Physics Letters A 426 (2022) 127900

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Theory of copper $K\alpha$ and $K\beta$ diagram lines, satellite spectra, and *ab initio* determination of single and double shake probabilities

T.V.B. Nguyen, H.A. Melia, F.I. Janssens, C.T. Chantler *

School of Physics, The University of Melbourne, Melbourne Australia

ARTICLE INFO

Article history:
Received 11 November 2021
Received in revised form 14 December 2021
Accepted 19 December 2021
Available online xxxx
Communicated by S. Khonina

Keywords:
Copper
Kα
Kβ
MCDHF
Characteristic radiation
Shake processes

ABSTRACT

High-accuracy MCDHF Cu $K\alpha$ and Cu $K\beta$ diagram spectra and major satellites are presented. Spectral eigenvalues reach a theoretical expansion convergence of 0.03 eV or 0.00025%, with gauge and amplitude convergence to 0.7% for Cu $K\alpha$ diagram spectra. Dominant theoretical spectral eigenvalues are shown to be within 0.032 eV of experimental data. *Ab initio* shake-off contributions are presented in terms of total probability from each subshell and as separated single and double shake probabilities. Discrepancies between theory and experiment in copper X-ray spectra arise from profile asymmetries, relativistic terms and shake spectra not yet accounted for. These results and this improved agreement provide key fundamental parameters for processes towards XFEL evolution and resolving key discrepancies between theory and experiment.

The $K\alpha$ spectrum results from the $2p \rightarrow 1s$ decay following photoionisation of the core $1s$ electron. For relatively heavy atoms, fine splitting between $2p$ states result in the two distinct peaks due to the transitions $2p_{3/2} \rightarrow 1s$ ($K\alpha_1$) and $2p_{1/2} \rightarrow 1s$ ($K\alpha_2$). The $K\beta$ spectrum arises from $3p_{3/2} \rightarrow 1s$ ($K\beta_1$) and $3p_{1/2} \rightarrow 1s$ ($K\beta_3$). The copper photoemission spectrum is the most commonly used radiation source in diffraction and scattering experiments. Hence, the Cu $K\alpha$ and $K\beta$ X-ray emission spectra are the most widely studied [1–12]. This recent collective effort is driven by the desire to understand and predict the asymmetric peaks that have been repeatedly observed experimentally. The asymmetry strongly suggests that there are other transitions beyond the simple bound-bound diagram transitions, pointing to physical processes yet to be explained or fully understood, referred to as satellite lines.

Several ideas have been proposed to explain the additional structure [13–16] and for molecular and solid state systems and crystals the influences of band and molecular orbital theory can be dominant. The most widely accepted view is that the additional structure, satellite lines, are caused by shake processes [17]. With the ionisation of a $1s$ electron, the system is no longer in an eigenstate of the atomic Hamiltonian. As the wavefunction relaxes, there is a probability that additional electron(s) are excited to higher shells (shake-up) or ejected into the continuum (shake-off), resulting in more excited state possibilities and hence additional transitions other than the diagram lines. Even within this picture, there are several explanations that have been proposed, depending on the incident photon or excitation energy [18–20]. In the high-energy limit, often referred to as the sudden approximation limit, the photoionisation occurs within a much shorter time frame than orbital relaxation, and thus the shake-off probability can be extracted from the wavefunction overlap between the initial and final state, which emphasise the need for highly accurate wavefunctions.

X-ray free electron laser (XFEL) sources involve similar processes and cross-sections as obtained by X-rays at synchrotrons or laboratory sources, especially at onset, but in time-resolved mode. The processes of detection of copper emission spectra are also similar. Data on the $3d$ transition metals has been collected at XFELs [21]. Theoretical understanding at the atomic level, as presented in this paper, is very much needed and an ongoing challenge because of the multiple ionisation processes, the cascade processes and hence of the satellite processes and spectra. XFELs provide a unique opportunity to investigate hollow atoms through K-shell double photoionisation [22]. Such investigations probe electron-electron correlation and require atomic theory calculations, such as the ones performed here, for the identification of spectral features and the hypersatellite spectra [23]. Complex

* Corresponding author.
E-mail addresses: b.nguyen6@student.unimelb.edu.au (T.V.B. Nguyen), hmelia@student.unimelb.edu.au (H.A. Melia), fjanssens@student.unimelb.edu.au (F.I. Janssens), chantler@unimelb.edu.au (C.T. Chantler).

https://doi.org/10.1016/j.physleta.2021.127900
0375-9601/

Table 1
Calculated results of copper $K\alpha$ and $K\beta$ diagram transitions. Spectral eigenvalues converge to ± 0.02 eV or 0.00025%; and gauge convergence to 0.7% is obtained for these diagram transitions. g_f values are provided in Coulomb gauge. Even at this level of 'simplicity', both the $p_{3/2} - s_{1/2}$ and the $p_{1/2} - s_{1/2}$ spectra are asymmetric being composed of 6 components and not just 2.

