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Resonant two-electron excitation in copper

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We present a calculation of the photoabsorption and photoemission cross sections of atomic copper in the neighborhood of the $3p$ threshold employing a time-dependent self-consistent-field approximation amended to include self-energy corrections necessary for a proper description of core-hole Auger decay. The calculated spectrum includes a contribution from a shake-up satellite in the two-particle spectrum which becomes resonant at the $3p$-$4s$ transition energy and is in good agreement with available absorption data. We present the relevant partial cross sections in the one-particle spectrum and include a brief discussion of the absorption above the $3p$ threshold with regard to the requirements of self-consistency.

I. INTRODUCTION

In this paper we report the results of quantitative calculations pertaining to resonant shake-up phenomena recently observed in a variety of narrow $3d$-band materials. Experiments have shown that direct photoemission from the $3d$ band is accompanied by a lower kinetic energy satellite whose generally weak intensity undergoes a dramatic resonant enhancement as the photon energy is tuned through the $3p$ threshold.[1,2] The satellite has been interpreted as a two-electron excitation in which a second $3d$ electron is promoted to an unoccupied level leaving two strongly correlated $3d$ holes bound to a single site. Support for this view has come from the decomposition of the satellite fine structure into atomic multiplets[2] as well as the quasi atomic Auger spectrum exhibited by these systems.[3] Nevertheless, the precise character of the final state corresponding to the satellite is still not completely understood regarding the role of the second "shake-up" electron. For the situation corresponding to the full d bands of copper, model calculations exist which exhibit a resonant two-hole satellite, where the $3d$ electron is promoted to either an essentially atomic $4s$ orbital[4,5] or to a conduction-band state at the Fermi level.[6,7] At present it is unknown whether either description would yield a resonant enhancement of magnitude consistent with experiment. Our purpose here is to begin to address this question purely within the context of the atomic model with a realistic calculation of photoabsorption and photoemission in the neighborhood of the $3p$ threshold of atomic copper.

We shall focus primarily on the photon energy dependence of the total photoabsorption cross section $\sigma_{\rm abs}(\omega)$, the various partial photoemission cross sections $\sigma_{nl}(\omega)$, and the shake-up satellite cross section $\sigma_{\rm sat}(\omega)$ which, in the absence of radiative decay, are related by

$$\sigma_{\rm abs}(\omega)=\sum_{n,l}\sigma_{nl}(\omega)+\sigma_{\rm sat}(\omega)\ . \tag{1}$$

The partial cross sections on the right-hand side of Eq. (1) are experimentally distinguishable due to the differing kinetic energy of the escaping photoelectrons. Before describing the calculation, we outline the important physical processes which define the problem, following the discussion of Wendin and co-workers.[4] First, consider the one-particle spectrum. Far below the $3p$ threshold the photoemission is dominated by transitions from the $3d$ shell to the continuum $\sigma_{3d}(\omega)$ described by

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$$\hbar\omega + 3d^{10}4s \rightarrow 3d^{9}4s + \epsilon\ , \tag{2}$$

where $\hbar\omega$ denotes the photon energy and ϵ the photoelectron. We shall ignore the oscillator strength due to emission from the $4s$ shell which is negligible at these energies. As the photon energy is increased, transitions become possible from the $3p$ level to the half-occupied $4s$ level which, in an independent-particle model are represented by a delta function in energy. In fact, however, the discrete $3p$-$4s$ and continuum $3d$-ϵl single-particle—hole channels interfere with one another to yield a typical Fano line shape[8] for the cross section. One may view this as a $3p$-hole lifetime effect in the sense that the discrete excitation autoionizes and decays into the continuum leaving a single hole in the $3d$ shell as the final state. Increasing the photon energy still further, direct photoemission from the $3p$ shell finally becomes possible according to

$$\hbar\omega + 3p^{6}3d^{10}4s \rightarrow 3p^{5}3d^{10}4s + \epsilon\ . \tag{3}$$

