



# Ab initio calculations of Auger electron kinetic energies: Breadth and depth

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## ABSTRACT

Ab initio theoretical calculations for Auger electron kinetic energies are presented for twenty prominent Auger peaks for the 3d transition metals ( $21 \leq Z \leq 30$ ). These are the twenty Auger peaks listed for these elemental solids in the National Institute of Standards and Technology (NIST) X-ray photoelectron spectroscopy database. Adding to these values, over one hundred Auger electron kinetic eigenenergies are calculated for titanium. Many of these transition lines are not established in current literature due to their relatively small yields and overlapping widths. These data can be of importance for determination of previously unaccounted Auger electron peaks with titanium and will be useful for X-ray fluorescence studies into the radiative Auger effect. The consistency between our values and the empirical data is an improvement compared with previous binding energy approaches and the methodology is convergent. The methods presented can be extended to other elements for future investigations of Auger electron kinetic energies which is particularly useful where current experimental values do not exist. Furthermore, these calculations provide evidence in the success of multiconfigurational Dirac–Hartree–Fock approaches in complex quantum mechanics.

## 1. Introduction

Atomic decay processes resulting from an initial K-shell hole provide valuable insight into many areas of modern physics. These decay processes yield electronic and photonic spectra with energies characteristic to the quantum system. Photon spectra from initial K-shell ionisations give rise to characteristic X-ray spectra and are important for industry, tests of complex atomic physics (Dean et al., 2019, 2020), relativistic quantum mechanics (Nguyen et al., 2022; Dean et al., 2022), and astrophysics (Chantler et al., 2013).

Here we focus on the Auger effect observed independently by Meitner (1922) and Auger (1923, 1924) in 1922 and 1923, respectively, first described and studied by Auger throughout the 1920s. Three electrons are involved in the Auger process and the three shells involved are used to designate the specific Auger electron. The naming convention for an Auger electron uses IUPAC X-ray nomenclature, an XYZ Auger electron is created from an initial X shell vacancy, where an electron in the Y shell relaxes into it, and the Auger electron is ejected from the Z shell.

Auger electrons offer insight into complex atomic physics with its main use in surface and materials science. Harris pioneered Auger electron spectroscopy (AES) in the late 1960s with studies of sulphur in nickel and various alloys of steel (Harris, 1968a,b). AES uses the sensitivity of Auger electrons to the elemental composition to determine surface properties of materials. The field has now expanded beyond

focussing solely on surfaces. It is an important component of X-ray photoelectron spectroscopy (XPS).

AES relies on accurate data for specific Auger electron kinetic energies, often referred to as Auger transitions, peaks, or energies. Much experimental work has characterised these to greater accuracies and precisions for both elemental substances and compounds. Results are used for industries such as metallurgy and microelectronics and by materials scientists to characterise the surface of a wide range of materials (Lu et al., 2021; Guseinov and Ilyin, 2021; Unger et al., 2020; Kosugi et al., 2020; Horio et al., 2020).

There is a new interest in an increasing range of elements and compounds shown by the industrial community for rare-earth-elements in battery, semiconductor, and photovoltaic cell technologies. For AES to be of use to studies involving elements and compounds, their respective Auger peaks must be well-characterised. Despite this, even common elements that have been studied many times are missing Auger transition information and less-common elements have even less information. The most comprehensive database, the National Institute of Standards and Technology (NIST) XPS database (Naumkin et al., 2012), only has Auger kinetic energies for 58 of the 92 naturally occurring elements. Hydrogen and helium have no Auger transitions in their natural state, and elements with fewer electrons have fewer possible transitions. For titanium, only three Auger transitions are listed out

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of over one-hundred allowed Auger transitions. Although a few Auger electron energies are dominant in a material; and some transitions have orders of magnitude lower yields than others, and may not be well-resolved, the current resolution is enough to cause significant problems with quantitative analysis.

As spectroscopic techniques improve, especially in different experimental techniques, more peaks will become well-resolved and observable. A lot of insight comes from recent technology and theory for X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES), including new progress on plasmon observation and theory. Since XPS and AES rely on a database of Auger electron energies, the more available peaks to compare with experimental data will benefit industry and scientific fields as more exotic materials are tested. A database can be purely experimental. However, theoretical values are also important, and essential when experimental values do not exist or are unresolvable. A comparison between the two reinforces the accuracy of both.

Performing advanced theoretical calculations and comparing with accurate experimental values is essential for testing the current standard. For this work, the multiconfigurational Dirac–Hartree–Fock (MCDHF) method is used to obtain values for Auger electron kinetic energies. Therefore, observing values consistent between these calculations and previous experiments (Naumkin et al., 2012) or predictions will provide added confidence to these methods.

While important to industry, condensed-matter science, and testing advanced quantum mechanics, the Auger peak is also important for state-of-the-art X-ray optics and atomic physics research. High-quality calibration of characteristic energies is pivotal for understanding key atomic physics phenomena. Understanding the radiative Auger emission (RAE) is becoming a new area of interest. RAE occurs when a photon is emitted along with the Auger electron. The total energy is shared between the Auger electron and photon, therefore, the edge photon energy occurs when the Auger electron has zero kinetic energy. From conservation of energy, this end-point energy will be the energy of the non-radiative Auger electron. Some of these are now seen in characteristic X-ray spectra, with an atomic and/or solid state band theory basis. Therefore, theoretical calculations are essential to achieve greater accuracies with future RAE satellites within characteristic X-ray spectra.

The previous theoretical standard for identifying Auger peaks uses binding energies of relevant energy levels. This method is improved upon by using a multi-configuration approach with a Dirac–Hartree–Fock potential by up to 5 eV. We demonstrate this in this work.

## 2. Background and theory

For an XYZ Auger electron, by conservation of energy, the kinetic energy of the Auger electron is:

$$E_{XYZ} = E_X - E_Y - E_Z \quad (1)$$

where  $E_{XYZ}$  is the kinetic energy of the XYZ Auger electron and  $E_i$  is the binding energy of the  $i$ th orbital. There are two main approaches to defining the zero or reference energy for these energies. The conventional solid state, condensed matter, materials perspective is to refer all to the relevant Fermi energy. The conventional atomic or fundamental parameters approach is to refer them to the vacuum level as for an isolated atom. The difference between these is the work function of the material, which is specific to the quantum system, crystallinity, surface plane and surface contamination and even temperature for example. Tabulations of Fermi energies relative to the vacuum level, that is to say the work function, are found in the literature (Tanuma et al., 1991; Shinotsuka et al., 2015; Chantler and Bourke, 2022). Kahn (2016) discusses differences and definitions of Fermi level, work function, vacuum level, ionisation energy, and electron affinity.

The NIST XPS database defines Auger electron kinetic energies with respect to the Fermi level. Our theoretical model uses free atoms and

**Table 1**

Work functions for elemental solids used in this work (Michaelson, 1977).

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Work function (eV)	3.5	4.33	4.3	4.5	4.1	4.5	5.0	5.15	4.65	4.33

references the vacuum energy level which is therefore independent of crystal structure. For comparison, we subtract the work function, listed for the particular crystal structure that we are comparing with, from our atomic calculation value. Sometimes the particular crystal structure is not given, or is polycrystalline, in this instances we compare with the polycrystalline work function for a particular elemental solid.

Table 1 presents the full list of work functions we use herein.

