Anomalous satellite intensity discrepancy in copper x-ray lines

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The copper $K\alpha$ spectrum contains asymmetries and satellite features due to secondary electron emission during ionization. Theoretical attempts at determining the intensities of these features are highly discrepant from experimental results. This discrepancy has been the subject of much discussion. In the present work we show that widely applied fitting procedures produce satellite intensities which depend strongly on assumptions regarding parametrization. We also show that recent high-accuracy satellite calculations can provide a copper $K\alpha$ spectrum in good agreement with experiment, thus resolving the discrepancy. This represents a major step toward a complete *ab initio* x-ray spectrum, a goal with significant implications for astrophysics, plasma physics, and tests of quantum electrodynamics.

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I. INTRODUCTION

The copper characteristic emission spectrum has been a topic of study for over half a century [1]. Copper x-ray lines are used as calibration for many experiments, and the copper photoemission spectrum is used in a variety of diffraction [2] and plasma experiments [3]. An accurate analytic representation of the copper spectrum would be highly useful for such experiments, as well as providing a test of many-body quantum mechanics and quantum electrodynamics.

It has long been known that an atom bombarded with electronic or photonic radiation produces "characteristic" radiation [4]. At energies greater than the $1s$-ionization threshold (the K edge) the most intense radiation is the $K\alpha$ line, which arises from the $2p \rightarrow 1s$ transition [5]. In heavier elements, relativistic splitting of the $2p$ shell divides the $K\alpha$ line into distinguishable $K\alpha_1$ and $K\alpha_2$ lines, arising from the $2p_{\frac{3}{2}} \rightarrow 1s_{\frac{1}{2}}$ and $2p_{\frac{1}{2}} \rightarrow 1s_{\frac{1}{2}}$ transitions, respectively. Additional features known as satellite lines have also been identified in early investigations.

Parratt [6] first proposed that the satellites arise due to "shake-off," a process in which an additional electron is ejected into the continuum during the ionization process. A population of atoms with both a core ionization *and* a shaken-off "spectator vacancy" will produce a distorted or shifted photoemission spectrum, which appears as satellites. Although alternative explanations for the satellites have been proposed [7,8] the adherence of the satellites to the adiabatic shake-off models (e.g., Refs. [9–11]) in the low-energy region provides strong evidence in support of a pure shake-off phenomenon [12–14], as do observations of the same satellite features in purely atomic species [15].

In the high-energy limit, photoionization takes place on a much shorter time scale than orbital relaxation. The outgoing photoelectron can be considered to leave the atom without perturbing the remaining electrons, which subsequently relax due to the increased effective nuclear charge. Under this approximation (the sudden approximation), shake-off occurs as a monopole transition between the unrelaxed atomic wave function and the fully relaxed wave function, where the final wave function may have one or more electrons shaken off into the continuum [16].

Numerous studies of the copper $K\alpha$ and $K\beta$ spectra have found the $3d$ satellite to contribute 14–30%. Deutsch *et al.* [17] were the first to measure the $K\alpha$ satellite contributions and considered numerous combinations of satellites in the $3s$, $3p$, and $3d$ shells in their analysis. This work found a $3d$ satellite contribution of 30%. Recent reanalyses of Deutsch *et al.*'s [18,19] experimental data have found $3d$ satellite contributions of 26% and 29%.

Galambosi *et al.*'s near-edge experiment found either a 26.2% shake-off contribution or a 13.5% shake-off contribution and a 12.7% shake-up contribution [20]. However, near-edge $K\beta$ experimental results from Enkisch *et al.* [21] found mainly shake-off behavior with a $3d$ contribution of 29%.

Two further studies [22,23] did not fit theoretical energy profiles to experimental results, but rather fit a series of Lorentzians. Ito *et al.* [23] explicitly associated the Lorentzian on the low-energy side of the main peak with the $3d$ satellite feature, while Holzer *et al.* [22] did not. Nevertheless, both experimental results are included in Table I for completeness, as are the experimental results discussed previously.

In contrast, theoretical studies have all predicted a $3d$ satellite intensity of 9%–15% [24–26] (Table I). Our recent work [26] has shown that adopting a multiconfiguration shake-off model improves the theoretical value only slightly for copper. It is the purpose of this paper to resolve this discrepancy.

Identification of the satellite contribution to the photoemission spectra is a difficult problem. Since the satellite emission lines overlap the diagram emission lines, spectra must be analyzed with the aid of atomic structure calculations. The procedure is as follows.

