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Theory of the Auger effect in solids: Plasmon effects in electron spectroscopies of valence states

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A theory of XPS and AES spectra of valence states of atoms in solids is proposed that allows for hole-plasmon interactions in the final state. The model Hamiltonian includes an interaction term between plasmon field and the resonant valence atomic orbital. The exact solution of the model is found for any shape of the unperturbed local density of states. Plasmon effects show up not only as plasmon satellites, but also as a very significant change in the shape of the main peak. The coupling to the boson field tends to localize the valence hole. Eventually, if the coupling is strong enough compared to the level width, sharp resonances appear in the spectra due to localized, small-polaron-like states. The degree of validity of a Born-Oppenheimer approximation is assessed by comparison with the present exact results.

I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) as applied to the investigation of valence states in solids show promise of becoming the key techniques for studying chemical bonds at surfaces in a near future. XPS and AES valence spectra are related to the local density of states and can tell us a great deal about bond strength, polarization, and symmetry, and about the geometrical arrangement of atoms belonging to or chemisorbed onto the solid.

While much experimental progress has been achieved recently and excellent data are now available in the literature, severe theoretical problems remain to be solved before the usefulness of such techniques can be substantially explored. Problems involving valence states are obviously much more difficult dynamical problems than those involving core states. Core holes in solids behave essentially as structureless, "external" potential sources acting on the elementary excitations of the system. Transient effects following the sudden switching of the core potential are now fully understood in terms of Mahan,[1] Nozières–De Dominicis[2] asymmetry (in the case of metals), and plasmon satellites. The problem of a structureless deep hole interacting with a sharp boson excitation field has been solved exactly by Langreth[3] several years ago. Valence holes, on the other hand, are dynamical potential sources that can react to the field of plasmon and other excitations by changing their wave functions. Since we are interested in obtaining the unperturbed valence density of states from the spectra, we are faced with the coupled transient problem of conduction-electron states and collective excitations relaxing together.

In the present paper I address the problem of electron spectroscopies of valence states in the presence of a long-wavelength plasmon excitation field. As Langreth[4] pointed out, long-wavelength plasmons are the only ones that behave as reasonably sharp excitations, while plasmons with larger wave vectors q tend to merge into the particle-hole continuum, and do not produce any prominent structure in the spectra. Particle-hole excitations will not be included in the present treatment for the sake of simplicity. Nevertheless, our procedure is quite meaningful even in the case of metals, when particle-hole shake-up is very extensive. The reason that it is permissible to deal with plasmons separately is that we can use the Born-Oppenheimer principle in reverse,[4] treating the plasmon coordinates as the "fast" variables, and the electron-hole coordinates as "slow" variables. Presumably, the particle-hole excitations will perturb our results (in the case of metals) by causing an extra relaxation shift and by making the line shapes somewhat more asymmetric. This effect could be included as a second stage in our treatment, by perturbation theory, or perhaps by extending Doniach's pseudoharmonic approximation.[5]

The (initially occupied) resonant valence orbital under investigation might be an impurity state, or a localized d state in a transition metal. It will be described within the familiar Anderson formalism[6] in terms of a localized atomic orbital $\varphi_a(\vec{r})$ and a set of (orthogonalized) band states $\varphi_k(\vec{r})$. In order to set up a reasonable model Hamiltonian for the coupled valence hole-plasmon system, we must assess the relative orders of magnitude of the various hole-plasmon interaction vertices. First, consider the vertex

$$I_{aaq} \sim \int d^3r \, |\varphi_a(\vec{r})|^2 V_q(\vec{r}) ,$$

where $V_q(\vec{r})$ is the potential associated with a plasmon having wave vector q. Clearly, this is a very important term, since plasmons interact strongly with a localized hole charge distribution, and we shall include it in the Hamiltonian. Next, there are vertices like

$$I_{akq} \sim \int d^3r\, \varphi_a(\vec{r})^* \varphi_k(\vec{r}) V_q(\vec{r})\,.$$

Since the potential of a long-wavelength plasmon is almost constant over an atomic wave function, these terms (of order $O(|q|)$ are negligible. Finally, terms like

$$I_{kk'q} \sim \int d^3r\, \varphi_k^*(\vec{r}) \varphi_{k'}(\vec{r}) V_q(\vec{r})$$

represent conduction electron-plasmon scattering. Long-wavelength plasmons are rather sharp excitations just because they do not interact with the Bloch states too strongly. Actually, our wavefunctions $\varphi_k(\vec{r})$ should represent modified Bloch states, orthogonalized to $\varphi_a(\vec{r})$, and the kinetic restrictions preventing scattering should be partially relaxed. However, since $I_{kk'q} = O(|q|)$, such vertices are still negligible in our problem.

