Observation of relativistic corrections to Moseley’s law at high atomic number

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Abstract

Transitions between low-lying electron states in atoms of heavy elements lead to electromagnetic radiation with discrete energies between about 0.1 keV and 100 keV (x rays) that are characteristic of the element. Moseley’s law — an empirical relation first described by Mosely in 1914 which supported predictions of the then-new Bohr model of atomic energy levels while simultaneously identifying the integer atomic number $Z$ as the measure of nuclear charge — predicts that the energy of these characteristic x rays scales as $Z^2$. The foundational nature of Moseley’s experiment has led to the popularity of Moseley’s law measurements in undergraduate advanced laboratory physics subjects. We report here observations of deviations from Moseley’s law in the characteristic $K\alpha$ x-ray emission of 13 elements ranging from $Z = 29$ to $Z = 92$. While following the square-law predictions of the Bohr model fairly well at low $Z$, the deviations become larger with increasing $Z$ ($p < 10^{-1000}$ by a $\chi^2$ test). We find that relativistic models of atomic structure are necessary to fit the full range of atomic numbers observed ($p = 0.23$ for the relativistic Bohr model). As has been argued by previous authors, measurements of the relativistic deviations from Moseley’s law are both pedagogically valuable at the advanced laboratory level and accessible with modern but modest apparatus. Here, we show that this pedagogical value can be be extended even further — to higher $Z$ elements, where the effects are more dramatically observable — using apparatus which is enhanced relative to more modest versions, but nevertheless still accessible for many teaching laboratories.
I. INTRODUCTION

Experimental tests of Moseley’s law using x-ray fluorescence spectroscopy appear commonly in advanced undergraduate physics laboratory subjects. Such experiments allow students to explore key supporting evidence for Bohr’s atomic theory while also introducing modern precision spectroscopy techniques.\textsuperscript{5–7} However, experiments testing Moseley’s law have the potential to teach undergraduates much more. Recent work by Soltis \textit{et al.}\textsuperscript{1} shows that with the accuracy of many modern detectors, Moseley’s law becomes inaccurate at high atomic number and requires first order relativistic corrections. By performing a Moseley’s law experiment, students recieve the opportunity to identify limitations in a commonly taught model, providing insight into the nature of experimental physics. In this paper, we build upon the work of Soltis \textit{et al} by measuring elements with even higher atomic number, which deviate further from Moseley’s law. We show that the approximation used by Soltis \textit{et al} remains inaccurate for these heavier elements and find that a more exact relativistic model is required, providing more aspects of the physics and modelling for students to explore.

II. BACKGROUND

In 1913, H. G. J. Moseley experimentally measured the wavelengths of characteristic x rays from a series of elements. Using his data in conjunction with Bohr’s recent theory describing the hydrogen atom, Moseley proposed that the energy of the transition scales quadratically with the atomic number \(Z\).\textsuperscript{5–7} This quadratic relation, called Moseley’s law, formed some of the first observational evidence for a quantum theory of atomic structure.

There are a number of ways to produce x rays in nature. They range from fluorescence to synchrotron radiation to extreme blue-shifting of radio waves. In this experiment, we focus on the first of these. X-ray fluorescence typically occurs when an electron is knocked out of a low-lying shell of a heavy element, leaving a hole in the electronic structure. This could be a consequence of bombardment by alpha rays, beta rays, gamma rays, or some more exotic process. The resulting hole is most often filled with an electron from a nearby higher shell,
emitting a photon in the process.

That electron leaves a new hole, which is then filled in much the same way, resulting in a cascade of electrons that each emit a photon. The brightest line in this spectrum comes from electrons transitioning between energy levels in the $n = 2$ and $n = 1$ shells, where $n$ is the usual principal quantum number. These highest energy x rays are denoted $K\alpha$ in Siegbahn notation. Bohr’s model predicts that electrons in shell $n$ have velocity $Z\alpha c/n$, where $Z$ is the atomic number, $\alpha$ is the fine structure constant (approximately $1/137$) and $c$ is the speed of light. This implies that the $K\alpha$ transition has energy $\frac{3}{8}m_ec^2\alpha^2c^2$. However, it also means that for a reasonably heavy element like gold ($Z = 79$), the innermost electrons are moving at more than half the speed of light. Therefore, it is possible that relativistic corrections may come into play. By using a relativistic Bohr-Sommerfeld approximation, we will find model fits to our data that improve upon the perturbation methods used by Soltis et al. This can help students understand the intricacies behind combining quantum mechanical theories with relativistic theories.

