsilon)}\ .$$

The diagonal T matrix is

$$g_k\bar{g}_k=v_k e^{i\delta_k}\sin\delta_k\ . \tag{4}$$

In the finite system of radius R the eigenvalues of H_i are

$$\epsilon_n=\frac{1}{2m}k_n^2=\frac{1}{2m}\left[\frac{n\pi}{R}\right]^2,$$

and the eigenvalues of H_f are:

$$\bar{\epsilon}_n=\epsilon_n-\frac{\delta_n v_n}{R}\ .$$

In the limit that $R\to\infty$, the scattering amplitude $\bar{g}_k$ can also be represented by a dispersion integral[24]

$$\lim_{R\to\infty}\bar{g}_k=g_k\exp\left[\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\delta(\omega)\,d\omega}{\omega-\epsilon_k-i\eta}\right]. \tag{5}$$

All of the above results we shall use in our theory.

III. MULTIPAIR EXPANSION

The core-hole Green's function at zero temperature is formally defined in terms of the creation ($d^\dagger$) and destruction (d) operators of the core hole.[16]:

$$G(t)=-i\Theta(t)\langle g\,|\,e^{iHt}d\,e^{-iHt}d^\dagger\,|\,g\rangle\ .$$

The ground state of the conduction-electron system $|\,g\,\rangle$ has no core holes, while $d^\dagger|\,g\,\rangle$ has one core hole. Thus one can exactly represent the Green's function by the equivalent formula[2,8]

$$G(t)=-i\Theta(t)\langle g\,|\,e^{iH_i t}e^{-iH_f t}\,|\,g\rangle\ , \tag{6}$$

where H_i and H_f are defined in Eq. (1). Our system is a sphere of radius R, in which a finite number of states N are occupied in the ground state. As shown by CN, (6) is equivalent to evaluating the determinant of a single-particle matrix elements

$$S_{ij}=\langle p_i\,|\,e^{-iH_f t}\,|\,p_j\rangle\ ,$$

where $|\,p\,\rangle$ are the occupied states in the ground state—i.e., those beneath the Fermi surface $p<F$. We have

$$G(t)=-i\Theta(t)e^{it(\epsilon_g-\epsilon_h)}\det\begin{vmatrix} S_{11} & S_{12} & S_{13} & \cdots & S_{1N} \\ S_{21} & S_{22} & \vdots & \cdots & S_{2N} \\ S_{N1} & \vdots & & \cdots & S_{NN} \end{vmatrix} . \tag{7}$$

The individual matrix elements in this determinant are difficult to evaluate, since $|p\rangle$ are eigenstates of H_i and not of H_f. In each matrix element we insert a complete set of states $\sum_\lambda |\bar{\lambda}\rangle\langle\bar{\lambda}|$ which are eigenstates of H_f:

$$S_{ij}=\sum_\lambda \langle p_i|\bar{\lambda}\rangle\langle\bar{\lambda}|p_j\rangle e^{-\bar{\epsilon}_\lambda t} .$$

This insertion is done for each matrix element in the determinant in Eq. (7). The next step is to notice that this determinant can be expressed as the determinant of the product of two matrices,

$$\det\{S_{ij}\}=\det\{A_{i\lambda}B_{\lambda j}\} ,$$

$$A_{i\lambda}=\begin{bmatrix} \langle p_1|\bar{\lambda}_1\rangle & \langle p_1|\bar{\lambda}_2\rangle & \langle p_1|\bar{\lambda}_3\rangle & \cdots & \langle p_1|\bar{\lambda}_M\rangle \\ \langle p_2|\bar{\lambda}_1\rangle & \langle p_2|\bar{\lambda}_2\rangle & \vdots & \cdots & \langle p_2|\bar{\lambda}_M\rangle \\ \langle p_N|\bar{\lambda}_1\rangle & \vdots & & \cdots & \langle p_N|\bar{\lambda}_M\rangle \end{bmatrix} ,$$

$$B_{\lambda j}=\begin{bmatrix} \langle\bar{\lambda}_1|p_1\rangle e^{-i\bar{\epsilon}_1 t} & \langle\bar{\lambda}_1|p_2\rangle e^{-i\bar{\epsilon}_1 t} & \cdots & \langle\bar{\lambda}_1|p_N\rangle e^{-i\bar{\epsilon}_1 t} \\ \langle\bar{\lambda}_2|p_1\rangle e^{-i\bar{\epsilon}_2 t} & \langle\bar{\lambda}_2|p_2\rangle e^{-i\bar{\epsilon}_2 t} & & \vdots \\ \langle\bar{\lambda}_M|p_1\rangle e^{-i\bar{\epsilon}_M t} & \vdots & \cdots & \langle\bar{\lambda}_M|p_N\rangle e^{-i\bar{\epsilon}_M t} \end{bmatrix} .$$

This step suggests that we evaluate the determinant by using the identity $\det(C)=\det(AB)$ $=\det(A)\det(B)$. This identity is incorrect in the present case because neither A nor B are square matrices. If there are M states in the band, and N are occupied in the ground state, then A is $N\times M$ while B is $M\times N$. We have that $N\leq M$.