Thus, we are led to the rather appealing physical picture of the valence hole being strongly screened by the plasmons as long as it remains localized at the atomic site where it was created, whereas a delocalized hole is effectively decoupled from the plasmons. Such description should be good, at least qualitatively, to deal with several transient problems involving boson excitations other than plasmons. It should be useful also in the theory of electron spectroscopies of chemisorbed molecules. In the latter case, the boson field should be identified with the surface-plasmon field which is largely responsible for the image potential,[7] and the present mathematical framework should be essentially adequate. The only point of real difference is that when dealing with surface plasmons one must be careful with the vertices I_{akq} that may not, generally speaking, be negligible.

From the mathematical viewpoint, the "localized" nature of the coupling term in the Hamiltonian leads to an exactly soluble problem. The method used is an extended version of the procedure by which I found the exact solution of the Auger XVV problem.[8] The special form of the coupling term is most directly exploited in looking for an algebraic equation for the appropriate expectation value of the nth power of the Hamiltonian.

In Sec. II, I demonstrate the simplicity of my mathematical procedure by working out Langreth's[3] core-hole problem. Section III is devoted to the formal theory of photoemission from a valence level. In Sec. IV the theory is extended to Auger transitions involving one final-state valence hole. The physical implications of the results are discussed in Sec. V. General conclusions are drawn in Sec. VI.

II. PHOTOEMISSION FROM A DEEP CORE LEVEL

As an introduction to the concepts and methods of Secs. III–VI we shall review the core-hole problem and solve it by a new technique. The model is the same as proposed by Lundquist and later solved exactly by Langreth.[3] Its simplicity lies in the fact that the deep hole has no internal degrees of freedom and only acts as an external perturbation on the boson excitation field of the solid. Thus, before the hole is created, the model Hamiltonian is just a free-boson Hamiltonian. In obvious notation,

$$H_0 = \sum_q \omega_q a_q^\dagger a_q\,, \tag{1}$$

and the system is in the ground state $|g\rangle$ with no bosons excited. After the sudden creation of the deep hole, the Hamiltonian becomes $H = H_0 + H_1$, with

$$H_1 = \sum_q g_q (a_q^\dagger + a_q)\,. \tag{2}$$

The density of states that we observe in the photoemission spectrum is

$$D(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle g | e^{-iHt} | g \rangle\,. \tag{3}$$

The Fourier transform $D(t)$ can be rewritten in form

$$D(t) = \sum_{n=0}^{\infty} \frac{(-it)^n}{n!} h_n\,,$$

with (4)

$$h_n = \langle g | H^n | g \rangle\,.$$

We can assume, without loss of generality, that $H_0 |g\rangle = 0$. Then clearly

$$h_n = \sum_q g_q \langle a_q H^{n-1} \rangle\,, \quad n > 0\,. \tag{5}$$

This is readily calculated because our Hamiltonian is such that

$$a_q H^k = (H + \omega_q)^k a_q + g_q \sum_{s=0}^{k-1} (H + \omega_q)^{k-s-1} H^s\,.$$

Therefore,

$$\langle a_q H^k \rangle = (g_q / \omega_q) [\langle (H + \omega_q)^k \rangle - \langle H^k \rangle]\,.$$

By summing the Taylor series, Eq. (4), we obtain

$$D(t)=1-i\sum_q \frac{g_q^2}{\omega_q}\int_0^t dt'\,D(t')(e^{-i\omega_q t'}-1)\,.$$

This equation is elementary and its solution

$$D(t)=\exp\left(-\sum_q \frac{g_q^2}{\omega_q^2}+\sum_q \frac{g_q^2}{\omega_q^2}(e^{-i\omega_q t}+i\omega_q t)\right) \tag{6}$$

coincides with Langreth's result. Our technique is quite simple and lends itself to generalization to cases in which the hole is free to react to the boson excitations, as we show below.