From the previous discussion, we expect to find the shake-up satellite in the two-particle spectrum. Far below the $3p$ threshold, the two $3d$-hole final states may be reached by direct excitation:

$$\hbar\omega + 3d^{10}4s \rightarrow 3d^{8}4s^{2} + \epsilon\ . \tag{4}$$

In addition, near the $3p$-$4s$ discrete transition energy, a resonant path to the presumed shake-up final state proceeds by super Coster-Kronig Auger decay of the $3p$ core hole:

$$\hbar\omega + 3p^{6}3d^{10}4s \rightarrow 3p^{5}3d^{10}4s^{2} \rightarrow 3p^{6}3d^{8}4s^{2} + \epsilon\ . \tag{5}$$

Clearly, the latter process also constitutes a hole-lifetime effect and the shape of the absorption spectrum near the discrete excitation energy will be determined by which process has the shorter lifetime between autoionization and Auger decay.[4,5]

This report is organized as follows. We address first the photoabsorption associated with the $3d$ shell in the absence of Auger lifetime effects, but including the interference between the $3p$-$4s$ discrete excitation and $3d$-ϵl continuum channel. This channel-mixing phenomenon is calculated within the context of a self-consistent treatment of electronic polarization based upon the local-density approximation. This preliminary calculation is primarily heuristic in character and illustrates that a proper description of the atomic absorption data[9] requires a more complete account of hole-lifetime (self-energy) effects. The remainder of the paper concerns the inclusion of the Auger decay of the $3p$ hole by an appropriate choice of self-energy corrections to the $3p$-hole energy and the calculation of the satellite intensity in a way which emphasizes the symmetry properties of the excited states. The direct shake-up channel is found to be very weak while the resonant shake-up channel produces a contribution which accounts for a significant feature in the experimental absorption spectrum. The pronounced Fano line shape which is present in the $3d$ partial photoemission cross section in the absence of Auger decay is destroyed, leaving only a weak modulation at the position of the satellite resonance. We conclude with a brief discussion of the influence of the satellite on the absorption spectrum above the $3p$ ionization threshold.

II. POLARIZATION EFFECTS

The photoabsorption and photoemission cross sections of valence shells can generally be computed using time-dependent self-consistent-field techniques.[10] In that picture the absorption is regarded as that produced by independent particles driven by a time-dependent local field $U(\vec{r}\,|\,\omega)$, equal to the sum of the external radiation field and an internally generated screening (or antiscreening) field induced by the polarization of the system. Let $\chi_0(\vec{r},\vec{r}\,'\,|\,\omega)$ denote the nonlocal frequency-dependent polarizability of a system of independent electrons. $\chi_0(\vec{r},\vec{r}\,'\,|\,\omega)$ may be represented diagrammatically as the sum of simple particle-hole bubbles such as the one shown in Fig. 1(a); each bubble stands for one term in the spectral representation of the polarizability and represents a possible single-particle excitation of the system. An approximation to the polarizability of the real interacting electron system, $\chi(\vec{r},\vec{r}\,'\,|\,\omega)$, which incorporates the dielectric effects discussed above, is found by solution of the RPA-type equation

$$\chi(\vec{r},\vec{r}\,'\,|\,\omega) = \chi_0(\vec{r},\vec{r}\,'\,|\,\omega) + \int \chi_0(\vec{r},\vec{r}_1\,|\,\omega) K(\vec{r}_1,\vec{r}_2) \chi(\vec{r}_2,\vec{r}\,'\,|\,\omega)\, d\vec{r}_1 d\vec{r}_2\ . \tag{6}$$

The frequency-independent kernel function $K(\vec{r},\vec{r}\,')$ reflects the effect of the Coulomb interaction between particle-hole pairs. The nonlinear dependence of $\chi(\vec{r},\vec{r}\,'\,|\,\omega)$ on $\chi_0(\vec{r},\vec{r}\,'\,|\,\omega)$ implied by the integral equation induces an interference between the particle-hole excitation channels of the

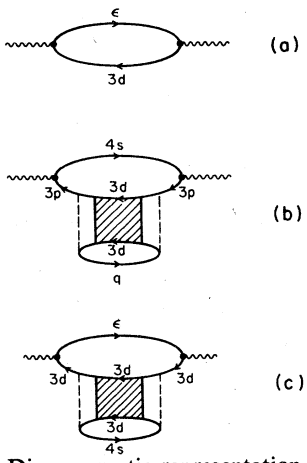

FIG. 1. Diagrammatic representation of contributions to the electronic polarizability $\chi_0(\vec{r},\vec{r}' \mid \omega)$ leading to photoemission : (a) direct $3d$-shell emission, Eq. (2), (b) resonant shake-up, Eq. (5), and (c) direct shake-up, Eq. (4).