We may use a theorem, independently found by Cauchy and Binet, for evaluating $\det(AB)$ when A and B are rectangular matrices. First, one takes the M different values of λ, and forms all different subsets of dimension N. Denote these subsets as $\{\lambda\}$. The theorem of Cauchy and Binet[25] is

$$\det\{S_{ij}\}=\sum_{\{\lambda\}}\det(A_{i\lambda})\det(B_{\lambda j}) .$$

One makes A and B square matrices by selecting a subset of values $\{\lambda\}$. Then one can use the equality $\det(AB)=\det(A)\det(B)$. The exact evaluation is the summation over all subsets.

In $\det(B)$, the factor $\exp(-it\bar{\epsilon}_\lambda)$ is the same for each row, and can be pulled outside of the determinant:

$$\det(B_{\lambda j})=\det(A_{j\lambda})^*\exp\left[-it\sum_\lambda\bar{\epsilon}_\lambda\right] .$$

The remaining part of $\det(B)$ is just the complex conjugate of $\det(A)$. Thus we arrive at the exact expression

$$G(t)=-i\Theta(t)e^{-it\epsilon_h}e^{itE_g}\times\sum_{\{\lambda\}}\exp\left[-it\sum_\lambda\bar{\epsilon}_\lambda\right]|\det(A_{i\lambda})|^2 . \tag{8}$$

The summation is over the different ways of arranging the M values of λ over sets of size N.

The set of states $|p_j\rangle$ are the initial states of the conduction-electron system. The creation of the core hole changes the electron states, and the new basis set is $|\bar{\lambda}_j\rangle$. The N electrons in the initial state may be arranged among the M different possible final states. Each arrangement has the probability given by Eq. (8).

The expansion in Eq. (8) lends itself naturally to a series over multiple excitations of electron-hole pairs in the final conduction-electron system. The first term is taken to be the case where all of the final electrons are in their ground state $\lambda<F$. The second term is where all but one electron is beneath the Fermi surface—i.e., there is one electron-hole pair. The third term has two electrons above the Fermi surface, and so has two electron-hole pairs. In this series, the $n+1$ term

gives the exact probability of making n pairs. We define P_n as the probability of making n pairs,

$$P_n(t)=\sum_{\{\lambda\}_n}|\det(A_{i\lambda})|^2\exp\left[-it\sum_{\lambda}\bar{\epsilon}_\lambda\right]e^{it\bar{E}}g\ ,$$

$$G(t)=-i\Theta(t)e^{-it(\epsilon_h+\Delta)}\sum_n P_n(t)\ , \tag{9}$$

$$\Delta=\bar{E}_g-E_g\ .$$

The summation on the right is taken over all sets of λ values which have n electrons above the Fermi energy and n empty states below.

The next step is to evaluate the determinants. An exact evaluation is possible for the case of a separable potential. The individual elements in the matrix are

$$\langle p_i\,|\,\bar{\lambda}_j\rangle=\frac{\langle p_i\,|\,V\,|\,\bar{\lambda}_j\rangle}{\bar{\epsilon}_j-\epsilon_i}=\frac{1}{R}\frac{g_i\bar{g}_j}{\bar{\epsilon}_j-\epsilon_i}\ .$$

In $\det(A_{i\lambda})$, the factor g_i is the same for each row and can be taken outside. Similarly, the factor $\bar{g}_j$ is the same for each column and can also be taken outside. There remains only the determinants of energy denominators, which may be obtained exactly,[26]

$$\det\left[\frac{1}{\bar{\epsilon}_j-\epsilon_i}\right]=\frac{\prod_{F\geq i>i'}(\epsilon_i-\epsilon_{i'})\prod_{m>n}(\bar{\epsilon}_m-\bar{\epsilon}_n)}{\prod_{i,m}(\epsilon_i-\bar{\epsilon}_m)}\ ,$$

so that

$$\det(A_{i\lambda})=\prod_{i\leq F}\left[\frac{g_i}{R}\right]\prod_m(\bar{g}_m)\frac{\prod_{i>i'}(\epsilon_i-\epsilon_{i'})\prod_{m>n}(\bar{\epsilon}_m-\bar{\epsilon}_n)}{\prod_{i,m}(\epsilon_i-\bar{\epsilon}_m)}\ . \tag{10}$$

Thus, we have found analytical expression for each term in the series (9). These terms simplify in the limit that $R\to\infty$.

