Comments on core-hole lifetime effects in deep-level spectroscopies*

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The effects of a finite core-hole lifetime on deep-level spectra in solids have recently attracted much interest. We here present a solvable model which enables a detailed analysis of lifetime effects. For x-ray photoemission and x-ray absorption, our analysis gives support for the usual convolution approach where the infinite lifetime spectrum is convoluted with a Lorentzian lifetime broadening. In particular, we demonstrate the inadequacy of a recent intuitive approach which predicts a suppression of the phonon broadening for short core-hole lifetimes. This is done by testing the different theories on our model. We also show that a straightforward diagrammatic analysis leads to the same conclusion. Finally, we discuss the phonon response to the total process of core-hole creation and subsequent annihilation in an x-ray or Auger emission event. It is explained in some detail that the lifetime independence of the shake-up connected with the first step in this process is in no contradiction with the fact that the phonon system is uneffected by the *total* deep-level process in the limit of short core-hole lifetimes. We also analyze the process of $1s$ hole creation and subsequent Auger K-LL emission and give explicit expressions for this process.

I. INTRODUCTION

Deep-level spectra in solids are always affected by the finite lifetime of the created core hole. The finite lifetime is caused by radiative and Auger processes. In x-ray photoemission (XPS) and x-ray absorption (SXA), the conventional way[1,2] to describe the spectra is to first calculate a spectrum corresponding to an infinite core-hole lifetime, and then convolute this spectrum with a Lorentzian lifetime broadening.

The possible limitations of this convolution approach have recently attracted much interest, and intuitive arguments which seem to invalidate it for short core-hole lifetimes have been presented. The intuitive arguments may be stated in the following way: When the core-hole lifetime width is comparable or larger than a typical shake-up excitation energy, i.e., a phonon, plasmon, or particle-hole pair energy, then the corresponding shake-up broadening must be suppressed. The reason for this should be that in a dynamical picture the core hole has disappeared before the excitations that couple to the core hole have had sufficient time to respond. This point of view has been developed into a theory for phonon broadening suppression in XPS by Šunjić and Lucas[3] (SL).

The SL theory predicts different phonon broadenings for different core levels in a solid. Since their arguments are quite general, the arguments should also apply to the particle-hole excitations responsible for the well-known asymmetry of the XPS line shape in a metal.[1] In this case the SL theory predicts a lifetime-dependent orthogonality index α. However, such effects have not been observed so far, and available experimental data seem to favor the convolution approach.

A different theory for lifetime and phonon broadening of core levels in solids has been proposed by Minnhagen.[4] In Sec. III of the present paper we show that a simplifying assumption in Ref. 4 is not in accordance with results from an exactly solvable model which contains true lifetime effects. Here we argue that the possible interference effects between shake-up excitations and higher-order Auger and radiative decay processes (see Sec. II) are in general probably small because higher-order decay terms in practice should be of little importance.

We consider in the present paper the effects of a finite core-hole lifetime on deep-level spectra in solids and find strong support for the usual convolution approach for XPS and SXA spectra. (The lifetime effects connected with the subsequent decay of the core hole, on the other hand, are more involved.[2,5-10]) Lifetime effects have also been considered by Citrin and Hamann who recently have presented an illuminating discussion.[11] Some aspects have been given by Parratt[12] and by Hedin,[2] and a short discussion has been given by Langreth.[13] Our analysis confirms the view presented in these papers.

In Sec. II we make a diagrammatic analysis of the core-electron spectrum. We treat the shake-up connected with the core-hole creation to all orders, and the lifetime effects are accounted for by dressing the bare core-electron propagator with respect to the decay self-energy parts. This leads to the usual convolution approach, and thus the diagrams considered by SL are accounted for in the above convolution theory.

In Sec. III we consider a solvable model which describes the essential physics connected with a decaying core hole immersed in a medium in which shake-up excitations can be created. Our model can be viewed as a modification of the Fano model[14] in atomic physics. SL's intuitive arguments should apply to this model since the core-hole density tends exponentially to zero after an initial excitation. In spite of this we find that the convolution approach gives the correct answer.

In Sec. IV we limit our discussion to phonon shake-up. We analyze in detail the lattice response to the total deep-level process of hole creation in the uppermost core shell and the subsequent emission in which the core hole is annihilated. It is explained why there is no contradiction between the lifetime independence of the phonon broadening observed in the first step and the fact that the lattice cannot be affected by the total process in the limit of short core-hole lifetimes. In this latter limit the phonon wave function does not change during the total process, or equivalently, the phonons emitted in the first step are completely reabsorbed in the subsequent step of the process. We also carry out a similar analysis of the process of, e.g., 1*s* hole creation and a subsequent *K-LL* Auger emission in which two core holes are created.

Finally, Sec. V contains summary and conclusions.

II. DIAGRAMMATIC APPROACH

A. General considerations

In this section we analyze the core-electron spectrum from a diagrammatic point of view. Our basic philosophy is to divide the core-valence (and phonon) diagrams into two classes, lifetime and nonlifetime diagrams. The reason for doing so is obvious: The nonlifetime diagrams give rise to a large relaxation shift of the threshold [for the simple metals this is of the order 5–10 eV (Refs. 15–17)], and have a complicated structure from particle-hole, phonon, and plasmon shake-up.[1,2] The core-valence lifetime diagrams, i.e., the diagrams corresponding to Auger and radiative processes, on the other hand, give only a small self-energy contribution (the lifetime width of, e.g., the uppermost core level in a simple metal is generally believed to be of the order 10–50 meV), and should have a smooth energy variation. The remaining intracore lifetime diagrams, if any, depend only very weakly on the solid-state environment.

We treat the nonlifetime diagrams (including valence-valence, core-valence, and phonon interactions) to all orders by applying Langreth's formally exact solution.[18] In this way we obtain the exact core spectrum $B_\infty(\epsilon)$ corresponding to the infinite lifetime case. We then dress all diagrams that contribute to B_∞ by lifetime self-energy parts. This leads, under conditions stated in Sec. II B and which should normally be fulfilled, to the usual convolution result. This means that the core spectrum is given by

$$B(\epsilon)=\int \frac{d\epsilon'}{2\pi}\,\frac{\Gamma}{(\epsilon-\epsilon')^2+\frac{1}{4}\Gamma^2}\,B_\infty(\epsilon')\,, \tag{1}$$

when all interactions are included. The parameter Γ is a sum of imaginary parts of (Auger and radiative) lifetime diagrams and thus represents the core-hole decay rate. Our analysis applies with minor modifications[18] also to x-ray absorption and gives the corresponding convolution result.