(1) Atomic structure calculations are used to determine the energies of the diagram and satellite lines.

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TABLE I. Theoretical and experimental values for the 3*d* satellite intensity in the literature. Experimental results differ by more than a factor of 2, with most results significantly higher than those predicted by theory. The present work resolves both the discrepancy within the experimental results and the discrepancy between theory and experiment.

	Shake-off Probability (%)
Theory	
Mukoyama and Taniguchi [24]	9.7
Kochur *et al*. [25]	12.3
Lowe *et al*. [26]	14.7
Experiment	
Galambosi *et al*. [20]	13.5
Hölzer *et al*. [22]	18.5
Ito *et al*. [23]	23.07
Chantler *et al*. [18]	26.0
Enkisch *et al*. [21]	20.0
Chantler *et al*. [19]	29.0
Deutsch *et al*. [17]	30.0

(2) These lines are convolved with a broadening function and then fit to an experimental spectum.

(3) The relative intensities of the broadened functions represent the percentage contribution of the diagram and satellite emissions.

Examples of this procedure can be seen in Refs. [18,19,27] for copper, and the same procedure is used with many other elements [23,28–30]. In each case, an experimentalist must assume that theoretical calculations are correct and that the best-fit shake-off value is representative of the true value.

Estimation of uncertainties is difficult. Not only are there correlated uncertainties in the fitting parameters but also the position of the lines themselves is uncertain—and this uncertainty can only be estimated based on the convergence of wave functions. There is no reliable and consistent method for evaluating this. It seems plausible, therefore, that this method of analyzing experimental spectra could be the cause of the discrepancy.

We show that the uncertainties in these values may be orders of magnitude larger than would be reported based on the usual covariance techniques. Despite a factor of 3 difference between the theoretical satellite intensities calculated in Ref. [26] and best-fit values found in Refs. [18,19,27], we are able to accurately reproduce the copper spectra with the theoretical values.

In all previous work on copper the valence electron configuration used in atomic structure calculation has been $3d^{10}4s^1$. For the purpose of completeness, here we consider the possibility that both $3d^{10}4s^1$ and $3d^9 4s^2$ configurations contribute to the spectrum.

II. CALCULATION

Detailed information on the multiconfiguration Dirac-Hartree-Fock (MCDHF) calculation of the copper spectrum can be found in our previous papers [18,19]. The present calculation follows the same procedure; however, the level of convergence obtained is slightly better than that obtained previously and we use an improved formulation of self-energy

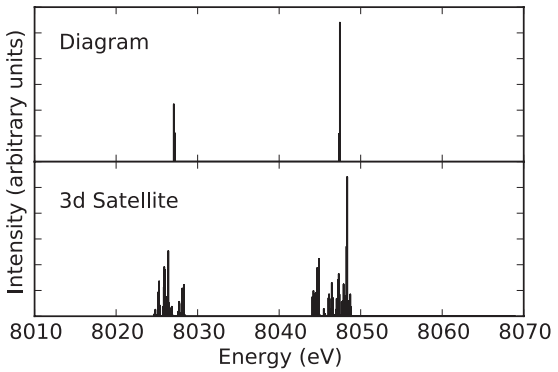

FIG. 1. Ouput of a multiconfiguration Dirac-Hartree-Fock (MCDHF) atomic transition calculation. Each line represents a transition, with the height of the line representing the transition strength (weighted statistically). Note that the relative intensity of the initial configurations (diagram and satellite) is not obtainable through standard MCDHF procedures.

contributions (to be discussed in future papers). The diagram lines were determined as in our previous work [19]; however, the satellite lines were determined using individual calculations for each atomic angular momentum eigenstate. The result is that the centroid of the $K\alpha_1$ satellite is approximately 0.2 eV closer to the diagram line, and the shape of the satellite is slightly different from our earlier calculation. Although these changes are small they significantly alter the fit to experimental data, further highlighting the extreme sensitivity of this procedure.

The output of an MCDHF calculation is a series of transition amplitudes and energies. The amplitudes represent the branching ratios from some initial state (assumed to be populated statistically) and, in order to be compared to experimental results, must be multiplied by a constant obtained through fitting to experimental data. A visual representation of this raw data is presented in Fig. 1. The relative intensity of the $K\alpha_1$ and $K\alpha_2$ lines is fixed by theory, as are the relative intensities of the multiplet components (most noticeable in the 3*d* satellite). The relative intensity of the satellite series compared to the diagram series must be obtained either through fitting to experimental data or through separate shake-off calculations (e.g., Refs. [24–26]).