III. RELATIVISTIC BOHR-SOMMERFELD APPROXIMATION

To better understand these relativistic corrections, we utilize the Bohr-Sommerfeld approximation. The Bohr-Sommerfeld quantization condition is a semiclassical rule that says in any closed orbit in a quantum system $\int_{\text{orbit}} p\,dx = 2\pi \hbar n$ for an integer $n$, where $p$ is the system momentum, $x$ the coordinate, and $\hbar = h/2\pi$ is the reduced Planck’s constant. If momentum can be thought of as the derivative of a quantum wavefunction’s phase, then this condition says that closed orbits are standing waves where the phase is the same at the beginning and end, as shown in Fig. 1. For circular orbits, the condition requires that angular momentum be $L = n\hbar$. This approximation can be combined with classical mechanics to derive Bohr’s atomic theory.

In the relativistic case, we still have $L = n\hbar$. However, $L$ is now $m_ecv/\sqrt{1 - v^2/c^2}$ instead of $m_ecv$, where $m_e$ is the mass of the electron, $v$ is the velocity, and $r$ is the radius of the orbit. The result\textsuperscript{2} is

$$E_n = m_ec^2\sqrt{1 - \left(\frac{\alpha(Z - 1)}{n}\right)^2},$$

where $E_n$ is the total energy of the system’s $n^{\text{th}}$ energy eigenstate, including the electron
mass-energy. The x-ray energy is then $E_{K_{\alpha}} = E_2 - E_1$. Bohr-Sommerfeld calculations are not exact — they are approximations to more accurate wave mechanics calculations. Remarkably, however, they do match the result of the exact wave mechanical calculation in the case of circular orbits. In the non-relativistic case, the correct equation to use would be the Schrodinger’s equation. In the relativistic case, the correct one would be Dirac’s equation. However, in both cases, the Bohr-Sommerfeld approximations are much easier to approach.

IV. APPARATUS AND PROCEDURE

To test Moseley’s law, we measure the energy of $K_{\alpha}$ radiation for a variety of elements. To do this, we expose selected elements to radiation from high-energy sources, inducing the emission of characteristic x rays. We then expose a high resolution energy detector to these x rays, generating a counting signal that is recorded by a multichannel analyzer (MCA). Once the MCA is calibrated, we can use its output to determine the energy of the x rays which hit the detector.
FIG. 2: Block diagram of the apparatus and signal chain. The detector, which is cooled with liquid nitrogen, contains a doped germanium crystal that generates pulses of electrical charge proportional to the energy deposited by each incident x ray. The charge pulses are integrated to a voltage, amplified, and categorized by amplitude by a multichannel analyzer.

A. Detector and calibration

The detector is a Canberra model BE2020 high-purity broad energy solid state x-ray detector system. The detector itself is a crystal of p-n doped germanium, biased at –1300 volts, and cooled with liquid nitrogen at 77 K to reduce noise. At the energy range we are studying, x-ray photons will excite electrons in the germanium through photoelectric absorption. These electrons, along with a few electrons excited through thermal noise, will enter the conduction band of the germanium crystal, producing a current signal in the detector. Since the number of excited electrons is proportional to the energy of the incident x ray, the magnitude of the integrated current signal is also proportional to the
energy of the x ray.

As shown in Fig. 2, the current signal from the germanium detector passes through a charge-integrating pre-amplifier and voltage amplifier to convert it to a voltage signal in the range 0–10 V, which can then be recorded by an MCA. The MCA sorts the signal into one of 2048 channels based on the voltage amplitude of the signal. We can then calibrate the MCA and obtain a relation between the MCA channel and the energy of the x ray which generated the recorded signal. We calibrate the MCA using a $^{57}$Co source (approximately 10 $\mu$Ci; see Fig. 3). We choose this isotope because it has radiation peaks in the tens of keV, the same range as the x-ray energies measured. We collect data on the $^{57}$Co spectra until we see clean peaks and calibrate the MCA channels to those peaks. The exact energy per channel depended on setting which we couldn’t keep constant, but was typically about .0556 keV per channel.

