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An Introduction to Coding with Matlab: Simulation of X-ray Photoelectron Spectroscopy by Employing Slater's Rules

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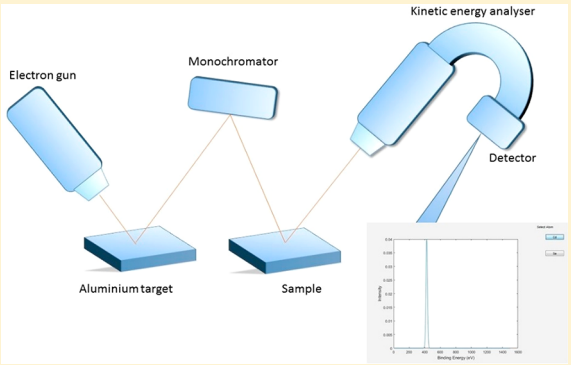
Supporting Information

ABSTRACT: Computational approaches toward simulating chemical systems and evaluating experimental data has gathered great momentum in recent years. The onset of more powerful computers and advanced software has been instrumental to this end. This manuscript presents a hands-on activity which trains students in basic coding skills within the Matlab framework. Moreover, students are able to simulate X-ray photoelectron spectroscopy (XPS) spectra of various elements using Slater's rules, a cornerstone of computational chemistry and a key topic in many undergraduate courses. A semiworked cadmium XPS example is introduced herein from which the XPS binding energy of the 3d electron may be calculated. Results are then compared with experimental values. The close agreement (within 10%) offers a real sense of student satisfaction and an appreciation of the value of computational techniques. Further elements and electronic configurations are subsequently explored. In sum, this practical develops understanding in the areas of quantum chemistry, spectroscopy, and coding skills simultaneously.



KEYWORDS: *First-Year Undergraduate, Atomic Properties, Computational Chemistry, Instrumental Methods, Spectroscopy*

INTRODUCTION

The rapid development in computational methods and equipment over the last few decades has led to computational languages becoming increasingly important.[1,2] In spite of this essential transferrable skill, many chemists struggle to code with confidence. This likely stems from several factors, including the contextual relevance of coding and inexperience. At a more specific level, an interesting study by Alzahrani et al. compared different coding languages, C++ versus Python, to identify any pedagogical advantages to using a specific computational language.[3] It was found that quality of the teaching, e.g. good learning resources and interesting assignments, outweighed the choice of coding language. In light of this, it is imperative that coding is introduced within a familiar chemical framework and at a level which complements the students prior experience. This idea of introducing coding within a familiar chemical context was adopted by Xie and Tinker, where they describe an undergraduate molecular dynamics (MD) simulation.[4] The MD simulations provide rich visual results, helping students conceptualize the often abstract math. In this project, Matlab was used to calculate binding energies of various elements using Slater's rules to predict X-ray photoelectron spectroscopy (XPS) spectra. This outputs a simulated spectrum akin to an experimental spectrum, thus uniting mathematical concepts with experimentally determined values.

XPS is itself an important tool to the physical/inorganic chemist.[5] It allows identification and quantitative analysis of materials and has been used in areas such as solar cells,[6] energy storage,[7] and catalysis.[8] Regrettably, the instrument is often delicate/expensive and is usually reserved for research purposes at most institutes. As a compromise, this practical demonstrates the key theoretical workings of XPS within a computer cluster environment using the Matlab software. The importance of Matlab and coding in general cannot be overstated. It is well-suited to carry out simulations of complex dynamic chemical systems, including quantum dot blinking,[9] atmospheric/environmental chemistry,[10] and combustion analysis.[11] Recently, the user interface of Matlab has undergone several improvements and software updates. In particular, we make use of the graphical user interface (GUIDE) function adopted by Fernández et al., which they employed to assist students with building an NMR data viewer.[12] The ease of use and drag and drop functionality of software helps prevent student discouragement early in the session. However, the GUI should be used with a note of caution because it can lead to a somewhat "black box" experience for students.[13] Matlab training is already commonplace at many universities yet largely resides within engineering and physics courses, where chemistry is in real danger of falling behind.[14,15] It is clear that further computational experiments must be developed within the Matlab syntax to complement

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the recent successes of utilizing Matlab to view NMR data to combat the surge in Matlab projects within other disciplines.