For example, our atomic calculation obtains a titanium  $L_3 M_3N_1$  Auger electron energy of 425.1 eV, subtracting the work function for titanium, 4.33 eV (Michaelson, 1977), from this yields the value in Table 2 of 420.8 eV relative to the Fermi level. Following e.g. Michaelson (1977), work functions for Fe (metal) can vary from 4.62 eV to 4.81 eV for different planes, and the polycrystalline value appears less than these by 0.12 to 0.31 eV. Whilst part of this is crystal-plane dependent, part of this may well be an estimated uncertainty of data consistency. These values are largely enshrined in the literature as work functions stemming from work prior to 1977, and little has changed to these values or their uncertainties since then. Similarly, Ni (metal) planes vary from 5.04 eV to 5.35 eV so from  $-0.11$  eV to  $+0.20$  eV relative to the polycrystalline reported value; and Cu (metal) planes vary by 0.5 eV, from 4.53 eV to 4.98 eV. Theoretical computations of the work functions using band predictions have been made (Skriver and Rosengard, 1992) and can also vary by 0.5 eV from the experimental tabulations. Greiner et al. (2012) provides a discussion of the challenges of defining a unique work function or Fermi level especially noting the surface or oxide contributions. Some uncertainties for materials such as polycrystalline Cu (metal) have been given as  $4.66 \pm 0.05$  eV under specific conditions.

## 3. Theoretical methods

Eq. (1) is incomplete since the transition itself alters the binding energies. Therefore, the most common theoretical approach to this is done by taking the mean of the binding energies of the shell of the atom in question and the shell of the  $Z+1$  atom, leading to a detailed binding energy method catalog of Auger transitions, primarily following an atomic-type model (Coghlan and Clausing, 1973):

$$E_{xyz} = E_x - E_{y'} - E_{z'} \quad (2)$$

where  $E_{y'}$  is:

$$E_{y'} = \frac{1}{2}(E_{y(Z)} + E_{y(Z+1)}) \quad (3)$$

and is the mean binding energy for the relaxing electron for the atom and the  $Z+1$  atom, similarly for  $E_{z'}$ . Since most work in AES is referenced to the Fermi energy, we must subtract the work function accordingly (Kahn, 2016; Coghlan and Clausing, 1973).

This method is referred to as the binding energy (BE) method and is used frequently as an easy way to calculate the Auger electron kinetic energy. It is particularly useful when empirical data is lacking, common for low yield peaks. However, greater accuracy is needed in many cases such as with overlapping peaks (von Busch et al., 1999), high intensity synchrotron experiments (Wallis et al., 2014), testing complex atomic physics with Auger cascades (Jonasas et al., 2008), and for characterising 4d metals ( $39 \leq Z \leq 48$ ) (Kleiman, 2002).

With the need for greater accuracy and precision calculations of Auger energies comes a need for a fully relativistic quantum approach, as opposed to the BE approximation of Eq. (3). This treatment must consider the atomic state functions (ASFs) of the initial, intermediate, and final states, and their interactions. These ASFs and interactions

**Table 2**

Auger electron Kinetic Energies (eV) referenced to the Fermi level ( $E_F$ ) for the theoretical results of this work compared with the NIST XPS database (Experiment, Naumkin et al. (2012)) and the BE method. Differences are defined as:  $\Delta = E_{theory} - E_{experiment}$  and  $\Delta_{BE} = E_{BE} - E_{experiment}$ . We compare the magnitude of differences between our theoretical values and the BE Method values to the experimental values in  $|\frac{\Delta_{BE}}{\Delta}|$ . The greater this value, the better our theoretical approach models the experimental values compared with the BE method. If greater than 1, the new approach is a better representation of the solid state spectra. We also give a statement of significance in dividing  $\Delta$  by our theoretical method uncertainty in  $|\frac{\Delta}{\sigma}|$ . Particular anomalies invite further experimental and theoretical investigation. The citing sources from the NIST XPS database (Naumkin et al., 2012) are given. The different nomenclature between atomic and solid state physics is shown. Numbers in brackets represent one standard deviation uncertainty from the variance.

	Nomenclature		Auger Electron Kinetic Energies Referenced to $E_F$ (eV)							
	Solid State	Atomic	Experiment, Naumkin et al. (2012)	Ref.	MCDHF Theory	$\Delta$	BE Method	$\Delta_{BE}$	$ \frac{\Delta_{BE}}{\Delta} $	$ \frac{\Delta}{\sigma} $
Sc	$L_2M_2M_3$	$L_2M_2M_3$	337.1(1.0)	Powell (2012)	337.3(4)	0.2	341.3	4.2	21	0.5
Ti	$KL_{23}L_{23}$	$KL_3L_3$	4002	Wittberg and Wang (1983)	4001.0(3)	-1.0	4004.3	2.3	2.3	3.3
	$L_{23}M_{23}V$	$L_3M_3N_1$	418.9(4)	Powell (2012)	420.8(4)	1.9	425.3	6.4	3.4	4.8
V	$L_{23}M_{23}V$	$L_3M_3N_1$	471.8(4)	Powell (2012)	472.4(5)	0.6	472.3	0.5	0.8	1.2
	$L_{23}VV$	$L_3M_2N_1$	510.2	Sawatzky and Post (1979)	510.7(6)	0.5	515.3	5.1	10.2	0.8
Cr	$L_{23}M_{23}V$	$L_3M_3N_1$	527.3(4)	Powell (2012)	528.0(3)	0.7	529.6	2.3	3.3	2.3
Mn	$L_{23}M_{23}V$	$L_2M_3N_1$	586.2(4)	Powell (2012)	587.5(4)	1.3	588.6	2.4	1.8	3.3
	$L_{23}M_{23}M_{23}$	$L_3M_3M_3$	544.3	Vayrynen (1981)	544.0(5)	-0.3	542.9	-1.4	4.7	0.6
	$L_{23}VV$	$L_2M_5N_1$	636.6	Vayrynen (1981)	634.8(7)	-1.8	634.2	-2.4	1.3	2.6
Fe	$L_{23}VV$	$L_3N_1N_1$	702.7(4)	Powell (2012)	701.9(6)	-0.8	701.8	-0.9	1.1	1.3
	$M_{23}VV$	$M_3M_4N_1$	48.6(3)	Kaurila et al. (1994)	48.2(3)	-0.4	47.4	-0.9	2.3	1.3
Co	$L_{23}VV$	$L_3M_5N_1$	773.4(4)	Powell (2012)	774.4(4)	1.0	772.9	-0.5	0.5	2.5
	$M_{23}VV$	$M_2M_4N_1$	53.6(7)	Powell (2012)	53.2(2)	-0.4	53.7	0.1	0.3	2.0
Ni	$L_{23}VV$	$L_3M_5N_1$	846.1	Powell et al. (1981)	845.2(3)	-0.9	848.0	1.9	2.1	3.0
	$M_{23}VV$	$M_2M_4N_1$	59.7(7)	Powell (2012)	60.2(3)	0.5	63.3	3.6	7.2	1.7
Cu	$L_2VV$	$L_2M_5N_1$	938.3	Mansour (1994)	939.9(6)	1.6	948.0	9.7	6.1	2.7
	$L_3VV$	$L_3M_5N_1$	914.1	Mansour (1994)	915.2(7)	1.1	928.4	14.3	13	1.6
	$M_{23}VV$	$M_2M_5N_1$	62.4	Seah (1998)	63.4(3)	1.0	70.8	8.4	8.4	3.3
Zn	$L_2M_{45}M_{45}$	$L_2M_4M_5$	1010.7(2)	Strohmeier (1994)	1008.3(7)	-2.4	1020.3	9.6	4.0	3.4
	$L_3M_{45}M_{45}$	$L_3M_5M_5$	992.4(4)	Powell (2012)	992.9(5)	0.5	997.2	4.8	9.6	1.0

are obtained and modelled using a MCDHF approach. This uses the Dirac–Coulomb–Breit Hamiltonian which includes electron–electron interactions and Breit interactions, which, in natural units ( $c = \hbar = 1$ ), is:

$$H_{DC} = \sum_i (\alpha_i \cdot p_i + (\beta_i - 1) + V_i) + \sum_{i>j} \left( \frac{1}{r_{ij}} + b_{ij} \right) \quad (4)$$

where the first term (Dirac) represents the individual electron contribution due to its kinetic energy with  $p_i$  being the momentum of the  $i$ th electron,  $\alpha$  and  $\beta$  are the  $4 \times 4$  Dirac matrices, and  $V_i^N$  is the monopole electron–nucleus Coulomb interaction. The second term (Coulomb) represents the two-body electron–electron Coulomb interactions including a Breit interaction term,  $b_{ij}$ :

$$b_{ij} = -(\alpha_i \cdot \alpha_j) \frac{\cos(\omega r_{ij})}{r_{ij}} + (\alpha_i \cdot \nabla_j)(\alpha_j \cdot \nabla_j) \frac{\cos(\omega r_{ij} - 1)}{\omega^2 r_{ij}} \quad (5)$$

where  $\omega = \epsilon_i - \epsilon_j$  is the difference in electron energies. For these equations, we use the zero-frequency approximation where  $\omega \rightarrow 0$ . This neglects all contributions of order  $\alpha^4 Z^3$  and above.