Transition	Energy (eV)	A^L/A^V	g_f
$K\alpha_1$			
$J=0 \rightarrow J=1$	8047.90 (±0.02)	1.0067	0.214935
$J=1 \rightarrow J=1$	8047.80 (±0.03)	1.0067	0.108004
$J=1 \rightarrow J=2$	8047.84 (±0.02)	1.0067	0.538166
$K\alpha_2$			
$J=0 \rightarrow J=1$	8027.99 (±0.02)	1.0069	0.110581
$J=1 \rightarrow J=0$	8027.92 (±0.02)	1.0069	0.109988
$J=1 \rightarrow J=1$	8027.90 (±0.03)	1.0069	0.219854
$K\beta_1$			
$J=0 \rightarrow J=1$	8903.61 (±0.02)	1.0064	0.0209132
$J=1 \rightarrow J=1$	8903.51 (±0.02)	1.0065	0.0131888
$J=1 \rightarrow J=2$	8903.70 (±0.03)	1.0065	0.0568483
$K\beta_3$			
$J=0 \rightarrow J=1$	8901.18 (±0.03)	1.0067	0.0134186
$J=1 \rightarrow J=0$	8901.18 (±0.03)	1.0067	0.0116048
$J=1 \rightarrow J=1$	8901.05 (±0.00)	1.0068	0.0213909

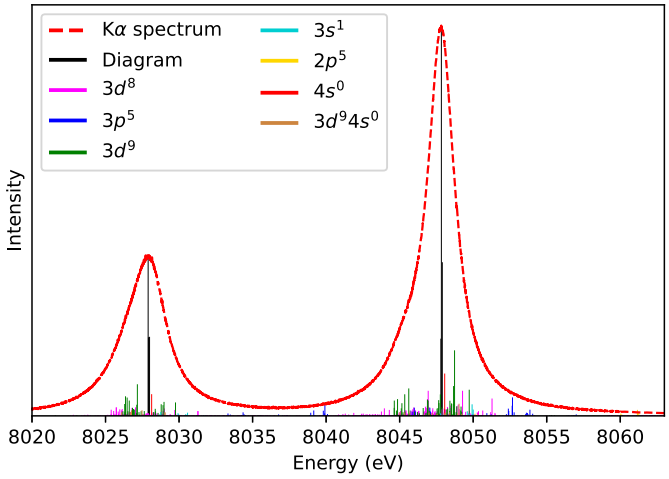

Fig. 1. Copper $K\alpha$ diagram and satellite transitions with relative intensity, compared with 2017 experiment with Cu metal foil [12]. The $K\alpha$ distinct peaks are clearly asymmetric due to the transitions beyond the characteristic diagram lines. The label convention here indicates the subshell where shake-off has occurred, and the number of electrons remaining. For example, $3d^8$ indicates 2 of the 10 d electrons were ejected from the $3d$ subshell as part of the shake process. Experiment and theory appear in very good agreement, possibly down to the convergence limit.

plasma dynamics such as in XFELs invoke many body processes for which satellite computations are required [24]. The method used here to calculate *ab initio* shake probabilities extends to a variety of multi-vacancy states that are expected at XFELs due to the high intensities and electric fields, especially including otherwise forbidden two-photon processes and many-body satellites.

Experimental efforts to resolve and understand the physical processes behind the Cu $K\alpha$ and $K\beta$ spectra are non-trivial because of numerous systematics associated with experiments [25,26]. High-accuracy theoretical data enables the isolation of the different transitions involved and better control of spectral characterisation. Our theoretical approach employing the multiconfiguration Dirac-Hartree-Fock method (MCDHF), implemented via the GRASP2K program [27] supplemented by our own codes and modifications [28], is a fully-relativistic method with Dirac wavefunctions. In using the MCDHF method, the total wavefunction is a linear combination of configuration state functions (CSFs), where each CSF is a single electronic wavefunction built from anti-symmetrised products of Dirac central field orbitals. MCDHF wavefunctions use the usual first-order base electronic structure of copper, but also include many other possible higher-order configurations to approximate the complete wavefunction.

