

Galore: Broadening and weighting for simulation of photoelectron spectroscopy

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Galore simplifies and automates the process of simulating photoelectron spectra from *ab initio* calculations. This replaces the tedious process of extracting and interpolating cross-sectional weights from reference data and generates tabulated data or publication-ready plots as needed. The broadening tools may also be used to obtain realistic simulated spectra from a theoretical set of discrete lines (e.g. infrared or Raman spectroscopy).

Photoelectron spectroscopy

Photoelectron spectroscopy (PES) is a family of methods used to characterise the chemical nature and electronic structure of materials. PES is based on the photoelectric effect, which was discovered by Hertz.¹ It was explored extensively by Rutherford and colleagues² and within a few years researchers including de Broglie³ and Robinson⁴ were using the technique to measure electron binding energies through the relationship

$$E_k = h\nu - E_B.$$

Photons with energies $h\nu$ ranging from 5 eV up to 12 keV eject electrons (referred to as “photoelectrons”) from the occupied orbitals of a sample. The kinetic energy E_k of each photoelectron therefore depends on its binding energy E_B . The names of various PES methods refer to the photon energy range used:

- ultraviolet photoelectron spectroscopy (UPS): 5–100 eV
- X-ray photoelectron spectroscopy (XPS): 0.3–2 keV
- hard X-ray photoelectron spectroscopy (HAXPES, HE-PES, HXPS, HX-PES): above 2 keV

These methods generate spectra that are directly related to the electronic density of states (DOS), a distribution which is routinely calculated in *ab initio* materials chemistry. When comparing the computed DOS with a PES measurement, it is often possible to identify general peak agreement simply by reversing the energy scale (i.e. replacing negative orbital energies with positive binding energies), applying a little broadening, and shifting the energy values to account for different references. This approach has been applied successfully where peak positions are of interest.^{5,6} Broadening is generally applied by convolution with a Gaussian and/or Lorentzian function: intrinsic lifetime broadening causes a Lorentzian energy distribution of the photoelectrons, while instrumental factors, including the width of the X-ray source and analyser resolution, give rise to a Gaussian line shape. Franck–Condon phonon broadening is caused by relaxation of atomic positions in response to creation of a photohole, as well as thermal population of vibrationally excited states before photoionisation, and gives around 0.8 eV Gaussian broadening in metal oxides.^{7–9}

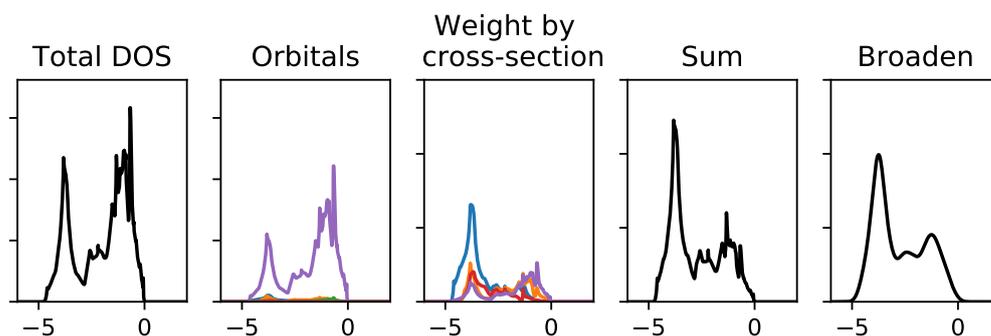


Figure 1: Procedure (left to right) for simulated photoelectron spectrum from *ab initio* DOS

Photoemission spectra for the same material will vary depending on the radiation source used. The probabilities of the underlying photoionisation events are based on the radiation and orbital energies, as well as the shape of the orbital. In order to account for this it is necessary to apply weighting to states according to their photoionisation cross-sections. This is accomplished by projecting the full DOS onto contributions from atomic *s*, *p*, *d*, *f* orbitals (PDOS), as is done routinely in analysis of *ab initio* calculations. It is then assumed that the contributions of these orbital-projected states to the total photoelectron spectrum will be proportional to the photoionisation cross-sections of corresponding orbitals in free atoms. (This is the Gelius model.^{10–12}) The free atom cross-sections have been computed by several methods and are available as reference data (e.g. 13). Implemented with ad-hoc scripts and spreadsheets, this method has already been used in many academic studies.^{14–18}

Known limitations and improvements

The Gelius model is based on photoelectrons with short wavelengths, such that the photoionisation matrix elements are dominated by regions of space close to the atomic nuclei.^{10–12} This model is expected to break down at longer wavelengths, and in the case of low-energy UPS it is likely that significant scattering effects would be neglected.

