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Auger Line Shapes of Free Atoms

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Quantitative calculations of Auger line shapes of free atoms after particle-impact ionization are presented. It is shown that the line shapes deviate from Lorentzians for all impact energies, due to long-range continuum interactions between the Auger electron and unobserved collision fragments. In particular, even at asymptotically high impact energies, the observed linewidth Γ_{FWHM} exceeds the decay width Γ_0 of the initial state by up to 10%; moreover, the line shapes are slightly, but noticeably shifted and asymmetrically distorted with respect to a Lorentzian. The magnitude of these effects was unknown in the past; possible implications for various subfields of physics are discussed.

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Auger spectra from free atoms have been obtained for more than 20 years, and so it may be surprising that the shape of Auger lines is still a subject of active research. In fact, it is frequently assumed that the Auger line shape can be described by a Lorentzian, with the position E_A^0 and the width Γ_0 being solely determined by the decay process of the inner-shell hole. This assumption essentially reflects the *two-step* hypothesis for resonance creation and decay, implying that the primary inner-shell ionization process is completely decoupled from the subsequent Auger process. Necessary conditions are (a) that the direct excitation amplitude of the final state is negligible (which is mostly true for Auger processes, in contrast to autoionization), and (b) that the lifetime of the intermediate resonance is sufficiently long to prevent final-state interactions between the Auger electron and any of the escaping collision partners.

Relying mostly on the two-step assumption, an unsurveyable wealth of data have been extracted from Auger spectra over the last 20 years, which were recorded with ever refined experimental techniques.[1] In fact, much of our knowledge on atomic inner-shell binding energies and transition probabilities arises from careful analysis of Auger line positions E_A^0 and widths Γ_0. Furthermore, the experimental data from free atoms have served as testing grounds for atomic structure calculations, and as reference standards in studies of atoms in various chemical environments, like molecules, surfaces, and solids.

In view of this situation it is necessary to reevaluate our knowledge about Auger line shapes on the basis of recent theoretical developments. In the present Letter we have focused our attention on Auger lines of free atoms following particle-impact ionization. It appears as if quantitative information on these line shapes is largely missing, although semiclassical and quantum-mechanical transition amplitudes have been derived and discussed to some extent.[2,3] However, for quantitative studies the kinematical situation of an actual collision experiment must be carefully regarded, since it is crucial for condition (b) of the two-step hypothesis. In a previous paper,[4] based on general properties of the Bethe-Born theory, we have given evidence that the two-step hypothesis is violated in *any collision experiment*, provided that the kinematics is not restricted by experimental coincidence techniques. The present Letter provides, for the first time, results of quantitative numerical line-shape calculations of Auger lines after electron impact. We find that the line shapes are generally asymmetric, and shifted with respect to the theoretical Auger energy E_A^0. Moreover, their width (FWHM) exceeds the decay width Γ_0 by a noticeable amount, which is on the order of 10% even in the limit of high impact energies. These are effects of appreciable magnitude which have mostly been disregarded in the past; one must expect that their quantitative knowledge gives rise to reevaluation of atomic parameters which have been derived from empirical line-shape analysis. Our theoretical work is complemented by the first experimental measurements of the proposed line shift at high impact energies, reported in a separate paper,[5] which shows excellent agreement with theory.

The effects to be considered arise from the "post collision interaction" (PCI) between the Auger electron and any other free particle originating from the primary collision event. At low impact energies, PCI is known to produce considerable Auger line-shape shifts and distortions, both in photoionization and particle-impact ionization. For *photoionization* various quantitative line-shape theories exist,[6–9] some of which are in excellent agreement with experiments.[10] A recent result of particular interest is the postulated disappearance of PCI in photoionization beyond a certain photon energy,[8,11] even if it holds strictly only for the case of isotropic photoelectron emission.[12] Classically, it is explained by the time delay between Auger emission and the Auger electron's interaction with the photoelectron ("retarded PCI"): The interaction vanishes when the initial photoelectron escapes with higher kinetic energy than the subsequently emitted Auger electron. Retarded isotropic PCI models automatically ensure condition (b) of the two-step hypothesis for sufficiently high photon energies, in contrast to earlier "sudden" PCI theories.[6,7]