III. PHOTOEMISSION FROM A VALENCE LEVEL

The model Hamiltonian for the noninteracting hole-boson system may be specified as follows:

$$H_0=\epsilon_a C_a^\dagger C_a+\sum_k \epsilon_k C_k^\dagger C_k+\sum_k V_{ak}(C_a^\dagger C_k+C_k^\dagger C_a)+\sum_q \omega_q a_q^\dagger a_q\,. \tag{7}$$

The first three terms of H_0 make up the well-known Anderson model, with ϵ_a, $C_a^\dagger$ denoting the atomic energy level and hole-creation operator, respectively, while ϵ_k and C_k refer to the band states. Thus, the V_{ak} are the familiar hopping matrix elements between the atomic and the Bloch states. Spin indices are suppressed, since they are unessential in the present problem. The last term in H_0 represents a free-boson field. Most collective excitations in solids may be conveniently described as bosons. Plasmons and optical phonons are often adequately represented by dispersionless bosons $\omega_q=\omega_p$ and the electron-hole excitations in an electron gas are approximated by a linear dispersion (ω_q proportional to q up to a certain cutoff value).

A common feature of such boson excitations is that they are strongly coupled to a localized charge (an electron or hole in an atomic orbital), but they are effectively decoupled from a delocalized Bloch electron. Therefore, the hole-boson coupling is of the form

$$H_1=n_a\sum_q g_q(a_q^\dagger+a_q)\,, \tag{8}$$

where $n_a=C_a^\dagger C_a$ and the coupling coefficients g_q are proportional to the qth Fourier component of the electrostatic potential produced by the localized charge. The factor n_a in H_1 ensures that the bosons interact with the valence hole only when it is in the localized state. Since the hole is free to diffuse back and forth from the solid, it acts essentially as a dynamic perturbation. In photoemission, a hole is produced at the atomic site, and the photoelectron spectrum is proportional to a square matrix element times a density of states $D(\omega)$ that carries all the interesting information. Before being photoionized, the system was in the ground state $|g\rangle$ of H_0.

Of course, $|g\rangle$ is a product of the vacuum state of the bosons and the ground state of the electron system, where we assume that the atomic orbital is occupied by an electron. The ionizing event instantaneously takes the system to the state $|i\rangle=C_a^\dagger|g\rangle$ (in the sudden approximation). The coupled electron-boson system will then relax to its new ground state. The density of states that we want to compute is given by

$$D(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle i|e^{-iHt}|i\rangle\,. \tag{9}$$

This can be calculated exactly as shown below.

The procedure essentially consists of a repeated application of the method that allowed us to solve the hole-hole interaction problem in the Auger spectra of solids.[8]

The Fourier transform of $D(\omega)$ is

$$D(t)=\sum_{n=0}^{\infty}\frac{(-it)^n}{n!}D_n\,,\quad D_n=\langle i|H^n|i\rangle\,. \tag{10}$$

If there were no electron-boson interaction ($H_1=0$) the corresponding quantities $D^0(t)$, D_n^0 could be computed by known methods. Thus, we should like to write down $D(t)$ in terms of $D^0(t)$.

To this end, we use the operator identity

$$H^n=H_0^n+\sum_{r=1}^{n}H_0^{r-1}H_1H^{n-r}\,. \tag{11}$$

It follows that

$$D_n=D_n^0+\sum_q g_q\sum_{r=1}^{n}\langle i|H_0^{r-1}|i\rangle\langle i|a_q H^{n-r}|i\rangle\,. \tag{12}$$

By defining

$$\Phi(q,t)=\langle i|a_q e^{-iHt}|i\rangle\,, \tag{13}$$

we obtain, by summing the Taylor series,

$$D(t)=D^0(t)-i\sum_q g_q\int_0^t dt'\,D^0(t-t')\Phi(q,t')\,. \tag{14}$$

The new unknown function $\Phi(q,t)$ can be treated in the same way, yielding the equation

$$\Phi(q,t)=-i\int_0^t dt'\,D^0(t-t')e^{-i\omega_q(t-t')},\times\left(\sum_{q_2}g_{q_2}\Phi(q_1q_2,t')+g_qD(t')\right)\,, \tag{15}$$

$$\Phi(q_1q_2,t)=\langle a_{q_1}a_{q_2}e^{-iHt}\rangle\,. \tag{16}$$

By iterating the process, we can form a set of infinitely many integral equations for a hierarchy of unknown functions. Define

$$\Phi(q_1,q_2,\ldots,q_k,t)=\langle a_{q_1}a_{q_2},\ldots,a_{q_k}e^{-iHt}\rangle . \qquad (17)$$