The general result (10) is how evaluated for the first few terms in the multipair expansion. First, we evaluate the term with no electron-hole pairs:

$$P_0^{1/2}=\prod_{i<F}\left[\frac{g_i\bar{g}_i}{R}\right]\frac{\prod_{F>i>i'}(\epsilon_i-\epsilon_{i'})\prod_{F>m>m'}(\bar{\epsilon}_m-\bar{\epsilon}_{m'})}{\prod_{F>i,m}(\epsilon_i-\bar{\epsilon}_m)}\ . \tag{11}$$

Next, we evaluate the term with one pair: a state β below the Fermi level ($\beta<F$) is empty, while a state λ above it ($\lambda>F$) is occupied:

$$P_1=\sum_{\substack{\beta<F\\ \lambda>F}}e^{-it(\bar{\epsilon}_\lambda-\bar{\epsilon}_\beta)}\left[\prod_{i<F}\left[\frac{g_i}{R}\right]\prod_{\substack{m<F\\ m\neq\beta}}(\bar{g}_m)\bar{g}_\lambda\frac{\prod_{i>i'}(\epsilon_i-\epsilon_{i'})\prod_{\substack{m>m'\\ \neq\beta}}(\bar{\epsilon}_m-\bar{\epsilon}_{m'})\prod_{m\neq\beta}(\bar{\epsilon}_m-\bar{\epsilon}_\lambda)}{\prod_{i,m\neq\beta}(\epsilon_i-\bar{\epsilon}_m)\prod_i(\epsilon_i-\bar{\epsilon}_\lambda)}\right]^2\ .$$

This expression is simplified by removing all factors which are P_0:

$$P_1=P_0\sum_{\substack{\beta<F\\ \lambda>F}}e^{-it(\bar{\epsilon}_\lambda-\bar{\epsilon}_\beta)}\left[\frac{\bar{g}_\lambda}{\bar{g}_\beta}\frac{(\epsilon_\beta-\bar{\epsilon}_\beta)}{(\bar{\epsilon}_\beta-\bar{\epsilon}_\lambda)}\prod_{\substack{i\neq\beta\\ i<F}}\left[\frac{\epsilon_i-\bar{\epsilon}_\beta}{\bar{\epsilon}_i-\bar{\epsilon}_\beta}\right]\prod_{i<F}\left[\frac{\bar{\epsilon}_i-\bar{\epsilon}_\lambda}{\epsilon_i-\bar{\epsilon}_\lambda}\right]\right]^2\ .$$

The next step is to take the limit of $R\to\infty$. This step is a delicate mathematical operation, which is described in the Appendix. There it is shown that

$$\lim_{R\to\infty}\prod_{\substack{i\neq\beta\\ i<F}}\left[\frac{\epsilon_i-\bar{\epsilon}_\beta}{\bar{\epsilon}_i-\bar{\epsilon}_\beta}\right]=\frac{\sin\delta_\beta}{\delta_\beta}\exp[\Delta(\epsilon_\beta)],\quad\lim_{R\to\infty}\prod_{i<F}\left[\frac{\bar{\epsilon}_i-\bar{\epsilon}_\lambda}{\epsilon_i-\bar{\epsilon}_\lambda}\right]=\exp[-\Delta(\epsilon_\lambda)]\ ,$$

$$\Delta(\epsilon)=\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{E_F}\frac{d\omega\,\delta(\omega)}{\omega-\epsilon}\ . \tag{12}$$

The two limiting expressions have a different prefactor, with $\sin(\delta_\beta)/\delta_\beta$ only in one case, because $\epsilon_\beta < E_F$ while $\epsilon_\lambda > E_F$. Also, recall that $\epsilon_\beta - \bar{\epsilon}_\beta = v_\beta \delta_\beta / R$ so we obtain for P_1 in the limit $R \to \infty$,

$$P_1(t) = P_0 \int_0^{k_F} \frac{dk_\beta}{\pi} \frac{v_\beta^2 \sin^2\delta_\beta}{\bar{g}_\beta^2} e^{2\Delta(\epsilon_\beta)} \int_{k_F}^{\infty} \frac{dk_\lambda}{\pi} \frac{g_\lambda^2}{(\epsilon_\beta - \epsilon_\lambda)^2} e^{-it(\epsilon_\lambda - \epsilon_\beta)} e^{-2\Delta(\epsilon_\lambda)} .$$

This expression is the exact probability, as a function of time, for creating a single electron-hole pair while creating the core hole.

This expression can be simplified by using some of the results of Sec. II for the one-particle T matrix. For example, from Eq. (4),

$$v_\beta \sin\delta_\beta / |\bar{g}_\beta| = g_\beta ,$$

$$P_1(t) = P_0 \int_0^{k_F} \frac{dk_\beta}{\pi} g_\beta^2 e^{2\Delta(\epsilon\beta)} \int_{k_F}^{\infty} \frac{dk_\lambda}{\pi} \frac{|\bar{g}_\lambda|^2}{(\epsilon_\beta - \epsilon_\lambda)^2} e^{-2\Delta(\epsilon_\lambda)} e^{-it(\epsilon_\lambda - \epsilon_\beta)} . \tag{13}$$

This result is the same as CN, or Mahan, since $g_\beta \bar{g}_\lambda = T_{\beta\lambda}$, except for the dispersion integrals $\exp[2\Delta(\epsilon_\beta) - 2\Delta(\epsilon_\lambda)]$. Our exact expression for the probability of creating a single electron-hole pair does contain these dispersion integrals. The earlier results, shown in Table I, do not have such factors, and are not the exact single-pair probabilities.