Table 1 details the characteristic diagram transitions of Cu $K\alpha$ and $K\beta$ numerically computed using the MCDHF method. Our approach utilised the Coulomb (relativistic velocity) and Babushkin (relativistic length) gauges as one of several key metrics to determine accuracy, with a ratio A^L/A^V close to unity being a necessary condition of convergence. The eigenvalue convergence seen to ± 0.02 eV or 0.00025% and the high degree of gauge convergence attest to the robustness of the methodology. The energies calculated here are smaller than the most accurate detailed previous theoretical work on Cu $K\alpha$ [29] by 0.03 eV to 0.19 eV, which is within the estimated accuracy of the previous work. The computational constraints of [29] did not allow convergence when handling a large basis set, so only a few primary lines were calculated and the rest were scaled accordingly. Herein, all diagram lines have been obtained simultaneously using the same basis set, and thus are expected to be more accurate. Earlier theoretical work [1] does not report discrete theoretical eigenvalues, so cannot be directly compared. Their results converged to an energy roughly 0.5 eV away from that found experimentally. A direct comparison between experimental peak energies and theoretical energy eigenvalues will not give a true reflection of accuracy for several reasons; widths, multiple transitions within the diagram lines, and satellite lines all shift the peak energy. Cu $K\alpha_1$ experimental peak energies of 8047.817(8) eV [12] from 2017 imply very good agreement (Fig. 1). Transition energies calculated to a high degree of accuracy and convergence point to much more accurate wavefunctions, which are fed into *ab initio* shake models that can be used in conjunction with experimental fittings to extract the underlying physical processes within the atomic spectra.

Fig. 1 presents the most recent Cu $K\alpha$ experimental reference spectrum with detailed error analysis [12], using copper metal foil, from the NIST standards laboratory, together with the array of diagram and satellite eigenvalue spectra from our theory, expanded to the 5s subshell. Computed transitions that may contribute to the observed spectrum are represented by the coloured sticks underneath the profile. The dominant characteristic diagram lines are the standard $K\alpha$ transitions. The ground state for neutral atomic copper is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$, with the diagram transitions from $1s^{-1}$ (a 1s hole) relaxing to $2p^{-1}$ (a 2p hole). Compared with this, the double shake-off satellite will have two fewer 3d electrons, designated $3d^8$. Note the complexity of the computations, and of the structure: the double shake-off satellite $3d^8$ (alone) contains 1506 independent eigenvalues (i.e. spectral lines) compared with the relatively straightforward 6 diagram spectral components for Cu $K\alpha$ or Cu $K\beta$. The $2p^5$ satellite eigenvalues lie within the high-energy tail of the spectrum and contribute to the $K\alpha_{3,4}$ complex [30,12].

Fig. 2 shows the Cu $K\beta$ spectrum with the diagram lines and satellite contributions, with the computation expanded to the 6g level. Eigenvalue convergence is to ± 0.03 eV and gauge convergence is to 0.6%, with some 91000 simultaneous CSF convergence. Similar to the $K\alpha$ spectrum (Fig. 1), the $3d^9$ is the most dominant satellite but is not the sole cause of asymmetry observed. The energy eigenvalues of the $K\beta_{1,3}$ diagram lines agree to within half an eV of the previous most detailed MCDHF calculations [11]. In addition, the satellite structures look consistent.

To better understand the contribution of each satellite, a shake model was developed following the sudden approximation implemented into the MCDHF framework. The validity of the sudden approximation limit relevant for the experimental reference data

Table 2
Total theoretical shake probabilities and extracted experimental shake probabilities for various satellite intensities in the literature. Early theoretical work underestimated all total shake probabilities. 4*s* satellite spectra are almost perfectly aligned with diagram spectra. All past experimental work extracting only a 3*d* satellite probability tended to overestimate the 3*d* probability by subsuming all others.

