Theoretical Determination of Characteristic X-Ray Lines and the Copper $K\alpha$ Spectrum

C. T. Chantler* and A. C. L. Hayward

School of Physics, University of Melbourne, Melbourne, Australia

I. P. Grant

Mathematical Institute, Oxford University, Oxford, United Kingdom

(Received 9 May 2009; published 16 September 2009)

Core excitations above the $K$ edge result in $K\alpha$ characteristic x-ray emission. Understanding these spectra is crucial for high accuracies in investigations into QED, near-edge x-ray structure and advanced crystallography. We address unresolved quantitative discrepancies between experiment and theory for copper. These discrepancies arise from an incomplete treatment of electronic interactions. By finding solutions to relativistic multiconfigurational Dirac-Fock equations accounting for correlation and exchange corrections, we obtain an accurate reproduction of the peak energies, excellent agreement of theory with experiment for the line shapes, good convergence between gauges, and account for the $K\alpha$ doublet ratio of $0.522 \pm 0.003:1$.

DOI: 10.1103/PhysRevLett.103.123002

PACS numbers: 32.30.Rj, 31.30.jf, 32.80.Hd

Spectroscopic lines resulting from atomic transitions gave the first insights into atomic structure and quantum mechanics [1]. Today, the most well tested theory in nature [2–4], quantum electrodynamics (QED), is probed using the same techniques. The $K\alpha$ spectrum, a designation from the early days of quantum mechanics, denotes the transition $2p \rightarrow 1s$. For heavier atoms, the fine splitting between the $2p$ states results in distinct peaks for the $2p_{1/2} \rightarrow 1s$ ($K\alpha_2$) and $2p_{3/2} \rightarrow 1s$ ($K\alpha_1$) transitions.

These diagram lines (Fig. 1) are the standard candles of x-ray spectroscopy. Wavelength-dispersive experiments, the cornerstone of high accuracies for most of the x-ray regime, are almost exclusively defined by angles, which must be calibrated to these peaks [5]. Alignment of experimental data with physical parameters requires positions and intensities of multiple peaks. Experiments usually have numerous systematics to account for, such as non-linear scaling, diffraction and slit broadening, and the constraint of key parameters yields more critical and definitive results [6,7].

Elementary statistical arguments suggest that the $K\alpha_2:K\alpha_1$ integrated intensity ratio should be 0.5:1; in reality this ratio increases slowly with atomic number $Z$ [8–11]. The simplest correct explanation is that the rate of deexcitation of the $1s$ hole by capture of a $2p_{1/2}$ electron is greater than that for capture of a $2p_{3/2}$ electron. Hence by virtue of the faster decay rate, the linewidth of $K\alpha_2$ is greater than that of $K\alpha_1$ [12,13]. The increase of the intensity ratio with $Z$ is supported by nonrelativistic Hartree-Fock calculations [14] especially when shell coupling is taken into account.

Relativistic effects become more pronounced as $Z$ increases in the transition metal region of the periodic table [15] and fully relativistic theory should be used. Indicators include the growth of intermediate coupling as $Z$ increases and the need to introduce energy offsets and dispersion scales [15–17] when trying to reconcile theory and experiment. Most earlier work modeled this by fitting spin-orbit parameters to experimental splittings of diagram lines [15,17]. Other studies indicated the need for relaxation and rearrangement of the atom prior to emission [15,18]. The outermost $4s$ has usually been ignored [17,19–22].

The complex structure of $K\alpha$ lines, which are not a simple sharp doublet, has been the source of much speculation: explanations invoke both atomic and solid state mechanisms [14,17]. Generally, the observed spectrum has been fitted to a sum of line profiles whose individual positions and strengths are determined solely by the fitting process without recourse to ab initio models. Explanations range from Kondo-like interaction of conduction electrons with core-hole states [23], final-state interactions between the core hole and the $d$ shell [24], electrostatic interactions of the $3d$ and $2p$ shells [25] to shake-up processes [13,19]. The first and last of these explanations have yielded good fits to particular subsets of data.