![Image](image.png)

**FIG. 3:** The multichannel analyzer is calibrated using $^{57}$Co, an isotope with known energies. This is a histogram of x-ray counts versus MCA channel number after five minutes of sampling.

**B. X ray sources and targets**

We use two high energy sources, $^{241}$Am and $^{133}$Ba isotopes, to generate x rays from pure samples of various elements. The $^{241}$Am isotope is part of a 10 mCi $^{241}$Am Amersham variable x-ray source, which emits alpha particles with energies near 5.4 MeV as it decays to $^{237}$Np. The alpha particles bombard one of six metals in a rotatable wheel on the apparatus.
and cause the metals to emit x rays (see Fig. 4b). The experimenter can rotate the wheel to select different metals, generating x rays from Cu, Rb, Mo, Ag, Ba, and Tb. (see Fig. 4a).

FIG. 4: The $^{241}$Am variable x ray source contains six different metals on a rotating wheel, each of which has its own characteristic x-ray spectrum. Emission from the source, mostly in the form of alpha particles, bombards the metals and causes them to emit x rays, which are detected by the germanium detector.

In addition to these six metals, we bombard prepared metal targets of high-purity with x rays from a 7 $\mu$Ci $^{133}$Ba check source that emits x rays at around 80 keV. We used this technique to measure Ta, W, Pt, Au, and Pb — all of which have x-ray lines below 80 keV. In this setup, the gold and platinum targets were foils held together by kapton tape. (Later, we bombard a pure ball of kapton tape with radiation from the $^{133}$Ba source, in order to ensure that the tape does not affect the peaks).

The final sample is uranium. The uranium sample comes not from a pure sample as above, but rather from a red-orange glazed Fiesta brand ceramic dinnerware plate. The bright red-orange glaze (branded “Fiesta red”) on these ceramics produced in the years 1936–1943 contains natural uranium oxide, while those produced in the years 1959–1972 contain the oxide of isotopically depleted uranium. Whether the present sample is of depleted or natural uranium has not been determined. Regardless, the sample’s own radioactivity is enough to induce x-ray fluorescence. We leave it in the detector for three days in order to determine the peak to within one channel. This is an important data point because of its high atomic number ($Z=92$), which gives a larger deviation from non-relativistic theories.
It is worth noting that there are several sources of error in the case of the uranium, which will be discussed in the next section.

Note the wide range of atomic numbers and the substantial gap between the second heaviest element, Pb, and the heaviest element, U. The relativistic model predicts that the innermost electrons in copper are moving with velocity $0.21c$ ($\gamma = 1.02$), while the innermost electrons in uranium are moving with velocity $0.67c$ ($\gamma = 1.35$), well into the relativistic regime.

Notably, all of these data points are metals. It would be interesting to include some heavy elements which are not metals — for example, an iodine tablet. This would let us detect if different categories of elements had different x-ray behavior.

V. DATA AND ANALYSIS

Once the system is calibrated, we use it to measure x rays produced by the methods described above. Table I shows the data collected for each element. Each point has a statistical error of about 0.06 keV due to the resolution of the peaks on the MCA.

![Image](a) ![Image](b)

FIG. 5: (a) The many peaks shown on the MCA from the Fiesta ceramic uranium-containing plate, and (b) a close up of the peak used to determine the uranium $K_\alpha$ energy.

In addition to statistical errors mentioned above, the uranium plate introduces several sources of possible error. First, the plate contained an oxide rather than elemental uranium. Since the experiment is mostly concerned with inner shell phenomena, we need to know if
TABLE I: Measured $K_\alpha$ x-ray energies for each element tested.

| Atomic number | Element | Peak (keV) |
|---------------|---------|------------|
| 29            | Cu      | 8.1        |
| 37            | Rb      | 13.45      |
| 42            | Mo      | 17.46      |
| 47            | Ag      | 22.14      |
| 56            | Ba      | 32.2       |
| 65            | Tb      | 44.4       |
| 73            | Ta      | 57.5       |
| 74            | W       | 59.3       |
| 78            | Pt      | 66.7       |
| 79            | Au      | 68.6       |
| 82            | Pb      | 74.9       |
| 92            | U       | 98.26      |

the valence-shell bonding would matter. Since the valence electrons are several times further away then the nucleus and have far less effective charge, we estimate that they cannot induce an error of more than one percent.