	Claimed Shake(-off) Probabilities (%)			
Theory	3*s*	3*p*	3*d*	4*s*
Mukoyama and Taniguchi (1987) [34]	0.34	2.5	9.7	9.7
Kochur et al. (2002) [35]		2.6	14.5	
Lowe et al. (2011) [10]			14.7	
Pham et al. (2016) [11]	0.32∓0.02	7.74∓0.10	19.94∓0.14	12.43∓0.15
This work (Total Shake to 6*g*)	**2.97**	**7.42**	**18.39**	**11.25**
Experiment (extracting only P(3d shake))				
Sauder et al. (1977) [17]			26.5±2	
Deutsch et al. (1995) [1]			26 - 30.0	
Hölzer et al. (1997) [4]			18.5	
Diamant et al. (2006) [36]			25±2	
Galambosi et al. (2003) [7]			25±2	
Enkisch et al. (2004) [8]			29.0	
Ito et al. (2006) [9]			23.1	
Chantler et al. (2009) [3]			29±2.5	
Chantler et al. (2010) [29]			26±1	
Chantler et al. (2012) [37]			15-30-39	

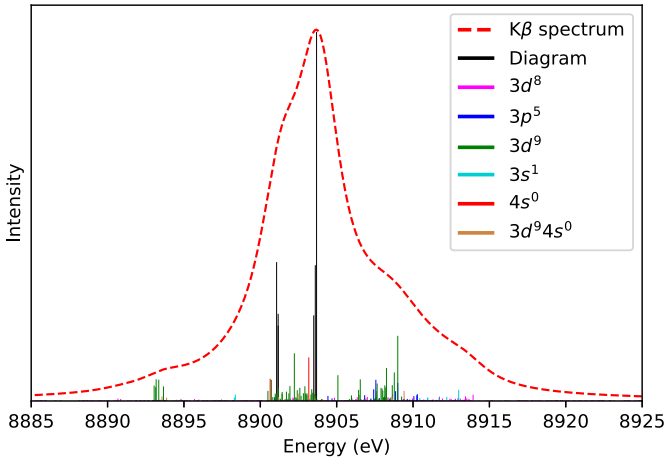

Fig. 2. Copper $K\beta$ diagram and satellite transitions with relative intensities from theory. The red curve is a simulated spectrum with typical experimental widths. The two primary diagram peaks are separated by only about 2 eV, yielding only one large unresolved but asymmetric peak. The $3d^9$ satellite is dominant relative to other satellites, but insufficient to fully explain the asymmetry. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

has been shown experimentally previously [31,32,11,33]. Near-threshold experiments [5] have suggested that satellites resulting from photoionised core electrons in medium-Z atoms are purely shake-off. The probability of electron shake-off from an $n\kappa$ subshell in the sudden approximation limit is

$$P_{n\kappa}^{shake} = 1 - \left| \sum_j \sum_k c_j d_k \langle \phi_{Bkn\kappa} | \phi_{Ajn\kappa} \rangle^{M_{n\kappa}} \right|^2, \quad (1)$$

where c_j and d_k represent the mixing coefficients in a multi-configuration framework and $M_{n\kappa}$ is the occupation number. The overlapping wavefunctions capture the moment immediately after ionisation of the 1*s* subshell but prior to orbital relaxation. Table 2 compares total shake-off calculations with literature. Satellite lines contribute significantly (10%-20%) to the spectrum and are the dominant contributors to the experimentally observed asymmetry. The variation of predicted percentage for a given satellite or for a total collection of satellites is discussed below and certainly varies according to the element even with the transition row series. Further, Table 2 reflects that experimental ansatzes yield 15-39%, an even bigger variation, whilst theoretical predictions have varied for a single component from 9.7% to 19.9%. Note implicitly that this variation implies that several of the determinations had uncertainties or systematic issues of order 10%. Indeed several of the earlier or experimental determinations definitely have systematic errors of 10%.

Theoretical results are smaller than those of experiment, not just in Table 2 with copper but e.g. also for scandium where the 3*p* satellite shake probability was predicted to be 7.8% [34] and 6% [35], compared with 15% extracted from experiment [38]. Results reported by [7] and [36] are similar, with a similar experimental approach. Enkisch et al. [8] measured the $K\beta$ spectrum, which is challenging to separate. Ito et al. [9] fitted four Lorentzians, with wildly different results. Chantler et al. fitted atomic structural calculations using MCDHF to experimental results, as did Deutsch et al. [1]. The uncertainty of extracting shake probabilities through fits to experimental data is far larger than that given by the fitting procedure [37], evident by the wide range of values given for the 3*d* shake probability (Table 2). This highlights the need for *ab initio* methods. Furthermore, the work of Deutsch et al. [1] has led to many researchers only modelling the diagram line and 3*d* satellites lines. In that case, the neglect of additional satellites artificially inflates the extracted 3*d* shake probability. Ref. [1] suggests that results from fitted atomic structure calculations are different from empirical experimental fitting. Empirical experimental fitting implies a shake probability of 18%, while fitting the results of atomic structure calculations indicates 3*d* shake probabilities for $K\alpha$ and $K\beta$ of 30% and 26%, respectively [1].