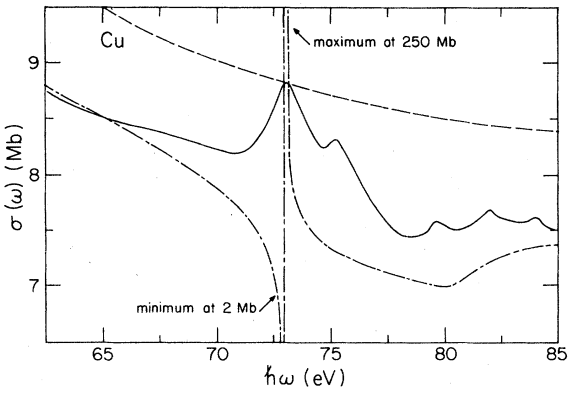

FIG. 2. Copper-vapor absorption data from Ref. 9 (solid line), calculated $3d$ partial photoemission cross section in the independent-particle approximation (dashed line), and the TDLDA (dashed-dot line) neglecting hole-lifetime effects. Data normalized to TDLDA calculation at 65 eV.

independent-particle system. In particular, as discussed in the Introduction, the $3p$-$4s$ discrete and $3d$-ϵl continuum excitations interfere to produce a Fano line shape in the absorption spectrum, which is proportional to $\mathrm{Im}\chi(\vec{r},\vec{r}' \mid \omega)$.

The present calculations employ a time-dependent self-consistent-field scheme based on the local-density approximation (LDA) which has been successfully applied to photoabsorption studies of the rare gases[11] and rare earths.[12] Specifically, the spectral representation of $\chi_0(\vec{r},\vec{r}' \mid \omega)$ is evaluated using wave functions and energy eigenvalues given by the LDA Kohn-Sham equations.[13] In this time-dependent local-density approximation (TDLDA), the local field contains both a direct Coulomb and exchange-correlation component. The polarization effects included by the solution of Eq. (6) may be represented by replacement of the external field by the local field in all dipole matrix elements; details may be found in Ref. 11. For example, the wiggly line vertices in Fig. 1(a), which stand for $\langle \epsilon \mid z \mid 3d \rangle$ in an independent-particle calculation should be reinterpreted as $\langle \epsilon \mid U(\vec{r} \mid \omega) \mid 3d \rangle$ in the self-consistent-field calculation.

In Fig. 2, the $3d$ partial photoemission cross section is shown in both the independent-particle approximation (dashed line) and the TDLDA (dashed-dot line). The theoretical curves have been shifted on the frequency axis to align the $3p$-$4s$ transition energy with the resonance structure of the experimental absorption data[9] since the discrete excitation energy based on local-density eigenvalues is, as is generally the case, in poor agreement with experiment. Below the $3p$ ionization threshold, the $3d$ partial cross section is nearly identical with the total photoabsorption cross section so that direct comparison with the experimental absorption spectrum is appropriate. In addition to the asymmetric Fano line shape, the difference in absolute magnitude between the two theoretical curves reflects the weak polarizability of the copper $3d$ shell.

The extremely narrow calculated resonance reflects the weakness of both the $3p$-$4s$ transition oscillator strength and the coupling of this discrete excitation to the degenerate $3d$-ϵl continuum channel. Furthermore, comparison of the theoretical linewidth with the observed peak width suggests that a fast decay mode is essential to reproduce the absorption spectrum. We emphasize that to this point the calculation has included only the self-consistent response of the atomic electrons which leads to photoemission final states containing a single hole relative to the ground state. We have included no two-electron excitations and therefore no satellite appears.