The lifetime effects in emission spectra are more involved, and the finite core-hole lifetime must be accounted for already in the lowest-order theory.[5-10] In cases when the folding result [Eq. (1)] applies to the absorption step (corresponding to SXA or XPS), the core-hole lifetime is included in the emission theory by the parameter Γ defined in Eq. (1).[6,8,9]

Of course the folding result [Eq. (1)] is commonly used and can be arrived at using other arguments than ours. For instance, it follows from the Born-Oppenheimer approximation if we consider only lifetime broadening and phonon shake-up. Our arguments, however, are not based on this approximation. A failure of the Born-Oppenheimer approximation may cause interference between, e.g., phonon and singular edge effects (which are both described by B_∞), but this failure can invalidate Eq. (1) *only* when it also causes a rapid energy variation of the Auger and radiative decay diagrams.

B. Detailed analysis

We now carry out a formal analysis based on the physical ideas presented in Sec. II A. We regroup the terms in the total Hamiltonian H (which describes the solid with all interactions of interest) into an unperturbed part without lifetime effects, and a perturbation

$$H=H_0+\epsilon_c b^\dagger b+bb^\dagger V+H_{\text{phot}}+Tb+b^\dagger T^\dagger\,. \tag{2}$$

Here H_0 is the Hamiltonian for the valence electrons and phonons when all core levels are filled. The second term is the core-electron energy (b is the annihilation operator for the core level under consideration). V contains the additional terms in the valence electron and phonon Hamiltonian when the core level is empty (V thus contains the major part of the core-valence Coulomb interaction as discussed in Sec. II A), and H_{phot} is the free radiation field. The remaining terms in Eq. (2) describe the core-hole decay and include the Auger part of the core-valence interaction and the coupling to the radiation field (see, e.g., Ref. 9).

For simplicity we consider the case when the uppermost core level is excited since then only this particular core level is involved in the dynamics. The corresponding operator b is explicitly indicated for reasons of clarity. We do not consider effects connected with, e.g., the spin degeneracy of the core level. The extension to deeper core levels is in principle simple and will be briefly indicated in the following.

When extrinsic effects are neglected, the XPS spectrum is described by the core-electron Green's function.[1,2] It is evident from a physical point of view that the effects of a finite core-hole lifetime enter in the intrinsic rather than the extrinsic part of the XPS spectrum. Our following analysis will therefore be centered on the properties of the core-electron Green's function G.

We first consider the diagrammatic expansion of G without lifetime effects. The core lines can now be extracted from the diagrams, and in this way the diagrams can be summed exactly using the linked-cluster theorem.[18] An approximation G_∞ to G which includes the relaxation part $bb^\dagger V$ to all orders, but no lifetime effects, is then obtained as (we use units such that $\hbar = 1$)

$$G_\infty(t) = i\theta(-t)\exp[-i\epsilon_c t + C(t)] . \tag{3}$$

When the nonadiabatic valence-electron–phonon interaction is neglected, the phonon part of G_∞ is separable from the electronic part, i.e., the cumulant C is the sum of a phonon term C_{ph} and a purely electronic term. The phonon part of G_∞ has been obtained by Bergersen *et al.*[19] and by Hedin[2] within an harmonic, adiabatic approximation and corresponds to the diagrams in Fig. 1. This class of diagrams defines the independent boson model[1,2] which was used by SL as a starting point. Also the electronic part of G_∞ corresponding to the lowest order cumulant may be represented by the diagrams in Fig. 1. In this case the boson propagator represents the dynamically screened Coulomb interaction.[18,20] Our arguments, however, are not restricted to any particular approximations for G_∞ other than those imposed by Eq. (2).

We now turn to the decay part of H. Taken alone,

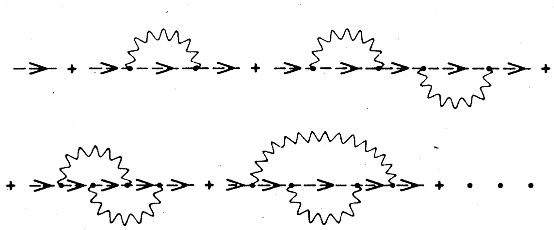

FIG. 1. Core-electron Green's function diagrams corresponding to the independent boson model. Dashed lines: bare Green's function; wiggly lines: the effective boson propagator.

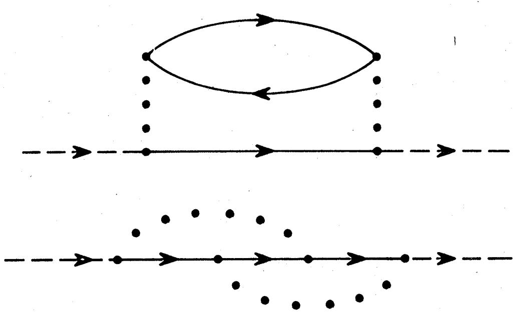

FIG. 2. Lowest-order C-VV Auger self-energy diagrams. The diagrams are of second order in the Auger part of the core-valence electron interaction and of order zero in the remaining interactions. Solid line: valence-electron Green's function; dotted line: bare Coulomb interaction; dashed line: core-electron Green's function. The core lines are not part of the self-energy diagrams.

the decay part gives a contribution $\Sigma_d(\omega)$ to the core-electron self-energy. For core levels with a binding energy $\lesssim 10$ keV, the Auger processes give the major contribution to Σ_d.[21] From purely phase space reasons it is expected that Σ_d varies on an core-electron energy scale and thus varies little over, e.g., the valence (or phonon) bandwidth.[13] This behavior may be verified for, e.g., the lowest order C-VV Auger diagrams shown in Fig. 2. $\Sigma_d(\omega)$ can then to a good approximation be replaced by a complex constant[22]

$$\Sigma_d(\epsilon_c + \Delta\epsilon_c + \tfrac{1}{2}i\Gamma) = \Delta\epsilon_c + \tfrac{1}{2}i\Gamma . \tag{4}$$

[Note that there is a misprint in SL's definition of the corresponding parameter Δ in their Eq. (2); see also Sec. III of the present paper.] In time space, Eq. (4) is equivalent to replacing the unperturbed Green's function

$$G_0(t) = i\theta(-t)e^{-i\epsilon_c t} , \tag{5}$$

by

$$G_d(t) = i\theta(-t)\exp[-i(\epsilon_c + \Delta\epsilon_c)t - \tfrac{1}{2}\Gamma |t|] . \tag{6}$$