![Diagram](image-url)

**FIG. 1.** Dominant radiative transitions between subshells. A statistical population would predict 0.5:1 for $K\alpha_2/K\alpha_1$, and 1:6 for $K\beta/K\alpha$. Quoted experimental ratios from [8].
Scofield [14] made Dirac-Hartree-Fock (DHF) calculations, and by comparing with earlier work, showed that exchange effects were essential to explain observed intensity ratios throughout the periodic table. Kuhn and Scott [15] made intermediate coupling calculations with Hartree-Fock wave functions suggesting that the most important $K\alpha$ satellites in the range $19 \leq Z \leq 32$ were due to an additional vacancy in the $2p$ subshell. More recently, modelling of $K\alpha$ spectra has exploited the multi-configurational DHF (MCDHF) computational framework of Grant et al. [26–28], often with modifications [8,17,29].

Modern ab initio theory for $N$ electron systems uses atomic state functions (ASFs) which are linear combinations of configuration state functions (CSFs). Each CSF is a sum of antisymmetrized products of atomic orbitals projected onto a subspace of total angular momentum $J$ and parity $\pi$ in which the $N$ electrons are distributed amongst open and closed subshells. The inner electrons of copper, $Z = 29$, show strong relativistic effects. Precise measurements of the spectra reveal asymmetric profiles. The importance of copper as a laboratory light source [30] meant that the satellite spectrum was understood empirically at an early stage. The excellent analysis of Deutsch et al. [17], using MCDHF calculations to locate the transition energies and amplitudes of the copper $K\alpha$, diagram and satellite lines, revealed that the $3d$ electron hole satellites could indeed account for the observed asymmetry (Fig. 2). These calculations were based on software [28] in which the calculation of transition rates used a common set of orbitals for upper and lower states. This average level model is optimal for neither of the states and limits the accuracy with which energies and transition rates can be predicted. As a starting point for this investigation and with assistance of Deutsch et al., we have reproduced their results.

Fischer and colleagues (Chapter 6, [31]) showed how the multiconfiguration Hartree-Fock procedure (MCHF) can be used for systematic studies of correlation in many-electron atoms. The active space approach focuses attention on extending the CSF set systematically, starting from a simple atomic configuration, to balance the description of correlation in the ASF. Such independent calculations change the orbitals and the CSF expansion. Calculations of line strengths, etc., based on a common set of orbitals must therefore be modified (Chapter 8, [32]). Olsen et al. [33] showed how to use orbital sets from separate calculations to construct a biorthogonal orbital system compatible with MCHF software, enabling striking improvements in predictions of strengths of resonance and intercombination lines in the C III spectrum [34]. These developments have been incorporated in GRASP2K software [35]. The strategies of using the new GRASP2K approach are non-trivial but the intrinsic biorthogonalization permits controlled convergence in difficult problems such as inner-shell hole spectra [36]. To deal with major challenges in core-hole excitation—modelling of convergence and false minima—the best approach is to slowly build up the wave function, beginning with the configuration state only, and adding extra orbitals in steps [32].

Tables I and II show the change in predicted positions of the energies and the transition strengths of the copper $K\alpha$ diagram lines with the systematic enlargement of the CSF set to include one or more excitations into the subshells, beginning with $3d^{10}4s^1$. Earlier MCDHF calculations have achieved agreement with observation to about 2 eV, contrasting with our agreement of 0.01 eV for $K\alpha_1$ and 0.06 eV for $K\alpha_2$. This eliminates the need to introduce additional fitting parameters when deconvolving the observed spectrum. The computational model starts from the matrix of the MCDHF atomic Hamiltonian in the chosen CSF space assuming that the electron-electron interaction is a Coulomb potential. The matrix of the fully retarded relativistic electron-electron interaction is then added and the diagonal matrix elements of the perturbed atomic Hamiltonian are also augmented with QED corrections for vacuum polarization and electron self-energy [32,36]. The eigenvalues and eigenvectors of this perturbed matrix give the energies and atomic wave functions used to cal-

**TABLE I.** Convergence of $K\alpha$ diagram energies. The two experimental values are as-reported for the full spectrum calibration [8] or reconstructed (Table II), including the satellite spectrum, which is nontrivial to deconvolve. However, expected diagram energies would be approximately 0.01 eV higher than the full spectrum for $K\alpha_1$ and perhaps a few 0.01 eVs for $K\alpha_2$ (see text).