Diagonalising the Dirac–Coulomb Hamiltonian provides coefficients,  $c_r$ , that are used with configuration state functions (CSFs),  $\Phi(\gamma, \Pi J M)$ , to give us the full ASFs,  $\Psi(\Pi J M)$ :

$$\Psi(\Pi J M) = \sum_r c_r \Phi(\gamma_r, \Pi J M) \quad (6)$$

These CSFs are Slater determinant solutions to the central field problem where parity,  $\Pi$ , angular momenta,  $J M$ , and electron configuration quantum numbers in  $\gamma$  are well defined and unique. These ASFs are obtained employing the GRASP2K interactive software which performs relativistic atomic structure calculations with the MCDHF method (Grant, 2007; Dyal et al., 1989; Parpia et al., 2006; Jönsson et al., 2007), modified to incorporate QED (quantum electrodynamics) contributions (Lowe et al., 2013) and Breit interactions (Chantler et al., 2014).

Once the ASFs are obtained for the initial, intermediate, and final atomic/ionic states transition amplitudes and energy eigenvalues are calculated. This is done using Fermi's Golden rule:

$$\langle \Psi(\alpha) | T_{DC} | \Psi(\beta) \rangle = \sum_{ij} c_i^*(\alpha) T_{ij} c_j(\beta) \quad (7)$$

where  $T$  is the transition operator. Solving for the transition operator is the last step in these calculations and is done using the Wigner–Eckart theorem. This step is done using the interactive RATIP software package (Fritzsche, 2001, 2012)

Within this framework, we make use of the sudden limit assumption during the ejection and relaxation processes. This states that the ASFs do not change over the time of electron ejection or electron relaxation (Thomas, 1984, 1986). This assumption is not a limiting factor to our calculations as it has proven to hold true to  $< 0.1 eV$  accuracy (Lowe et al., 2013; Chantler et al., 2014, 2010).

The calculations are complex, especially for the  $3d$  metals due to their open shells. Depending on the species and the level of accuracy calculating for some ASFs require upwards of 100,000 CSFs. Calculations can be performed considering only the shells that contain electrons in the supposed ground state or, preferably, the ASF can be extended to allow contributions from higher energy shells, providing second- and third-order CSFs. The first-order CSFs are those which only contain electrons in the canonical ground state, second-order CSFs allow one electron to be excited above this level and third-order allow for two. Higher-order CSFs account for deficiencies in the radial wavefunction, electron–electron correlations and incomplete basis sets. The increased accuracy and convergence naturally increases computational time. For example, there are four first-order, 1,114 second-order (one excitation), and 144,925 third-order (two excitations) CSFs for the ground state scandium ion with a K-shell hole.

This process is more time consuming than simple binding energy approaches. However, our results, below, show that the added effort is important and significant.

#### 4. Prominent Auger peaks of 3d transition metals results (breadth)

Numerous databases list experimental Auger electron kinetic energies (Seah, 1989; Powell, 1995a,b; Seah, 1998, 2003; Powell, 2010, 2012). However, no substantial work has been done on comparison between these and calculations derived from a full relativistic quantum mechanical treatment of the Auger process. Whilst this present work is not comprehensive, it sheds light on the full treatment of the problem and encourages those who require Auger energies for transitions not found in the literature to use these methods over the BE method. Of course, an isolated atomic computation is not obviously a mimic of a specific band structure problem. The latter may have large widths of e.g. 6 eV and may be dominated by the method or averaging over orientation, even ignoring surface or contamination effects. Hence the current results are most accurate in reference to the vacuum level, for which the work function estimates given earlier would be subtracted.

The NIST XPS database gives twenty separate empirically derived Auger electron kinetic energies for the 3d transition metals (Naumkin et al., 2012). Within each transition there are many different values given from different experiments and different compounds. We cite, where possible, the pure metal form(s) and results reported by the NIST XPS database as ‘good’ quality data, and include the sources in Table 2 for each. Unfortunately, many of the values listed do not give the specific crystal structure of the solid and therefore we are unable to account for varying work functions. For these, we use the polycrystalline reference.

Another issue when comparing between experimental values from solids and theoretical values as calculated for free atoms is the outermost electron shells couple with the valence band and are sometimes poorly defined. This is seen when looking through databases of Auger kinetic energies that list a particular transition with a ‘V’, for ‘valence’, in place of IUPAC atomic orbitals. Since we calculate for isolated atoms using atomic orbitals, we use IUPAC X-ray naming conventions. While this is a limitation to predict bound systems e.g. oxides, it is striking that we obtain values closer to the experimental tables for materials than the current binding energy methods.

Due to the closeness of certain orbital energies, experimental methods often cannot resolve different eigenenergies and there can be band structure and level crossing perturbations. For example, the titanium  $L_3 M_3 N_1$  Auger electron energy we calculate has no exactly, directly corresponding experimental value in the NIST XPS database. Rather, there is an entry for  $L_{23} M_{23} V$ . This Auger electron spectral line would consist of at least four energy eigenvalues when parsing  $L_{23}$  into  $L_2$  and  $L_3$  and similarly for the M shell. There is also further separation of the valence shells between the  $M_4$ ,  $M_5$ , and  $N_1$  shells.

Due to the orbital mixing of outermost orbitals into less well-defined valence orbitals and the closeness of these orbitals with widths resulting in overlapping energies many experimental values give a dominant or average peak energy rather than separate transitions. Sometimes, the separate peaks are well-resolved, as is the case for the NIST XPS database entries for Cu  $L_3 VV$  and Cu  $L_2 VV$  list five and two values respectively all from the same experiment. These values come from Plots 191-4, 191-9, and 191-14 in Mansour (1994) (Mansour, 1994). Despite the experiment resolving separate peaks well, all are labelled with the same Valence label. The BE Method is not accurate enough to determine the origins of the separate peaks; but a full MCDHF treatment of the problem as presented here is able to give each transition peak its atomic orbital origin. Plot 191-4 from the Mansour work show five discernible peaks for the Cu  $L_3 VV$  which we believe are attributable to the atomic orbitals  $M_4$ ,  $M_5$ , and  $N_1$ . These three orbitals would result in six separated peaks but due to different yields and widths one has been hidden. Ultimately, this explains the critical importance of atomic theory with solid state experiments. Even with orbital mixing of valence shells, and potential level crossing, the atomic theory that leads to separate peaks being observed remains true. In particular, the NIST XPS label  $L_{23}$  is clearly incorrect, this is (purely)  $L_3$  and the  $L_2$  Auger spectra

are well-defined in the experimental data in a separate energy — indeed where they should be from ab initio theory. This is assisted in context by the experimental resolution being of order 1 eV (the authors claim energy resolution down to 0.13 eV, perhaps with experimental and spectral broadening towards 1 eV, where these multiplets are clearly separated.