Prior to fitting, the transition lines presented in Fig. 1 must be broadened. Typically, all transitions corresponding to the $K\alpha_1$ transition are broadened equally, and all transitions corresponding to the $K\alpha_2$ transition are broadened equally. A third parameter is used to account for the *additional* broadening due to a spectator vacancy. Strictly speaking, each transition should have a unique natural linewidth. In practice, however, *ab initio* linewidths are not in sufficiently good agreement with experiment for this to take place. The present parametrization is a compromise between physical accuracy and limiting the number of free parameters, and can be interpreted as assuming that upper- and lower-level state lifetimes are dominated by auger effects. The resulting spectra consists of the sum of the lines in Fig. 1, each of which has been convolved with some broadening function. In the present work this function is a Lorentzian, as experimental broadening has already been accounted for [17].

The experimental data used in this work were extracted from the work of Deutsch *et al.* [17]. The residuals from Deutsch *et al.*'s original fitting have been scanned and added to Deutsch *et al.*'s parametrization to provide a more accurate experimental reconstruction and meaningful χ^2_{reduced} values. We note that the random fluctuations in Deutsch *et al.*'s original work appear to be smaller than the expected 2σ and that this causes a χ^2_{reduced} that can be lower than 1.

III. RESULTS AND DISCUSSION

In the first column of Table II [fit (a)], we reproduce the fitting method used by most previous investigations, using six parameters (some previous studies have used more than six, but none have used less). The parameters allow for a linear scaling of the theoretical spectra (reported here as $K\alpha_1$ and $K\alpha_2$ energy shifts), for $K\alpha_1$ and $K\alpha_2$ broadening, for the intensity of the $3d$ spectator contribution, and for additional broadening of the $3d$ spectator contribution.

The best-fit $3d$ satellite intensity is 39%, significantly higher than our previous result of 26% [19]. The theoretical values used in the present work are slightly different from our previous results due to improved optimization and convergence, and the original experimental data are used in this work whereas previous work used a parametrization, hence the different ansatz. This emphasizes the sensitivity of the fitted parameters to slight changes in the fitting procedure or theoretical method.

In fits (b) to (d) of Table II we consider the same theoretical and experimental data, but remove some parameters from our fitting. In fit (b) the fitting procedure is identical to that of fit (a) except that we do not allow additional spectator broadening. This increases the χ^2_{reduced} by only 0.17 but reduces the satellite intensity to 30%. In fit (c) we allow satellite broadening but constrain the small (<0.15 eV) energy offsets to 0. The resultant χ^2_{reduced} (1.21) is still close to 1, but perhaps surprisingly the fitted satellite intensity has now increased to 49%. It is clear that by choosing different fitting parameters the satellite intensity can change enormously while still producing a $\chi^2_{\text{reduced}} \simeq 1$.

In fits (e) to (h) we constrain the satellite intensity to the theoretical value of 14.7% [26]. This increases the χ^2_{reduced} relative to fits (a) and (b), but still permits $\chi^2_{\text{reduced}} \approx 1$ for fits (e) and (f). Negative relative $3d$ spectator broadening is *possible* but quite *improbable* in fits (e) and (g). This is probably an artifact of the fitting, and in both cases setting the broadening to 0 has a negligible impact on the χ^2_{reduced}. Comparing columns (b) and (f) (highlighted), $\chi^2_{\text{reduced}} \simeq 1$ with the satellite intensity in the range 0.30 to the theoretical value of 0.147. In both cases, the additional spectator broadening commonly used in this method of fitting is not required to obtain a good match to experimental data.

Fits (a) and (f) are presented in Figs. 2 and 3. The residuals are nearly identical for the $K\alpha_2$ line, even though the satellite intensity has been reduced by almost a factor of 3. The theoretical result slightly underestimates the asymmetry of the $K\alpha_1$ line on the low-energy side, although this could also be explained by a small uncertainty in the energy of the $3d$ satellite.

Fits (b), (c), and (f) all provide good agreement with experiment, with value of χ^2_{reduced} of 0.73, 1.21, and 1.01, respectively. Each case fixes either the spectator broadening to 0, the experimental-theoretical offset to 0, or the shake-off probability to the theoretical value. The shake-off probabilities that are determined from these fits range from the theoretical value of 14.7% up to a maximum of 49% in fit (c). This provides a clear indication that the method produces unreliable shake-off determination at the current level of experimental and theoretical accuracy.