Let us now consider both interactions together. An obvious approach is to dress all diagrams included in G_∞ with self-energy part Σ_d from the decay terms. This means that we leave out mixed vertices between the two interactions, i.e., mixed vertices between relaxation and decay processes. These vertices have been discussed by Minnhagen.[4] It may probably be assumed that the decay in most cases is well described in lowest (second) order in the decay terms.[21] In this lowest-order theory the above dressing is exact since the lowest-order relaxation-decay vertex diagrams are of fourth order in the decay interaction. (An example of a lowest-order Auger-C-VV-phonon vertex diagram is given in Fig. 3.) As described above, Σ_d in the

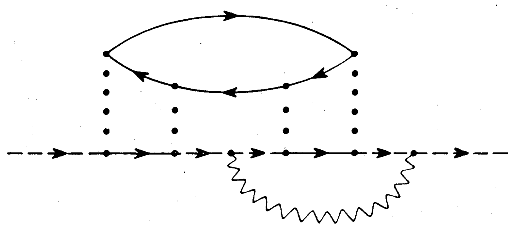

FIG. 3. Lowest-order Auger-C-VV-phonon vertex diagram. Solid line: valence electron Green's function; dotted line: Coulomb interaction; wiggly line: effective boson propagator; dashed line: core-electron Green's function.

dressed diagrams may be replaced by a complex constant, and going back to time space we find that the core lines can again be extracted. Thus the diagrams can still be summed exactly using the linked-cluster theorem. The result is simply

$$G(t)=i\theta(-t)e^{-\Gamma|t|/2}\exp[-i(\epsilon_c+\Delta\epsilon_c)t+C(t)] \qquad (7)$$

and corresponds to the convolution result in Eq. (1) if we absorb the radiative and Auger contribution $\Delta\epsilon_c$ to the core-level energy in ϵ_c. The shift $\Delta\epsilon_c$ should be of the same order as the lifetime width and thus be small. The crucial point in arriving at Eq. (7) is that (within the one-pole approximation for G_d) the dressed core function only propagates in one direction in time space and contains only one single (in this case complex) frequency, precisely as in the case without lifetime effects [compare Eqs. (5) and (6)].

Note that the independent boson model need not be invoked in the derivation of Eqs. (1) and (7). Specializing now to this latter approximation it is seen that we have summed the diagrams in Fig. 1 to all order in the core-hole boson interaction using core propagators that are dressed with respect to the decay part of H. By doing so, however, we have obtained the usual convolution result which is incompatible with SL's Eq. (1), which they claim corresponds to the same class of diagrams. It should also be noted that since SL describe the lifetime processes by a simple exponential decay their approach is limited to the one-pole approximation for G_d that we used above.

The relaxation part ($bb^\dagger V$) of H will in general influence the size of Γ since Σ_d includes (in the lowest-order theory) diagrams of lowest order in the decay part of H [the last two terms in Eq. (2)], but of all orders in the other interaction. This means that Σ_d includes the diagrams obtained by dressing the skeletons in Fig. 2 with respect to the interactions in H_0 and $bb^\dagger V$. Diagrams that can be viewed as dressed relaxation self-energy part are excluded from Σ_d since these diagrams are accounted for by dressing G_∞. Γ can also be obtained from the emission theories.[5-10] Owing to the interaction $bb^\dagger V$, the valence electrons will be strongly polarized at the core hole before it decays, and this will enhance the Auger rate. This point has been stressed by McMullen and Bergensen.[6] The calculation of Γ for the uppermost core level in a metal is a complex many-body problem due to the final-state interaction; the most recent estimate has been made by Glick and Hagen.[23] However, these solid-state effects on Σ_d do not invalidate our derivation of the line shape in Eq. (1), provided we dress G_∞ with the complete lifetime self-energy part Σ_d.

Deeper core holes will decay mainly through intracore transition. A $1s$ hole in Na or Al, for example, will decay mainly via K-LL Auger transitions.[21] It is easy to see that the arguments used in the derivation of Eq. (7) will apply for these levels also, provided Σ_d is smooth enough. The main difference is that Σ_d in this case is dominated by intracore transitions, but this does not change the basic structure of the diagrams for G in terms of lifetime and nonlifetime diagrams.

Finally, we draw attention to some anomalous cases where $\Sigma_d(\omega)$ is large and rapidly varying, such as in the $4s$-$4p$ region in Xe.[24] We are then completely outside the range when the simple picture of an exponentially decaying core hole applies, and the relaxation and decay parts in H must now be treated on the same basis.[24]

III. SOLVABLE MODEL

The lifetime broadening of core levels in a solid is caused by the Auger part of the Coulomb interaction and the coupling to the radiation field, and the exact solution to this full problem as defined in Eq. (2) is probably out of reach. In this section we consider a simple model which describes the same basic physics as the full deep-level problem. In the full problem, the states where the core level is empty are degenerate with a continuum of states where the core level is filled and a high-energy x-ray photon or Auger electron is present. The decay part of H will mix the empty core-level states with the continuum, and this is the cause of the lifetime broadening of the core level.

A simple model which contains this decay mechanism consists of a sharp fermion level immersed in a continuum. The model is very similar to the one used by Fano[14] for describing auto-ionizing atomic states. We also include a Bose field (representing, e.g., the phonons in the full problem) which couples to the sharp level. This model is summarized in the Hamiltonian

FIG. 4. "Core" Green's function self-energy diagram for the solvable model. Full line: continuum Green's function; dashed line: "core" electron Green's function.

$$H=\epsilon_c b^\dagger b+\sum_k \epsilon_k c_k^\dagger c_k+\omega a^\dagger a$$

$$+\alpha b b^\dagger(a+a^\dagger)+\sum_k A(\epsilon_k)(c_k^\dagger b+b^\dagger c_k)\,. \tag{8}$$

Here b, c_k, and a are annihilation operators for the sharp fermion level, the Fermi continuum, and the Bose field, respectively, and ϵ_c, ϵ_k, and ω are the corresponding mode energies. α and $A(\epsilon_k)$ are the coupling constants (A is taken real for simplicity).