Apparently, a similar PCI cutoff (or at least a monotonic decrease) has long been assumed for the case of particle-impact ionization, even though it was never derived theoretically. Various experiments have investigated collisional PCI line shifts $\Delta\epsilon$ as a function of impact energy T; however, most of them focus on the region of low impact energies (up to a few times the ionization limit), where the T dependence is largest.[13] Moreover, instrumental line broadening, space charges, and contact potentials usually prevent the *absolute* measurement of line-shape parameters, such as the shift $\Delta\epsilon(T)$ of the maximum of the line. This, together with the absence of well founded theories to compare with, explains why previous assumptions about Auger line shapes after particle-impact ionization were mostly not based on solid ground.

Our calculation of the Auger line shape $L(T,E_A)$, representing the probability distribution for observation of the kinetic Auger energy E_A, proceeds as follows: In noncoincident Auger spectroscopy experiments, none of the fragments of the primary collision are observed; hence, the collision kinematics remains unknown. The observed Auger line shape L is then an incoherent average over line shapes $l(E',E'',E_A)$ occurring in single collisions with well determined kinematics; the averaged distribution L depends parametrically on the incident energy T. Within the common approximation of an *isotropic* post collision interaction, the kinematics of a single collision is fully specified through T and the energies E' and E'' of the ejected electron and scattered projectile, respectively. The following relation holds:

$$E'+E''=E_1(T)=T-E_B\,, \tag{1}$$

where E_B is the binding energy of the ejected electron, and $E_1(T)$ is commonly called the "excess energy" of the collision. With (1), the averaging process reduces to a single integral over line shapes $l(E',E'',E_A)$, weighted by differential impact-ionization cross sections $d\sigma/dE'$:

$$L(T,E_A)=[\sigma(T)]^{-1}\int_0^{T-E_B} l(E',E'',E_A)\frac{d\sigma}{dE'}dE'\,. \tag{2}$$

Normalization of $L(T,E_A)$ is maintained through division by the total ionization cross section $\sigma(T)$ for the inner-shell hole under consideration, provided that the functions $l(E',E'',E_A)$ are normalized to $\int l(E',E'',E_A)dE_A=1$.

The line shapes $l(E',E'',E_A)$ were numerically calculated from the semiclassical PCI theory of Russek and Mehlhorn;[8] they are in complete analogy to the photoionization Auger line shapes discussed in great detail there. The present extension to *two* final-state particles is straightforward,[8] but requires considerably higher computational efforts. Based on experience with the photoionization case,[10] we expect the functions $l(E',E'',E_A)$ to be excellent representations of Auger energy distributions, at least for collisions leading to dissimilar energies E' and E'' of the outgoing particles, which is most likely at high impact energies. We note that $l(E',E'',E_A)$ generally depends on the charges and masses of the particles involved; in the following we shall restrict the discussion to electron-impact ionization (two outgoing electrons) only. The more general collision process differs only in magnitude from this example, with the main conclusions remaining valid, as will be shown in a forthcoming publication.

The cross sections $d\sigma/dE'$ and $\sigma(T)$ were calculated in nonrelativistic first Born approximation (BA). One expects BA to be adequate for investigation of PCI-related effects as they mostly arise from the presence of a slow atomic electron released in a "soft" (or "glancing") collision.[4] The approximation should, however, break down at threshold, when all ionizing collisions are necessarily "hard" collisions, and exchange effects and long-range correlations between the projectile and the ejected electron become important.[2] The BA cross sections can be reformulated in terms of generalized oscillator strengths, which are analytically known for various atomic subshells if screened hydrogenic wave functions are employed. We found good agreement with Hartree-Slater cross sections for the innermost atomic shells when the effect of "outer screening" is taken into account, which is also crucial for the correct kinematical condition of Eq. (1). We have used the generalized-oscillator-strength formulas of Vriens and Bonsen,[14] modified for outer screening according to Walske.[15]