A modern XPS spectrometer relies on the photoelectric effect. Typically, a focused X-ray beam is directed toward the specimen, which ejects electrons from the sample. These electrons are then directed by a set of electromagnetic lenses toward a kinetic energy analyzer (KEA) yielding the binding energy.[16] The binding energy may be estimated, using Slater's rules, as the difference in energy between the parent atom and the produced ion. The physicist John C. Slater introduced these empirical rules in 1930 to describe shielding of the nuclear charge by inner-shell electrons.[17] Since the early calculations of Slater, other groups have proposed more accurate screening factors.[18] For simplicity, this experiment deals only with the historical application of Slater's rules.

BACKGROUND

The effective nuclear charge is introduced by eq 1 below:

$$Z_{\text{eff}} = Z - s \tag{1}$$

where Z_{eff} is the effective nuclear charge, Z is the nuclear charge, and s is the shielding factor. The shielding factor is calculated using Slater's rules highlighted in Table 1.

Table 1. Slater's Rules for Electron Shielding[a]

Group	Other Electrons in the Same Group	Electrons in Group(s) with Principal Quantum Number n and Azimuthal Quantum Number <l	Electrons in Group(s) with Principal Quantum Number $n-1$	Electrons in All Group(s) with Principal Quantum Number $\leq n-2$
1s	0.3			
ns,np	0.35		0.85	1
nd,nf	0.35	1	1	1

[a]At greater principal quantum numbers, the effective nuclear charge decreases due to screening by inner-shell electrons. Hence, 1s electrons experience the greatest effective nuclear charge, whilst the nuclear charge is highly screened for electrons in the d and f shells.

As an example calculation, consider the cadmium atom $Z = 48$. To determine the shielding constant for an electron in the 2s orbital, look at the group ns,np in the above table. There are a total of 7 other electrons in the same group as the electron of interest, i.e. $2s^1\ 2p^6$, which has a shielding factor of 0.35. Furthermore, there are 2 electrons ($1s^2$) in the group with a principal quantum number of $n-1$, which has a shielding factor of 0.85. Hence, the total shielding constant in this example is $(2 \times 0.85) + (7 \times 0.35) = 4.15$. Using this information, it is possible, using eq 2, to calculate the total energy of an N-electron atom:

$$E = -\sum_{i=1}^{N}\left(\frac{Z - s_i}{n_i}\right)^2 \tag{2}$$

where E is the total energy (Rydbergs) of an N-electron system, Z is the nuclear charge, s_i is the shielding constant of the i^{th} electron, and n_i is the principal quantum number of the i^{th} electron. Evaluating the total energy of an N-electron atom pre- and postionization and converting to electron volts yields an estimate of the binding energy. A table of elements frequently analyzed using XPS and their electron configurations is given in Table 2.

PROCEDURE AND RESULTS

Coding forms an important basis across all scientific disciplines, including chemistry, engineering, and biology, to name but a few. Unfortunately, many students find coding concepts difficult because they may not have been exposed to coding basics. Conversely, some students find coding comes somewhat naturally to them and as a result may find a Matlab practical intellectually unstimulating. This XPS practical may be tailored to suit the level of the students, whereby inexperienced Matlab users would be supplied with a heavily annotated script, which walks them through the code in a step-by-step fashion (Supporting Information). Students who are competent using Matlab software, on the other hand, may be given a reduced script and expected to fill in the blanks. This adaptability makes the XPS experiment relevant for a range of educational levels from first year undergraduate chemists through to finalists. Moreover, the XPS technique is not limited to chemistry students. This analytical tool exhibits an exceptionally broad scope and may find application in physics, engineering, and life sciences.

The raw code is explored more fully in the Supporting Information, and the major computational steps are illustrated by the flowchart in Figure 1. To summarize the important steps in the coding process, the student must (i) initiate the graphical user interface and build their output window, which will display the simulated spectra, (ii) enter the shielding constants outlined by Slaters' rules and assign the numerical values as variables, (iii) calculate the shielding constants and the total energy of the N-electron parent atom, (iv) calculate the shielding constants and total energy of the N-electron defect ion, (v) determine the electron binding energy by subtracting the total energy of the defect ion from the parent ion, and (vi) use the Matlab software and graphical user interface to plot the simulated XPS spectrum.