The general equation is

$$\begin{aligned}\Phi(q_1,\ldots,q_k,t) &= -i\int_0^t \exp[-i(\omega_{q_1}+\cdots+\omega_{q_k})(t-t')]D^0(t-t') \\ &\quad\times\Big[g_{q_1}\Phi(q_2,\ldots,q_k,t')+\cdots \\ &\quad + g_{q_k}\Phi(q_1,\ldots,q_{k-1},t') \\ &\quad + \sum_{q'} g_{q'}\Phi(q_1,\ldots,q_k,q',t')\Big]\,dt' . \qquad (18)\end{aligned}$$

If the hole is strictly localized ($D^0(t)=1$) the above set of equations is solved by the ansatz

$$\Phi(q_1,\ldots,q_k,t)=f(q_1,t)f(q_2,t)\ldots f(q_k,t)D(t) .$$

It turns out that

$$f(q,t)=(g_q/\omega_q)(e^{-i\omega_q t}-1) ,$$

and $D(t)$ coincides with Langreth's solution, Eq. (6). For general $D^0(t)$ and general boson dispersion law, our set of equations looks rather awkward. In the following, we shall concentrate on the case of dispersionless plasmons $\omega_q=\omega_p$, with general D^0.

It is convenient to define the quantities

$$\Phi_k(t)=\sum_{q_1}\cdots\sum_{q_k} g_{q_1}g_{q_2}\cdots g_{q_k}\Phi(q_1,q_2,\ldots q_k,t) , \qquad (19)$$

and to Laplace transform our equations. They become

$$\begin{aligned} D(s)&=D^0(s)-iD^0(s)\Phi_1(s) \\ \Phi_1(s)&=-iD^0(s+i\omega_p)[\beta D(s)+\Phi_2(s)] \\ \Phi_k(s)&=-iD^0(s+ik\omega_p)[k\beta\Phi_{k-1}(s)+\Phi_{k+1}(s)] , \\ &\cdots \end{aligned} \qquad (20)$$

where $\beta=\sum g_q^2$.

The procedure for solving the above infinite system involves a limiting process. One can assume $\Phi_{L+1}=0$, solve the first L equations, and finally let $L\rightarrow\infty$. Clearly, $\phi_L\rightarrow 0$ for $L\rightarrow\infty$. The result can be expressed as a continuous fraction

$$D(s)=\cfrac{D^0(s)}{1+\cfrac{\beta D^0(s)D^0(s+i\omega_p)}{1+\cfrac{2\beta D^0(s+i\omega_p)D^0(s+2i\omega_p)}{1+\cdots}}} . \qquad (21)$$

This is our closed-form exact solution.

The density of states that we need is finally given by

$$D(\omega)=\frac{1}{\pi}\lim_{\substack{\delta\rightarrow 0\\ \delta>0}} \mathrm{Re}\,D(s=\delta-i\omega) . \qquad (22)$$

The continuous fraction of Eq. (21) is difficult to handle analytically, but its numerical evaluation is straightforward.

The density of states $D(\omega)$ that we have computed is just the diagonal component $D_{aa}(\omega)$ of a density of states matrix $D_{mm'}(\omega)$, with the indices m and m' running over the complete set of single-electron valence states of the sample. In general, along with $D_{aa}(\omega)$ one must consider other components $D_{ka}(\omega)$ and $D_{kk'}(\omega)$, where k now refers to the band states in the Hamiltonian [Eq. (7)]. The photoelectron yield per unit time will be proportional to $\sum_{mm'} M_{mp}M^*_{m'p}D_{mm'}(\omega)$, where the matrix elements M_{mp} may be written as usual

$$M_{mp}=\int d^3r\,\vec{\epsilon}_q\langle p|-i\vec{\nabla}|m\rangle e^{i\vec{q}\cdot\vec{r}} . \qquad (23)$$

Here $\vec{\epsilon}_q$ and $\vec{q}$ are the polarization vector and wave vector of the incoming x ray and $|p\rangle$ is the outgoing fast electron state. Since the band states $|k\rangle$ have to be orthogonalized to the localized state $|a\rangle$, they will give nonvanishing matrix elements M_{kp} and, will contribute to the photoelectron yield. However, once $D(s)\equiv D_{aa}(s)$ is known from Eq. (21), the other components of the matrix $D_{mm'}(s)$ can also be specified. It is easily seen that

$$D_{ka}(s)=-i\frac{V_{ka}}{s+i\epsilon_k}D_{aa}(s) \qquad (24)$$

and

$$D_{kk'}(s)=\frac{\delta_{kk'}}{s+i\epsilon_k}-\frac{V_{ak}V_{ak'}}{(s+i\epsilon_k)(s+i\epsilon_{k'})}D_{aa}(s) . \qquad (25)$$

Equations (21)–(25) allow us to compute all the contributions to the photoelectron cross section.

