

Atomic form factors and photoelectric absorption cross-sections near absorption edges in the soft X-ray region

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Abstract. Reliable knowledge of the complex X-ray form factor [$\text{Re}(f)$ and $\text{Im}(f)$] and the photoelectric attenuation coefficient (σ_{PE}) is required for crystallography, medical diagnosis, radiation safety and XAFS studies. Key discrepancies in earlier theoretical work are due to the smoothing of edge structure, the use of non-relativistic wave functions, and the lack of appropriate convergence of wave functions. These discrepancies lead to significant corrections for most comprehensive (i.e. all-Z) tabulations. This work has led to a major comprehensive database tabulation [Chantler, C. T. (2000). *J. Phys. Chem. Ref. Data*, 29, 597-1048] which serves as a sequel and companion to earlier relativistic Dirac-Fock computations [Chantler, C. T. (1995). *J. Phys. Chem. Ref. Data*, 24, 71-643]. The paper finds that earlier work needs improvement in the near-edge region for soft X-ray energies, and derives new theoretical results of substantially higher accuracy in near-edge soft X-ray regions. Fine grids near edges are tabulated demonstrating the current comparison with alternate theory and with available experimental data. The best experimental data and the observed experimental structure as a function of energy are strong indicators of the validity of the current approach. New developments in experimental measurement hold great promise in making critical comparisons with theory in the near future. This work forms the latest component of the FFAST NIST database [<http://physics.nist.gov/PhysRefData/FFast02/Text/cover.html>].

INTRODUCTION

Tables for form factors and anomalous dispersion are of general use in the UV, x-ray and γ -ray communities. Much of the recent theoretical basis for these was contributed by Cromer, Mann and Liberman[1] while much of the experimental data was synthesised by Henke et al.[2] The generality of these works has entailed numerous simplifications compared to detailed relativistic S-matrix calculations. Detailed S-matrix results do not appear to give convenient tabular application for the range of Z and energy of general interest, while the tables have limited validity across extended regimes.

Earlier relativistic Dirac-Fock computations[3] addressed the primary interactions of X-rays with isolated atoms from $Z = 1$ (hydrogen) to $Z = 92$ (uranium) and computed them within a self-consistent Dirac-Hartree-Fock framework. This has general application across the range of energy from 1-10 eV to 400-1000 keV, with limitations as the low- and high-energy extremes are approached. Tabulations are provided for the f_1 and f_2 components of the form factors, together with the photoelectric attenuation coefficient for the atom, μ , as functions of energy and wavelength. This work has lead to significant quantitative improvement above 30 keV to 60 keV energies, near absorption edges, and at 0.03 keV to 3 keV energies. Recent experimental syntheses are often complementary

to this sort of approach.

Discrepancies between currently used theoretical approaches [4, 5, 6, 7, 3] of 200 % exist for numerous elements from 1 keV to 3 keV X-ray energies. This level of inconsistency may be surprising to some users who have conventionally viewed log-log plots covering decades in energy and attenuation coefficient, but these discrepancies have been present in the literature for decades.

A major comprehensive database tabulation [8] addresses these key discrepancies and derives new theoretical results of substantially higher accuracy in near-edge soft X-ray regions (0.1 keV to 10 keV). The grid size and spacing of the reported tabulation is given with synchrotron users in mind, where fine grids near edges are necessary and continuous energy scans are possible. All energies above 0.1 keV, and all elements to $Z=92$, were investigated in this computation. Estimates for the expected accuracy of the pair of publications[3, 8] is given across the full range of Z and energy, including near-edge limitations of wavefunction convergence and near-edge structure itself. An obvious point, for XAFS and MAD users, is the absence of near-edge structure, and perhaps a deviation of the edge onset from a particular solid-state system. This is an advantage, which serves to separate the oscillatory near-edge structure and discrete lines or near-edge zeroes from a reference baseline for the given element.

This paper summarises new results in areas of critical recent discussion, and some preparation towards a proper resolution of theoretical and experimental flaws.

MAJOR DISCREPANCIES

Compilations of experimental data for form factors are widespread, particularly for common elements such as silicon, copper, silver and gold over the central X-ray energies[5]. These are particularly useful in evaluating the reliability of a particular measurement, or the difficulty of an experiment in a given energy regime. However, the range of the imaginary coefficient in such compilations often varies by 10% to 30% [Figure 1]. This implies in general that claimed experimental accuracies of 1%-3% are not reliable.

