Threshold Singularities in Appearance-Potential Spectroscopy*

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The model Hamiltonian used by Nozieres and De Dominicis in calculating the threshold behavior of x-ray emission and absorption in metals is applied to the situation where a core excitation is created by a fast electron. Explicit expressions are given for the exponent governing the threshold behavior. For transitions involving s-state core levels it is possible for stronger threshold divergences to occur than for the x-ray problem.

Threshold singularities are well-known phenomena in x-ray absorption and emission.[1-3] Recent theoretical work shows that this singular behavior is due to the interaction of the suddenly created (in the case of absorption) or annihilated (in the case of emission) core hole with the low-lying single-particle excitations of the conduction electrons.[4-11] In this Letter we use the model of Nozières and De Dominicis[7] (hereafter referred to as ND) to show that threshold singularities are expected in appearance-potential spectroscopy[12-13] (APS) and to calculate the critical exponents expected for the divergences.

Briefly, in APS a fast electron (100–1000 eV) is used to create a core excitation, leaving the system in a final state which has a core hole and two additional electrons in the conduction band. Experimentally one measures the total yield of soft x rays produced when the core hole de-excites as a function of the incident electron energy and thus measures a quantity proportional to the cross section for exciting the core hole. At threshold the two additional conduction electrons are at the Fermi level.

We consider free conduction electrons which only interact with the potential of the core hole, and assume a structureless deep hole. Although there are strong plasmon satellites in APS,[12-15] here we only consider the threshold behavior of the primary core-hole excitation. Thus we take as the model Hamiltonian describing the dynamics of the solid[7]

$$H=\sum_k \epsilon_k C_k^\dagger C_k + \Delta a a^\dagger + \sum_{k_a,k_b} V(\vec{k}_a,\vec{k}_b)\vec{C}_{k_a}^\dagger C_{k_b} a a^\dagger, \tag{1}$$

where $C_k^\dagger$ is the operator which creates a conduction electron in the momentum state $\vec{k}$ (we implicitly include the spin index in the k label but assume spin-independent interactions), a is the operator which annihilates the core electron in the deep state under consideration, and $-\Delta$ is the energy of the deep level ($\Delta>0$), and the potential V is the same one which enters the x-ray problem. We take as the part of the Hamiltonian describing the creation of the core hole by the incident electron beam

$$H_1=\sum_{k,k_1,k_2} W(\vec{k};\vec{k},\vec{k}_2) C_{k_1}^\dagger C_{k_2}^\dagger C_k a. \tag{2}$$

We treat the high-energy incident electron as distinguishable from the other electrons of the solid and hence, for an incident beam of energy ϵ_{k_i} the cross section for creating the core hole is[16]

$$d\sigma \propto \int dt\, \exp[i\epsilon_{k_i} t] \sum_{k_1,k_2,k_3,k_4} W(\vec{k}_i;\vec{k}_3,\vec{k}_4) W^*(\vec{k}_i;\vec{k}_2,\vec{k}_1) \langle C_{k_1}(t) C_{k_2}(t) a^\dagger(t) a(0) C_{k_3}^\dagger(0) C_{k_4}^\dagger(0)\rangle, \tag{3}$$

where angular brackets indicate the expectation value in the initial ground state of the system which contains no core holes. The time dependence of the operators in Eq. (3) is described by the Heisenberg representation[17] for the Hamiltonian given by Eq. (1). Thus the scattering cross section is determined by the function

$$\Gamma_{k_1,k_2,k_3,k_4}(t_1,t_2,t_3,t_4;\tau_1,\tau_2) = \langle T C_{k_1}(t_1) C_{k_2}(t_2) C_{k_3}^\dagger(t_3) C_{k_4}^\dagger(t_4) a(\tau_1) a^\dagger(\tau_2)\rangle. \tag{4}$$