Experimental values have difficulty separating the components and are often empirical. Theoretical values to date have been total shake probabilities. However, $P_{n\kappa}$ is the probability of at least one electron being removed from the $n\kappa$ subshell. For the purpose of experimental fitting and comparison it is important to distinguish the difference between single and double shake probabilities within a $n\kappa$ subshell. Using the binomial theorem, single and double shake probabilities can be extracted.

We must also consider the effects of two shake events occurring across different subshells. The isolated single and double shake-off probability is the probability that a shake event occurs only in a particular $n\kappa$ subshell whilst leaving the other subshells

Table 3
Isolated single and double shake-off probabilities (%): the probability that either one or two electrons removed from particular subshell, while all the electrons from other subshells remain as is. The $3d$, $4s$ and $3p$ single shake processes are expected to be dominant according to the shake probabilities.

$n\kappa$	$1,-1$	$2,-1$	$2,1$	$2,-2$	$3,-1$	$3,1$	$3,-2$	$3,2$	$3,-3$	$4,-1$
P(%)	1.57	1.6	1.67	1.72	1.79	2.04	2.45	4.84	6.65	7.47
$n_1l_1\,n_2l_2$	$3d4s$	$3d^2$	$3p3d$	$3p4s$	$3s3d$	$3s4s$	$3p^2$	$3s3p$	$2p3d$	$2p4s$
P(%)	1.458	0.9087	0.8747	0.5686	0.3490	0.2269	0.1403	0.1362	0.6622	0.4305

unchanged. Single shake probabilities calculated here (Table 3) are for electrons from any particular $n\kappa$ subshell, whereas the double shake probabilities are presented for two electrons from subshells n_1l_1 and n_2l_2. Separating single and double shake events within and across subshells has not been considered in the literature and provides a more complete picture from which atomic structure calculations can be applied to experimental data. Previous attempts to calculate double shake probabilities from $P_{n\kappa}$ or $P_{n\ell}$ have been limited in their approach [35].

The energy and amplitude eigenvalues of 3698 transitions contributing to the Cu $K\alpha$ and Cu $K\beta$ spectra have been calculated. Many have been determined for the first time. Gauge convergence of $< 0.7\%$ for both sets of diagram transitions, along with energy convergence to 0.03 eV, indicate the stability of the wavefunctions and a near-complete inclusion of correlation effects. The *ab initio* shake probabilities highlights the requirement of a multi-configurational framework when dealing with open shell systems and confirm the $3d^8$ and $3d^94s^0$ double hole satellites as the two most dominant double-shake processes. Shake probabilities have been dissected and reported down to the subshell level. Previously only the total $3d$ has been reported, whereas here we present $3d-$ and $3d$ as well as other subshells, including double shake processes.

Up until recently, even the best theoretical computations showed eigenvalue convergence issues internally and compared with experiment at the level of eV or more. [25] appears reliably to reach below 1 eV and perhaps below 0.5 eV, and here we present formal convergence below 0.10 eV, though of course the theory and modelling may or may not correspond with a physical quantum system. Hence, the convergence of energy eigenvalues with the expansion of the active set is not a proof of accuracy with respect to a particular experimental system; rather it approximates the uncertainty resulting from using a finite basis set and a particular theoretical approach. The gauge and amplitude convergence are based on the transition probability and if fully relativistic can approach the 0.7% stated. The amplitude convergence can often be significantly better than the gauge convergence marker, for the recommended gauge. Previous satellite probabilities have been challenged by the level of theory available, by the formula used to derive the probability and by the lack of wavefunction biorthogonalisation. There has been a key question about the meaning and usage of a given theoretical computation and hence its convergence for a particular system.

X-ray free electron laser (XFEL) sources [21,22] require theoretical understanding at the atomic level, as presented in this paper, which is an ongoing challenge because of the multiple ionisation and cascade processes and hence of the satellite processes and spectra. Understanding ionisation, Auger and multiple ionisation processes is challenging, for which experimental and theoretical data remains quite limited. In particular, the semi-empirical coefficients used widely in XFEL evolution modelling will be improved by more detailed and advanced ionisation and cascade computations.