Strictly, one or two of the results in such compilations could indeed reach the claimed accuracy, but the remainder must then be in error by up to 10σ . The effect of a 10% error is similar to a 10% error in the thickness of the sample, or a 10% error in the exponent of the probability of photoabsorption through a sample. This variation seems almost independent of the year of the experiment, or the specification for high or low energy measurements.

A second general source for an experimental best-fit line is given by the Centre for X-Ray Optics, Lawrence Berkeley Laboratory[2, 6, 9]. These references present experimental-theoretical syntheses for the complex form factor in the softer X-ray regime. As a weighted evaluation of experimental data, they are extremely useful. They are also extremely valuable in the very soft X-ray regime where multi-electron interactions occur which are not addressed by general IPA (independent particle approximation) theories. However, no variation or error bar is associated with this single fit, and in soft X-ray regimes, near-edge regimes and other areas the result may be in sharp discrepancy with theory and expected results, or with the best available data. The deviations lie at the

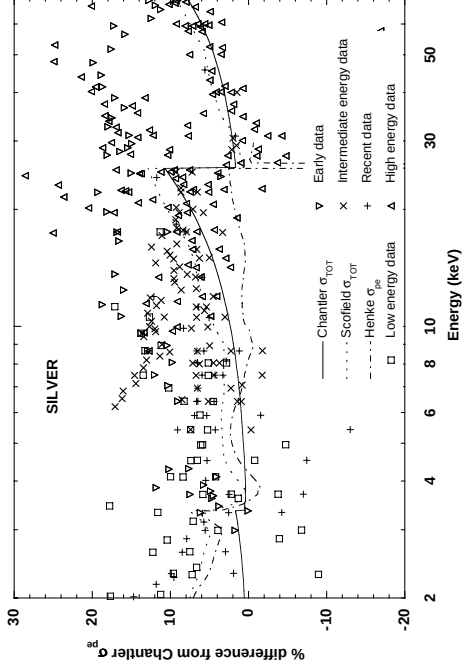


FIGURE 1. Attenuation in silver relative to Chantler (1995) σ_{PE} . Scattering indicated by Chantler σ_{TOT} . Silver shows an array of data [7] quoted at 1% - 3%, but with variation of 28%, or 16% for more recent measurements. Theory shows variations of 7%.

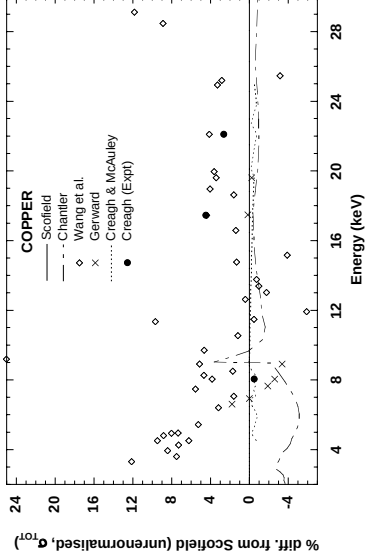


FIGURE 2. Major discrepancies in the form factor of copper. Scattering is minor. Quoted experimental uncertainty given by symbol size [7, 10, 11, 17]. Measurements of f'' or σ_{PE} for copper have quoted 1% accuracy, but discrepancies reach 25% near edges and 8% away from edges. This has been stressed recently. Theories disagree by 6%, and experiment and theory disagree by 12% away from edges.

same 10% - 30% level as the variation of less critical compilations.

RELIABILITY CRITERIA FOR EXPERIMENTAL RESULTS: WHICH SHOULD ONE CONSULT?

Turning exclusively to measurements claiming high accuracy, i.e. 1%, for copper, we narrow the spectrum of measurements only slightly [10, 11] [Figure 2]. Rather than referencing papers claiming high accuracy, one can require that optimal or preferred experimental techniques are followed in papers used for comparison or reference. This would include

- (i) accurate determination of thickness, composition and purity of samples

- (ii) accurate energy calibration and monochromatic sources
- (iii) accurate orientation and alignment techniques
- (iv) control of harmonic contamination and source divergence
- (v) other criteria including statistical precision and detection linearity [12, 13, 14].

In the case of silicon, these criteria were carefully evaluated as part of an international effort to address such variations. The result was a very accurate and consistent set of measurements for silicon, including contributions by Creagh, Barnea, Gerward, Kerr del Grande and others [12, 15]. These same principles were applied, in the experimental references cited, and specifically for the copper examples given in Fig. 2; and yet the variation and discrepancies remain. Hence, a number of systematic error sources are not accounted for. For experimentalists these (unknown) error sources represent an intriguing limitation to X-ray investigations of all types, and hence an issue of fundamental importance.