Γ obeys the following equation of motion:

$$\begin{aligned}[\partial/\partial t_1 + i\epsilon_k]\Gamma_{k_1,k_2,k_3,k_4}(t_1,t_2,t_3,t_4;\tau_1,\tau_2) &= \delta(t_1-t_4)\delta_{k_1,k_4} F_{k_2,k_3}(t_2,t_3;\tau_1,\tau_2) - \delta(t_1-t_3)\delta_{k_1,k_3} F_{k_2,k_4}(t_2,t_4;\tau_1,\tau_2) \\ &\quad - i\sum_{k_b} V(\vec{k}_1,\vec{k}_b)\langle T C_{k_b}(\,)a(t_1) a^\dagger(t_1) C_{k_2}(t_2) C_{k_3}^\dagger(t_3) C_{k_4}^\dagger(t_4) a(\tau_1) a^\dagger(\tau_2)\rangle,\end{aligned} \tag{5}$$

where

$$F_{k_2,k_3}(t_2,t_3;\tau_1,\tau_2)=\langle TC_{k_2}(t_2)C_{k_3}{}^{\dagger}(t_3)a(\tau_1)a^{\dagger}(\tau_2)\rangle. \tag{6}$$

Although it is possible to calculate the function F from its equation of motion,[9] it suffices to note that F determines the response function in the case of the creation of a core hole by an x ray and so we can simply take over the results of ND for it. Next we note in analogy to the x-ray calculation that the last term on the right-hand side of Eq. (5) vanishes unless $\tau_2>t_1>\tau_1$, and for this particular time ordering

$$a(t_1)a^{\dagger}(t_1)=1. \tag{7}$$

Thus the equation of motion for Γ closes and does not involve higher-order correlation functions. This is a direct consequence of the "assumed" structureless nature of the deep hole. Noting that the term in brackets on the left-hand side of Eq. (5) is the inverse of the free-electron Green's function G, we rewrite Eq. (5) as the following integral equation:

$$\Gamma_{k_1,k_2,k_3,k_4}(t_1,t_2,t_3,t_4;\tau_1,\tau_2)=G_{k_1,k_4}(t_1-t_4)F_{k_2,k_3}(t_2,t_3;\tau_1,\tau_2)-G_{k_1,k_3}(t_1-t_3)F_{k_2,k_4}(t_2,t_4;\tau_1,\tau_2)$$
$$-i\int_{\tau_1}^{\tau_2}dt\sum_{q_1,q_2}G_{k_1,q_1}(t_1-t)V(\vec{q}_1,\vec{q}_2)\Gamma_{q_2,k_2,k_3,k_4}(t,t_2,t_3,t_4;\tau_1,\tau_2). \tag{8}$$

To proceed further, we expand the deep hole potential in spherical harmonics as

$$V(\vec{q}_1,\vec{q}_2)=\textstyle\sum_{lm}V_l(q_1,q_2)Y_{lm}{}^{*}(\Omega_{q_1})Y_{lm}(\Omega_{q_2}). \tag{9a}$$

Furthermore, we assume that each component of V_l is separable, i.e.,

$$V_l(q_1,q_2)=V_l\,U_l(\epsilon_{q_1})U_l(\epsilon_{q_2}), \tag{9b}$$

where U_l is a cutoff function centered somewhere near the Fermi surface.[7] With the form of the potential specified by Eqs. (9), the momentum sums in Eq. (8) can be immediately performed leaving only the time variable to consider. In what follows, we illustrate how the calculation proceeds for the specific case of s-wave scattering, and then discuss the generalization to the higher partial-wave components.