When all $\{A(\epsilon_k)\}$ vanish we are back to the independent boson model which we discussed in Sec. II. We now temporarily put $\alpha=0$ and study the decay part of the model. The self-energy for the "core" Green's function

$$G(t)=-i\langle T[b(t)b^\dagger(0)]\rangle$$

is now given by the diagram in Fig. 4, and its explicit form is

$$\Sigma_d(\omega)\equiv\Delta(\omega)-\tfrac{1}{2}i\Gamma(\omega)\,\mathrm{sgn}(\omega-\epsilon_F)$$

$$=\int\frac{P}{\omega-\epsilon}A^2(\epsilon)\nu(\epsilon)\,d\epsilon$$

$$-\,i\pi\,\mathrm{sgn}(\omega-\epsilon_F)\nu(\omega)A^2(\omega)\,. \tag{9}$$

Here $\nu(\epsilon)$ is the fermion density of states,

$$\nu(\epsilon)=\sum_k\delta(\epsilon-\epsilon_k)\,,$$

and ϵ_F is the Fermi energy.

In order for $\Sigma_d(\omega)$ to be slowly varying in the vicinity of $\omega=\epsilon_c$, ϵ_F should be well separated from ϵ_c, and we choose ϵ_F well above ϵ_c in order to keep the similarity with the deep-level problem. By choosing $\nu(\epsilon)A^2(\epsilon)$ to be slowly varying over a large interval around ϵ_c, we can make $\Sigma_d(\omega)$ as slowly varying as desired. We may, for example, take

$$\nu(\epsilon)A^2(\epsilon)=\begin{cases}a^2 \text{ when } |\epsilon-\epsilon_c|<\Omega\,,\\ 0 \text{ otherwise}\,.\end{cases} \tag{10}$$

Σ_d is then given by

$$\Sigma_d(\omega)=a^2\left(\ln\left|\frac{\omega-\epsilon_c+\Omega}{\omega-\epsilon_c-\Omega}\right|-i\pi\,\mathrm{sgn}(\omega-\epsilon_F)\right.$$

$$\left.\times\,\theta(\omega-\epsilon_c+\Omega)\theta(\Omega+\epsilon_c-\omega)\right)\,. \tag{11}$$

In this particular example, Ω gives the scale of variation for $\Sigma_d(\omega)$, while as discussed in Sec. II this role is played by the core-level binding energy in the full problem. Since we can make $\Sigma_d(\omega)$ as slowly varying as we wish, we can obtain a "core-level" line shape (i.e., the spectral function for $G=G_d$)

$$B_d(\epsilon)=\frac{1}{\pi}\,|\mathrm{Im}G_d(\epsilon)|$$

$$=\frac{1}{2\pi}\frac{\Gamma(\epsilon)}{[\epsilon-\epsilon_c-\Delta(\epsilon)]^2+\frac{1}{4}\Gamma^2(\epsilon)} \tag{12}$$

arbitrarily close to a Lorentzian.

The above results may also be obtained by a direct diagonalization of the model Hamiltonian H in Eq. (8). In this approach we are looking for a unitary transformation

$$c_i=\sum_k u(\epsilon_k,\epsilon_i)d_k\,, \tag{13a}$$

$$b=\sum_k v(\epsilon_k)d_k \tag{13b}$$

to new fermion operators $\{d_k\}$. The requirement that H is diagonal in $\{d_k\}$ leads to the equations

$$(\epsilon'-\epsilon)u(\epsilon,\epsilon')+v(\epsilon)A(\epsilon')=0\,,$$

$$(\epsilon_c-\epsilon)\nu(\epsilon)+\int\nu(\epsilon')A(\epsilon')u(\epsilon,\epsilon')d\epsilon'=0\,.$$

These equations are identical with Eqs. (3a) and (3b) in Fano's paper,[14] so we just give the solution

$$u(\epsilon,\epsilon')=\frac{1}{\nu(\epsilon)}\left(\delta(\epsilon-\epsilon')\cos\delta(\epsilon)\right.$$

$$\left.+\frac{P}{\pi(\epsilon-\epsilon')}\frac{A(\epsilon')}{A(\epsilon)}\sin\delta(\epsilon)\right)\,, \tag{14a}$$

$$v(\epsilon)=\frac{1}{\nu(\epsilon)}\frac{\sin\delta(\epsilon)}{\pi A(\epsilon)}=\left(\frac{1}{\nu(\epsilon)}B_d(\epsilon)\right)^{1/2}\,. \tag{14b}$$

Here the "phase shift" $\delta(\epsilon)$ is given by

$$\tan\delta(\epsilon)=\pi\nu(\epsilon)A^2(\epsilon)/[\epsilon-\epsilon_c-\Delta(\epsilon)]$$

and varies rapidly from 0 to π around $\epsilon=\epsilon_c+\Delta\epsilon_c$, indicating the presence of one full resonance at this energy [$\Delta\epsilon_c$ is the shift defined as in Eq. (4)].

Since H is diagonal in the operators $\{d_k\}$, any correlation function can be written down directly in terms of the transformation coefficients in Eq. (13); e.g., the "core" Green's function is obtained as

$$G_d(t)=-i\sum_k v^2(\epsilon_k)\langle T[d_k(t)d_k^\dagger(0)]\rangle\,. \tag{15}$$

It is readily verified that this expression is equivalent to Eqs. (9) and (12) given above.

The core Green's function G_d has a decay in the present model since $\mathrm{Im}\Sigma_d\neq 0$, but this does not necessarily imply the presence of true lifetime effects. It has been pointed out[6,8,9] that in the full problem (see Sec. II) the particle-hole[25] and phonon[2,19,26] interactions in the relaxation term $bb^\dagger V$ will cause the core-electron Green's function to decay also when the core-hole lifetime is infinite. The true lifetime effects are connected with the decay of the *core hole* rather than the decay of G.[6,8,9] We therefore consider the time evolution of a core hole created at time zero, or more precisely the core-hole density at times $t>0$,

$$n_h(t)=\langle b^\dagger(0)b(t)b^\dagger(t)b(0)\rangle \tag{16}$$

after an initial excitation at $t=0$. The core-hole density is a special case of the four-point function

$$\Lambda(t_1,t_2,t_3,t_4)=\langle b^\dagger(t_1)b(t_2)b^\dagger(t_3)b(t_4)\rangle\ . \tag{17}$$

This can be calculated exactly in the present model [Eq. (8)] using, e.g., the transformation in Eq. (13), (or by Wick's theorem and analytic continuation), and the result is

$$\Lambda(t_1,t_2,t_3,t_4)=\langle b^\dagger(t_1)b(t_4)\rangle\langle b(t_2)b^\dagger(t_3)\rangle + \langle b^\dagger(t_1)b(t_2)\rangle\langle b^\dagger(t_3)b(t_4)\rangle\ . \tag{18}$$