Another way to manipulate this expression is to use (5) and to replace the integrand of (13) the right-hand side of

$$|\bar{g}_\lambda|^2 \exp[-2\Delta(\epsilon_\lambda)] = g_\lambda^2 \exp[2p(\epsilon_\lambda)], \quad p(\epsilon) = \frac{1}{\pi} \int_{E_F}^{\infty} \frac{d\omega\, \delta(\omega)}{\omega - \epsilon} .$$

In Ref. 24 the exact multipair expression for the Mahan singularity at the absorption edge was derived. There it was found that one could take the Born approximation results and modify them with the factors of $\exp[2\Delta(\epsilon_\beta)]$ for holes and $\exp[2p(\epsilon_\lambda)]$ for electron lines. The same result is found here for the core-hole Green's function.

Similar steps can be taken to derive the two-pair, three-pair, and n-pair probabilities. These are

$$P_2(t) = \frac{1}{(2!)^2} \int_0^{k_F} \frac{dk_\alpha}{\pi} g_\alpha^2 e^{2\Delta(\epsilon_\alpha)} \int_0^{k_F} \frac{dk_\beta}{\pi} g_\beta^2 e^{2\Delta(\epsilon_\beta)} \int_{k_F}^{\infty} \frac{dk_\lambda}{\pi} g_\lambda^2 e^{2p(\epsilon_\lambda)} \int_{k_F}^{\infty} \frac{dk_\phi}{\pi} g_\phi^2 e^{2p(\epsilon_\phi)} \times \frac{\exp[-it(\epsilon_\lambda + \epsilon_\phi - \epsilon_\alpha - \epsilon_\beta)](\epsilon_\alpha - \epsilon_\beta)^2 (\epsilon_\lambda - \epsilon_\phi)^2}{(\epsilon_\alpha - \epsilon_\lambda)^2 (\epsilon_\alpha - \epsilon_\phi)^2 (\epsilon_\beta - \epsilon_\lambda)^2 (\epsilon_\beta - \epsilon_\phi)^2} , \tag{14}$$

$$P_n(t) = \frac{1}{(n!)^2} \prod_{\alpha,\lambda}^{n} \left[\int_0^{k_F} \frac{dk_\alpha}{\pi} g_\alpha^2 e^{2\Delta(\epsilon_\alpha)} e^{it\epsilon_\alpha} \int_{k_F}^{\infty} \frac{dk_\lambda}{\pi} g_\lambda^2 e^{2p(\epsilon_\lambda)} e^{-it\epsilon_\lambda} \right] \frac{\prod_{\alpha<\beta}^{n} (\epsilon_\alpha - \epsilon_\beta)^2 \prod_{\lambda>\phi}^{n} (\epsilon_\lambda - \epsilon_\phi)^2}{\prod_{\alpha,\lambda}^{n} (\epsilon_\alpha - \epsilon_\lambda)^2} .$$

The subscripts α and β denote hole states, while λ and ϕ denote electron states. The prefactor of $(n!)^{-2}$ accounts for the equivalent ways of counting the same configuration of electrons or holes.

An exact expression has been found for the core-hole Green's function. In Eq. (9) it is expressed as a summation over the probabilities $P_n(t)$ of making n pairs. We have derived an exact expression for the terms in this series, and therefore have an exact mathematical expression for the Green's function.

IV. LINKED CLUSTER EXPANSION

Although we have found an exact expression for $G(t)$, it is in a form which is inconvenient to use. When taking the Fourier transform of $G(t)$, each term in the series diverges in the limit of low frequency. This divergence is the well known infrared divergence, which is caused by the emission of many low-energy electron-hole pairs. The customary method of eliminating this divergence is by resumming the series in a linked cluster expan-

sion.[17] We shall now do this, and derive the first two terms for the kernel in (3).

The general procedure is to solve the equation

$$\sum_n P_n(t)=\exp[-\phi(t)] ,$$

$$\phi(t)=\int_0^\infty \frac{du}{u}(1-e^{-iut})\sum_{j=1}^{\infty}\rho^{(j)}(u) .$$

Thus we must find the kernel functions $\rho^{(j)}(u)$ which will reproduce the original series over $P_n(t)$. Using the fact that $\phi(t=0)=0$, one can establish that the first term in the series is

$$P_0=\exp\left[-\int_0^\infty \frac{du}{u}\rho(u)\right] .$$

The quantities on both sides of the equal sign are zero in the limit of $R\to\infty$. The divergence is caused by the infinite number of electron-hole pairs made in the infinite system.