Finally, we consider in Table III the case where both the $3d^{10}4s^1$ and $3d^9 4s^2$ configurations contribute to the experimental spectrum. This would occur if both valence configurations were partially occupied prior to ionization or if the ionization event itself populated the higher-energy

TABLE II. Fitting of theoretical data to experimental copper $K\alpha$ spectrum. Parameters constrained to 0 for a particular fit are indicated with a blank space. Columns (a)–(d) correspond to fittings in which the satellite intensity is allowed to vary; columns (e)–(h) correspond to fittings in which the satellite intensity is set to its theoretical value. The theoretical modeling of $3d$ satellite structure (model f) yields a perfectly plausible result with a good fit.

	Cu $3d^{10}4s^1$ fitting parameters							
	(a)	**(b)**	(c)	(d)	(e)	**(f)**	(g)	(h)
Fitted values								
$K\alpha_1$ width (eV)	1.94	**2.26**	1.70	2.15	2.49	**2.45**	2.52	2.42
$K\alpha_2$ width (eV)	2.64	**2.97**	2.41	2.89	3.16	**3.11**	3.18	3.07
Δexperimental $K\alpha_1$ (eV)	−0.12	**−0.14**			−0.16	**−0.12**		
Δexperimental $K\alpha_2$ (eV)	−0.12	**−0.14**			−0.22	**−0.23**		
$3d$ spectator broadening (eV)	0.94		1.13		−0.46		−0.90	
$3d$ shake-off (Probability)	0.39	**0.30**	0.49	0.38				
Fixed values								
$3d$ shake-off (Probability)					0.147	**0.147**	0.147	0.147
Derived values								
Total spectrum peak ($K\alpha_1$) (eV)	8047.82	**8047.84**	8047.88	8047.93	8047.88	**8047.89**	8048.02	8048.02
Total spectrum peak ($K\alpha_2$) (eV)	8027.75	**8027.68**	8027.82	8027.82	8027.68	**8027.86**	8027.82	8027.89
χ^2_{reduced}	0.56	**0.73**	1.21	1.71	1.00	**1.01**	2.67	2.74

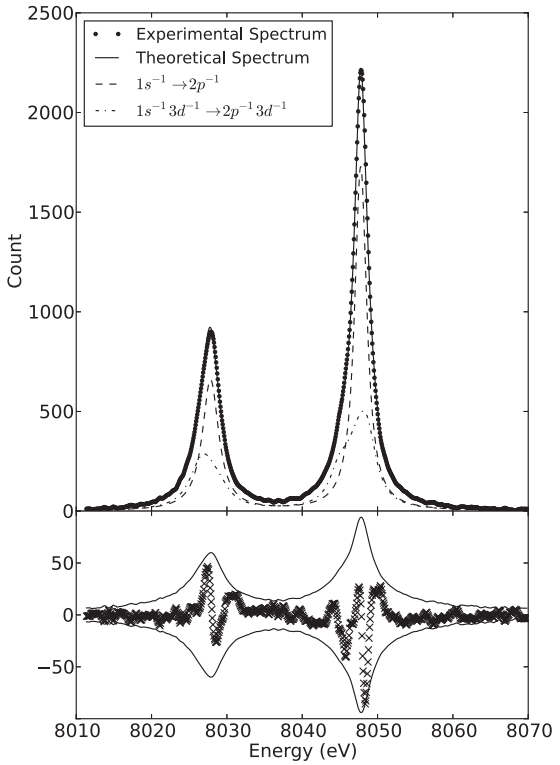

FIG. 2. Copper spectrum fitted with all parameters free (see Table II). This best-fit satellite intensity is 39.7%, almost 3 times greater than that predicted theoretically (cf. Fig. 3). The lower plot contains residuals, with the solid lines representing $\pm 2\sigma$.