IV. AUGER CORE-CORE-VALENCE TRANSITIONS

Auger transitions involving valence electrons can provide a powerful probe of chemisorption bonds and impurity states. By properly analyzing the Auger core-valence-valence (or XVV) spectra, involving two valence holes in the final state, we can obtain the local density-of-states matrix of valence electrons.[8] The analysis is simplest in the case of Auger core-core-valence (or XX′V) spectra, involving one final-state hole in an inner level and another hole in the valence band. In principle, XX′V spectra are directly related to the local single-electron density of states. However, in order to perform an accurate quantitative analysis of the experimental data, we have to deal with the complications due to the presence of collective excitations. In the present paper we are interested in the effect of plasmons on XX′V Auger spectra of chemisorbed or impurity atoms.

In the initial state, there is one deep hole in the core of the atom that polarizes the plasmons. The hole lifetime before the Auger transition is assumed to be long enough to allow for the complete relaxation of plasmons and valence electrons. The Auger transition eventually replaces the core hole by another core hole plus a valence hole. The core-hole potential will not change with the transition, provided the symmetry of the core hole is the same in the initial and in the final state. If the core-hole symmetry varies, the higher multipoles of the core potential will also vary. In such cases, the interaction between the core and plasmons of appropriate symmetries will be suddenly turned on or off. In the present paper we confine ourselves to cases in which the latter effects are negligible, or to the case of the equal deep-hole symmetries in the initial and final states.

The valence hole can be represented by the Anderson model Hamiltonian as in Sec. III, namely,

$$H_h=\epsilon_a n_a+\sum_k \epsilon_k n_k+\sum_k V_{ak}(C_a^\dagger C_k+C_k^\dagger C_a)\,. \tag{26}$$

The valence-hole correlation function, in the absence of plasmons,

$$D_h(t)=\langle g_h|C_a e^{-iH_h t}C_a^\dagger|g_h\rangle\,, \tag{27}$$

where $|g_h\rangle$ is the hole vacuum, can be calculated exactly,[6] and characterizes the electronic structure of the undisturbed atom. Our task will be to see how it appears in the Auger spectrum.

The model Hamiltonian of the coupled hole-plasmon system in the initial state is

$$H_i=H_h+Un_a+\sum_q \omega_q a_q^\dagger a_q+\sum_q d_q(a_q+a_q^\dagger) +n_a\sum_q g_q(a_q^\dagger+a_q)\,. \tag{28}$$

The term Un_a represents the shift of the valence level due to the core-hole potential. The next term is the free-plasmon Hamiltonian. The last two terms represent the coupling of plasmons to the core and valence holes, respectively. The plasmon-valence hole interaction is taken to be localized, as discussed above. Before the Auger transition takes place, the system is in the ground-state $|g\rangle$ of H_i with no valence holes. The (intra-atomic) transition suddenly takes the system to the state $C_a^\dagger|g\rangle$, while the Hamiltonian becomes the final-state Hamiltonian,

$$H_f=H_i+\Delta E_c\,. \tag{29}$$

Here, ΔE_c is the energy difference between the initial and final core-hole states. Again, we are using the sudden approximation. Interatomic transitions would bring about the states $C_k^\dagger|g\rangle$, in analogy with the XPS case (Sec. III). However, it is an important feature of the Auger effect, when compared to photoemission, that such terms are, generally speaking, rather unimportant (see, e.g., Ref. 9).