To determine the dominant threshold behavior we need only the asymptotic solution of Eq. (8) for large time intervals. Thus we nay use the following asymptotic expression[7] for G:

$$G(t)=-i\nu_0[\mathrm{P}(1/t+\tan\theta\,\delta(t)], \tag{10}$$

where we are measuring energies relative to the Fermi energy μ, P denotes the principal-value integral,

$$\nu_0=\nu(\mu)U^2(\mu), \tag{11a}$$

$\nu(\epsilon)$ is the density of states, $\tan\theta$ is related to the scattering phase shift at the Fermi energy $[\delta(\mu)=\delta]$ by

$$\tan\delta=\pi g/(1-\pi\tan\theta), \tag{11b}$$

and $g=\nu_0V_{l=0}$. Using the form of G given by Eq. (10) we find that Eq. (8) can be rewritten as (dropping the momentum subscripts as a notational convenience)

$$\Gamma(t_1,t_2,t_3,t_4;\tau_1,\tau_2)=\frac{G(t_1-t_4)F(t_2,t_3;\tau_1,\tau_2)-G(t_1-t_3)F(t_2,t_4;\tau_1,\tau_2)}{1-\pi g\tan\theta}$$
$$+\frac{\tan\delta}{\pi}\int_{\tau_1}^{\tau_2}dt\,\mathrm{P}\left(\frac{1}{t_1-t}\right)\Gamma(t,t_2,t_3,t_4;\tau_1,\tau_2). \tag{12}$$

Equation (12) is essentially the same integral equation faced by ND and is a member of a class of singular integral equations discussed at some length by Muskhelishvili.[18] We take the perturbative solution and obtain

$$\Gamma(t_1,t_2,t_3,t_4;\tau_1,\tau_2)=F(t_2,t_3;\tau_1,\tau_2)\varphi^a(t_1,t_4;\tau_1,\tau_2)-F(t_2,t_4;\tau_1,\tau_2)\varphi^a(t_1,t_3;\tau_1,\tau_2), \tag{13a}$$

where

$$\varphi^a(t_1, t_4; \tau_1, \tau_2) = \cos^2\delta\left[\frac{G(t_1-t_4)}{1-\pi g\tan\theta} - \frac{1}{\pi}\tan\delta\left(\frac{t_1-\tau_1}{\tau_2-t_1}\right)^{\delta/\pi}\int_{\tau_1}^{\tau_2} dt\left(\frac{\tau_2-t}{t-\tau_1}\right)^{\delta/\pi}\frac{G(t-t_4)}{1-\pi g\tan\theta}\,\mathrm{P}\left(\frac{1}{t-t_1}\right)\right] \quad (13b)$$

φ^a is simply the one-electron Green's function in the presence of the transient core-hole potential.[7] Since[9]

$$F(t_2, t_3; \tau_1, \tau_2) = g(\tau_1-\tau_2)\varphi^a(t_2, t_3; \tau_1, \tau_2), \quad (14a)$$

where

$$g(\tau_1-\tau_2) = \langle Ta(\tau_1)a^\dagger(\tau_2)\rangle, \quad (14b)$$

we see that Eq. (13) has a simple physical interpretation. Γ is simply the deep hole propagator multiplied by an antisymmetrized product of one-electron Green's functions in the presence of the core-hole potential. The generalization of the calculation to any number of final-state electrons is obvious. For the time ordering entering[7] Eq. (3),

$$g \sim e^{-i\Delta t}/(i\xi_0 t)^{2(\delta/\pi)^2}, \quad (15a)$$

$$\varphi_{k_2,k_3}{}^a \sim (e^{-i\mu t} i\nu_0)/t(i\xi_0 t)^{2\delta/\pi}\delta_{k_2,k_3}, \quad (15b)$$

where ξ_0 is a cutoff factor of the order of the conduction bandwidth and the effects of spin are included in determining the exponents in Eqs. (15). Hence, as far as its asymptotic behaivor goes

$$\langle C_{k_1}(t)C_{k_2}(t)a^\dagger(t)a(0)C_{k_3}{}^\dagger(0)C_{k_4}{}^\dagger(0)\rangle \sim \frac{e^{-i\Delta t}}{(i\xi_0 t)^{2(\delta^2/\pi^2)}}\frac{e^{-2i\mu t}(i\nu_0)^2}{t^2}(i\xi_0 t)^{4\delta/\pi}[\delta_{k_2,k_3}\delta_{k_1,k_4} - \delta_{k_2,k_4}\delta_{k_1,k_3}], \quad (16)$$