Results we obtain show the relevance and accuracy of atomic theory to solid state experiment for Auger structure and spectra. These results surpass the binding energy methods still used to obtain Auger energies for unknown transitions. The differences between these values obtained via state-of-the-art MCDHF atomic theory calculations and the current experiments offer avenues for future research into theoretical solid state physics. There is ambiguity when comparing with experimental tabulations which merge or cannot resolve orbitals using, as example, ‘V’ or  $M_{23}$ . As mentioned for Cu  $L_3 VV$  this notation arises from valence orbital mixing and the closeness in energies of orbitals resulting in overlapping peaks. For example, only one value is given in the NIST XPS database for Ti  $L_3 M_{23} V$  where there may be up to six,  $M_{23} \in \{M_2, M_3\}$ ,  $V \in \{M_4, M_5, N_1\}$ . Notice that for copper as discussed,  $M_{23}$  should be experimentally separable into  $\{M_2, M_3\}$ , whereas the small energy separations of e.g.  $\{M_4, M_5, N_1\}$  may be merged, unresolved, or subject to larger perturbations from band structure mixing and level crossing. This can be seen in works that present figures of the full spectra rather than tables of peak energies. Wagner (1972) (Wagner, 1972) presents data which shows one asymmetric peak for Ti  $L_3 M_{23} V$  which implies it is composed of several transitions. Hence in Table 2, we choose the atomic states corresponding to the experimental energies, hopefully representing the dominant single process, where there is any ambiguity. We present our theoretical values with the work function subtracted from the MCDHF value which enables us to directly compare with the standard way for reporting experimental values referenced to the Fermi energy. Furthermore, we also do this for the BE method.

The BE method uses Eqs. (2) and (3) with the binding energies following (Bearden and Burr, 1967; Cardona and Ley, 1978; Fuggle and Mårtensson, 1980). There may be more accurate data for binding energies – e.g. a 1995 work by Cedric Powell has a greater accuracies for the  $2p_{3/2}$  binding energies for the 3d transition metals (Powell, 1995a) – however, we use these references as does the Lawrence Berkeley National Laboratory X-ray data booklet (Thompson et al., 2009) due to their completeness across all shells of each element.

Table 2 compares 3d transition metals with two metrics for determining the increased accuracy of the MCDHF approach. We define the difference between the prediction of the BE method and the reported values in the NIST XPS database as  $\Delta_{BE} = E_{BE} - E_{experiment}$ , and the difference between our result and the NIST XPS database as  $\Delta = E_{theory} - E_{experiment}$ . We present the ratio  $\Delta_{BE}/\Delta$  where the greater the value the better the MCDHF method calculated in this work models the experimental data than the BE method. Most results show this to be greater than unity — that is, the new results are a closer representation of the material experimental data than the BE method.

The second metric is the difference between our result and the NIST XPS database (Naumkin et al., 2012),  $\Delta$ , divided by the uncertainty,  $\sigma$ , in our work. The error we report comes from the square of the variance of the set of energy eigenvalues obtained for each transition. Each single transition has a set of energy eigenvalues due to the nature of electron–electron spin coupling for a given atomic state and the spread of these lead to an uncertainty. In most cases  $\Delta$  is less than 1 eV or perhaps two  $\sigma_E$  of the experimental variation; and in most cases  $\Delta/\sigma$  is less than 3 — that is less than three estimated standard deviations.

These results show remarkable agreement between the MCDHF approach and the best available experimental data especially compared with BE approaches. This is not the only benefit in using this approach. There are many more Auger transitions than exist in the NIST XPS database. For example, titanium has two entries whereas there are over one-hundred (atomic or solid state) transitions. Theoretical models allow predictions for these processes especially if experimental values

**Table 3**

*Ab initio* MCDHF calculations for Titanium Auger electron Energies (eV) for initial K-shell vacancies compared with the BE method. The binding energies are taken from Fuggle and Mårtensson (1980). The difference between our theoretical values and the values obtained from the BE method are given as:  $\Delta_{BE-th} = E_{BE} - E_{theory}$ . Estimated significance is given by  $\frac{\Delta_{BE-th}}{\sigma}$ . Apparently, no sources give the  $M_{45}$  binding energies of titanium. \* 'Same as above' since the source gives the same  $M_2$  and  $M_3$  energies.

Energy levels	Auger Electron Kinetic Energies (eV)					
	Spectral Line	MCDHF Theory	BE Method	$\Delta_{BE-th}$	$\frac{\Delta_{BE-th}}{\sigma}$	
KLL	KL <sub>1</sub> L <sub>1</sub>	3779.9(3)	3782.7	2.8	9.3	
	KL <sub>1</sub> L <sub>2</sub>	3883.5(4)	3886.5	3.0	7.5	
	KL <sub>1</sub> L <sub>3</sub>	3891.2(3)	3893.6	2.4	8.0	
Ti Z=22	KL <sub>2</sub> L <sub>2</sub>	3989.3(4)	3990.3	1.0	2.5	
	KL <sub>2</sub> L <sub>3</sub>	3995.6(3)	3997.4	1.8	6.0	
	KL <sub>3</sub> L <sub>3</sub>	4001.0(3)	4004.4	3.4	11.3	
KLM	KL <sub>1</sub> M <sub>1</sub>	4311.2(4)	4314.0	2.8	7.0	
	KL <sub>1</sub> M <sub>2</sub>	4338.5(5)	4341.6	3.1	6.3	
	KL <sub>1</sub> M <sub>3</sub>	4339.0(4)	*	2.4	8.0	
	KL <sub>1</sub> M <sub>4</sub>	4351.3(4)	-	-	-	
	KL <sub>1</sub> M <sub>5</sub>	4351.6(5)	-	-	-	
	KL <sub>2</sub> M <sub>1</sub>	4415.2(4)	4417.8	2.6	6.5	
	KL <sub>2</sub> M <sub>2</sub>	4442.2(4)	4445.4	3.2	8.0	
	KL <sub>2</sub> M <sub>3</sub>	4442.7(4)	*	2.7	6.8	
	KL <sub>2</sub> M <sub>4</sub>	4454.2(3)	-	-	-	
	KL <sub>2</sub> M <sub>5</sub>	4455.3(4)	-	-	-	
	KL <sub>3</sub> M <sub>1</sub>	4422.0(6)	4424.9	2.9	4.8	
	KL <sub>3</sub> M <sub>2</sub>	4449.3(4)	4452.5	3.2	8.0	
	KL <sub>3</sub> M <sub>3</sub>	4449.9(7)	*	2.6	3.4	
	KL <sub>3</sub> M <sub>4</sub>	4461.2(5)	-	-	-	
	KL <sub>3</sub> M <sub>5</sub>	4461.6(4)	-	-	-	
	KMM	KM <sub>1</sub> M <sub>1</sub>	4841.9(6)	4845.3	3.4	5.7
		KM <sub>1</sub> M <sub>2</sub>	4869.7(5)	4872.9	3.2	6.4
		KM <sub>1</sub> M <sub>3</sub>	4870.3(5)	*	2.6	5.2
		KM <sub>1</sub> M <sub>4</sub>	4882.4(4)	-	-	-
		KM <sub>1</sub> M <sub>5</sub>	4882.7(3)	-	-	-
		KM <sub>2</sub> M <sub>2</sub>	4897.7(6)	4900.5	2.8	4.7
KM <sub>2</sub> M <sub>3</sub>		4898.6(5)	*	1.9	3.8	
KM <sub>2</sub> M <sub>4</sub>		4909.6(5)	-	-	-	
KM <sub>2</sub> M <sub>5</sub>		4909.7(5)	-	-	-	
KM <sub>3</sub> M <sub>3</sub>		4898.3(5)	4900.5	2.2	4.4	
KM <sub>3</sub> M <sub>4</sub>		4909.9(3)	-	-	-	
KM <sub>3</sub> M <sub>5</sub>		4910.2(2)	-	-	-	
KM <sub>4</sub> M <sub>4</sub>		4918.1(4)	-	-	-	
KM <sub>4</sub> M <sub>5</sub>		4918.8(2)	-	-	-	
KM <sub>5</sub> M <sub>5</sub>		4920.0(2)	-	-	-	

are limited by broadening or limited substructure. Due to the broadening and overlapping of spectra, it becomes even more important to characterise the peak energies with greater accuracy, which we achieve with the MCDHF approach over the BE approach.