In this respect, the difference between Auger and XPS lies mainly in the form of the matrix elements that allows us to consider AES an almost ideally local technique. Therefore we do not worry about the off-diagonal terms of the density-of-states matrix (see Sec. III); our unknown is rather the diagonal term

$$D(t)=\langle g|C_a e^{-iH_f t}C_a^\dagger|g\rangle\,. \tag{30}$$

In order to proceed, it is convenient to introduce new boson coordinates A_q, defined by[3]

$$a_q=A_q-d_q/\omega_q\,. \tag{31}$$

The canonically transformed Hamiltonian is $\tilde{H}_f=H_0+H_1$, with

$$H_0=H_h+\left(U-2\sum_q \frac{d_q g_q}{\omega_q}\right)n_a+\sum_q \omega_q A_q^\dagger A_q -\sum_q \frac{d_q^2}{\omega_q}+\Delta E_c, \tag{32}$$

$$H_1=n_a\sum_q g_q(A_q^\dagger+A_q)\,. \tag{33}$$

The transformed ground state $|\tilde{g}\rangle$ is the vacuum state for the A_q and the plasmon variables do not contribute to the correlation function $D^0(t)$ defined in terms of H_0 alone as

$$D^0(t)=\langle\tilde{g}|c_a e^{-iH_0 t}C_a^\dagger|\tilde{g}\rangle\,. \tag{34}$$

Now let $W=U-2\sum_q(d_q\tilde{g}_q/\omega_q)$. The function $D^0(t)$ differs from $D_h(t)$ [Eq. (27)] by a phase factor $\exp\{-i\,[\Delta E_c+\sum(d_q^2/\omega_q)]t\}$ and by a level shift Wn_a in the Hamiltonian. This implies that $D^0(t)$ can be readily written down in terms of $D_h(t)$. In fact, the analog of Eq. (14) in this case is a Dyson equation yielding

$$D^0(s)=D_h(s+i\eta)/\left[1+iWD_h(s+i\eta)\right]\,, \tag{35}$$

with

$$\eta=\Delta E_c-\sum_q d_q^2/\omega_q\,.$$

Our final task is to write down $D(s)$ in terms of $D^0(s)$. Since this problem is the same as the XPS problem, the exact solution has already been found in Sec. III [Eq. (21)].

V. DISCUSSION

The above results may be summarized as follows. X-ray photoelectron spectroscopy and Auger spectra involving one valence hole in the final state can be discussed in terms of a local density of states $D_{aa}(\omega)$ calculated in the presence of the hole-boson coupling. Off-diagonal elements of the density-of-states matrix should be of minor importance, at least in AES; however, they can be expressed in terms of $D_{aa}(\omega)$ as in Eqs. (24) and (25). Moreover, $D_{aa}(\omega)$ can be written down in terms of a local density of states $D^0_{aa}(\omega)$ calculated in the absence of any coupling with the boson field. In the case of dispersionless plasmons the only other ingredients needed to specify D in terms of D^0 are the plasma frequency ω_p and the square coupling constant $\beta = \sum_q g_q^2$. In principle, $D^0_{aa}(\omega)$ is easy to calculate. In the case of XPS, D^0 is just the single-electron density of states as obtained from an Anderson model, and contains the information about the unperturbed local electronic structure that we are interested in.[10] In the case of AES, the relevant D^0 is related to the unperturbed density of states through a simple "impurity state" formula [Eq. (35)] involving the "screened" deep-hole potential W. Therefore, the main physical point of our discussion is the relationship between the "observed" density of states D and its "bare hole" counterpart D^0 [Eq. (21)].

In a very simpleminded approach one could have guessed that $D(\omega)$ should be something like a convolution of $D^0(\omega)$ with Langreth's function [as given by the Fourier transform of Eq. (6)]. This corresponds to the idea behind the Doniach and Sunjic[11] treatment of XPS line shapes in metals. In fact, this is true in just one case. If $D^0(\omega)$ is taken to be a Lorentzian, it is not hard to see that the solution of Eq. (20) is the same as Langreth's function, with all the δ-function peaks broadened into Lorentzians. This "obvious" case is very pathological in several respects. Mathematically, a Lorentzian $D^0(\omega)$ implies that the one-electron Hamiltonian does not have finite moments, and cannot represent any realistic valence band. Physically, the convolution result implies a complete lack of correlation between the decay of the hole and the plasmon field. Therefore, while the trivial solution may be useful in introducing core-hole lifetime effects, it is certainly irrelevant to the problem of valence holes.