Asymmetry corrections may be applied to the photoionisation cross-sections to account for the polarisation of sources and angular acceptance range of electron detectors. This is especially relevant for HAXPES measurements where the experimental geometry may be deliberately changed in order to manipulate the spectrum and expose different contributions.¹⁹ A best-practice approach is to integrate the relevant equations over a range of angles depending on the equipment geometry.²⁰ Currently this data is not included in Galore, but users are able to include corrected cross-sections from a JSON-formatted data file if available.

At high photon energies, it has been observed that intensity changes in oxides do not correlate with photon energy as predicted by the available tabulated data; in particular the intensity of O-2p states in CdO, PbO₂ and In₂O₃ seem to vary more linearly than predicted.²⁰

Further reading

For further information about PES there are some helpful reviews in the academic literature, including Refs 21, 22 and 23.

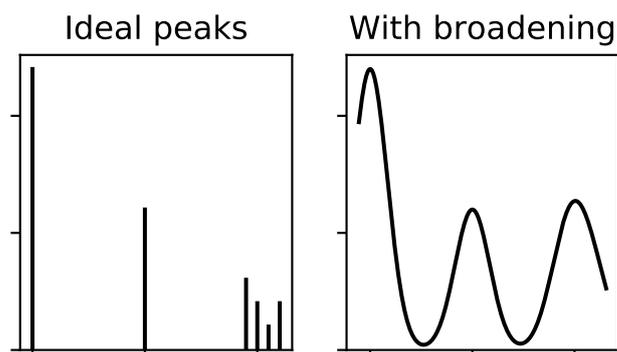


Figure 2: Schematic example of misleading peak intensities due to overlap

Vibrational spectroscopy (IR and Raman)

In infrared (IR) spectroscopy, low-energy photons are absorbed corresponding to the energies of lattice vibrations and an absorption spectrum is obtained. In a highly-crystalline system, symmetry selection rules limit the absorption activity to a small number of possible excitations with zero crystal momentum (“Gamma-point phonons”). In Raman spectroscopy another optical method is used to observe lattice vibrations and different selection rules apply; again, the resulting spectrum corresponds to a limited selection of Gamma-point movements.

It is possible to predict the frequencies and intensities of these vibrational modes by performing *ab initio* lattice dynamics calculations. Usually these will be performed within density-functional theory, either using variations of density-functional perturbation theory (based on the work of Gonze²⁴) or the frozen-phonon (“direct”) method (see Refs 25, 26). When the underlying set of vibrational frequencies and mode intensities has been calculated it is typical to broaden the data by convolution with a Gaussian–Lorentzian function.^{27,28} This is necessary to correctly interpret the effect of overlapping peaks; for example, Figure 2 shows a case in which a group of peaks with low intensities combine to form a large peak in the broadened spectrum.

Galore

Galore provides a command-line tool and Python API to import data and resample it to a dense, regular X-Y series. This mesh can then be convolved with Gaussian and Lorentzian functions to yield a smooth output, in the form of a plot or data file. Numpy functions are used for data manipulation and convolution on a finite grid and Matplotlib is used for plotting.^{29,30} As well as simple tabular data files, the electronic DOS or PDOS may be imported directly from the output of the VASP or GPAW codes.

The Gaussian and Lorentzian functions employed have the forms:

$$y = \exp\left(\frac{-(f - f_0)^2}{2c^2}\right) \quad \text{where} \quad c = \frac{\gamma}{2\sqrt{2\log 2}}$$

and

$$y = \frac{0.5\gamma}{\pi(f - f_0)^2 + (0.5\gamma)^2}$$

where f is the x-axis value, f_0 is the mid-point, γ is the full-width-half-maximum of the peak.

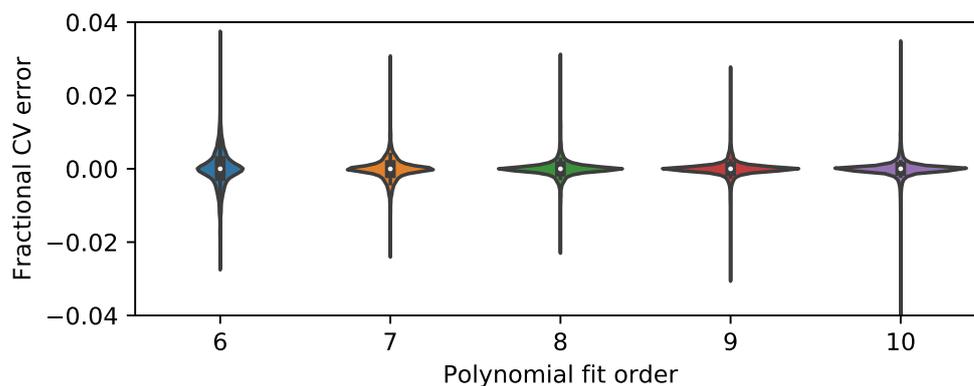


Figure 3: Cross-validation error of HAXPES data fitting over full energy range across all elements and orbitals