### 5. Titanium Auger electron kinetic energies (depth)

Here we provide and illustrate the depth of calculations possible for a particular element, titanium. Most of these eigenvalues do not exist in experimentally compiled tabulations. Most of these values cannot be derived from binding energy approaches: because binding energies are not given for the  $M_4$  ( $3d_{3/2}$ ),  $M_5$  ( $3d_{5/2}$ ), or  $N_1$  ( $4s_{1/2}$ ) shells; or e.g. Fuggle and Mårtensson (1980) does not differentiate between the  $M_2$  ( $3p_{1/2}$ ) and  $M_3$  ( $3p_{3/2}$ ) electron energies for titanium; and especially because electron coupling produces separated levels. Yet our MCDHF approach is able to predict this complexity. Hence *ab initio* calculations of Auger peaks are particularly important, since these peaks may be unnoticed or unaccounted for in high accuracy AES experiments. While the lack of empirical or BE method values demonstrates the importance of this work, it means comparisons are generally future work.

We split the results into three tables, one for initial vacancy in the K shell, Table 3, and two for the initial vacancy in the L shell, Tables 4 and 5. We compare our results with the BE approach where possible. Results can be achieved through high accuracy MCDHF modelling of Auger transitions, and will be valuable to the AES community and the X-ray physics community for characterising RAE satellites.

**Table 4**

Results for Titanium Auger peaks for an initial L-shell hole. Labels as per Table 3.

Energy levels	Auger Electron Kinetic Energies (eV)				
	Spectral Line	MCDHF Theory	BE Method	$\Delta_{BE-th}$	$\frac{\Delta_{BE-th}}{\sigma}$
LLM	L <sub>1</sub> L <sub>2</sub> M <sub>1</sub>	10.3(4)	12.7	2.4	8.0
	L <sub>1</sub> L <sub>2</sub> M <sub>2</sub>	38.8(5)	40.3	2.5	5.0
Titanium Z=22	L <sub>1</sub> L <sub>2</sub> M <sub>3</sub>	39.1(4)	*	2.2	5.5
	L <sub>1</sub> L <sub>2</sub> M <sub>4</sub>	49.9(6)	-	-	-
	L <sub>1</sub> L <sub>2</sub> M <sub>5</sub>	50.0(5)	-	-	-
	L <sub>1</sub> L <sub>3</sub> M <sub>1</sub>	16.8(6)	19.8	3.0	5.0
	L <sub>1</sub> L <sub>3</sub> M <sub>2</sub>	44.5(4)	47.4	2.9	7.3
	L <sub>1</sub> L <sub>3</sub> M <sub>3</sub>	45.1(3)	*	2.3	7.7
	L <sub>1</sub> L <sub>3</sub> M <sub>4</sub>	56.4(6)	-	-	-
	L <sub>1</sub> L <sub>3</sub> M <sub>5</sub>	57.0(7)	-	-	-
	L <sub>1</sub> MM	L <sub>1</sub> M <sub>1</sub> M <sub>1</sub>	436.9(5)	440.2	3.3
L <sub>1</sub> M <sub>1</sub> M <sub>2</sub>		465.2(5)	467.8	2.6	5.2
L <sub>1</sub> M <sub>1</sub> M <sub>3</sub>		465.5(4)	*	2.3	5.8
L <sub>1</sub> M <sub>1</sub> M <sub>4</sub>		477.2(4)	-	-	-
L <sub>1</sub> M <sub>1</sub> M <sub>5</sub>		478.3(2)	-	-	-
L <sub>1</sub> M <sub>2</sub> M <sub>2</sub>		491.8(6)	495.4	3.6	6.0
L <sub>1</sub> M <sub>2</sub> M <sub>3</sub>		492.0(3)	*	3.4	11.3
L <sub>1</sub> M <sub>2</sub> M <sub>4</sub>		504.7(6)	-	-	-
L <sub>1</sub> M <sub>2</sub> M <sub>5</sub>		505.0(4)	-	-	-
L <sub>1</sub> M <sub>3</sub> M <sub>3</sub>		492.1(8)	495.4	3.3	4.1
L <sub>1</sub> M <sub>3</sub> M <sub>4</sub>		505.1(5)	-	-	-
L <sub>1</sub> M <sub>3</sub> M <sub>5</sub>		505.5(5)	-	-	-
L <sub>1</sub> M <sub>4</sub> M <sub>4</sub>		506.2(6)	-	-	-
L <sub>1</sub> M <sub>4</sub> M <sub>5</sub>		506.6(5)	-	-	-
L <sub>1</sub> M <sub>5</sub> M <sub>5</sub>		506.7(7)	-	-	-
L <sub>2</sub> MM	L <sub>2</sub> M <sub>1</sub> M <sub>1</sub>	336.3(5)	339.5	3.2	6.4
	L <sub>2</sub> M <sub>1</sub> M <sub>2</sub>	362.9(8)	367.1	4.2	5.3
	L <sub>2</sub> M <sub>1</sub> M <sub>3</sub>	361.3(4)	*	3.8	9.5
	L <sub>2</sub> M <sub>1</sub> M <sub>4</sub>	376.3(3)	-	-	-
	L <sub>2</sub> M <sub>1</sub> M <sub>5</sub>	376.5(5)	-	-	-
	L <sub>2</sub> M <sub>2</sub> M <sub>2</sub>	390.1(6)	394.7	4.6	7.8
	L <sub>2</sub> M <sub>2</sub> M <sub>3</sub>	390.5(4)	*	4.2	10.5
	L <sub>2</sub> M <sub>2</sub> M <sub>4</sub>	403.4(7)	-	-	-
	L <sub>2</sub> M <sub>2</sub> M <sub>5</sub>	403.5(6)	-	-	-
	L <sub>2</sub> M <sub>3</sub> M <sub>3</sub>	391.4(7)	-	-	-
	L <sub>2</sub> M <sub>3</sub> M <sub>4</sub>	404.2(5)	-	-	-
	L <sub>2</sub> M <sub>3</sub> M <sub>5</sub>	404.4(6)	-	-	-
	L <sub>2</sub> M <sub>4</sub> M <sub>4</sub>	404.8(5)	-	-	-
	L <sub>2</sub> M <sub>4</sub> M <sub>5</sub>	405.1(6)	-	-	-
	L <sub>2</sub> M <sub>5</sub> M <sub>5</sub>	405.2(5)	-	-	-

### 6. Discussion

AES is widely used for materials characterisation as it provides high resolution compositional information about the layers near the surface of a material. Auger electrons have low energies and are readily scattered, or absorbed, by their surrounding material, so only the Auger electrons produced by the top few atomic monolayers (0.5 nm–5 nm) can escape the sample (Ecke et al., 2007; Grainger and Castner, 2011). This makes AES an excellent technique for analysing the composition of nanoparticles and surfaces. XPS and AES are preferred techniques for analysing conductive materials. Heavier elements can have numerous overlapping Auger electron peaks, the peak widths increase with energy, and the peaks can have very small intensities compared with the background continuum. These effects can lead to difficulties in identifying the characteristic peaks of different elements (Raja and Barron, 2022; Bishop, 2014; Marie and Torbjörn, 2007).