The experiment was run as part of a second year undergraduate module (Bonding and Spectroscopy) and would be well-suited to many computational and/or spectroscopy modules in general. The session lasted a maximum of 4 h, where most students completed the experiment within 2−3 h.

Table 2. Common Elements Analyzed Using XPS[a]

Element	Parent Atom	Defect Ion
Cd	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2 4p^6 4d^{10} 5s^2$
Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2 4p^4$
Rh	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^8 5s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2 4p^6 4d^8 5s^1$
In	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10} 5s^2 5p^1$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9 4p^6 4d^{10} 5s^2 5p^1$

[a]The electron configurations of the parent atom (pre-XPS) and defect ion (post-XPS) are provided. The electron configuration of the defect ion highlights a missing electron in the 3d shell for cadmium, selenium, rhodium, and indium. The energy difference between these two species approximates to the binding energy observed in XPS.

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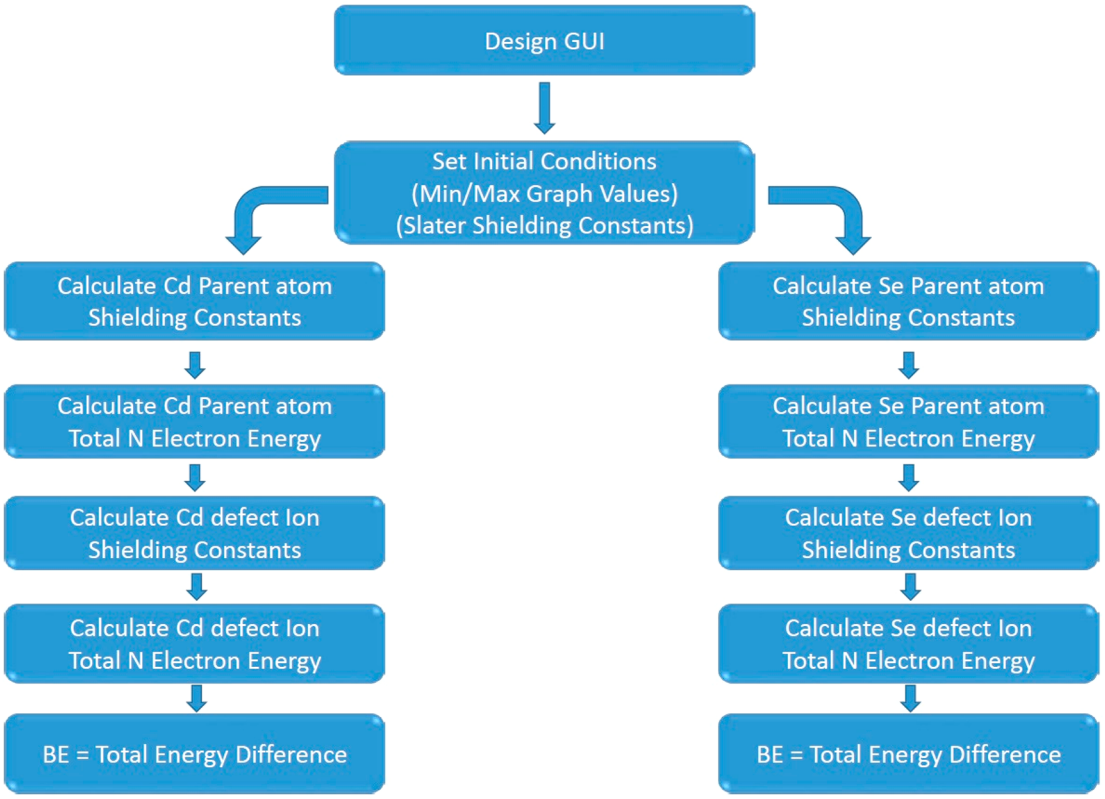

Figure 1. Flow diagram highlighting the main computational steps for XPS calculations. (Top to bottom) The GUI is generated using the in-built "Guide" function in the Matlab software. Next, the graph minimum and maximum *x*-axis values are defined, and Slater shielding constants are assigned. The calculations then split into similar computational steps for both cadmium and selenium. (Left) The shielding constants for each electron in each subshell are calculated using Slaters rules. These shielding constants are then used to calculate the total energy of the *N*-electron parent atom according to eq 2. The process of calculating the shielding constants and total energy is then repeated for the defect ion. Lastly, the binding energy is determined as the difference in total energy between the parent atom total *N*-electron energy and the defect ion. (Right) Analogous calculations using the electron configuration and atomic number of selenium yields the selenium binding energy.