The next term in the linked cluster expansion is $P_1(t)$ which determines the first term $\rho^{(1)}(u)$:

$$\rho^{(1)}(u)=u\int_{-\infty}^{\infty}\frac{dt\,e^{iut}}{2\pi}\frac{P_1(t)}{P_0} ,$$

$$\rho^{(1)}(u)=\frac{1}{u}\int_0^{k_F}\frac{dk_\beta}{\pi}g_\beta^2 e^{2\Delta(\epsilon_\beta)} \times\int_{k_F}^{\infty}\frac{dk_\lambda}{\pi}g_\lambda^2 e^{2p(\epsilon_\lambda)} \times\delta(u+\epsilon_\beta-\epsilon_\lambda) . \tag{15}$$

The above form for $\rho^{(1)}(u)$ is correct only when no bound states are present. Whenever bound states are present in the final state, they must be included in the summations. For example, when there is a single bound state below the band, then the hole in the electron-hole pairs can originate from this state. One has the additional term in $\rho^{(1)}(u)$:

$$\delta\rho^{(1)}(u)=\frac{f_b}{u}\int_{k_F}^{\infty}\frac{dk_\lambda}{\pi}\delta(u+\epsilon_b-\epsilon_\lambda) \times\bar{g}_\lambda^2 e^{-2\Delta(\epsilon_\lambda)} ,$$

$$f_b=f_b^{(0)}\exp[-2p(\epsilon_b)] ,$$

where ϵ_b is the binding energy, and $f_b^{(0)}$ is the oscillator strength for hole transitions to the empty band, defined by

$$N_\beta\bar{g}_\beta^2\to f_b^{(0)}\delta(\epsilon_\beta-\epsilon_b) ,$$

where $N_\beta=(\pi v_\beta)^{-1}$ is the density of states. A numerical example for this expression will be given below.

The second term in the series (3) is

$$\rho^{(2)}(u)=u\int_{-\infty}^{\infty}dt\,e^{iut}\left[\frac{P_2(t)}{P_0}-\frac{1}{2!}\left[\frac{P_1(t)}{P_0}\right]^2\right] .$$

There will be two electrons (k_λ,k_ϕ) and two holes (k_α,k_β). In the term P_1^2 there are two choices for pairing the electron-hole variables: either (k_α,k_λ) (k_β,k_ϕ), or (k_α,k_ϕ), (k_β,k_λ). We take both possibilities and divide by two. From (13) and (14) we obtain

$$\rho^{(2)}(u)=\frac{u}{4\pi^4}\int_0^{k_F}dk_\alpha g_\alpha^2 e^{2\Delta(\epsilon_\alpha)}\int_0^{k_F}dk_\beta g_\beta^2 e^{2\Delta(\epsilon_\beta)}\int_{k_F}^{\infty}dk_\lambda g_\lambda^2 e^{2p(\epsilon_\lambda)}\int_{k_F}^{\infty}dk_\phi g_\phi^2 e^{2p(\epsilon_\phi)} \times\delta(u+\epsilon_\alpha+\epsilon_\beta-\epsilon_\lambda-\epsilon_\phi)\left[\frac{(\epsilon_\alpha-\epsilon_\beta)^2(\epsilon_\lambda-\epsilon_\phi)^2}{(\epsilon_\alpha-\epsilon_\lambda)^2(\epsilon_\alpha-\epsilon_\phi)^2(\epsilon_\beta-\epsilon_\lambda)^2(\epsilon_\beta-\epsilon_\phi)^2} -\frac{1}{(\epsilon_\alpha-\epsilon_\lambda)^2(\epsilon_\beta-\epsilon_\phi)^2}-\frac{1}{(\epsilon_\alpha-\epsilon_\phi)^2(\epsilon_\beta-\epsilon_\lambda)^2}\right] .$$

By only algebraic manipulations the polynomial in the integrand can be simplified, and so we find

$$\rho^{(2)}(u)=-\frac{u}{2\pi^4}\int_0^{k_F}dk_\alpha g_\alpha^2 e^{2\Delta(\epsilon_\alpha)}\int_0^{k_F}dk_\beta g_\beta^2 e^{2\Delta(\epsilon_\beta)}\int_{k_F}^{\infty}dk_\lambda g_\lambda^2 e^{2p(\epsilon_\lambda)}\int_{k_F}^{\infty}dk_\phi g_\phi^2 e^{2p(\epsilon_\phi)} \times\frac{\delta(u+\epsilon_\alpha+\epsilon_\beta-\epsilon_\lambda-\epsilon_\phi)}{(\epsilon_\alpha-\epsilon_\lambda)(\epsilon_\alpha-\epsilon_\phi)(\epsilon_\beta-\epsilon_\lambda)(\epsilon_\beta-\epsilon_\phi)} . \tag{16}$$

We also tried to derive the next term $\rho^{(3)}(u)$ but we were overwhelmed by the several hundred terms in the polynomial in its integrand.

One feature of both experimental and theoretical interest is the exponent of the power-law singularity associated with the infrared divergence.[5] The singularity comes from the long time behavior of the function $\phi(t)$, which generally has a depen-

dence that is logarithmic[2]:

$$\lim_{t\to\infty}\phi(t)=g\ln(t)\ ,$$

$$g=\lim_{u\to 0}\rho(u)\ .$$

The coefficient g becomes the exponent of the power-law singularity for the spectral function. Nozières and de Dominicis[2] showed that the exact exponent should be $g=\delta_F^2/\pi^2$. The approximate theories summarized in Table I do not have the exact limiting value. In two cases they give $g=\sin^2\delta_F/\pi^2$.