Spectra are further complicated by chemical state effects that can cause energy shifts or variations in the line-shape (Davis et al., 1976; Unger et al., 2020). Positively, these measurable changes to the spectra can differentiate between compounds of the same elements (Marie and Torbjörn, 2007; Unger et al., 2020). As the nanoscience and thin film industries continue to grow, better approaches will be needed to characterise new materials, provide quality control, and facilitate monitoring of potential environmental contaminants (Rades et al., 2014). Major features in AES, XPS, XAS and XES can be explained

**Table 5**  
Results for Titanium Auger peaks for an initial L-shell hole. Labels as per Table 3.

Energy levels	Auger Electron Kinetic Energies (eV)				
	Spectral Line	MCDHF Theory	BE Method	$\Delta_{BE-th}$	$\frac{\Delta_{BE-th}}{\sigma}$
L <sub>3</sub> MM Titanium Z=22	L <sub>3</sub> M <sub>1</sub> M <sub>1</sub>	329.6(5)	333.1	3.5	7.0
	L <sub>3</sub> M <sub>1</sub> M <sub>2</sub>	357.9(4)	360.7	2.8	7.0
	L <sub>3</sub> M <sub>1</sub> M <sub>3</sub>	358.4(6)	*	2.3	3.8
	L <sub>3</sub> M <sub>1</sub> M <sub>4</sub>	369.9(3)	–	–	–
	L <sub>3</sub> M <sub>1</sub> M <sub>5</sub>	367.2(5)	–	–	–
	L <sub>3</sub> M <sub>2</sub> M <sub>2</sub>	384.0(4)	388.3	4.3	10.8
	L <sub>3</sub> M <sub>2</sub> M <sub>3</sub>	384.6(4)	*	3.7	9.3
	L <sub>3</sub> M <sub>2</sub> M <sub>4</sub>	397.5(5)	–	–	–
	L <sub>3</sub> M <sub>2</sub> M <sub>5</sub>	397.8(5)	–	–	–
	L <sub>3</sub> M <sub>3</sub> M <sub>3</sub>	386.2(6)	388.3	2.1	3.5
	L <sub>3</sub> M <sub>3</sub> M <sub>4</sub>	398.6(5)	–	–	–
	L <sub>3</sub> M <sub>3</sub> M <sub>5</sub>	399.0(3)	–	–	–
	L <sub>3</sub> M <sub>4</sub> M <sub>4</sub>	410.7(7)	–	–	–
	L <sub>3</sub> M <sub>4</sub> M <sub>5</sub>	411.0(5)	–	–	–
	L <sub>3</sub> M <sub>5</sub> M <sub>5</sub>	411.2(5)	–	–	–
LMN	L <sub>1</sub> M <sub>1</sub> N <sub>1</sub>	494.1(5)	–	–	–
	L <sub>1</sub> M <sub>2</sub> N <sub>1</sub>	521.7(6)	–	–	–
	L <sub>1</sub> M <sub>3</sub> N <sub>1</sub>	521.9(7)	–	–	–
	L <sub>1</sub> M <sub>4</sub> N <sub>1</sub>	535.2(4)	–	–	–
	L <sub>1</sub> M <sub>5</sub> N <sub>1</sub>	535.2(5)	–	–	–
	L <sub>2</sub> M <sub>1</sub> N <sub>1</sub>	393.2(7)	–	–	–
	L <sub>2</sub> M <sub>2</sub> N <sub>1</sub>	421.0(6)	–	–	–
	L <sub>2</sub> M <sub>3</sub> N <sub>1</sub>	421.5(8)	–	–	–
	L <sub>2</sub> M <sub>4</sub> N <sub>1</sub>	434.5(7)	–	–	–
	L <sub>2</sub> M <sub>5</sub> N <sub>1</sub>	434.9(5)	–	–	–
	L <sub>3</sub> M <sub>1</sub> N <sub>1</sub>	387.0(5)	–	–	–
	L <sub>3</sub> M <sub>2</sub> N <sub>1</sub>	416.6(6)	–	–	–
	L <sub>3</sub> M <sub>3</sub> N <sub>1</sub>	420.8(4)	–	–	–
	L <sub>3</sub> M <sub>4</sub> N <sub>1</sub>	428.1(5)	–	–	–
	L <sub>3</sub> M <sub>5</sub> N <sub>1</sub>	428.4(7)	–	–	–

with the help of atomic theory. In particular, Larkins (1982) emphasised angular momentum coupling of states as a perturbation of shell eigenvalues; and authors such as Lund et al. (1997) have recognised that key components of the spectrum can be viewed, as we present, as atomic or quasi-atomic. Indeed, the complexity of the density of states (DOS) while composed of atomic and quasiatomic resonances, also can include band distribution. It remains compelling to recognise and address these in order of dominance in the appropriate perturbation theory in relativistic quantum mechanics.

All of these research areas require a comprehensive database of Auger peak energies. When the literature lacks a particular peak energy it is typical to use the BE method. We have shown that this can lead to incorrect energies of up to 4 eV which are improved upon by using ab initio MCDHF calculations.

## 7. Conclusion

Ab initio MCDHF calculations for Auger electron energies have been performed and show that atomic calculations are typically accurate to within the 1 eV level. This is in spite of the range of solid state phenomena that impact upon the measured Auger transition energy. The atomic calculation is referenced to the vacuum level, and by subtracting the work function the separation of e.g. eigenvalues is often dominant and present in solid state spectra. These calculations are an improvement to the BE method in obtaining Auger transition energies that are still used where experimental data is lacking. This work is important for: X-ray optics in obtaining radiative Auger peak energies, future works on the interplay between solid state and atomic physics, and materials science and industry for nominating Auger peaks in data that may not have a current database entry.

## CRedit authorship contribution statement

**J.W. Dean:** Conceptualization, Methodology, Writing. **C.T. Chantler:** Supervision, funding acquisition, Writing. **B. Ganly:** Funding acquisition, Writing.

## 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.

## Data availability

The code used is freely available from the references listed. No raw data is used.

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## References

- Auger, P., 1923. Sur les rayons  $\beta$  secondaires produits dans un gaz par des rayons X (On  $\beta$  rays as a secondary product in a gas to X-rays). *Compt. R. L'Academie Des Sci.* 177, 169–171.
- Auger, P., 1924. Sur les rayons  $\beta$  secondaires produits dans un gaz par des rayons X (On  $\beta$  rays as a secondary product in a gas to X-rays). *Compt. R. L'Academie Des Sci.* 178, 1535–1536.
- Bearden, J.A., Burr, A.F., 1967. Reevaluation of X-ray atomic energy levels. *Rev. Modern Phys.* 39 (1), 125–142. <http://dx.doi.org/10.1103/RevModPhys.39.125>.
- Bishop, H., 2014. The role of the background in auger electron spectroscopy. *Scanning Electron Microsc.* 1982 (1), 22.
- Cardona, M., Ley, L., 1978. Photoemission in Solids I: General Principles. In: *Topics in Applied Physics*, Springer-Verlag, Berlin Heidelberg, <http://dx.doi.org/10.1007/3-540-08685-4>.
- Chantler, C.T., Bourke, J.D., 2022. Key physico-chemical parameters and significance, and tabulations. In: Chantler, C.T., Boscherini, F., Bunker, B. (Eds.), *International Tables for Crystallography*. Vol. I, Kluwer Academic Publishers, Dordrecht.
- Chantler, C.T., Lowe, J.A., Grant, I.P., 2010. Multiconfiguration Dirac-Fock calculations in open-shell atoms: Convergence methods and satellite spectra of the copper  $K\alpha$  photoemission spectrum. *Phys. Rev. A* 82 (5), 52505.
- Chantler, C.T., Nguyen, T.V.B., Lowe, J.A., Grant, I.P., 2013. Relativistic calculation of transition probabilities for 557.7 nm and 297.2 nm emission lines in oxygen. *Agron. J.* 769 (1), 3–7. <http://dx.doi.org/10.1088/0004-637X/769/1/84>.
- Chantler, C.T., Nguyen, T.V.B., Lowe, J.A., Grant, I.P., 2014. Convergence of the Breit interaction in self-consistent and configuration-interaction approaches. *Phys. Rev. A* 90 (6), 1–8. <http://dx.doi.org/10.1103/PhysRevA.90.062504>.
- Coghlan, W., Clausing, R., 1973. Auger catalog: Calculated transition energies listed by energy and element. *At. Data* 5, 317–469.
- Davis, L., MacDonald, N., Palmberg, P., Reach, G., Weber, R., 1976. *Handbook of Auger Electron Spectroscopy*. Physical Electronics Division.
- Dean, J.W., Chantler, C.T., Melia, H.A., Smale, L.F., 2019. High accuracy characterisation for the absolute energy of scandium  $K\alpha$ . *J. Phys. B* 52 (16), 165002–165013.
- Dean, J.W., Chantler, C.T., Smale, L.F., Melia, H.A., 2020. An absolute energy characterisation of scandium  $K\beta$  to 2 parts per million. *J. Phys. B* 53 (20), 205004–205014. <http://dx.doi.org/10.1088/1361-6455/abb1ff>.
- Dean, J.W., Pushkarna, P., Melia, H.A., Nguyen, T.V.B., Chantler, C.T., 2022. Theoretical calculation of characteristic radiation: multiconfiguration Dirac-Hartree-Fock calculations in scandium  $K\alpha$  and  $K\beta$ . *J. Phys. B* 55 (7), 075002. <http://dx.doi.org/10.1088/1361-6455/ac61ed>.
- Dyall, K.G., Grant, I.P., Johnson, C.T., Parpia, F.A., Plummer, E.P., 1989. GRASP: a general-purpose relativistic atomic structure program. *Comput. Phys. Comm.* 55, 425–456.
- Ecke, G., Cimalla, V., Tonisch, K., Lebedev, V., Romanus, H., Ambacher, O., Liday, J., 2007. Analysis of nanostructures by means of Auger electron spectroscopy. *J. Electr. Eng.* 58 (6), 301–306.
- Fritzsche, S., 2001. RATIP – a toolbox for studying the properties of open-shell atoms and ions. *J. Electron Spect. Rel. Phenom.* 114–116, 1155–1164. [http://dx.doi.org/10.1016/S0368-2048\(00\)00257-7](http://dx.doi.org/10.1016/S0368-2048(00)00257-7).
- Fritzsche, S., 2012. The RATIP program for relativistic calculations of atomic transition, ionization and recombination properties. *Comp. Phys. Comm.* 183 (7), 1525–1559. <http://dx.doi.org/10.1016/j.cpc.2012.02.016>.
- Fuggie, J., Mårtensson, N., 1980. Core-level binding energies in metals. *J. Electron Spect. Rel. Phenom.* 39 (21), 275.
- Grainger, D., Castner, D., 2011. 3.301 - Surface analysis and biointerfaces: Vacuum and ambient in situ techniques. In: Ducheyne, P. (Ed.), *Comprehensive Biomaterials*. Elsevier, Oxford, pp. 1–22. <http://dx.doi.org/10.1016/B978-0-08-055294-1.00082-9>.