Typical results for one selected Auger line, Ar $L_3M_{2,3}M_{2,3}$, are presented in Figs. 1 and 2. Normalized line shapes $L(T,E_A)$ are shown for a variety of excess energies $E_1=T-E_B$ in Fig. 1, whereby the energy scale

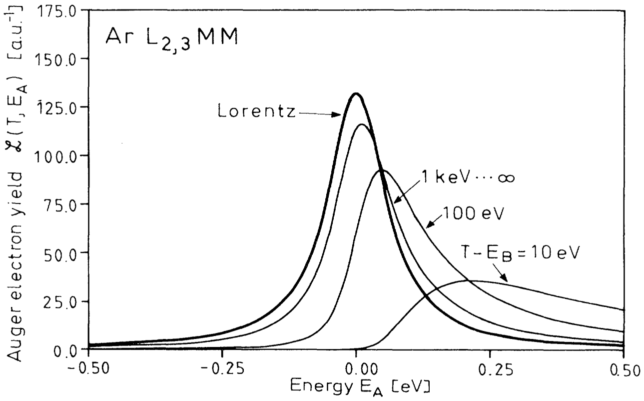

FIG. 1. Calculated line shapes of the argon $L_{2,3}$-*MM* Auger line after electron-impact ionization. Line shapes are shown for different values of the excess energy $T-E_B$, where T is the impact energy, and $E_B=248$ eV is the $L_{2,3}$-shell binding energy in argon. Note that the line shape does not visibly change for excess energies larger than 1 keV; in particular, a Lorentzian line shape, also shown for comparison, is never reached. The Auger energy scale E_A is plotted relative to the nominal Auger energy $E_A^0=201$ eV (center of the Lorentzian); the width Γ_0 of this transition is 130 meV.

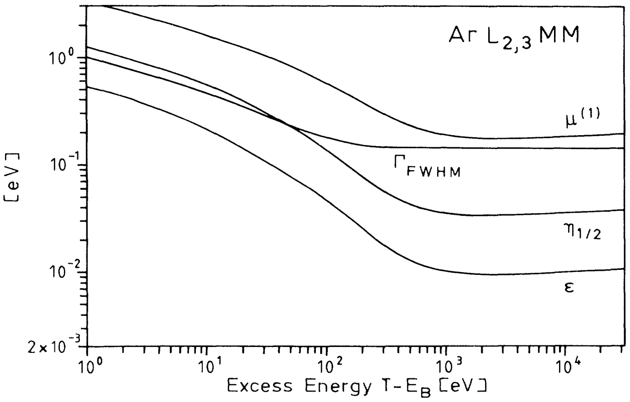

FIG. 2. Evolution of some characteristic Auger line-shape parameters as a function of the excess energy $T-E_B$. Shown are the full width at half maximum, Γ_{FWHM}; the position of the maximum, ϵ; the median, $\eta_{1/2}$; and the mean (or first moment), $\mu^{(1)}$, of the argon $L_{2,3}$-MM Auger line. The parameters ϵ, $\eta_{1/2}$, and $\mu^{(1)}$ are calculated with respect to the nominal Auger energy $E_A^0=201$ eV; hence their values would vanish identically if the line shape were Lorentzian.

E_A is plotted relative to the unperturbed Auger energy $E_A^0=201$ eV. One sees that the line shapes are severely distorted near the ionization threshold $E_1 \rightarrow 0$, where the present BA calculations yield only qualitative results, and almost look like Lorentzians in the limit of high excess energies, $E_1 \rightarrow \infty$, (equivalent to high impact energies $T\rightarrow \infty$), where BA is certainly valid. The important result is that the Lorentzians, predicted by the two-step hypothesis, are never reached. In fact the asymptotic line shapes $L(T\rightarrow \infty, E_A)$ exhibit noticeable shifts towards higher energies and are certainly broader than the Lorentzian, as can immediately be seen from the maximum position and height of the normalized lines.