In order to obtain the exact result $g=\delta_F^2/\pi^2$, one apparently has to obtain the limiting behavior of every term in the kernel,

$$g=\lim_{u\to 0}\sum_{j=1}^{\infty}\rho^{(j)}(u)\ .$$

So far we have been able to obtain an analytical expression for $\rho^{(1)}(u=0)$, and not for $\rho^{(2)}(0)$. The problem, of course, is that the dispersion factors $\exp(2\Delta)$ and $\exp(2p)$ do affect the result, and render the integrals difficult. For the first term we obtain.

$$\rho^{(1)}(0)=\frac{\delta_F\tan\delta_F}{\pi^2}\ .$$

For most potentials of physical interest, the phase shifts have the range of values $0<\delta<\pi/2$. In this range, we have that $\sin^2\delta<\delta^2<\delta\tan\delta$. Thus, our values tend to be an approximation to the exact g, which is too large. One expects the next term in the kernel to be negative, which is the case, as shown in (16).

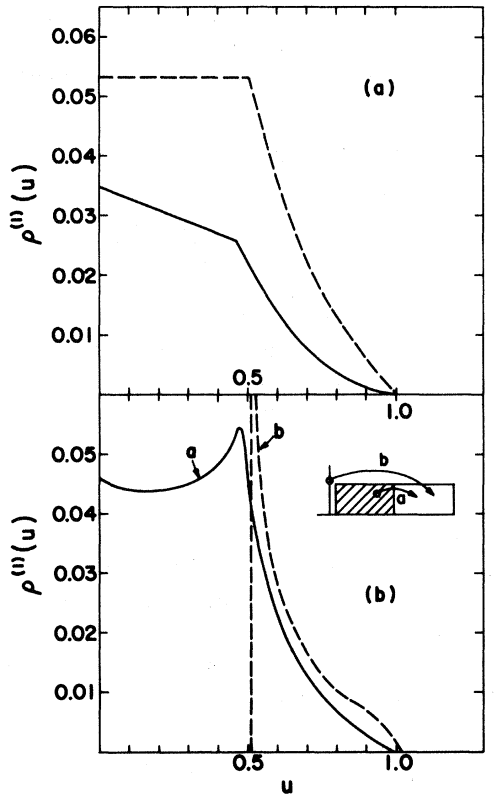

FIG. 1. Different theories for the first cumulant term in the core-hole Green's function. The numerical example is for a conduction band of unit width, half full, constant density of states, and $U=\pi^{-1}\tan(\pi/5)$. In part (a) the dashed line is the second Born approximation, and the solid line is the T-matrix approximation. (b) is the present theory which has the T-matrix plus dispersion integrals. The solid line is the present theory but without the core hole in the bound state. The dashed line shows the transitions $\delta\rho$ which leaves the hole in the bound state. The final $\rho^{(1)}$ in (b) should be the sum of the two curves.

V. DISCUSSION

An exact solution is presented for the core-hole Green's function for a class of model Hamiltonians. The Green's function was represented as a series of terms, which represent multiple excitations of electrons and holes. An analytical expression is given for each term in this series, so a formally exact solution is obtained. Furthermore, this series was resummed as a linked cluster expansion and recast as an exponential series. The first two terms were presented for this resummation. Our series is an expansion in the exact probabilities of making electron-hole pairs.

The various approximations are compared by a numerical example shown in Fig. 1. For this illustration we use a contact model $U=0.281$ with a constant density of states in a band of unit width which is 50% occupied. This model, which has been well studied,[15,24] has a phase shift at the Fermi surface of $\delta_F=\pi/5$, and therefore an exact value of $\rho(0)=\delta_F^2/\pi^2=0.040$. In Fig. 1(a), the dashed curve is the second Born approximation of Langreth. Here the kernel of the integrand of $\rho^{(0)}(u)$ is the constant $U^2=0.0535$, and the variations with u occur from the joint density of states for electron and hole. The solid line is the CN result, which has the kernel equal to $\sin^2\delta(\epsilon)$. The present result calculated from Eq. (15) is given in Fig. 1(b). Here the kernel is also $\sin^2\delta(\epsilon)$ plus the

additional dispersion factors. They have an important effect, since the solid line in part (b) is much different than the solid line in part (a).

The model we are solving has a single bound state beneath the bottom of the occupied conduction band. The bound state affects $\rho^{(1)}(u)$ in two ways. The first is to permit the hole to be in the bound state, so electron-hole transitions are allowed from the bound states. These have an oscillator strength $f_b=0.0108$ in the present case, and cause the big jump at $u=0.51=-\epsilon_b$. The second effect of the bound states also has an important influence upon the shape of $\rho^{(1)}(u)$: It affects the dispersion integral. The phase shift is considered to have a constant value of π between the bound state energy ϵ_b and the bottom of the band energy ϵ_0. Thus, the integral in (12) may be written as

$$\Delta(\epsilon)=\ln\left|\frac{\epsilon_o-\epsilon}{\epsilon_b-\epsilon}\right|+\frac{1}{\pi}\int_{\epsilon_0}^{E_F}\frac{d\omega\,\delta(\omega)}{\omega-\epsilon}\ .$$

The first term on the right of this equation is caused by the bound state, and it has a big influence upon the result. In our numerical example $\epsilon_b=-0.513\,42$ while $\epsilon_0=-0.50$.