- Grant, I.P., 2007. *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation*. Springer.
- Greiner, M.T., Chai, L., Helander, M.G., Tang, W.-M., Lu, Z.-H., 2012. Transition metal oxide work functions: The influence of cation oxidation state and oxygen vacancies. *Adv. Funct. Mater.* 22 (21), 4557–4568. <http://dx.doi.org/10.1002/adfm.201200615>.
- Guseinov, N.R., Ilyin, A.M., 2021. Electrostatic energy analyzer for nanotechnology applications. *J. Electron Spect. Rel. Phenom.* 246, <http://dx.doi.org/10.1016/j.elspec.2020.147031>.
- Harris, L.A., 1968a. Analysis of materials by electron-excited auger electrons. *J. Appl. Phys.* 39 (3), 1419–1427. <http://dx.doi.org/10.1063/1.1656374>.
- Harris, L.A., 1968b. Some observations of surface segregation by auger electron emission. *J. Appl. Phys.* 39 (3), 1428–1431. <http://dx.doi.org/10.1063/1.1656375>.
- Horio, Y., Nakahara, H., Yuhara, J., Takakuwa, Y., 2020. Beam rocking auger electron spectroscopy of a Si(111)root 3x root 3-ag surface. *E-J. Surf. Sci. Nanotech.* 18, 139–145. <http://dx.doi.org/10.1380/ejssnt.2020.139>.
- Jonauskas, V., Karazija, R., Kučas, S., 2008. The essential role of many-electron Auger transitions in the cascades following the photoionization of 3p and 3d shells of Kr. *J. Phys. B* 41 (21), 215005. <http://dx.doi.org/10.1088/0953-4075/41/21/215005>.
- Jönsson, P., He, X., Froese Fischer, C., Grant, I.P., 2007. The GRASP2K relativistic atomic structure package. *Comput. Phys. Comm.* 177 (7), 597–622. <http://dx.doi.org/10.1016/j.cpc.2007.06.002>.
- Kahn, A., 2016. Fermi level, work function and vacuum level. *Mater. Horiz.* 3, 7–10. <http://dx.doi.org/10.1039/C5MH00160A>.
- Kaurila, T., Saisa, L., Vayrynen, J., 1994. Resonant photoemission from iron films on copper. *J. Phys. Cond. Matter* 6 (27), 5053. <http://dx.doi.org/10.1088/0953-8984/6/27/014>.
- Kleiman, G., 2002. High-resolution Auger spectroscopy of 4d metals and alloys. *J. Electron Spect. Rel. Phenom.* 127 (1-2), 53–63. [http://dx.doi.org/10.1016/S0368-2048\(02\)00172-X](http://dx.doi.org/10.1016/S0368-2048(02)00172-X).
- Kosugi, S., Martins, J., Hosseini, F., Marchenko, T., Travnikova, O., Bozek, J.D., Ito, K., Sokell, E., Piancastelli, M.N., Simon, M., Koike, F., Azuma, Y., 2020. Conjugate photoelectron recapture peaks in the high resolution Auger electron spectra following near-threshold Ar 2p photoionization. *J. Phys. B* 53 (12), <http://dx.doi.org/10.1088/1361-6455/ab7fc1>.
- Larkins, F.P., 1982. Theoretical developments in high resolution auger electron studies of solids. *Appl. Surf. Sci.* 34 (13), 4–34.
- Lowe, J.A., Chantler, C.T., Grant, I.P., 2013. Self-energy screening approximations in multi-electron atoms. *Radiat. Phys. Chem.* 85, 118–123. <http://dx.doi.org/10.1016/j.radphyschem.2013.01.004>.
- Lu, D., Goto, K., Da, B., Liu, J., Yoshikawa, H., Tanuma, S., Ding, Z.J., 2021. Secondary electron-, Auger electron- and reflected electron-spectroscopy study on sp(2)-hybridization carbon materials: HOPG, carbon glass and carbon fiber. *J. Electron Spect. Rel. Phenom.* 250, <http://dx.doi.org/10.1016/j.elspec.2021.147086>.
- Lund, C.P., Thurgate, S.M., Wedding, A.B., 1997. Auger photoelectron coincidence spectroscopy studies: Trends in the  $L_{2,3} - M_{4,5} M_{4,5}$  line shapes across the 3d transition-metal series. *Phys. Rev. B* 55 (8), 5455–5465.
- Mansour, A.N., 1994. Copper Mg  $k\alpha$  XPS spectra from the physical electronics model 5400 spectrometer. *Surf. Sci. Spectra* 3, 202. <http://dx.doi.org/10.1116/1.1247748>.
- Marie, E., Torbjörn, W., 2007. 4 - surface analytical techniques applied to cleaning processes. In: Johansson, I., Somasundaran, P. (Eds.), *Handbook for Cleaning/Decontamination of Surfaces*. Elsevier Science B.V., Amsterdam, pp. 747–789. <http://dx.doi.org/10.1016/B978-0-44451664-0/50023-1>.
- Meitner, L., 1922. Über die Entstehung der  $\beta$ -Strahl-Spektren radioaktiver Substanzen. *Zeitschrift Für Physik* 9 (1), 22. <http://dx.doi.org/10.1007/BF01326962>.
- Michaelson, H.B., 1977. The work function of the elements and its periodicity. *J. Appl. Phys.* 48 (11), 4729–4733. <http://dx.doi.org/10.1063/1.323539>.
- Naumkin, A.V., Kraut-Vass, A., Gaarenstroom, S.W., Powell, C.J., 2012. NIST X-ray photoelectron spectroscopy database. NIST Standard Reference Database 20, Version 4.1, Measurement Services Division of the National Institute of Standards and Technology (NIST), <http://dx.doi.org/10.18434/T4T88K>, <https://srdata.nist.gov/xps/selEnergyType.aspx>.
- Nguyen, T.V.B., Melia, H.A., Janssens, F.I., Chantler, C.T., 2022. Theory of copper  $K\alpha$  and  $K\beta$  diagram lines, satellite spectra, and ab initio determination of single and double shake probabilities. *Phys. Lett. A* 426, 127900. <http://dx.doi.org/10.1016/j.physleta.2021.127900>.
- Parpia, F.A., Froese Fischer, C., Grant, I.P., 2006. GRASP92: a package for large-scale relativistic atomic structure calculations. *Comput. Phys. Comm.* 175 (11–12), 745–747. <http://dx.doi.org/10.1016/j.cpc.2006.07.021>.
- Powell, C.J., 1995a. Elemental binding-energies for X-Ray photoelectron-spectroscopy. *Appl. Surf. Sci.* 89 (2), 141–149. [http://dx.doi.org/10.1016/0169-4332\(95\)00027-5](http://dx.doi.org/10.1016/0169-4332(95)00027-5).