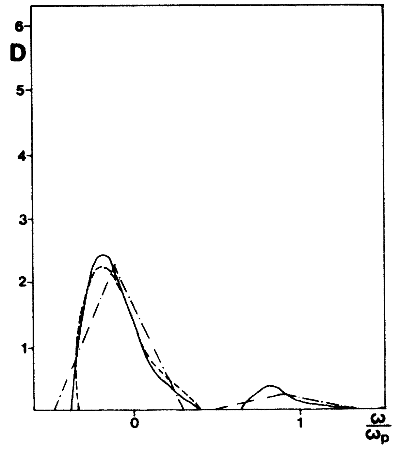

FIG. 1. Density of states $D(\omega)$ for $a=0.1$ and $\delta=0.2\omega_p$ (see text). The dot-dash line represents the unperturbed D_0 (Eq. 36) convoluted with Langreth's function; the dashed line is the Born-Oppenheimer approximation normalized to e^{-a}; the solid line is the exact solution.

Hole-plasmon correlation effects are important provided D^0 is allowed to have finite moments, as it should be. In order to bring out the main physical features, it is convenient to assume a simple model. Let $D^0(\omega)$ be the symmetric, triangular-shaped function having a half-width δ at half-maximum

$$D^0(\omega) = (1/2\delta - |\omega|/4\delta^2)\Theta(2\delta - |\omega|), \tag{36}$$

where Θ is Heaviside's step function. In our numerical computation we also need the Hilbert transform $I^0(\omega)$, given by

$$\Pi I^0(\omega) = \frac{1}{2\delta}\ln\left|\frac{\omega+2\delta}{\omega-2\delta}\right| + \frac{\omega}{4\delta^2}\ln\left|\frac{\omega^2-4\delta^2}{\omega^2}\right| . \tag{37}$$

In Figs. 1–3, we see the resulting $D(\omega)$ for several values of the width parameter δ/ω_p and of the coupling strength $a = \beta/\omega_p^2$. The convolution of D^0 with Langreth's function is also shown for comparison. We notice that, besides producing satellite peaks, the plasmons affect the shape of the main peak in a characteristic way.

For weak coupling ($a < \delta/\omega_p$) the peaks become asymmetric with a tail on the same side as the energy losses due, e.g., to electron hole and other excitations. Thus, asymmetries due to plasmons may superimpose on those due to energy losses, even though their origin is different. This point can be important in analyzing the experimental spectra. For stronger coupling ($a \sim \delta/\omega_p$) the peaks become very much sharper than the unperturbed ones. The reason for this narrowing is clearly that the plasmons can only screen a localized hole and tend to favor localization. Eventually, for $a > \delta/\omega_p$, the hole may become self-trapped, and a localized state develops that recalls a small polaron. Indeed, as a byproduct of our calculation, we have also obtained the exact ground-state energy of our final-state Hamiltonian that could be interpreted as a continuous model for a polaron

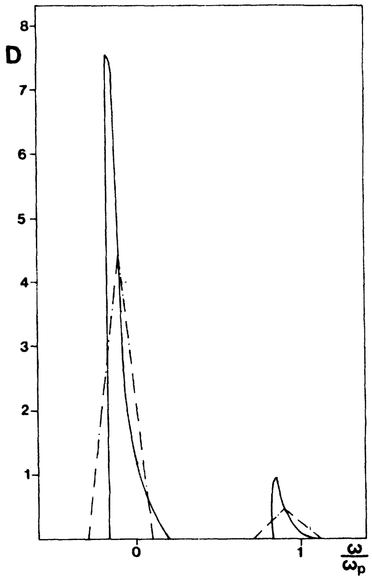

FIG. 2. Density of states $D(\omega)$ for $a=0.1$ and $\delta=0.1\omega_p$. Dot-dash line: simple convolution result. Solid line: exact result. The peaks tend to become sharp and asymmetric because the plasmons tend to localize the hold.

bound to our impurity. I note in passing that the position and intensity of the δ-function peak are best obtained, in a numerical evaluation of Eq. (21) by looking at the pole in the imaginary part of $D(s)$.

The results shown in the figures refer to situations in which the level width δ is much less than the plasma frequency, since this is usually true in solids. In such conditions, the plasmon variables may be considered as fast variables as compared to the hole coordinates. It may be interesting to know how good the Born-Oppenheimer approximation would be in calculating the shape of the main peak. The Born-Oppenheimer approximation would consist in assuming that the plasmons "have time" to relax completely around the resonant orbital before the hole moves, and the hole effectively sees the potential of a static screening cloud. Thus, the problem would reduce to a simple impurity problem, and the result would be given by Eq. (35) with $\eta=0$ and $W=-a\omega_p$. The "Born-Oppenheimer" density of states D_{BH}, normalized to e^{-a} to allow for the presence of plasmon satellites, is shown in Fig. (1) for the sake of comparison. As far as I know, this is the first time that the degree of validity of a Born-Oppenheimer approximation can be assessed by direct comparison with an exact result. It can be seen that for $\delta/\omega_p=0.2$, D_{BH} turns out to be qualitatively correct, and a much better approximation than the simple convolution results.