No exact results for $\rho(u)$ are available in the literature, so we are unable to compare with the exact solution. Those authors presenting computer solutions[13–15] are capable of obtaining $\rho(u)$ but have not presented the result. Only von Barth and Grossmann[12] present results for $\rho(u)$, which they call $\alpha(\omega)$. Our results are quite similar to theirs, although the results cannot be compared directly since the two calculations assumed a different single-particle density of states.

The present results show how dispersion integrals affect the core-hole Green's function. The first use of dispersion theory in the x-ray edge problem was by Lloyd,[27] who tried to solve the problem by using canonical transformation. He was unable to solve the canonical transformation for the general case, but did for the trival example of a constant phase shift and found dispersion results similar to those here. Pardee and Mahan[28] showed that dispersion theory was a simple and elegant way of solving the Mahan singularity. Recently, Penn, Girvin, and Mahan[24] solved the exciton singularity exactly for the contact and separable potentials. They showed that the results could be presented in a simple way and did contain dispersion integrals as suggested by Pardee and Mahan. The present theory is an extension of this work to the case of the core-hole Green's function.

Finally, in Refs. 20–23 there is another approach to the time-dependent pair spectra, whose relationship to the present work is still unclear.

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APPENDIX

The mathematical approach in the present theory has been to confine the system of electrons to a large sphere of radius R. After evaluating the determinants, we then take the limit $R\to\infty$. There are several situations, particularly in the case of resonant energy denominators, where this limit has to be taken with great care.

The first case we will derive is

$$H(k_m)=\lim_{R\to\infty}\sum_{n>F}h\left[\frac{n\pi}{R}\right]\langle n\,|\,\bar{m}\rangle\ ,$$

$$\langle n\,|\,\bar{m}\rangle=\frac{1}{R}\frac{g\left[\frac{n\pi}{R}\right]\bar{g}\left[\frac{m\pi}{R}\right]}{\epsilon_n-\bar{\epsilon}_m}\ ,$$

where $h(k)$ is any function of k. In the limit $R\to\infty$, the particle wave vectors $n\pi/R=k_n$ go to the continuum values k_n, and the summation becomes an integral over this continuum. We ignore bound states in this analysis since they are easily included in the results as a sum over their discrete states: it is the continuum states which must be treated carefully. In the continuum limit, one might be tempted to set

$$H(k_m)\overset{?}{=}\frac{\bar{g}(k_m)}{\pi}\int_{k_F}^{\infty}dk\frac{h(k)g(k)}{\epsilon_k-\epsilon_m}\ .$$

This formula is correct when $k_m<k_F$. However, it is incorrect when $k_m>k_F$ because an additional term arises from the resonance region $k\sim k_m$.

Thus we set $k_m>k_F$ and reexamine the resonance region more closely. The summation is divided into four separate pieces:

$$H(k_m)=\lim_{R\to\infty}\frac{\bar{g}(k_m)}{R}\left[\left[\sum_{n=F}^{m-L}+\sum_{n=m-L}^{m+L}+\sum_{n=m+L}^{\infty}\right]\frac{h(k_n)g(k_n)/v_n}{k_n-k_m+\delta_m/R}+\sum_{n=F}^{\infty}\frac{h(k_n)g(k_n)/v_n}{k_n+k_m-\delta_m/R}\right]. \tag{A1}$$

The last term, where the energy denominators are not resonant, can be evaluated by taking the straightforward continuum limit,

$$\lim_{R\to\infty}\frac{\bar{g}(k_m)}{R}\sum_{n=F}^{\infty}\frac{h(k_n)g(k_n)/v_n}{k_n+k_m-\delta_m/R}=\frac{\bar{g}(k_m)}{\pi}\int_{k_F}^{\infty}\frac{dk}{v_k}\frac{h(k)g(k)}{k+k_m}.$$

In the limit that $R\to\infty$, the integers n, m, and F also go to infinity, so that the ratios $\pi F/R\to k_F$, $\pi n/R\to k_n$, etc. remain finite. The integer L we assume does not increase as fast as R, so that the ratio $\epsilon=\pi L/R$ goes to zero as $R\to\infty$. Thus the first and third terms in (A1) become

$$\lim_{R\to\infty}\frac{\bar{g}(k_m)}{R}\left[\sum_{n=F}^{m-L}+\sum_{n=m+L}^{\infty}\right]\frac{hg/v_n}{k_n-k_m+\delta_m/R}=\frac{\bar{g}(k_m)}{\pi}\left[\int_{k_F}^{k_m-\epsilon}dk+\int_{k_m+\epsilon}^{\infty}dk\right]\times\frac{h(k)g(k)}{v_k(k-k_m)}.$$

This integral is recognized as the definition of the principal part of the integral over the integrand with a vanishing denominator.