III. SELF-ENERGY EFFECTS

The physical origin of the satellite spectrum is the nonstationary character of the state produced by the sudden creation of a $3p$ core hole. The Auger decay of this state, indicated in Eq. (5), is represented diagrammatically in Fig. 1(b) which describes a low-order contribution to the $3p$-hole self-energy. The premise of this work is that the dominant contributions to this self-energy are con-

figurations involving two $3d$ holes and a particle in either the $4s$ level or higher bound levels or continuum states.[14] The box in Fig. 1(b) represents the multiple scattering of the two holes from one another. If such scattering is restricted so the holes remain in the $3d$ shell, the result is equivalent to an elementary multiplet calculation which neglects configuration interaction. According to this diagram, the initial angular momentum of the $3p$ hole, a ^2P state, can be conserved by decay to any of the multiplets of the $3d^8$ complex ($^1S,^3P,^1D,^3F,^1G$) since the photoelectron, denoted by q, can provide any needed angular momemtum. Indeed, the observed kinetic energy distribution of the satellite fine structure in bulk copper[2] and quasiatomic Cu-phthalocyanine[15] is consistent with such decay.

Technically, our choice of this self-energy diagram represents an approximation to the two-particle Green's function in which the only internal lines correspond to $3d$-hole propagation. Here, the $3p$-hole self-energy may be written in the form

$$\Sigma_{3p}(\omega)=\sum_{q,\lambda}\frac{|A_{\lambda q}|^2}{\hbar\omega+E_{\lambda 0}+\epsilon_q-i\delta}\ . \tag{7}$$

The two $3d$-hole multiplets are denoted by $\lambda\equiv\{LSM_LM_s\}$. $E_{\lambda 0}$ is the energy of the multiplet with respect to the ground state which reduces to $-2\epsilon_{3d}$ in the absence of multiplet splitting. Each of the two-hole multiplets enters the self-energy with an amplitude determined by Coulomb matrix elements and factors which involve the multiplet wave functions. A concise formula is

$$|A_{\lambda q}|^2=\sum_{ijkl}\langle 0|d_i^\dagger d_j^\dagger|\lambda\rangle\langle\lambda|d_k d_l|0\rangle \times\langle pq|V|kl\rangle\langle ji|V|pq\rangle\ , \tag{8}$$

where d_i denotes a destruction operator for a $3d$ electron with magnetic and spin quantum numbers $i\equiv\{M_LM_S\}$. We evaluate the above expressions by noting that the energy denominator in Eq. (7) and q orbitals in Eq. (8) may be combined to form the spectral representation of the one-particle Green's function appropriate to the LDA potential,

$$G(E)=\sum_q\frac{|q\rangle\langle q|}{E-\epsilon_q+i\delta}\ , \tag{9}$$

and hence may be exactly evaluated.[11] For convenience (and since we are not concerned with the satellite binding energy) we have ignored the multiplet splittings in the evaluation of Eq. (7). These splittings may be easily included and may even be modified in an *ad hoc* manner to include polarization corrections.[16] We find this contribution to the $3p$-hole self-energy to be weakly energy dependent (10% variation over the energy range of interest), with a mean value of the imaginary part corresponding to an Auger lifetime of 3.75×10^{-16} sec.

To incorporate this self-energy, and generate the shake-up satellite, we must modify the independent-particle response function, $\chi_0(\vec{r},\vec{r}'|\omega)$, which has the spectral representation

$$\chi_0(\vec{r},\vec{r}'|\omega)=\sum_{i,j}(f_i-f_j)\frac{\psi_i^*(\vec{r})\psi_j(\vec{r})\psi_j^*(\vec{r}')\psi_i(\vec{r}')}{\hbar\omega-(\epsilon_j-\epsilon_i)+i\delta}\ , \tag{10}$$

where f_i and $\psi_i(\vec{r})$ denote a Fermi occupation factor and atomic single-particle orbital, respectively. Consistent with the presumed satellite excitation sequence, Eq. (5), we isolate the term responsible for $3p$-$4s$ transitions and make the substitution

$$\frac{1}{\hbar\omega-\epsilon_{4s}+\epsilon_{3p}+i\delta} \rightarrow\frac{1}{\hbar\omega-\epsilon_{4s}+\epsilon_{3p}+\Sigma_{3p}(\omega_{4s}-\omega)}\ . \tag{11}$$