Since

$$\langle b(t_2)b^\dagger(t_3)\rangle=\int_{\epsilon_F}^{\infty}d\epsilon B(\epsilon)\,e^{-i\epsilon(t_2-t_3)}\ ,$$

we can make the first term in Eq. (18) as small as we wish by choosing ϵ_F large enough. The asymptotic behavior of Λ is then

$$\Lambda(t_1,t_2,t_3,t_4)\sim\exp[\,i(\epsilon_c+\Delta\epsilon_c)(t_1-t_2+t_3-t_4) - \tfrac{1}{2}\Gamma|t_1-t_2| - \tfrac{1}{2}\Gamma|t_3-t_4|\,]\ ,$$

when t_1 and t_3 are sufficiently well separated from t_2 and t_4, respectively (see below). The cusps at $t_1=t_2$ and $t_3=t_4$ are artifacts of the asymptotic exponential approximation, and it is readily verified that the exact Λ fulfills the well-known analyticity conditions. With the specific choice of $A(\epsilon)$ in Eq. (10), the asymptotic approximation is valid when the time separations are large compared to $1/\Omega$. As special cases we find (in the asymptotic region)

$$n_h(t)=e^{-\Gamma t} \tag{19}$$

and

$$\langle T[b^\dagger(t_1)b(t_2)b^\dagger(t_2)b(0)]\rangle = \theta(t_1-t_2)\theta(t_2)\exp[\,i(\epsilon_c+\Delta\epsilon_c)t_1-\tfrac{1}{2}\Gamma t_1\,]\ . \tag{20}$$

Equation (19) shows that a created core hole is physically annihilated with a rate given by twice the imaginary part of Σ_d, and thus lifetime effects in a real sense are present in our model [Eq. (8)]. Equation (19) also shows that SL's arguments should apply to the model, since $n_h(t)$ has an exponential decay.

It is interesting that no lifetime decay with respect to t_2 is present in the time-ordered correlation in Eq. (20) in spite of the fact that the path-ordered correlation $n_h(t)$ decays exponentially. Since the correlation in Eq. (20) does not depend on t_2 in the asymptotic region, we also have asymptotically

$$\left\langle T\left(b^\dagger(t_1)\,\frac{d}{dt_2}\,[\,b(t_2)b^\dagger(t_2)\,]b(0)\right)\right\rangle=0\ . \tag{21}$$

When the decay is caused by Auger processes, higher-order Auger diagrams may possibly give contributions which are nonzero in the asymptotic region. However, the present model shows that deviations from Eq. (21) will not be directly related to the core-hole decay in a simple way, as, e.g., was suggested in Ref. 4, and corrections to Eq. (21) can only be of higher order in the decay interactions.

We now go back to the case when both couplings [α and $\{A(\epsilon_k)\}$] are nonzero. As in Sec. II we dress all diagrams in the independent boson model (see Fig. 1) with self-energy parts corresponding to core-hole decay (see Fig. 4). We then make the one-pole approximation [Eq. (6)] to the dressed core Green's function [as defined in Eqs. (9) and (15)], and arrive at Eq. (7), i.e., the usual convolution result. The difference from Sec. II is that by dressing the independent boson diagrams by self-energy parts corresponding to the "core-hole" decay we obtain the *exact* Green's function G in the present model [Eq. (8)].[27] The reason for this is that the decay part of H does not give rise to any vertex diagrams. The second step, namely the use of the one-pole approximation for the dressed Green's function, can be made as accurate as desired by a suitable choice of the parameters ϵ_F and $\{A(\epsilon_k)\}$ in our model. *We have thus proved that one can construct a model which contains true lifetime effects in the sense that* $n_h(t)\to 0$ *when* $t\to\infty$, *and for which the folding approximation as defined in Eqs.* (1) *and* (7) *hold with any prescribed degree of accuracy.* Therefore, we believe that our model gives conclusive arguments against the SL approach [their only real assumption about the lifetime processes is equivalent to our Eq. (19)]. Our model also shows the danger inherent in using classical arguments for describing a quantum-mechanical process.

A finite lifetime of the deep core hole is necessarily connected with fluctuations in the core-level occupation number. However, there need not be any appreciable fluctuations of the occupation number in the ground state. This comes out very clearly in the present model [Eq. (8)]. Let us choose the decay coupling as in Eq. (10). We then have three independent parameters in the decay part of H: ϵ_F, Ω, and a^2. ϵ_F controls the core-level fluctuations in the ground state, and these fluctuations can be made negligible by a suitable choice of ϵ_F; the core electron can then only propagate in one direction in time space. Ω controls the accuracy of the Lorentzian approximation, and the core-hole lifetime is determined by a^2. Thus, a short core-hole lifetime is not incompatible with small ground state fluctuations. The same holds for the full problem where the smallness of the ground state fluctuations [as well as the scale of variation of $\Sigma_d(\omega)$] are determined by the core-level binding energy, while the core-hole lifetime depends on the size of the decay interaction.

IV. ASPECTS ON THE TOTAL PROCESS OF CORE-HOLE CREATION AND SUBSEQUENT EMISSION

So far we have discussed the XPS experiment and found that, e.g., the phonon broadening of the XPS line should to a good approximation be independent of the core-hole lifetime. In view of this it is interesting to ask for the phonon state when the core hole has disappeared again. This information could in principle be obtained from an experiment where the emitted XPS electron and the subsequently emitted Auger electron or x-ray photon are measured in coincidence. The number of shake-up phonons remaining after the total process is obtained as the number of phonons excited when the core hole is created plus the number of phonons excited when it disappears again. (The number of created phonons in the last step is not necessarily positive since phonons may also be reabsorbed.) One of the authors (C.-O.A.) has recently developed a theory on phonon effects in x-ray emission[9] from which the phonon broadening connected with the total process can be obtained. Phonon effects in x-ray emission have also been considered by Mahan.[10] The fundamentals of this theory can be viewed as a solid-state version of the well-known theory of resonance fluorescence.[28] It is thus based on a dressing of diagrams with decay self-energy parts in a similar way as was outlined in Sec. II. The phonon broadening observed in the total process of core-level excitation and subsequent emission can according to this theory be written as[9]

$$D_{\text{tot}}(\Omega) = 2\pi \int_0^\infty dt\, \Gamma e^{-\Gamma t} \sum_{i,f} \rho_i \left| \langle f | b^\dagger(t) b(0) | i \rangle \right|^2 \times \delta(\Omega + E_i - E_f) . \quad (22)$$

Here $|i\rangle$ and $|f\rangle$ are initial and final phonon states, respectively, and ρ_i is the statistical probability that the crystal is in state $|i\rangle$ before the deep-level process. (For simplicity the electronic degrees of freedom are suppressed, compared Ref. 9.) We may interpret Eq. (22) in the following way: The phonons experience a sudden switch on of the core-hole potential at time zero, and subsequently a sudden switch off at a later time t. The sudden switch on and switch off will cause transitions to other phonon states. The Golden Rule gives the probability per unit time that the phonons will end up in a final state which differs by the energy Ω from that of the initial state. This basic transition probability is then multiplied with the probability ($\Gamma \exp[-\Gamma t]$) that the switch off occurs at time t, i.e., the probability that the core hole survives to the time t. Finally the total probability is obtained by integrating over all possible times t.