- Powell, C.J., 1995b. Energy calibration of x-ray photoelectron spectrometers - results of an interlaboratory comparison to evaluate a proposed calibration procedure. *Surf. Interface Anal.* 23 (3), 121–132. <http://dx.doi.org/10.1002/sia.740230302>.
- Powell, C.J., 2010. Recommended auger-electron kinetic energies for 42 elemental solids. *J. Electron Spect. Rel. Phenom.* 182 (2), 11–18. <http://dx.doi.org/10.1016/j.elspec.2010.05.012>.
- Powell, C.J., 2012. Recommended Auger parameters for 42 elemental solids. *J. Electron Spect. Rel. Phenom.* 185 (2), 3. <http://dx.doi.org/10.1016/j.elspec.2011.12.001>.
- Powell, C.J., Erickson, N.E., Jach, T., 1981. L3VV auger-electron line-shapes and peak positions for near-threshold electron-excitation in nickel and copper. *Phys. Rev. Lett.* 46 (14), 953–956. <http://dx.doi.org/10.1103/PhysRevLett.46.953>.
- Rades, S., Wirth, T., Unger, W., 2014. Investigation of silica nanoparticles by auger electron spectroscopy (AES). *Surf. Interface Anal.* 46 (10–11), 952–956. <http://dx.doi.org/10.1002/sia.5378>.
- Raja, P., Barron, A., 2022. *Physical methods in chemistry and nano science*. In: *Physical Methods in Chemistry and Nano Science*. LibreTexts.
- Sawatzky, G., Post, D., 1979. X-ray photoelectron and auger spectroscopy study of some vanadium oxides. *Phys. Rev. B* 20, 1546. <http://dx.doi.org/10.1103/PhysRevB.20.1546>.
- Seah, M.P., 1989. Post-1989 calibration energies for X-Ray photoelectron spectrometers and the 1990 joesphson constant. *Surf. Interface Anal.* 14 (8), 488. <http://dx.doi.org/10.1002/Sia.740140813>.
- Seah, M.P., 1998. AES: Energy calibration of electron spectrometers. IV. A re-evaluation of the reference energies. *J. Electron Spect. Rel. Phenom.* 97 (3), 235–241. [http://dx.doi.org/10.1016/S0368-2048\(98\)00299-0](http://dx.doi.org/10.1016/S0368-2048(98)00299-0).
- Seah, M.P., 2003. Summary of Iso/Tc 201 Standard Xi. Iso 17974 : 2002 - surface chemical analysis - high-resolution auger electron spectrometers - calibration of energy scales for elemental and chemical-state analysis. *Surf. Interface Anal.* 35 (3), 327–328. <http://dx.doi.org/10.1002/Sia.1529>.
- Shinotsuka, H., Tanuma, S., Powell, C.J., Penn, D.R., 2015. Calculations of electron inelastic mean free paths. X. Data for 41 elemental solids over the 50 eV to 200 keV range with the relativistic full Penn algorithm. *Surf. Interface Anal.* 47 (9), 871–888. <http://dx.doi.org/10.1002/sia.5789>.
- Skriver, H.L., Rosengaard, N.M., 1992. Surface energy and work function of elemental metals. *Phys. Rev. B* 46, 7157–7168. <http://dx.doi.org/10.1103/PhysRevB.46.7157>.
- Strohmeier, B.R., 1994. Influence of surface-composition on initial hydration of aluminium in boiling water. *Surf. Sci. Spectra* 81 (2), 273–275. [http://dx.doi.org/10.1016/0169-4332\(94\)00179-0](http://dx.doi.org/10.1016/0169-4332(94)00179-0).
- Tanuma, S., Powell, C.J., Penn, D.R., 1991. Calculations of electron inelastic mean free paths. II. Data for 27 elements over the 50–2000 eV range. *Surf. Interface Anal.* 17 (13), 911–926. <http://dx.doi.org/10.1002/sia.740171304>.
- Thomas, T.D., 1984. Transition from adiabatic to sudden excitation of core electrons. *Phys. Rev. Lett.* 52 (6), 417–420. <http://dx.doi.org/10.1103/PhysRevLett.52.417>.
- Thomas, T.D., 1986. Is ionization adiabatic near threshold? *J. Electron Spect. Rel. Phenom.* 40 (3), 259–269. [http://dx.doi.org/10.1016/0368-2048\(86\)80024-X](http://dx.doi.org/10.1016/0368-2048(86)80024-X).
- Thompson, A., Lindau, I., Attwood, D., Liu, Y., Gullikson, E., Pianetta, P., Howells, M., Robinson, A., Kim, K.-J., Scofield, J., Kirz, J., Underwood, J., Kortright, J., Williams, G., Winick, H., 2009. *X-Ray Data Booklet*. University of California, Berkeley, California 94720.
- Unger, W.E., Wirth, T., Hodoroaba, V.-D., 2020. Chapter 4.3.2 - auger electron spectroscopy. In: Hodoroaba, V.-D., Unger, W.E., Shard, A.G. (Eds.), *Characterization of Nanoparticles*. In: *Micro and Nano Technologies*, Elsevier, pp. 373–395. <http://dx.doi.org/10.1016/B978-0-12-814182-3.00020-1>.
- Vayrynen, J., 1981. Differences in L<sub>2</sub>, 3MM auger-electron spectra of atomic and metallic manganese. *J. Electron Spect. Rel. Phenom.* 22 (1), 27–42. [http://dx.doi.org/10.1016/0368-2048\(81\)85002-5](http://dx.doi.org/10.1016/0368-2048(81)85002-5).
- von Busch, F., Kuetgens, U., Doppelfeld, J., Fritzsche, S., 1999. L<sub>23</sub>[L<sub>23</sub>]-MM[L<sub>23</sub>] and L<sub>23</sub>[M<sup>2</sup>]-MM[M<sub>2</sub>] Auger vacancy satellite spectra of argon. *Phys. Rev. A* 59, 2030–2042. <http://dx.doi.org/10.1103/PhysRevA.59.2030>.
- Wagner, C., 1972. Auger lines in X-Ray photoelectron spectrometry. *Anal. Chem.* 44 (6), 967.
- Wallis, A.O.G., Lodi, L., Emmanouilidou, A., 2014. Auger spectra following inner-shell ionization of argon by a free-electron laser. *Phys. Rev. A* 89, 063417. <http://dx.doi.org/10.1103/PhysRevA.89.063417>.
- Wittberg, T., Wang, P., 1983. The ti KLL spectra of TiO<sub>2</sub> and TiH generated by bremsstrahlung-excited auger spectroscopy. *J. Electron Spect. Rel. Phenom.* 31 (1), 81–83. [http://dx.doi.org/10.1016/0368-2048\(83\)85016-6](http://dx.doi.org/10.1016/0368-2048(83)85016-6).