<table>
<thead>
<tr>
<th>CSFs</th>
<th>Excitations</th>
<th>Orbitals</th>
<th>$2p_{1/2} \rightarrow 1s$ (eV)</th>
<th>$2p_{3/2} \rightarrow 1s$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>⋯</td>
<td>8030.79</td>
<td>8050.82</td>
</tr>
<tr>
<td>53</td>
<td>1</td>
<td>$4d$</td>
<td>8028.85</td>
<td>8048.67</td>
</tr>
<tr>
<td>203</td>
<td>1</td>
<td>$4p4d4f$</td>
<td>8026.92</td>
<td>8046.87</td>
</tr>
<tr>
<td>20897</td>
<td>2</td>
<td>$4p4d4f$</td>
<td>8027.91</td>
<td>8047.84</td>
</tr>
<tr>
<td>Reconstructed [8]</td>
<td></td>
<td></td>
<td>8027.88(0.13)</td>
<td>8047.84(0.06)</td>
</tr>
<tr>
<td>Full Spectrum [8]</td>
<td></td>
<td></td>
<td>8027.85(0.01)</td>
<td>8047.83(0.01)</td>
</tr>
</tbody>
</table>

![FIG. 2. Calculated energies and relative intensities resulting from diagram and satellite transitions for Copper $K\alpha$, overlaid with the experimental spectrum and normalized.](image-url)
calculate transition probabilities. The improved agreement of
the oscillator strengths in the length and velocity gauges
$A^L$ and $A^V$ as the CSF set is enlarged (Table II) strongly
endorses the quality of the ASF representations. The dif-
fERENCE in transition strengths between the two gauges
remains one of the few methods \[31,37\] for demonstrating
convergence without reference to experiment. Although
this is already the most elaborate calculation yet published
for the Cu $K\alpha$ lines, we are continuing to investigate the
effect of adding further configurational states to ensure that
important correlation effects have not been omitted.

Deutsch et al. fitted their experimental spectrum with a
sum of Lorentzians, including offsets for energy noncon-
vergence. The line strengths were calculated using orbitals
from the initial state: Deutsch et al. did not have bio-
orthogonal software so performed configuration interaction cal-
culations with frozen orbitals to calculate oscillator
strengths. The difference between $A^L$ and $A^V$ was within
about 10% for all and 5% for the strongest line. Table II
shows that our theoretical strengths for diagram lines agree
agrees to $<1\%$ for the simplest calculation, improving to $<0.04\%$
in the most elaborate calculation. Our predicted energies
and relative intensities of the diagram lines are shown in
Fig. 2.

The lower part of Fig. 2 shows our predictions for
satellite lines. Our procedure differs from that of Deutsch
et al. as we include the weakly bound $4s$ electron. In their
calculation, the two lower atomic states, $2p_{1/2}$ and $2p_{3/2}$
were obtained using different energy functionals, which
repressed potentially crucial mixing of the inner orbitals.
We therefore retained the $4s$ electron, and calculated the
$J = 1$ states, so we could use the same orbital basis for the
common upper state as well as both lower states. This
assumption gives a good description of the $1s$ hole state
for other values of $J$. A spectator $3d$ hole breaks the
symmetry of the single hole configuration, giving structure
to the $K\alpha$ spectrum. The number of CSFs needed to
describe these states increases greatly so that convergence
with enlargement of the CSF set is more difficult to
achieve. The most effective procedure appears to start
with the lowest state of each set of split diagram lines
and to add CSFs progressively with single and double
excitations from the $n = 3$ to $n = 4$ subshells. This gave
oscillator strengths whose gauge differences were within
about 1%. We then performed more modest MCDHF
calculations for each $J\pi$ symmetry to get a representation
of the whole spectrum. This enabled us to avoid difficulties
of false convergences among the closely split levels.

Figure 2 shows that the $[3d]$ hole states make the $2p_{3/2}$
orbital more diffuse so that its overlap with $1s$ is less than
that of the $2p_{1/2}$ orbital. The experimental spectrum can
now be fitted with just three parameters: the widths of $K\alpha_1$
and $K\alpha_2$ lines and a Gaussian difference width $w_d$
between the widths of the diagram and satellite lines (satellite lines
will be broader than diagram lines). The resulting level of
accuracy is not surpassed in the literature to our
knowledge.