which gives the following divergent behavior of the cross section near threshold[19]:

$$d\sigma \sim \frac{\nu_0^2}{\xi_0}\left(\frac{\xi_0}{\epsilon_i - \Delta - 2\mu}\right)^\gamma, \quad (17a)$$

where the exponent characterizing the threshold behavior is given by

$$\gamma = (4\delta/\pi - 1) - 2(\delta/\pi)^2 = (2\delta/\pi - 1) + \alpha. \quad (17b)$$

In Eq. (17b) $\alpha = 2\delta/\pi - 2(\delta/\pi)^2$ is the exponent governing the divergence in the x-ray problem.[7] When we have predominantly s-wave scattering, the Friedel sum rule tells us that $\delta \simeq \frac{1}{2}\pi$. For this case $\gamma \simeq \alpha$ and the APS and the x-ray threshold behavior should be the same.

It is straightforward to generalize the preceding discussion to take into account the effects of higher partial waves. We expand the transition matrix element in terms of partial waves, obtaining

$$W(\vec{k}_i; \vec{k}_1, \vec{k}_2) = \sum_{(lm)(l'm')} W_{(lm)(l'm')}(\vec{k}_i; k_1, k_2)Y_{(lm)}(\Omega_{k_1})Y_{(l'm')}(\Omega_{k_2}). \quad (18)$$

As was the case in the x-ray problem, each angular momentum component (lm) defines an independent channel,[7] and thus we may directly take over the results of ND for g and φ^a. The result is

$$d\sigma \sim \sum_{(lm)(l'm')} |W_{(lm)(l'm')}|^2 \frac{\nu_0^2}{\xi_0}\left(\frac{\xi_0}{\epsilon_{k_i} - \Delta - 2\mu}\right)^{\gamma_{ll'}} \quad (19a)$$

where the exponent governing the threshold behavior of each term in Eq. (19a) is

$$\gamma_{ll'} = \frac{2(\delta_l + \delta_{l'})}{\pi} - 1 - 2\sum_{\bar{l}}(2\bar{l}+1)\left(\frac{\delta_{\bar{l}}}{\pi}\right)^2. \quad (19b)$$

An expression similar to Eq. (19a) has been found for the Auger emission threshold.[20]

In the case of an x-ray–induced transition there is a $\Delta l = \pm 1$ selection rule. This is not the case for an electron-induced transition where near threshold we expect conservation of angular momentum. Since we have a high-energy incident electron, it effectively has many angular momentum components and so there are probably no angular momentum selection rules involved in the APS transition. Hence

it is possible for a transition involving an s-state core level to have a divergent threshold behavior for APS and not for the x-ray case.

In conclusion we note that many simplifying physical assumptions are embodied in the model Hamiltonian and just as in the x-ray case,[7] additional effects may tend to smear the threshold behavior. However, the contrasts between APS and x-ray threshold behavior hopefully will encourage experimental tests of the predictions of the model.

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Direct Evidence for Disorder Effects on the Electronic Structure of Selenium

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The electron states of amorphous and single-crystal trigonal selenium were investigated by high-resolution photoemission spectroscopy. Structures due to a high density of states 0.2 eV below and 6.9 eV above the valence-band edge for crystalline Se are absent in the amorphous phase, but structures due to deeper valence-band density-of-states features remain. The results provide the first direct evidence for disorder effects on the Se valence and conduction bands and agree with calculations for amorphous Se using a pseudopotential formalism.

There have been a number of band-structure calculations for trigonal selenium, the most recent due to Sandrock[1] using the pseudopotential method. A pseudopotential formalism was also adopted recently by Kramer and co-workers[2-4] in their approach to the problem of calculating