The theory and formal convergence is valid strictly only for an isolated copper atom - i.e. for atomic physics. The solid state effect of delocalisation and conduction electrons can be large for copper metal, for $3d$ and $4s$ electrons. If the hybridisation between the X-ray emitting atom and its neighbour atoms are large, the shake-off probability might become low because the core hole perturbation is not felt by these delocalised electrons. So *prima facie* it might not apply to a molecule, solid or even metal. Fig. 1 shows that our results for energy eigenvalues of the diagram lines agrees well with the experimental peak energy measured by Mendenhall et al. [12]. The weighted mean line energy of our $K\alpha_1$ and $K\alpha_2$ energy eigenvalues are 8047.848(23) and 8027.927(24) eV, respectively. Mendenhall et al. report experimental peak energies: $K\alpha_1^0 = 8047.8162(4)$ and $K\alpha_2^0 = 8027.9435(22)$ eV. These two measures should not be in perfect agreement because the peak energy is affected by line widths, satellite intensities and experimental broadening. The two measures give energies to within 0.032 eV indicating, along with the convergence of eigenvalues with the active set, that the method used is capable of reproducing theoretical spectrum in agreement with experimental to below 0.1 eV. If Doniac asymmetries are present [15] then their effect must be small; and although the conduction band of the Cu metal system is very different from the isolated atomic $4s$ electron orbital (delocalisation [39,40]), the influence of this upon the Cu metal spectrum appears to be small.

The influence of the $4s$ electron, whether included or omitted in our theoretical computation, shifts the energy eigenvalue of our diagram lines by only 0.21 eV (from difference between our $K\alpha_1$ diagram and $K\alpha-_1$ $4s$ satellite line energy eigenvalues). Previous work, whether omitting [1] or including [3,29] the conduction band electron was able to match atomic structure calculation to experimental data taken on metallic Cu well with $\chi_r^2 \approx 1$. Hence any theory or conduction band effects on the diagram and key satellite eigenvalues must be small.

We know that a naïve application to e.g. an oxide with a different oxidation state, Fermi level and symmetry will be fraught (i.e. invalid). The observed line shape is then governed by the discrete valence electron response such as shake-off, but also by avoided crossing due to spontaneous covalence or delocalisation [41] for CuO, and also free-electron-like conduction electron response to the creation of a core hole [15].

However, molecular orbital theory gives support for the individual theoretical satellite contribution being valid yet for the overlap intensities varying widely as expected. Band theory is much less accurate an approximation than these computations, yet contains key partitioning into band structure. Hence there is scope for significant application and significant further work in this regard. We think there is clear evidence that for metal foils the influence is much less than sometimes realised, but of course the impact of band theory is dominant for conduction bands and visible spectroscopy.

CRediT authorship contribution statement

T.V.B. Nguyen: Writing – original draft, Writing – review & editing, Validation, Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software. **H.A. Melia:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **F.I. Janssens:**

Formal analysis, Investigation, Methodology. **C.T. Chantler:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We acknowledge the Australian Research Council (DP210100795) for the research grant for this work.