The variance of the broadening function D_{tot} is given by[9]

$$\sigma^2 = 2\Delta^2(T) + \Delta_\Gamma^2 - \Delta_{12}^2(\Gamma, T) . \quad (23)$$

Here $\Delta(T)$ is the phonon broadening observed in the first step[2,19,26]

$$\Delta^2(T) = \int_0^\infty d\omega\, \omega^2 g(\omega)[2n(\beta\omega) + 1] , \quad (24)$$

Δ_Γ is the additional, lifetime-dependent contribution to the phonon broadening observed in the subsequent emission

$$\Delta_\Gamma^2 = 2 \int_0^\infty d\omega\, d\omega'\, \omega\omega' g(\omega) g(\omega') \times \left(\frac{\Gamma^2}{(\omega+\omega')^2 + \Gamma^2} + \frac{\Gamma^2}{(\omega-\omega')^2 + \Gamma^2} - \frac{2\Gamma^4}{(\omega^2+\Gamma^2)(\omega'^2+\Gamma^2)} \right) , \quad (25)$$

and Δ_{12} is a cross term

$$\Delta_{12}^2(\Gamma, T) = 2 \int_0^\infty d\omega\, \omega^2 g(\omega)[2n(\beta\omega) + 1] \frac{\Gamma^2}{\omega^2 + \Gamma^2} . \quad (26)$$

In these formulas Γ is the lifetime full width at half-maximum, $g(\omega)$ is the phonon strength function introduced in Refs. 2, 19, and 26 (we follow the notation in Refs. 2, 9, and 26), and $n(\beta\omega)$ is the Bose function at temperature T ($\beta = 1/kT$). For a single boson mode, as in Sec. III, we have $g(\omega) = (\alpha^2/\omega_0^2)\delta(\omega - \omega_0)$, α being the coupling constant, while in the general case $g(\omega)$ involves a summation over the continuous phonon spectrum.[2,19,26]

The interference between the switch on and switch off processes is a consequence of the finite core-hole lifetime and will disappear only in the limit $\Gamma \to 0$, as is seen from Δ_Γ^2 and Δ_{12}^2 in Eqs. (25) and

(26). In this limit the phonon width is $\sqrt{2}\Delta(T)$, and is thus the same as if the phonon system had independently first been subject to a sudden potential change V_{ph}, and then, after a local equilibrium has been obtained, a sudden potential change $-V_{\text{ph}}$. [V_{ph} is the core-hole potential seen by the phonons, i.e., the phonon part of the relaxation term in Eq. (2).] The interference is zero since the excitations created in the switch on process have spatially moved away from the core hole before it disappears. Thus, as seen from Eq. (25) this is not the case for a dispersionless single-frequency distribution $g(\omega)=n_0\delta(\omega-\omega_0)$, since in this case the shake-up phonons from the first step stay at the core hole forever, and we have $\Delta_\Gamma^2 \to 2n_0^2\omega_0^2>0$ when $\Gamma\to 0$.

In the limit $\Gamma\to\infty$, the broadening σ for the total process must be zero. The reason for this is that the lattice has no time to respond to the total deep-level process, and we must end up in the initial phonon state. It is seen from Eqs. (23)–(26) that the theory in Ref. 9 gives the correct value $\sigma=0$ in the limit $\Gamma\to\infty$, in spite of the fact that it gives a lifetime-independent phonon width $[\Delta(T)]$ to the core level as observed in the first step, in accordance with the analysis in Secs. II and III. It is also seen from Eqs. (23)–(26) that the limiting case $\Gamma\to\infty$ is approached when Γ is large compared to a typical phonon energy. The phonon broadening may still be comparable or larger than Γ since in many cases several shake-up phonons are involved.

At first sight it is somewhat surprising that *on one hand* the phonon broadening corresponding to the total deep-level process including the core-hole annihilation is completely suppressed in the limit $\Gamma\to\infty$, and yet on *the other hand* the phonon broadening corresponding to the creation of the core hole is independent of Γ. One may wonder how the shake-up phonons responsible for the XPS phonon broadening can be brought into existence when the core hole is present only a very short time.

From a quantum-mechanical point of view the answer is that an excitation spectrum is always related to the Hamiltonian relevant to the measurement. In the XPS case the observed phonon broadening corresponds to lattice excitations measured with respect to the Hamiltonian H_1 which includes the core-hole potential V_{ph} seen by the phonons. In the XPS case we are thus analyzing the ground state (or more generally the equilibrium ensemble) corresponding to a *filled* core level with a Hamiltonian H_1 corresponding to an *unfilled* core level. This leads to a lifetime-independent phonon broadening[2,29]

$$\Delta^2(T)=\langle V_{\text{ph}}^2\rangle-\langle V_{\text{ph}}\rangle^2\,, \tag{27}$$

where the averages are taken over the no core-hole equilibrium ensemble. [In the case of harmonic phonons with a linear core-hole coupling, Eqs. (27) and (24) are equivalent.] The phonon broadening σ^2 for the total process, on the other hand, corresponds to shake-up excitations measured with respect to the *no-core-hole Hamiltonian* H_0, and this broadening is indeed dynamically suppressed for short core-hole lifetimes. The SL theory does not distinguish between the above two pictures, and in our opinion this is one reason why it is not satisfactory.