For a more quantitative discussion, we shall consider various parameters that characterize the Auger line shapes. Figure 2 displays the impact-energy dependence of the apparent width $\Gamma_{\mathrm{FWHM}}(T)$, the maximum position $\epsilon(T)$, the median $\eta(T)$, and the mean (or first moment) $\mu^{(1)}(T)$ of the calculated lines $L(T,E_A)$. Note that ϵ, η, and $\mu^{(1)}$ are computed with respect to the unperturbed Auger energy E_A^0, and hence their values vanish identically for a Lorentzian. It follows from the definition of the median $\eta(T)$,

$$\tfrac{1}{2}=\int_{-\infty}^{\eta(T)} L(T,E_A)dE_A\,, \tag{3}$$

and from the definition of the first moment $\mu^{(1)}(T)$,

$$\mu^{(1)}(T)=\int_{-\infty}^{\infty} L(T,E_A)E_A dE_A\,, \tag{4}$$

that a line shape is certainly asymmetric when $\epsilon \neq \eta \neq \mu^{(1)}$. We found that the relation $\epsilon<\eta<\mu^{(1)}$ generally holds (indicating a line asymmetry with a high-energy tail), and that for not too high impact energies T all line-shape parameters decrease monotonically with increasing excess energy $E_1=T-E_B$, as shown in Fig. 2. Both results were qualitatively known from previous electron-impact experiments.[13] The interesting new result emerges in the limit of high (nonrelativistic) impact energies: There, the calculated line-shape parameters ϵ, η, and $\mu^{(1)}$ *tend towards finite values of appreciable magnitude;* they prove that Auger lines of free atoms always carry considerable non-Lorentzian contributions when observed after particle-impact ionization, in distinct contrast to photoionization. We emphasize that the present numerical results are of general validity; they follow from the fact that a finite fraction of the secondary electrons tend to be very slow after an ionizing collision at high impact energies T. Asymptotically[16] the (unnormalized) probability distribution $P(E')$ for these secondary electrons' energy E' approaches E^{-1} times the optical oscillator strength distribution df/dE for inner-shell ionization (where $E=E'+E_B$), a function which is not only finite but in most cases even peaking around $E'\approx 0$. Hence, one generally expects a nonnegligible fraction of secondary electrons to participate in PCI and, thus, to violate condition (b) of the two-step hypothesis. Considerations of this kind have already led to analytical predictions[3,4] for the shift $\epsilon(T)$, which were derived without explicit knowledge of the line shape $L(T,E_A)$ itself.

In Table I we have summarized the results of our cal-

TABLE I. Reduced line-shape parameters for several Auger transitions after high-energy ($T\rightarrow\infty$) electron-impact ionization. The first column specifies the Auger transition and the second lists values for the nominal Auger energy E_A^0 and the initial-state decay width Γ_0. The following columns present reduced (divided by Γ_0) values of the actual Auger linewidth Γ_{FWHM}, the position of the maximum ϵ, the median $\eta_{1/2}$, and the first moment $\mu^{(1)}$, respectively. For details, see text.

Auger line	E_A^0, Γ_0 (eV)	Asymptotic ($T\rightarrow\infty$) reduced parameters $\frac{\Gamma_{\mathrm{FWHM}}}{\Gamma_0}$ (%)	$\frac{\epsilon}{\Gamma_0}$ (%)	$\frac{\eta}{\Gamma_0}$ (%)	$\frac{\mu^{(1)}}{\Gamma_0}$ (%)
Ne K-LL	804, 0.27	104	5.2	17.8	90
Ar K-LL	2660, 0.68[a]	102	3	11.0	48
Ar L_1-MM	257, 2.0	107	6.3	19.4	64
Ar L_3-MM	201, 0.13	110	8.5	29.2	151
Kr $L_{2,3}$-MM	1460, 1.17	103	4.1	13.5	56
Ca L_3-MM	275, 0.21	108	7.1	24.3	121