There remains the interesting term, which is the second one on the right in Eq. (A1). Here we set $l=n-m$ and examine

$$\lim_{R\to\infty}\bar{g}(k_m)\sum_{l=-L}^{L}\frac{h\left[k_m+\frac{\pi l}{R}\right]g\left[k_m+\frac{\pi l}{R}\right]\Big/v_n}{l\pi+\delta_m}.$$

In the limit of $R\to\infty$, this series converges to a value independent of L, as long as L is large. The factors in the numerator can be evaluated at the value $k_n=k_m$, and the remaining summation is an expression for the cotangent

$$\frac{\bar{g}(k_m)h(k_m)g(k_m)}{v_m}\sum_{l=-\infty}^{\infty}\frac{1}{l\pi+\delta_m}=\frac{\bar{g}(k_m)h(k_m)g(k_m)\cot(\delta_m)}{v_m}.$$

Thus we can collect our various terms and obtain the final result:

$$H(k_m)=\bar{g}(k_m)\left[\frac{h(k_m)g(k_m)\cot\delta_m}{v_m}+\mathcal{P}\int_{k_F}^{\infty}\frac{dk}{\pi}\frac{h(k)g(k)}{\epsilon_k-\epsilon_m}\right]. \tag{A2}$$

The first term on the right comes from the resonant denominator, and this term only occurs when $k_m>k_F$. This result was employed in Ref. 24 but without a proof.

The second case we will derive is Eq. (12). Gottfried[29] has discussed the method of evaluating this limit. However, when $m<F$ there is a resonant term, similar to the one above, which Gottfried overlooked. In order to find it, we follow his steps by expressing the product an an exponential series:

$$J(k_m)=\lim_{R\to\infty}\prod_{\substack{n<F\\ n\neq m}}\left[\frac{\epsilon_n-\bar{\epsilon}_m}{\bar{\epsilon}_n-\bar{\epsilon}_m}\right]=\lim_{R\to\infty}\exp(\Xi), \tag{A3}$$

$$\Xi=\sum_{\substack{n=1\\ n\neq m}}^{F}\ln\left[\frac{k_n^2-(k_m-\delta_m/R)^2}{(k_n-\delta_n/R)^2-(k_m-\delta_m/R)^2}\right],$$

$$\Xi=\left[\sum_{n=1}^{m-L}+\sum_{n=m-L}^{m+L}+\sum_{n=M+L}^{F}\right]\ln\left[\frac{k_n-k_m+\delta_{m/R}}{k_n-k_m-(\delta_n-\delta_m)/R}\right]+\sum_{n=1}^{F}\ln\left[\frac{k_n+k_m-\delta_m/R}{k_n+k_m-(\delta_n+\delta_m)/R}\right]. \tag{A4}$$

Again the summation has been broken into four terms. In the limit $R\to\infty$, the argument of the logarithm approaches unity. A finite result is obtained by expanding this argument. For example, the last term in the above equation becomes

$$\lim_{R\to\infty}\sum_{n=1}^{F}\ln\left[\frac{k_n+k_m-\delta_m/R}{k_n+k_m-(\delta_n+\delta_m)/R}\right]=\lim_{R\to\infty}\left[\frac{1}{R}\sum_{n=1}^{F}\frac{\delta_n}{k_n+k_m-\delta_m/R}+O\left[\frac{1}{R^2}\right]\right]=\int_0^{k_F}\frac{dk}{\pi}\frac{\delta(k)}{k+k_m}\ .$$

In the first and third terms in (A4), we again get the definition of principal parts:

$$\lim_{R\to\infty}\left[\sum_{n=1}^{m-L}+\sum_{n=m+L}^{F}\right]\ln[\ ]=\mathscr{P}\int_0^{k_F}\frac{dk}{\pi}\frac{\delta_k}{k-k_m}\ .$$

Again the interesting term is the second one in (A4). Here it is important to recall that the term $n=m$ is omitted from the series, according to the original expression (A3). Again letting $l=n-m$, we have to evaluate the series

$$\sum_{\substack{l=-L\\ l\neq 0}}^{L}\ln\left[\frac{\pi l+\delta_m}{\pi l+\delta_m-\delta_{m+l}}\right]\to\sum_{\substack{l=-\infty\\ l\neq 0}}^{\infty}\ln\left[\frac{\pi l+\delta_m}{\pi l}\right]=\ln\left[\frac{\sin(\delta_m)}{\delta_m}\right]\ .$$

By collecting all of these terms, we obtain the final result:

$$J(k_m)=\frac{\sin\delta_m}{\delta_m}\exp[\Delta(k_m)]\ .$$

The prefactor of $\sin(\delta)/\delta$ only occurs whenever $k_m<k_F$, since it comes from the resonant denominator in the summation. This prefactor was not obtained in Ref. 29.

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