From a classical point of view the x-ray photoelectron energy will depend on the instantaneous positions $\{\vec{R}_i\}$ of the ions at the moment of core-hole creation. Let the potential energy for the ion configuration $\{\vec{R}_i\}$ be $V_1(\vec{R}_i)$ and $V_0(\vec{R}_i)$ with and without the core hole, respectively ($V_{\text{ph}}=V_1-V_0$). The energy given to the ions in the particular configuration $\{\vec{R}_i\}$ will then be

$$\Delta E_{\text{XPS}}(\vec{R}_i)=V_1(\vec{R}_i)-V_0(\vec{R}_i)=V_{\text{ph}}(\vec{R}_i) \tag{28}$$

in the first step. Each configuration $\{\vec{R}_i\}$ has a certain probability $p(\vec{R}_i)$ to occur, and the statistical spread in the ion positions gives a phonon broadening with a width

$$\Delta^2=\sum p(\vec{R}_i)V_{\text{ph}}^2(\vec{R}_i)-\Big(\sum p(\vec{R}_i)V_{\text{ph}}(\vec{R}_i)\Big)^2\,,$$

which is equivalent to Eq. (27) if quantum-mechanical probabilities $p(R_i)$ are used. If the ions were at rest there would be no phonon broadening. Of course, the ions will always vibrate due to zero-point and temperature fluctuations. Thus, from a classical point of view the phonon broadening in XPS is due to the ion vibrations at the moment of core-hole creation, in accordance with the ideas presented already by Parratt.[12] Also in this context compare the illuminating discussion by Citrin and Hamann.[11] In the subsequent core-hole annihilation, the energy taken from the ions will depend on the ion configuration $\{R_i'\}$ at a later time, in similar way as in Eq. (28). Therefore, the energy given to the ions in the total process is

$$\Delta E_{\text{tot}}(\vec{R}_i,\vec{R}_i')=V_{\text{ph}}(\vec{R}_i)-V_{\text{ph}}(\vec{R}_i')\,,$$

and this energy will evidently tend to zero when $\Gamma\to\infty$ since the two ion configurations $\{\vec{R}_i\}$ and $\{\vec{R}_i'\}$ are then the same.

For deeper core levels, the dominating decay mechanism is usually intracore Auger transitions in which the core hole in one core shell decays into two core holes in another shell.[21] A $1s$ hole in Na, for example, decays predominantly via a K-$L_{2,3}L_{2,3}$ transition.[21] The SL intuitive arguments should here give a lifetime dependent XPS broadening *enhancement*, since the phonon coupling increases when the initial core hole decays. However, as we showed in the previous sections, the shake-up created in the initial excitation process is (to a good approximation) *independent* of the core-hole lifetime also in this case. This applies in particular to the XPS phonon broadening, which is still given by Eq. (27).

In an appendix we give the extension of the theory in Ref. 9 necessary to describe, e.g., an Auger K-LL process. Also in this case the phonon broadening observed in the first step of core-hole creation is $\Delta(T)$, and the phonon broadening in the subsequent Auger K-LL emission is $[\Delta^2(T)+\Delta_\Gamma^2]^{1/2}$. The broadening connected with the total process of core-hole creation and subsequent K-LL emission is described by a relation analogous to Eq. (22). The only difference is that in this case the final states refer to the Hamiltonian H_2 which includes the two-core-hole potential V_2 seen by the phonons. The energy spread (standard deviation) of the phonons after the K-LL emission is σ_{KLL}, where

$$\sigma_{KLL}^2=2\Delta^2(T)+\Delta_\Gamma^2+\Delta_{12}^2(\Gamma,T). \quad (29)$$

The difference from Eq. (23), which applies to the uppermost core level, is that the cross term Δ_{12}^2 enters with the opposite sign.

In the limit $\Gamma\to 0$ we have as before complete relaxation, and thus $\sigma_{KLL}^2=2\Delta^2(T)$. In practice, however, the deeper core levels have an appreciable lifetime width.

In the limit $\Gamma\to\infty$, the lattice has no time to respond to the $1s$ hole before the Auger emission takes place, and σ_{KLL} is now the same as if the lattice had been subject to a sudden potential change V_2-V_0. We are thus analyzing the no-core-hole equilibrium ensemble using the two-core-hole Hamiltonian H_2, and the corresponding phonon broadening is $\sigma_{KLL}^2=\langle V_{20}^2\rangle-\langle V_{20}\rangle^2$. When the core-hole coupling is linear ($V_{20}=2V_{\mathrm{ph}}$), the above expression is equivalent to the $\Gamma\to\infty$ limit of Eq. (29). In the first step of core-hole creation, on the other hand, we are analyzing the same no-core-hole ensemble using the *one-core-hole Hamiltonian* H_1, and the corresponding phonon broadening is still given by Eq. (27) (for all values of Γ). From Eq. (A9) it is readily verified that the phonon broadening observed in the second step of Auger K-LL emission is ($V_{21}=V_2-V_1$)

$$\Delta_{KLL}^2(\Gamma=\infty)=\langle V_{21}^2\rangle-\langle V_{21}\rangle^2 .$$

This is the same as the XPS width Δ [Eq. (27)] if the core-hole coupling is linear. Thus, if $\Delta_{KLL}\neq\Delta$ this may be due either to a nonlinear core-hole coupling or to incomplete relaxation effects, i.e., deviations from the limit $\Gamma\to\infty$.

V. CONCLUSIONS

We have analyzed the effects of a finite core-hole lifetime on deep-level spectra in solids. We have found that the usual convolution approach in which the infinite lifetime spectrum is convoluted with a lifetime broadening should in general give a good approximation of XPS and x-ray absorption (SXA) spectra. It is shown that the arguments for a phonon broadening suppression do not apply to the XPS experiment. In particular we present a solvable model which provides conclusive arguments in favor of the convolution approach. We infer from this that a description of the absorption step, as measured in XPS or SXA, and which goes beyond the convolution approximation must necessarily involve a more detailed description of the decay processes.

We also discuss the lifetime effects in connection with the total process of creation and subsequent annihilation of the core hole. We illustrate in detail why there is no contradiction inherent in the fact that the XPS phonon broadening is lifetime independent and yet the lattice is completely unaffected by the deep-level process in the limit of short core-hole lifetimes. We have extended the analysis to include deeper core levels, which decay mainly via intracore Auger transitions.

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APPENDIX

In this appendix we give the modifications of the theory in Ref. 9 required to describe the phonon effects in Auger K-LL emission. The process of core-hole creation and subsequent emission is described by a four-time correlation function[8,9]

$$\hat{\Lambda}(t_1,t_2,t_3,t_4)=\langle T_1^\dagger(t_1)T_2(t_2)T_2^\dagger(t_3)T_1(t_4)\rangle . \quad (A1)$$

In the case of, e.g., Auger K-$L_{2,3}L_{2,2}$ emission, T_1 is the transition operator for the first step in which the $1s$ hole is created, and T_2 the transition operator for the K-LL emission in which the $1s$ hole is filled and two $2p$ holes are created. As in Ref. 9 we exclude the nonadiabatic valence-electron phonon interaction; $\hat{\Lambda}$ then factorizes in an electronic part and a phonon part $\hat{\Lambda}_{KLL}$.