UNCERTAINTIES NEAR SOFT X-RAY LII, LIII, MIV, MV EDGES

The greatest discrepancies between these theories occur near edges, with deviations by factors of 5 or more between predictions. The cause of near-edge error in theoretical computations is often inadequate interpolation, extrapolation or integration methods. These introduce oscillations or discontinuities into the data [16]. The cause of near-edge error in experimental compilations is often due to neglect of the edge region or smoothing through edge structure [6]. The cause of near-edge error in specific experiments is often due to the dramatic variation of form factor with energy, requiring both accurate absolute intensity measurement and also precision energy calibration [13].

Assuming that these issues have been correctly addressed, theory will disagree with experiment near edges by large factors due to XAFS and related structure. This can reach a 200% discrepancy between IPA theory and a solid-state experiment [17]. Even if the experiment is performed on a monatomic gas, there may be pressure-dependent structure and other strong oscillatory behaviour near edges. Some of this structure (shape resonances and Cooper minima) may be qualitatively predicted by some theoretical approaches, but often the experimental result will show significant quantitative discrepancy [18].

The largest discrepancies between Chantler (1995) and the Scofield theory are not due to any of these causes. Chantler (1995) claims uncertainties of up to a factor of two in soft X-ray near-edge regions. Saloman, Hubbell and Scofield (1988) refers to 10% - 20% discrepancies from experimental data in the medium-Z regime, which may be taken as an uncertainty estimate. In most elements and regions, the near-edge variation falls within these error bars. Such experimental data is not sufficiently precise to distinguish between these two theories, or even to observe edge structure.

In the region 1 keV – 2 keV for particular edges in medium or high-Z elements, large discrepancies are observed between these two theoretical treatments. This is illustrated in Fig. 3 for Zn, $Z=30$. This is not due to XAFS or any such near edge oscillation.

Relative to appropriate high-energy theory, which would yield well-defined edges and smooth behaviour for each orbital on a log-log plot, the results of Scofield, Chantler

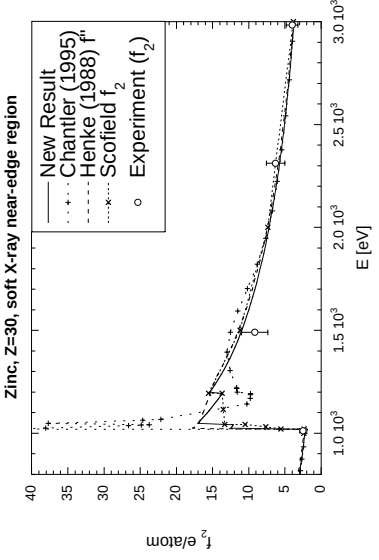


FIGURE 3. Attenuation in Zn ($Z=30$), represented by $\text{Im}(f)$. Experimental data from [7]. Refs [3, 2, 4] agree with available experiment, but all have large error, as indicated by the new result [8].

and Henke are all in error. This error arises from an accumulation of minor errors in inner shell electronic wavefunctions. Particularly for near-edge energies, these errors accumulate, which is a strong reason for the low accuracy claimed by theory in this region. The K and LI shell are accurately computed, and the form factors for these sub-shells are accurate; but the errors for LII and LIII are amplified, and also fall in increasingly difficult soft X-ray energies. Hence the wavefunction solution for the orbital radial electron density, which leads to the computation of the near-edge form factor, becomes unreliable and increasingly inaccurate.

Within the convergence criteria for the DHF wavefunctions, this may be more or less difficult to address, depending upon the exchange potential and method used. We have been able to retain the original formalism and to require a better and more uniform convergence in these regions.

When the wavefunctions are thereby improved and this issue is addressed, we obtain the ‘New Result’ [Figure 3]. Appropriate high-energy theory would expect a behaviour very closely following this. This then obtains the theoretically expected IPA edge structure. The precision of these results is dramatically improved. The accuracy is still limited as discussed above. We would claim no better than 20% - 30% accuracy in this region, even though experiment may agree to better than 10%.

The largest effects are represented by Zn $Z=30$ and Pm $Z=61$. These represent 1.5 σ errors for the 1995 tabulation, where σ is estimated as 50%, as stated above. In these cases the Scofield result yields 160% and 220% errors near the edge (or 4-5 σ errors); conversely, [3] yielded maximum 68% and 87% errors respectively at the same locations. We believe that the cause of the Scofield discrepancies lies in the same problem regarding the electron distribution. This will be affected by the formalism used to derive wavefunctions. The Chantler (1995) errors tended to be extended over slightly larger energy ranges (i.e. 40-50% versus 20-30% above the edge).