Cross-sectional weights are included for some standard energy values (He(II) UPS and Al k-alpha) from tabulated *ab initio* calculations.¹³ Users may provide their own weighting values in the same human-readable JSON file format. Higher-energy (HAXPES) spectra may be simulated using cross-sections from fitted data over an energy range 1-1500 keV. Tabulated data³¹ was fitted to an order-8 polynomial on a log-log scale, and coefficients for each element and orbital shape are stored in a database file. The fitting error is generally below 1%, with outliers in the region of 2–3%. The order-8 fit was selected based on cross-validation in order to avoid over-fitting (Figure 3).

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This would have been much more painful if not for the excellent scientific Python ecosystem, and the Python Materials Genome project spared us the pain of writing Yet Another Vasp Parser.

References

- (1) Hertz, H. Ueber einen Einfluss des ultravioletten Lichtes auf die electrische Entladung. *Ann. der Phys. und Chemie* **1887**, 267 (8), 983–1000.

- (2) Rutherford, E. The Connexion between the β and γ Ray Spectra. *Phil. Mag.* **1914**, *28* (165), 305–319.
- (3) de Broglie, M. Les phénomènes photo-électriques pour les rayons x et les spectres corpusculaires des éléments. *J. Phys. Radium* **1921**, *2* (9), 265–287.
- (4) Robinson, H. The Secondary Corpuscular Rays Produced by Homogeneous X-Rays. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **1923**, *104* (727), 455–479.
- (5) Veal, T. D.; Feldberg, N.; Quackenbush, N. F.; Linhart, W. M.; Scanlon, D. O.; Piper, L. F. J.; Durbin, S. M. Band Gap Dependence on Cation Disorder in ZnSnN_2 Solar Absorber. *Adv. Energy Mater.* **2015**, *5* (24), 1501462.
- (6) Savory, C. N.; Ganose, A. M.; Travis, W.; Atri, R. S.; Palgrave, R. G.; Scanlon, D. O. An assessment of silver copper sulfides for photovoltaic applications: theoretical and experimental insights. *J. Mater. Chem. A* **2016**, *4* (32), 12648–12657.
- (7) Cox, P. A.; Egdell, R. G.; Goodenough, J. B.; Hamnett, A.; Naish, C. C. The metal-to-semiconductor transition in ternary ruthenium (IV) oxides: a study by electron spectroscopy. *J. Phys. C Solid State Phys.* **1983**, *16* (32), 6221–6239.
- (8) Nelin, C. J.; Bagus, P. S.; Brown, M. A.; Sterrer, M.; Freund, H.-J. Analysis of the Broadening of X-ray Photoelectron Spectroscopy Peaks for Ionic Crystals. *Angew. Chem. Int. Ed.* **2011**, *50* (43), 10174–10177.
- (9) Regoutz, A.; Egdell, R.; Morgan, D.; Palgrave, R.; Téllez, H.; Skinner, S.; Payne, D.; Watson, G.; Scanlon, D. Electronic and surface properties of Ga-doped In_2O_3 ceramics. *Appl. Surf. Sci.* **2015**, *349*, 970–982.
- (10) Gelius, U.; Siegbahn, K. ESCA studies of molecular core and valence levels in the gas phase. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 257.
- (11) Gelius, U. Molecular Orbitals and Line Intensities in ESCA Spectra. In *Electron spectrosc.*; Shirley, D. A., Ed.; North-Holland: Amsterdam, 1972; p 311.
- (12) Gelius, U. Recent progress in ESCA studies of gases. *J. Electron Spectros. Relat. Phenomena* **1974**, *5* (1), 985–1057.
- (13) Yeh, J.; Lindau, I. Atomic subshell photoionization cross sections and asymmetry parameters: $1 \leq Z \leq 103$. *At. Data Nucl. Data Tables* **1985**, *32* (1), 1–155.
- (14) Dou, Y.; Egdell, R. G.; Law, D. S. L.; Harrison, N. M.; Searle, B. G. An experimental and theoretical investigation of the electronic structure of CdO. *J. Phys. Condens. Matter* **1998**, *10* (38), 8447–8458.
- (15) Morris, D.; Dou, Y.; Rebane, J.; Mitchell, C. E. J.; Egdell, R. G.; Law, D. S. L.; Vittadini, A.; Casarin, M. Photoemission and STM study of the electronic structure of Nb-doped TiO_2 . *Phys. Rev. B* **2000**, *61* (20), 13445–13457.
- (16) Glans, P.-A.; Learmonth, T.; Smith, K. E.; Guo, J.; Walsh, A.; Watson, G. W.; Terzi, F.; Egdell, R. G. Experimental and theoretical study of the electronic structure of HgO and Tl_2O_3 . *Phys. Rev. B* **2005**, *71* (23), 235109.
- (17) Farahani, S. K. V.; Veal, T. D.; Mudd, J. J.; Scanlon, D. O.; Watson, G. W.; Bierwagen, O.; White, M. E.; Speck, J. S.; McConville, C. F. Valence-band density of states and surface electron accumulation in epitaxial SnO_2 films. *Phys. Rev. B* **2014**, *90*, 155413.
- (18) Sathasivam, S.; Williamson, B. A. D.; Al Thabaiti, S. A.; Obaid, A. Y.; Basahel, S. N.; Mokhtar, M.; Scanlon, D. O.; Carmalt, C. J.; Parkin, I. P. Chemical Vapor Deposition Synthesis and Optical Properties of Nb_2O_5 thin films with Hybrid Functional Theoretical Insight into Band Structure and Band Gaps. *ACS Appl. Mater. Interfaces* **2017**, *9*, 18031–18038.