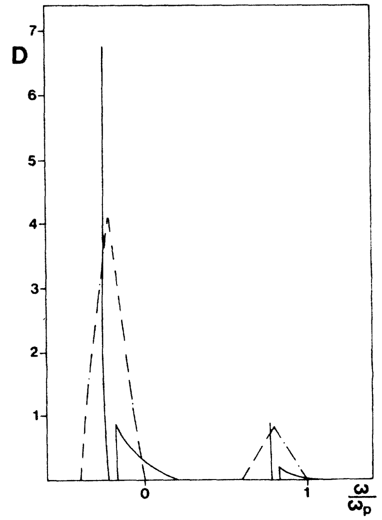

FIG. 3. Density of states $D(\omega)$ for $a=0.2$ and $\delta=0.1\omega_p$. Dot-dash line: simple convolution result. Solid line: exact result. The vertical bars represent δ-like singularities due to localized states of the hole.

VI. CONCLUSION

Any attempt to obtain density-of-states information from XPS and Auger valence spectra should be based on a separation of one-electron properties from many-body final-state relaxation effects.

In the above discussion it has been shown that the hole-plasmon coupling can produce not only plasmon satellites, but also an important change in the shape of the peaks. If the coupling is strong enough compared to the single-electron level width, the plasmons will cause the localization of the final-state hole and the occurrence of sharp resonances in the spectra.

The present treatment is based on a model Hamiltonian that includes those coupling terms that are important for long-wavelength bulk plasmons. A new mathematical technique has been proposed that allows us to solve the problem exactly in the dispersionless limit. The results should allow for the comparison of specific one-electron local-density-of-states calculations with experiment, or, equivalently, for a first-principles calculation of the spectra. Such a calculation, though feasible nowadays, involves complex numerical computations that are outside the scope of the present paper.

Finally, I should like to mention several related problems that are still open. The inclusion of boson dispersion in the present scheme, though probably fairly unimportant in the case of plasmons,[12] would be of interest in problems involving acoustical phonons and electron-hole excitations. However, this generalization does not seem to be a trivial one. Another challenging problem arises in the connection with the coupling of holes to surface plasmons. Since the latter may cause large electric-field fluctuations close to the surface, it may be necessary to use a more complicated Hamiltonian than the present one, as pointed out in Sec. I. Instead, a theory of x-ray emission from a valence band, including plasmon effects, can be built up within the present model, and a solution can be obtained by the present formalism. This sort of calculation is currently in progress, and the results will be reported elsewhere. The important new result of the present paper is the exact density of states calculated in the presence of the hole-plasmon coupling. The solution of a model field theory is interesting on its own right and we have shown that nontrivial effects should be found in the experimental spectra. However, inelastic-scattering effects due to the outgoing electron are also important in many cases and should be included in a complete theory. We already have a good physical understanding of such effects. They could be taken care of by extending well-known treatments given by Chang and Langreth[13] and Sunjic and Sokcevic.[14] Such important refinements, as well as the approximate inclusion of electron-hole shakeup,[15] are deferred to a future publication. To sum up, the application of electron spectroscopies to the investigation of valence states involves a very interesting area of theoretical research, and, despite many intriguing problems, the idea of getting reliable densities of states from such techniques is rapidly becoming a practical proposition.

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[12] Plasmon dispersion should have little influence on the shape of the no-loss peak, as can be inferred by analogy with the core-hole case. It will produce a slight distortion of the "Born-Oppenheimer" potential seen by the hole (see Sec. V), and a small correction to the line shapes considered here. The shapes of the satellites are less interesting since in actual spectra they contain substantial contributions from extrinsic effects (see below).

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[15] Recoil effects due to the finite hole mass are known to remove the threshold singularity, and the finite width of the valence level will contribute further to smear out the energy losses to electron-hole pairs over a sizable energy range. Moreover, a valence hole will tend to be more delocalized than a core hole and to scatter conduction electrons less strongly. As a result, electron-hole shake-up effects can be expected to produce a relatively weak, smooth background in valence-state electron spectroscopies. Nevertheless, they may still be of some importance for a detailed quantitative analysis and they deserve a separate treatment.