The modified response function replaces $\chi_0(\vec{r},\vec{r}'|\omega)$ in the integral equation, which is solved to yield the overall response of the system. We briefly defer a discussion of the validity of this approach and present the resulting calculated absorption spectrum for atomic copper in Fig. 3. Here, as in the previous figure, the relative absorption data of Bruhn *et al.*[9] was normalized to the calculation below the resonance structure. We find the width and relative intensity of the peak in good agreement with the data although the $3p$-level spin-orbit splitting near 75 eV is not reproduced in our nonrelativistic calculation. Decomposition of the calculated absorption according to Eq. (1) reveals only a weak modulation of the $3d$ partial photoemission cross section (dashed-dot line) in the vicinity of the $3p$-$4s$ transition energy: the observed peak structure is due to the nearly Lorentzian profile of the two-electron satellite. This behavior is consistent with the analyses of Wendin[4] and Yafet[5] for the case when the Auger lifetime is much shorter than the autonionization lifetime.

The explicit formula for the resonant contribution to the shake-up satellite cross section clearly

shows that each multiplet undergoes the same magnitude of resonance enhancement while their *relative* intensities are always determined by the $A_\lambda q$ (see Table I). The partial shake-up cross section in which the $3d$ shell is left in the multiplet state λ is

$$\sigma_\lambda(\omega)=4\pi^2\alpha\hbar\omega\frac{|\langle 4s\,|\,U(\vec{r}\,|\,\omega)\,|\,3p\rangle\,|^2}{|\,\hbar\omega-\epsilon_{4s}+\epsilon_{3p}+\Sigma_{3p}(\omega_{4s}-\omega)\,|^2}\sum_q |A_{\lambda q}|^2\delta(\hbar\omega+E_{\lambda 0}+\epsilon_q)\,. \tag{12}$$

The cross section differs from a Lorentzian line due to the frequency dependence of both the self-energy and the local field. However, as noted earlier, the latter effect is small (about 10%) because the $3d$ shell of transition metals is not highly polarizable due to the absence of a strongly overlapping unoccupied orbital accessible by a dipole transition.[17] Although no partial photoemission cross-section data is available for the atom, bulk copper shows very similar features for the $3d$-band[18] and satellite[2] emission. In the bulk case, however, the position of the shake-up resonance maximum and the onset for continuous absorption both occur at the Fermi-level excitation energy, whereas in the atom these processes are separated by the $4s$-level binding energy so that the absorption spectrum of copper vapor and copper bulk metal are not identical.[9]

The direct shake-up process, Eq. (4), may be represented by a self-energy correction to the $3d$-hole propagator, as shown in Fig. 1(c), in the same approximation as previously discussed for the $3p$ hole, i.e., we consider only the sudden approximation which neglects the interaction of the residual ion with the photoelectron. We find this process to be nearly energy independent and to contribute to the cross section with an intensity only 1% of the main line, as observed far from resonance. This shake-up mechanism scales with the $\langle\epsilon\,|\,U\,|\,3d\rangle$ dipole photon vertex rather than the $\langle 4s\,|\,U\,|\,3p\rangle$ vertex of the resonant diagram. Finally, only the ^1D component of the $3d^8$ multiplet can be excited in this case since only the $l=0$ $4s$ particle state, rather than the escaping photoelectron, can provide the missing angular momentum. Nonetheless, in the condensed state the shake-up electron may reside in a hybridized state with significant $3d$ ($l=2$) admixture, in which case even the nonresonant shake-up process would couple to all the multiplets. Our particular choice of direct shake-up, Eq. (4), was chosen because it leads to exactly the same final state as the dominant resonant sequence, Eq. (5).

With both satellite processes leading to the $3d^8 4s^2$ final state, there exists in principle an interference between the two.[5] A proper description of this effect involves diagrams we have omitted. In fact, the substitution indicated by Eq. (11) followed by solution of the SCF integral equation does not generate a solution of the optical linear-response problem in the presence of self-energy effects which satisfies the conservation laws. In particular, our computed cross section does not satisfy the f sum rule. Baym and Kadanoff[19] have outlined a procedure which determines a linear integral equation for $\chi(\vec{r},\vec{r}\,'\,|\,\omega)$ [a Bethe-Salpeter equation generally different from Eq. (6)] for any particular self-energy choice. In such a "conserving approximation," new diagrams would be generated, some of which may be identified as those responsible for the interference phenomenon in the two-particle spectrum mentioned above. Indeed,