[a] For Ar K-LL transitions, the decay width Γ_0 is 0.68 eV; however, the unperturbed (Lorentzian) Auger line is additionally broadened by the decay widths of the two final L-shell hole states. This additional broadening due to final-state decay is not included in the present work.

culations in terms of reduced line-shape parameters, i.e., parameters divided by Γ_0, the decay width of the initial inner-shell hole (which coincides with the unperturbed linewidth for Auger transitions leading to a stable final state). This is a convenient representation both for spectroscopic purposes as well as for comparison between different Auger transitions. The results are listed for a total of six prominent K and L Auger lines; the reduced parameters are those in the limit of high impact energies T (the energy dependence of the reduced parameters is very similar in all cases and resembles Fig. 2). The restriction to K and L Auger lines is appropriate for our use of screened hydrogenic wave functions; more sophisticated calculations with higher demands on computer time are certainly required for intermediate- and outer-shell Auger transitions.

One important result evolving from Table I concerns the apparent width Γ_{FWHM} of the Auger line, which exceeds the decay width Γ_0 by up to 10%. Such a systematic deviation is substantial, considering that much of our knowledge about Auger transitions comes from observed linewidths, and that comparison with theory is frequently performed at an uncertainty level well below 10%. We must expect that reevaluation of experimental data will lead to revised Auger transition probabilities in some cases. Apart from atomic physics, this may affect those disciplines where Auger line shapes are analyzed for additional broadening and distortion due to environmental effects on the emitting atom ("chemical shift"), as is usually done in molecular and solid-state physics. For instance, the treatment of dynamic screening of Auger transitions in solids[17] is mathematically equivalent to that of PCI, and the effects on the line shape are very similar; hence, comparison with Auger lines from free atoms may lead to misinterpretations if the effects considered here are neglected.

The relevance of the other reduced parameters, ϵ, η, and $\mu^{(1)}$, is somewhat more subtle, even though the large difference between them implies a distinct asymmetry of the lines. Empirical determination of both η and $\mu^{(1)}$ is almost impossible since these parameters receive large contributions from the far wings of the line, where experimental data are unreliable due to background and statistics. Only the shift ϵ of the maximum can be measured, as has been recently demonstrated.[5,13] Nevertheless, the asymmetry of the Auger lines persists and may lead to considerable errors due to asymmetric "pileup" effects in spectra with many overlapping lines, or to erroneous intensity ratios or line decompositions when Lorentzians are used in fitting routines. For example, a recent reevaluation of a section of the Ca L_3-MM Auger spectrum yielded a decomposition into only nineteen Auger lines when line shapes similar to the present ones were used, as opposed to 26 lines from an earlier analysis of the same spectrum with Lorentzians.[18]

In summary, we have performed quantitative studies on Auger lines of free atoms, confirming that they are never Lorentzians when obtained from noncoincident electron-impact experiments. The most conspicuous result concerns the apparent linewidth, which exceeds the decay width by up to 10% even at highest impact energies. Furthermore, the lines are generally asymmetric, which leads to noticeable distortions in spectra with many overlapping lines. One expects various implications for atomic, molecular, and solid-state physics from these effects, which were qualitatively unknown in the past. Physically, they arise from long-range continuum interactions (PCI) with unobserved slow collision products, i.e., from a violation of the two-step hypothesis for resonance creation and decay. Although demonstrated by specific examples, the present results are easily generalized and remain essentially valid for any collision process, including multiple ionization of atoms. Hence, it now seems established that non-Lorentzian Auger line shapes of free atoms are the rule rather than the exception, and can only be avoided under carefully selected kinematical conditions, as occur in high-energy photoionization or in coincidence experiments with one or more of the collision fragments.

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