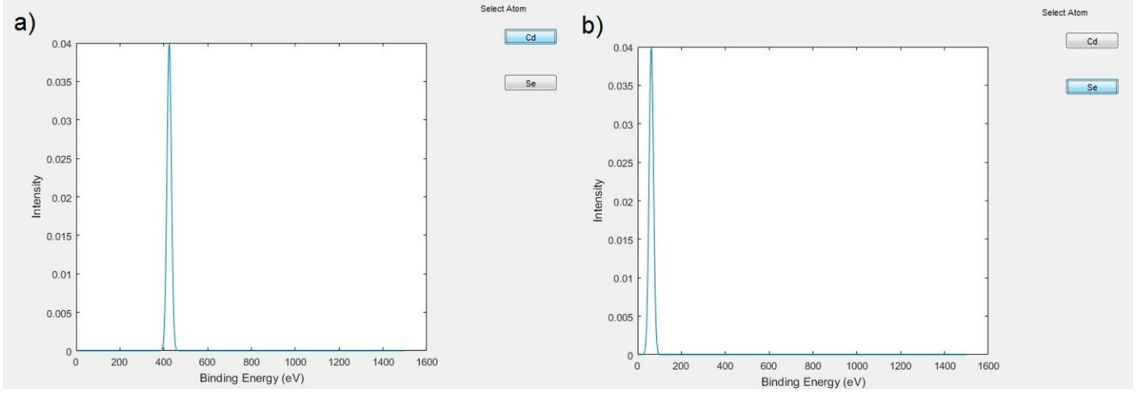

Figure 2. Simulated XPS spectra of cadmium and selenium. (a) XPS spectrum generated for cadmium. Axis labels and units have been generated within the Matlab syntax. The line shape takes the form of a normal distribution where the mean value is the calculated binding energy. The intensity of the transition has not been rigorously calculated and remains arbitrary for simplicity in this case. The mean binding energy is about 410 eV. (b) XPS spectrum of selenium calculated using Slater's rules. Axis labels and units have been generated within the Matlab syntax. The mean binding energy is about 60 eV. Other elements, including rhodium and indium, can be simulated using the same method.

The experimental duration may be tuned by asking the students to calculate the XPS of more complex elements, i.e. more electron subshells or shortened by simulating the XPS of simple electronic configurations such as carbon or nitrogen. A laboratory demonstrator was present during the entire session to ensure that assistance was available with a staff to student ratio of 1:12. The session is highly flexible, however, and one may envisage running a 1 h tutorial before the Matlab practical, where only minimal practical supervision is required.

Model simulation data are given by Figure 2 for the cadmium 3d and selenium 3d binding energies. Each of these approximate well to experimentally determined values. As mentioned earlier, the script may be extended to cover additional elements, and the XPS spectra of rhodium and indium are given in the Supporting Information.

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CONCLUSION

Matlab is an invaluable skill within both academia and industry; however, many students, particularly at the undergraduate level, find it difficult to realize its importance and find coding challenging. The work presented here introduces Matlab in a user-friendly way with a hands-on experience of coding. This introductory practical will be useful for introducing more advanced scripts, including looping and conditional statements, in future projects. Moreover, this work helps reinforce typical undergraduate computational material (Slater's rules) and spectroscopy. In particular, it demonstrates well the relationship between atomic structure, the organization of electron subshells, and observables in XPS. Calculated XPS binding energies, for the examples shown, fall within 10% of the experimental values.[19−22] It is easy to envisage using other elements besides cadmium, selenium, rhodium, and indium, opening up multiple coding opportunities. More complex and challenging ideas may also be introduced in the form of angular momentum coupling (Russel−Saunders coupling) and spatial quantization concepts.[23]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.9b00236.

Raw annotated coding for all elements and figures for the elements rhodium and indium (PDF)

Raw coding for simulations (ZIP)

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Notes

The author declares no competing financial interest.

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