Figure 3 shows the fitted spectrum, with contributions
from both $1s$ and $1s3d$ initial states, with residuals in
Fig. 4. The $\chi^2$ of the fit using only diagram lines gave $\chi^2 =
2.65$ while inclusion of satellites dropped this to 0.46.
Using the relative populations $p_d$ and $p_s$ of the diagram
and satellite lines yields a total integrated intensity ratio
$I(K\alpha_1)/I(K\alpha_2) = 0.522 \pm 0.003$. The ratio has been re-
ported as low as 0.507 $\pm$ 0.014 \[11\], while the most reli-
able determination is 0.518 $\pm$ 0.021 \[8\], both consistent
with our result. Theoretical and derived (experimental)
component widths are presented in Table III. While total
spectral widths vary widely depending upon the resolution,
authors have attempted to derive raw widths by removing

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{CSFs} & \text{Excitations} & \text{Orbitals} & A^L \text{ (10}^{14} \text{ s}^{-1}) & A^V \text{ (10}^{14} \text{ s}^{-1}) & A^L/A^V \\
\hline
2p_{1/2} \rightarrow 1s & 3 & 0 & \cdots & 2.07250 & 2.08825 & 0.9926 \\
53 & 1 & 4d & 2.03613 & 2.05011 & 1.1518 \\
203 & 1 & 4p4d4f & 2.05644 & 2.06283 & 0.9969 \\
20897 & 2 & 4p4d4f & 2.04922 & 2.04854 & 1.0003 \\
2p_{3/2} \rightarrow 1s & 3 & 0 & \cdots & 1.02343 & 1.03100 & 0.9926 \\
53 & 1 & 4d & 1.00653 & 1.01317 & 0.9934 \\
203 & 1 & 4p4d4f & 1.00574 & 1.00929 & 0.9965 \\
20897 & 2 & 4d4p4f & 1.00580 & 1.00544 & 1.0004 \\
\hline
\end{array}
\]
instrumental broadening. Results vary from 2.28 eV to 2.47 eV for Kα₁ and from 2.78 eV to 3.49 eV for Kα₂. A few authors have attempted to fit diagram or satellite subcomponent widths as in Table III with similar results. This is a limitation of the current and previous approaches, in that the subcomponent widths are fitted and there is little constraint from good theory. Whilst excellent results have been obtained, there is clearly room for improvement of experiment and theory.

The summed spectral profile is well accounted for by the presence of the spectator lines. The relatively large variation in the fitted satellite contributions from Table III is due to correlation of the fitting approaches with noise in the experimental data. The residual in Fig. 4 is well bounded by the statistical error. The theoretical understanding of shake processes is still developing. Estimations for satellite and diagram cross sections vary greatly [14,40,41] and the agreement with experiment (Table III) is relatively poor. This suggests the need to investigate these effects across a broad range of atomic systems. Comparisons with other similar elements can provide insight into the magnitude and nature of these poorly understood processes.

We have shown that the ratio of Kα line intensities can be explained by considering the atomic wave function in detail. Using biorthogonal CSF sets, we have investigated a difficult problem involving near degenerate eigenstates, slowly converging sets of levels, and calculated the diagram line profiles of copper to within 0.05% of their experimental value, with even better convergence on their energies. We have produced an ab initio derivation of the intensities and energies of diagram and spectator lines for copper that were able to account, to a high degree of accuracy, for the full Kα spectrum (Fig. 3). In particular, our determination of the ratio for I(Kα₂)/I(Kα₁), 0.522 ± 0.003, is in agreement with experiment. This gives confidence in the quality of the theoretical model and the care taken for the corresponding experiments.

*chantler@unimelb.edu.au


---

**TABLE III.** Parameters and standard deviations for Kα.

<table>
<thead>
<tr>
<th>Component</th>
<th>Present [17]</th>
<th>[19]</th>
<th>literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p₃/2</td>
<td>2.55(11)</td>
<td>2.68</td>
<td>1.81(5)</td>
</tr>
<tr>
<td>2p₁/2</td>
<td>1.87(10)</td>
<td>2.08</td>
<td>2.93(7)</td>
</tr>
<tr>
<td>2p₃/2 3d</td>
<td>3.86(24)</td>
<td>2.75</td>
<td>1.21(15)</td>
</tr>
<tr>
<td>2p₁/2 3d</td>
<td>3.18(25)</td>
<td>2.75</td>
<td>1.09(15)</td>
</tr>
</tbody>
</table>

% Populations

<table>
<thead>
<tr>
<th>Diagram</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>71.0(25)</td>
<td>69</td>
<td>72(3)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Satellite</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>29.0(25)</td>
<td>31</td>
<td>28(3)</td>
<td>5.5 [40]</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>[41]</td>
<td></td>
</tr>
</tbody>
</table>

---