The phonon part $\hat{\Lambda}_{KLL}$ describes the phonons under the influence of the different number of core holes involved in the process, and is in the present case given by

$$\hat{\Lambda}_{KLL}(t_1,t_2,t_3,t_4)=\langle U_0^\dagger(t_1)U_1(t_1-t_2)U_2\ (t_2-t_3)U_1(t_3-t_4)\ U_0(t_4)\rangle . \quad (A2)$$

Here $U_n(t)=e^{-iH_nt}$ is the time evolution operator for the phonons under the influence of n core holes.

We now specialize to the case of harmonic phonons, i.e.,

$$H_0=\sum_n \omega_n a_n^\dagger a_n ,$$

and a linear core-hole coupling $V\equiv V_{\rm ph}$ which we assume to be the same for different types of core holes. We then have $H_n=H_0+nV$, where

$$V=\sum_n B_n(a_n+a_n^\dagger) .$$

H_n is diagonalized by the nth power of the unitary transformation[18]

$$S=\exp\left[\sum_n\left(\frac{B_n}{\omega_n}(a_n-a_n^\dagger)\right)\right] ,$$

and from an analysis analogous to the one given in Ref. 9, we find

$$\begin{aligned}\hat{\Lambda}_{KLL}&(t_1,t_2,t_3,t_4)\\ &=\exp[i\epsilon_0(t_1+3t_2-3t_3-t_4)]\,\langle S^\dagger(t_1)S^\dagger(t_2)S(t_3)S(t_4)\rangle ,\end{aligned}$$

and finally,

$$\begin{aligned}\hat{\Lambda}_{KLL}(t_1,t_2,t_3,t_4)=\exp[&i\epsilon_0(t_1+3t_2-3t_3-t_4)+f(t_4-t_1)\\ &+f(t_3-t_2)-f(t_2-t_1)+f(t_4-t_2)\\ &+f(t_3-t_1)-f(t_4-t_3)] .\end{aligned} \tag{A3}$$

Here $f(t)$ is given by

$$\begin{aligned}f(t)=\int_0^\infty & d\omega\, g(\omega)\\ &\times\{[2n(\beta\,\omega)+1](\cos\omega t-1)+i\sin\omega t\} ,\end{aligned}$$

and

$$\epsilon_0=\int \omega g(\omega)\,d\omega .$$

The probability for 1s-level excitation and subsequent K-LL emission is obtained by folding the electronic parts of the excitation and K-LL emission probabilities by the phonon and lifetime-broadening function

$$\begin{aligned}\Lambda_{KLL}&(\omega_1,\omega_2;\Gamma)\\ &=\int_{-\infty}^{\infty}d\tau\int_0^\infty dt\,dt'\,\hat{\Lambda}_{KLL}(\tau,t+\tau,t',0)\\ &\qquad\times\exp[\,i(\omega_1-\omega_2)\tau-i\omega_2(t-t')\\ &\qquad-\tfrac{1}{2}\Gamma(t+t')] .\end{aligned} \tag{A4}$$

Here ω_1 and ω_2 correspond to the excitation and emission steps, respectively, and Γ is the 1s lifetime full width at half-maximum from all available radiative and Auger channels. No effects of the finite 2p hole lifetime are included above. Considerations analogous to those in Sec. II shows that the only effect of the finite 2p-hole lifetime on the K-$L_{2,3}L_{2,3}$ spectrum should be an additional, Lorentzian broadening of the emission spectrum given by Eq. (A4).

Λ_{KLL} is non-negative and normalized to $(2\pi)^2/\Gamma$. As in Ref. 9 it is readily verified that the phonon and lifetime broadening function for the initial excitation

$$\frac{2\pi}{\Gamma}\int \Lambda_{KLL}(\omega,\omega_2;\Gamma)\,d\omega_2$$

is the same as the broadening from the theory in Refs. 2, 19, and 29, and thus given by Eq. (27).

The broadening in the total process of 1s-hole creation and subsequent K-LL emission is described by the variable $\Omega=\omega_1-\omega_2$, and the corresponding broadening function is

$$D_{KLL}^{\rm tot}(\Omega,\Gamma)=\Gamma\int\frac{d\omega_2}{2\pi}\,\Lambda_{KLL}(\Omega+\omega_2,\omega_2;\Gamma) . \tag{A5}$$

The above expression may be rewritten in a form similar to Eq. (22). The moments $\langle\Omega^n\rangle_\Gamma$ of $D_{KLL}^{\rm tot}$ are obtained from the appropriate time derivatives of Λ_{KLL}. In particular, the mean energy that is absorbed by the phonon system is

$$\langle\Omega\rangle_\Gamma=-2\epsilon_0+2\int_0^\infty d\omega\,\omega g(\omega)\,\frac{\Gamma^2}{\omega^2+\Gamma^2} \tag{A6}$$

and is thus negative, contrary to the case of x-ray emission from the uppermost core level. The energy spread σ_{KLL} is given by Eq. (29).

The phonon and lifetime broadening in the emission step is obtained from Eq. (A4) by integrating over ω_1 (compare Ref. 9). By splitting off a Lorentzian we obtain a lifetime-dependent phonon broadening D_{KLL} for the emission step. The no-phonon line in emission appears at the energy $3\epsilon_0$, as required in a linear coupling theory for K-LL emission. The first moment of D_{KLL} is

$$\langle\omega\rangle_\Gamma=2\epsilon_0-\int_0^\infty d\omega\,\omega g(\omega)\,\frac{\Gamma^2}{\omega^2+\Gamma^2} , \tag{A7}$$

and the energy spread is

$$\langle\omega^2\rangle_\Gamma-\langle\omega\rangle_\Gamma^2=\Delta^2(T)+\Delta_\Gamma^2 , \tag{A8}$$

where $\Delta(T)$ and Δ_Γ are given in Eqs. (24) and (25). In the limit $\Gamma\to\infty$, D_{KLL} is the Fourier transform of

$$\begin{aligned}\hat{D}_{KLL}(t,\infty)&=\hat{\Lambda}_{KLL}(0,t,0,0)\\ &=\langle U_1^\dagger(t)U_2(t)\rangle ,\end{aligned} \tag{A9}$$

and is equal to the absorption broadening function within a linear harmonic approximation.

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