- (19) Regoutz, A.; Oropeza, F.; Poll, C.; Payne, D.; Palgrave, R.; Panaccione, G.; Borgatti, F.; Agrestini, S.; Utsumi, Y.; Tsuei, K.; et al. Identification of metal s states in Sn-doped anatase by polarisation dependent hard X-ray photoelectron spectroscopy. *Chem. Phys. Lett.* **2016**, *647*, 59–63.
- (20) Mudd, J. J.; Lee, T. L.; Muñoz-Sanjosé, V.; Zúñiga-Pérez, J.; Payne, D. J.; Egdell, R. G.; McConville, C. F. Valence-band orbital character of CdO: A synchrotron-radiation photoelectron spectroscopy and density functional theory study. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2014**, *89* (16), 1–7.
- (21) Hüfner, S.; Schmidt, S.; Reinert, F. Photoelectron spectroscopy – An overview. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2005**, *547*, 8–23.
- (22) Fadley, C. S. X-ray photoelectron spectroscopy: From origins to future directions. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2009**, *601*, 8–31.
- (23) Fadley, Charles S. X-ray photoelectron spectroscopy: Progress and perspectives. *J. Electron Spectrosc. Relat. Phenom.* **2010**, *178–179*, 2–32.
- (24) Gonze, X. First-principles responses of solids to atomic displacements and homogeneous electric fields: Implementation of a conjugate-gradient algorithm. *Phys. Rev. B* **1997**, *55* (16), 10337–10354.
- (25) Parlinski, K.; Li, Z. Q.; Kawazoe, Y. First-Principles Determination of the Soft Mode in Cubic ZrO₂. *Phys. Rev. Lett.* **1997**, *78* (21), 4063–4066.
- (26) Togo, A.; Oba, F.; Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. *Phys. Rev. B* **2008**, *78* (13), 134106.
- (27) Hills, G.; Jones, W. J. Raman spectra of asymmetric top molecules. Part 1. – The pure rotational spectrum of ethylene. *J. Chem. Soc. Faraday Trans. II* **1975**, *71*, 812–826.
- (28) Grevels, F.-W.; Kerpen, K.; Klotzbücher, W. E.; McClung, R. E. D.; Russell, G.; Viotte, M.; Schaffner, K. The Very Low Barrier of CO Site Exchange in Tricarbonyl (η^4 -1, 5-cyclooctadiene) iron: Picosecond Kinetics in Solution Investigated by Line Shape Simulation of the ν (CO) IR Bands and Complementary Evidence from the Course of ¹³CO Incorporation in a Low-Temperature Matrix. *J. Am. Chem. Soc.* **1998**, *120* (40), 10423–10433.
- (29) van der Walt, S.; Colbert, S. C.; Varoquaux, G. The NumPy Array: A Structure for Efficient Numerical Computation. *Comput. Sci. Eng.* **2011**, *13*, 22–30.
- (30) Hunter, J. D. Matplotlib: A 2D graphics environment. *Comput. Sci. Eng.* **2007**, *9*, 90–95.
- (31) Scofield, J. H. *Theoretical photoionization cross sections from 1 to 1500 keV*; UCRL-51326; Lawrence Livermore National Laboratory, 1973.