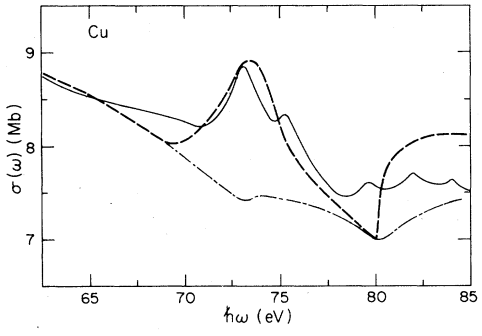

FIG. 3. Copper-vapor absorption data from Ref. 9 (solid line), calculated total photoabsorption cross section including Auger decay of $3p$-hole (dashed line), and $3d$ partial photoemission cross section (dashed-dot line). Satellite cross section is the difference between the two theoretical curves below 80 eV. Above 80 eV, this difference represents the $3p$ partial photoemission cross section. Data normalized to calculation at 65 eV.

TABLE I. Relative intensities (normalized to ^1G) of the shake-up multiplets calculated from Eq. (8). The dependence of $|A_{\lambda q}|^2$ on the photoelectron kinetic energy is very weak in the photon energy range of interest.

Multiplet	^1G	^3F	^1D	^3P	^1S
$\lvert A_{\lambda q}\rvert^2$	100	45	13	3	5

Wendin[17] and Amusia[20] have discussed such better approximations in a somewhat different context. To reiterate, neither a self-energy-corrected independent-particle approximation employing only $\chi_0(\vec{r},\vec{r}' \mid \omega)$, nor a self-energy-corrected TDLDA employing Eq. (6) strictly generates a conserving approximation for the optical response. Nevertheless, the quite reasonable results we obtain for the shakeup structure with our simplified TDLDA calculation suggests that the corrections to it must be distributed to other parts of the absorption spectrum.

In fact, the behavior of the calculated spectrum above the $3p$ threshold immediately indicates where some corrections ought to occur. The small features above 80 eV in the experimental curve have been associated with transitions to high-lying rydberg states, implying a $3p$ ionization limit of about 85 eV. The calculation yields a $3p$ threshold at lower binding energy (again, typical of a local-density approximation) and an abrupt $3p$ to continuum absorption step not observed in the data. First, we note that no self-energy corrections were applied to the $3p$-hole propagator above threshold, the inclusion of which would broaden the calculated sharp edge. More important, however, is the interaction of the slowly escaping photoelectron with the residual ion. The Coulomb attraction between the slow electron and either the $3p$ core hole or (for sufficiently fast decay) the two-hole Auger final state is known to suppress core-level photoemission near threshold.[17,21]

One way to approximate the core-hole interaction involves calculation of the photoemission using final states appropriate to the atomic system completely relaxed around the core hole. Amusia has presented a diagrammatic discussion of this procedure[20] and we note that some of the terms required by a Baym-Kadanoff analysis of the shakeup self-energy-corrected polarizability are thereby approximately counted. Indeed, we find that this approach yields a $3p$ partial photoemission cross section of about 0.5 Mb near threshold, i.e., only half as large as that indicated in Fig. 3, and thus bringing the total absorption into reasonable accord with the data. Nevertheless, we feel that a proper description of absorption phenomena above a near-core threshold still awaits a full self-consistent theoretical treatment.

IV. SUMMARY

We have shown that a previously developed mean-field theory of atomic photoabsorption may be simply adapted to quantitatively account for near-core-hole Auger decay to a two $3d$-hole shake-up final state in atomic copper. Our attention has focused on the photon energy dependence of the total photoabsorption from the $3p$ and $3d$ shells as well as the satellite emission. Proper account of the $3p$-hole lifetime in the $3p$-$4s$ excitation channel yields a satellite containing a strong resonance in all the $3d^8$ multiplets centered at the $3p$-$4s$ transition energy. In addition, a weak nonresonant process generates a satellite only in the ^1D multiplet component which exists at all energies. A significant feature in the experimental atomic absorption data may be ascribed to the resonant two-electron excitation while the one-hole spectrum exhibits no dramatic modulation. Generally, we find good agreement with the available data except very near the $3p$ ionization threshold.

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