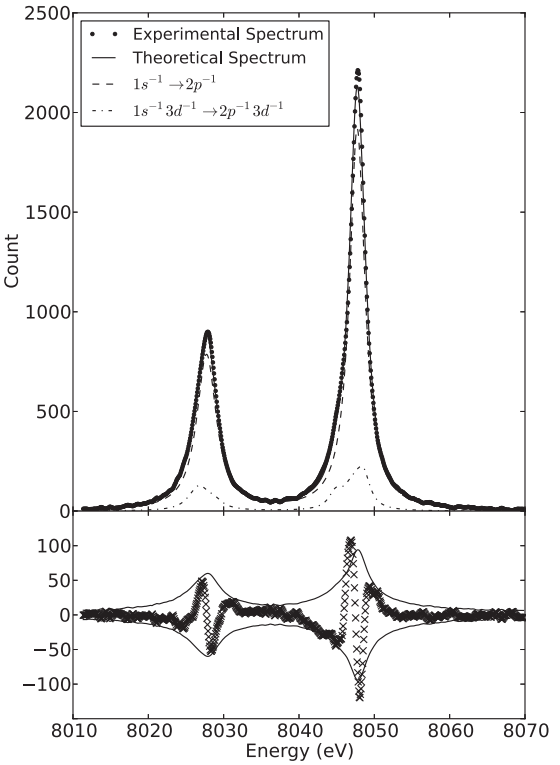

FIG. 3. Copper spectrum with $3d$ satellite intensity set to 14.7%, as calculated by *ab initio* multiconfiguration shake-off calculations [26] (see Table II). This fit has a χ^2_{reduced} of 1.01 (cf. Fig. 2). The lower plot contains residuals, with the solid lines representing $\pm 2\sigma$.

$3d^9 4s^2$ levels. Two fits were carried out, one with the energy offsets as free parameters and one with the offsets fixed by theory. Neither case observes any contribution from $3d^9 4s^2$, thereby justifying earlier theoretical assumptions; so that fit (i) $\equiv$ fit (a).

IV. CONCLUSION

Without a physical justification for the numerous parameters fitted in previous work, satellite intensities can *at best* be determined with an accuracy of $\pm 10\%$. Of the fitting procedures used in this paper the best-fit satellite intensity (30%), the satellite intensity with no theoretical-experimental offset (49%), and the theoretical value (14.7%) all result in fits with a χ^2_{reduced} close to 1. The range of these values is far greater than would be reported using the usual covariance matrix.

The *maximum* offset required in any of the fits here is 0.2 eV. Ultimately, the satellite intensity in copper may not be determinable without higher-accuracy experimental data. The considerations outlined here, however, are transferable to other atomic systems with better-resolved experimental spectra.

The results presented herein suggest that existing methods of fitting satellite intensities to experimental results can produce best-fit values with an uncertainty much greater than that of the least-squares estimate. Parameters can be highly correlated and highly sensitive to inaccuracies in calculations. Altering the assumptions made in the fitting process yields significantly different results by the earlier criterion. We have shown that recent *ab initio* determinations of satellite intensities are consistent with experimental results, thus resolving the discrepancy observed by previous researchers. The critical requirement is for new higher-accuracy experimental data to investigate these satellites further and thereby accurately constrain the experimentally determined shake-off probability. Having *ab inito* calculations that are able to reproduce the satellite intensity and spectra asymmetry represents a vital

TABLE III. Fitting parameters for a mixture of valence configurations $3d^9 4s^2$ and $3d^{10} 4s^1$. The first column allows an experimental-theoretical offset, while the second does not. The results imply that the $3d^9 4s^2$ configuration is not at all populated.

	Cu $3d^9 4s^2 + 3d^{10} 4s^1$	
	(i)	(j)
Fitted values		
$3d^{10} 4s^1$ contribution	100.0%	100.0%
$3d^9 4s^2$ contribution	0.0%	0.0%
Δexperimental $K\alpha_1$ (eV)	−0.11	
Δexperimental $K\alpha_2$ (eV)	−0.11	
$3d^{10} 4s^1$ parameters		
$K\alpha_1$ width (eV)	1.94	1.70
$K\alpha_2$ width (eV)	2.64	2.41
$3d$ shakeoff (Probability)	0.39	0.49
$3d^9 4s^2$ parameters		
$3d$ Shake-off (probability)	0.00	0.00
χ^2_{reduced}	0.56	1.21

step toward complete *ab initio* agreement with experiment, with significant implications for astrophysics, x-ray calibration standards, and tests of quantum electrodynamics.

Several lines of investigation could further help to resolve the problem. If our interpretation of the satellite features is correct—that they arise due to vacancies present prior to the transition—then other spectra in the K series should be reproducible using the methods presented here. Equally, additional studies into the remaining transition metals are necessary. In particular, multiconfiguration atomic structure calculations have been performed previously for scandium. The shape of the scandium profile also depends distinctly on the relative widths of the diagram and satellite lines and represents a good candidate for further study.

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