References

[1] M. Deutsch, G. Hölzer, J. Härtwig, J. Wolf, M. Fritsch, E. Förster, $K\alpha$ and $K\beta$ x-ray emission spectra of copper, Phys. Rev. A 51 (1995) 283–296.
[2] M. Deutsch, O. Gang, K. Hämäläinen, C.C. Kao, Onset and near threshold evolution of the Cu $K\alpha$ X-ray satellites, Phys. Rev. Lett. 76 (14) (1996) 2424–2427.
[3] C.T. Chantler, A.C.L. Hayward, I.P. Grant, Theoretical determination of characteristic X-ray lines and the copper $K\alpha$ spectrum, Phys. Rev. Lett. 103 (2009) 123002.
[4] G. Hölzer, M. Fritsch, M. Deutsch, J. Härtwig, E. Förster, $K\alpha_{1,2}$ and $K\beta_{1,3}$ x-ray emission lines of the 3*d* transition metals, Phys. Rev. A 56 (Dec 1997) 4554–4568.
[5] M. Fritsch, C.C. Kao, K. Hämäläinen, O. Gang, E. Forster, M. Deutsch, Evolution of the Cu $K\alpha_{3,4}$ satellites from threshold to saturation, Phys. Rev. A 57 (3) (1998) 1686–1697.
[6] R. Diamant, S. Huotari, K. Hämäläinen, C.C. Kao, M. Deutsch, Evolution from threshold of a hollow atom's X-ray emission spectrum: the Cu $K^h\alpha_{1,2}$ hypersatellites, Phys. Rev. Lett. 84 (Apr 2000) 3278–3281.
[7] S. Galambosi, H. Sutinen, A. Mattila, K. Hämäläinen, R. Sharon, C.C. Kao, M. Deutsch, Near-threshold multielectronic effects in the Cu $K\alpha_{1,2}$ x-ray spectrum, Phys. Rev. A 67 (2003) 022510.
[8] H. Enkisch, C. Sternemann, M. Paulus, M. Volmer, W. Schülke, 3*d* spectator hole satellites of the Cu $K\beta_{1,3}$ and $K\beta_{2,5}$ emission spectrum, Phys. Rev. A 70 (Aug 2004) 022508.
[9] Y. Ito, T. Tochio, H. Oohashi, A. Vlaicu, Contribution of the [1s3d] shake process to $K\alpha_{1,2}$ spectra in 3*d* elements, Radiat. Phys. Chem. 75 (11) (2006) 1534–1537.
[10] J.A. Lowe, C.T. Chantler, I.P. Grant, Ab initio determination of satellite intensities in transition-metal photoemission spectroscopy using a multiconfiguration framework, Phys. Rev. A Rapid Commun. 83 (2011) 060501.
[11] T.L.H. Pham, T.V.B. Nguyen, J.A. Lowe, I.P. Grant, C.T. Chantler, Characterization of the copper Kβ x-ray emission profile: an ab initio multi-configuration Dirac-Hartree-Fock approach with Bayesian constraints, J. Phys. B 49 (2016) 035601.
[12] M.H. Mendenhall, A. Henins, L.T. Hudson, C.I. Szabo, D. Windover, J.P. Cline, High-precision measurement of the x-ray Cu $K\alpha$ spectrum, J. Phys. B 50 (11) (2017) 115004.
[13] M. Deutsch, M. Hart, Wavelength, energy shape, and structure of the Cu $K\alpha_1$ x-ray emission line, Phys. Rev. B 26 (1982) 5558–5567.
[14] L.G. Parratt, Electronic band structure of solids by X-ray spectroscopy, Rev. Mod. Phys. 31 (1959) 616–645.
[15] S. Doniach, M. Sunjic, Many-electron singularity in X-ray photoemission and X-ray line spectra from metals, J. Phys. C 3 (2) (1970) 285–291.
[16] P. Nozieres, A. Blandin, Kondo effect in real metals, J. Phys. 26 (1980) 193–211.
[17] W.C. Sauder, J.R. Huddle, J.D. Wilson, R.E. Lavilla, Detection of multiplet structure in Cu $K\alpha_{1,2}$ by means of a monolithic double crystal spectrometer, Phys. Lett. A 63 (3) (1977) 313–315.
[18] T.D. Thomas, Transition from adiabatic to sudden excitation of core electrons, Phys. Rev. Lett. 52 (Feb 1984) 417–420.
[19] E. Vatai, Energy dependence of the electron shakeup and shakeoff: evidence of different levels of nonseparability, Phys. Rev. A 38 (Oct 1988) 3777–3780.
[20] M. Roy, J.D. Lindsay, S. Louch, S.J. Gurman, Multiple-electron excitation in X-ray absorption: a simple generic model, J. Synchrotron Radiat. 8 (Jul 2001) 1103–1108.
[21] J. Hoszowska, A.K. Kheifets, J. Dousse, M. Berset, I. Bray, W. Cao, K. Fennane, Y. Kayser, M. Kavčič, J. Szlachetko, et al., Physical mechanisms and scaling laws of k-shell double photoionization, Phys. Rev. Lett. 102 (7) (2009) 073006.