Usually the experimental data is inadequate to make a critical comparison of theory. However, the general trend is given by Kr $Z=36$ [Fig. 4] [19]. The predicted new structure matches up well with such optimum experiments, as opposed to alternative theoretical structures.

Recent work by our research group has reinvestigated copper explicitly, and yielded

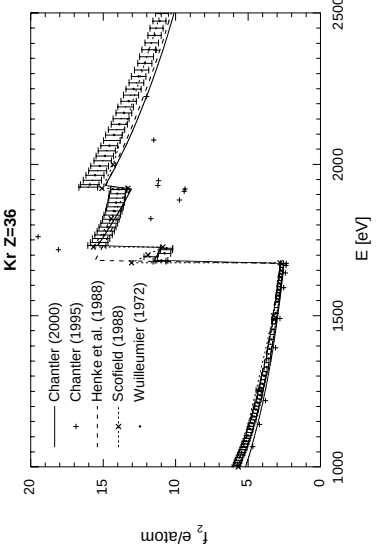


FIGURE 4. Plot illustrating the consistency of near-edge structure between experiment [19] and [8], as opposed to earlier theory. $\text{Im}(f) = f_2$. Experimental values include contributions from scattering. $[\mu/\rho]$ (in cm^2/g) = f_2 (e/atom) $\times 5.02152 \times 10^5$.

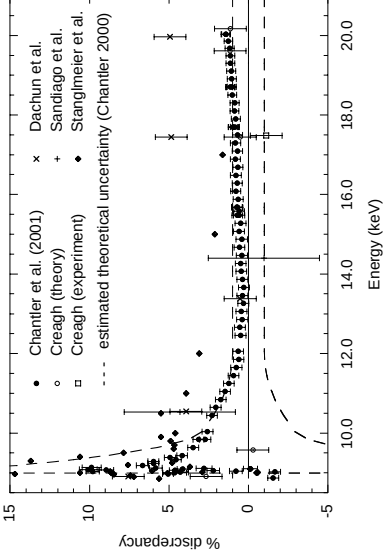


FIGURE 5. Comparison between [14] and earlier measurements [20, 10, 21, 17] for copper. Data are compared to theory [3, 8], $\left\{ \% = \frac{[\mu/\rho] - [\mu/\rho]_{\text{theory}}}{[\mu/\rho]_{\text{theory}}} \right\}$, with theoretical uncertainty given by the region between dashed lines, which increases to 20% near the K-edge. The comparison of mass absorption coefficient is identical to that of $\text{Im}(f)$. An alternate theory [17] agrees with the reference theory, and agreement of the experimental data with current theory is good.

dramatically reduced error bars [Fig. 5]. This result with 0.3% uncertainty is able to verify theory in a conclusive manner, in this energy regime, for the first time.

CURRENT EXPERIMENTAL ISSUES

Figures 4,5 show a potential significant absolute experimental offset at the 1σ level. In fact, there is a common tendency towards experimental results lying higher than theoretical predictions. In some cases this is partly due to an inadequate control of scattering, divergence and alignment. Misalignment or significant divergence will both lead to measured attenuation coefficients lying higher than correct values, while the effect of uncertainty in scattering depends on the model assumed for the given sample.

This remains an issue for experimental comparisons. This sort of discrepancy is strong motivation for high accuracy experiments to address these issues.

Experimental and theoretical difficulties remain in central X-ray energies, but also at VUV energies where the IPA assumption fails, and at very high energies. In both regimes experimental measurement difficulties arise, and at high energies it is very difficult to isolate problems of the photoeffect computation from those of the computation of scattering contributions. The other difficulty at high energies relates to exactly what type of sample (gas, foil, crystal or other) is under investigation, because this will change the dominant scattering contributions by orders of magnitude.

CONCLUSION

Several generic difficulties with theoretical determinations of the atomic form factor in the X-ray region have been resolved. Selected experimental data sets suggest the accuracy of [8] compared to most alternatives. Key discrepancies are often due to the smoothing of edge structure, the use of non-relativistic wavefunctions, and the lack of appropriate convergence of wavefunctions.

In general experimental data are not sufficiently accurate to assess theory at the level required. However, the best experimental data and the observed experimental structure as a function of energy are strong indicators of the validity of the current approach. New developments in experimental measurement hold great promise in making critical comparisons with theory in the near future.

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