[22] J. Hoszowska, J. Szlachetko, J.-C. Dousse, W. Błachucki, Y. Kayser, C. Milne, M. Pajek, S. Boutet, M. Messerschmidt, G. Williams, et al., X-ray two-photon absorption with high fluence xfel pulses, J. Phys. Conf. Ser. 635 (10) (2015) 102009.
[23] C.T. Chantler, J.D. Silver, X-ray spectra of recoil ions from fast beam interaction with Mg and MgF_2 solid targets, Nucl. Instrum. Methods B 31 (1988) 59–69.
[24] C.T. Chantler, Charge and state population in dilute plasmas from beam-foil spectroscopy, Can. J. Phys. 86 (2008) 331–350.
[25] H.A. Melia, C.T. Chantler, L.F. Smale, A.J. Illig, The characteristic radiation of copper $K\alpha_{1,2,3,4}$, Acta Crystallogr., Sect. A 75 (2019) 527–540.
[26] H.A. Melia, C.T. Chantler, L.F. Smale, A.J. Illig, The characteristic radiation of copper $K\beta$ including radiative Auger processes, J. Phys. B, At. Mol. Opt. Phys. 53 (2019) 195002.
[27] P. Jönsson, G. Gaigalas, J. Bieroń, C. Froese-Fischer, I.P. Grant, New version: Grasp2k relativistic atomic structure package, Comput. Phys. Commun. 184 (9) (2013) 2197–2203.
[28] T.V.B. Nguyen, J.A. Lowe, T.L.H. Pham, I.P. Grant, C.T. Chantler, Self-energy corrections in GRASP2K: update and benchmark, with code for QED and gauge investigations, The modified GRASP2K package, '1.15', available from https://www.ph.unimelb.edu.au/~chantler/opticshome/softwarepackagedownloads.html#GRASP2KRCISE, 2015.
[29] C.T. Chantler, J.A. Lowe, I.P. Grant, Multiconfiguration Dirac Fock calculations in open shell atoms: convergence methods and satellite spectra of copper Kα photoemission spectrum, Phys. Rev. A 82 (2010) 052505.
[30] M. Deutsch, E. Förster, G. Hölzer, J. Härtwig, K. Hämäläinen, C.C. Kao, S. Huotari, R. Diamant, X-ray spectroscopy of copper: news results on an old subject, J. Res. NIST 109 (2004) 75–98.
[31] T.A. Carlson, M.O. Krause, Electron shake-off resulting from K-shell ionization in neon measured as a function of photoelectron velocity, Phys. Rev. 140 (Nov 1965) A1057–A1064.
[32] O. Mauron, J.-C. Dousse, J. Hoszowska, J.P. Marques, F. Parente, M. Polasik, l-shell shake processes resulting from 1s photoionization in elements $11 \leq Z \leq 17$, Phys. Rev. A 62 (Nov 2000) 062508.
[33] Y. Ito, T. Tochio, M. Yamashita, S. Fukushima, A.M. Vlaicu, L. Syrocki, K. Słabkowska, E. Weder, M. Polasik, K. Sawicka, P. Indelicato, J.P. Marques, J.M. Sampaio, M. Guerra, J.P. Santos, F. Parente, Structure of high-resolution $K\beta_{1,3}$ x-ray emission spectra for the elements from Ca to Ge, Phys. Rev. A 97 (2018) 052505.
[34] T. Mukoyama, K. Taniguchi, Atomic excitation as the result of inner-shell vacancy production, Phys. Rev. A 36 (Jul 1987) 693–698.
[35] A.G. Kochur, A.I. Dudenko, D. Petrini, Shake process probabilities for outer-shell electrons in atoms with Z < 71, J. Phys. B, At. Mol. Opt. Phys. 35 (2) (2002) 395–399.
[36] R. Diamant, S. Huotari, K. Hämäläinen, R. Sharon, C.C. Kao, M. Deutsch, The evolution of inner-shell multielectronic X-ray spectra from threshold to saturation for low- to high-Z atoms, Radiat. Phys. Chem. 75 (11 SPEC. ISS.) (2006) 1434–1446.
[37] C.T. Chantler, J.A. Lowe, I.P. Grant, Anomalous satellite intensity discrepancy in copper x-ray lines, Phys. Rev. A 85 (3) (2012) 1.
[38] D.F. Anagnostopoulos, R. Sharon, D. Gotta, M. Deutsch, $K\alpha$ and $K\beta$ x-ray emission spectra of metallic scandium, Phys. Rev. A 60 (Sep 1999) 2018–2033.
[39] J. Kawai, E. Nakamura, Y. Nihei, K. Fujisawa, Y. Gohshi, Charge transfer effects on the chemical shift and the line width of the Cu Kα X-ray fluorescence spectra of copper oxides, Spectrochim. Acta, Part B, At. Spectrosc. 45 (4–5) (1990) 463–479.
[40] J. Kawai, T. Konishi, High resolution titanium Ka X-ray fluorescence spectra, Spectrochim. Acta 49B (7) (1994) 725–738.
[41] J. Kawai, Y. Nihei, M. Fujinami, Y. Higashi, S. Fukushima, Y. Gohshi, Sc Kα, and Kβ X-ray fluorescence spectra, Solid State Commun. 70 (5) (1989) 567–571.