Another error may be introduced by the spectrum’s many peaks as seen in Fig. 5a. The plate contains uranium, a host of decay products, and many other fluorescing materials. It is possible that there was another peak overlapping with the uranium one. However, the peak, shown in Fig. 5b, is narrow, with a full width at half maximum of about 2.3 eV, and a global maximum between channels 867 and 868. Using Poisson statistics, the counts for these channels are higher than the counts for channels 866 and 869 with p-values of $1.3 \times 10^{-12}$ and $2.4 \times 10^{-4}$ respectively. Because of this, we believe the error introduced is at most one channel.

Fig. 6a shows a linear fit between the atomic number and the square root of the energy, testing Moseley’s original law and the Bohr model. Our fit suggests an electron mass of $593 \pm 10_{\text{stat}} \pm 6_{\text{sys}}$ keV, which is seven sigma away from values found in other experiments. The line appears to be a good fit, but the $\chi^2$ value is over 8000 with just 11 degrees of
freedom, naively corresponding to a p-value of less than $10^{-1500}$. This suggests a bad fit and providing a valuable learning opportunity.

To verify that the theory behind Moseley’s law is inaccurate, we plot the residuals to this linear fit in Fig. 6b. The clear pattern in the residual combined with a $\chi^2$ of over 8000 and an electron mass over $7\sigma$ off supports our believe that a new theory is required.

We next test the model described by Soltis et al. This paper used the formula $E_{K\alpha} = \hbar c R_\infty \left(\frac{3}{4}(Z - 1)^2 + \frac{15}{64} \alpha^2 (Z - 1)^4\right)$. We again see a strong trend in the residuals, shown in Fig. 7 and find a high $\chi^2$ value: 885 with 11 degrees of freedom, corresponding to a p-value of about $10^{-180}$. While this is clearly an improved fit over Moseley’s law, the large $\chi^2$ value provides us motivation to search for a still better theory.

We finally use the fit presented in Eq. 1 to find $m_e c^2$ and test our claim that the Bohr-Sommerfeld approximation provides a more accurate theory. The residuals from this fit are shown in Fig. 8. Fig. 8 indicates no significant trend. This fit has a $\chi^2$ value of 13.4 and 11 degrees of freedom, consistent with random noise, indicating that the fully relativistic theory is the most accurate of the theories tested. The p-value of the relativistic hypothesis is .25 so it is not rejected. In addition, we find that $m_e c^2 = 502 \pm 6$ keV, only 1.5 standard deviation from the well-known value of 511 keV found in other experiments.

FIG. 6: Linear fit suggested by Moseley’s law (a) with residuals of data to that fit (b).
VI. CONCLUSIONS

This paper examines a correction to Moseley’s law that accounts for relativistic effects. It shows that the corrected version better explains measured data than both the non-relativistic version and alternative theories tested in the past. The non-relativistic version of the law gives an electron mass inconsistent with the other experiments while the relativistic version agrees within 1.5 standard deviations.

This experiment is a valuable teaching opportunity, as it requires experimenters to look at residual plots to clearly reveal incorrect theories. In addition, the theory presented here is fundamentally both relativistic and quantum. That means that this paper not only demonstrates that a well known model, Moseley’s law, is inaccurate, but it also tests both
relativity and quantum mechanics at the same time. The combined theory is accurate to the limit of the experimental apparatus and allows students to explore the process of discovering new explanations as data becomes more accurate.

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1 T. Soltis, L. M. Folan, and W. Eltareb, American Journal of Physics 85, 352 (2017).
2 D. Kraft, American Journal of Physics 42, 837 (1974).
3 Germanium Detectors, User’s Manual, Canberra Industries, Inc. (2003).
4 X-Ray Fluorescence (XRF): Understanding Characteristic X-Rays, AMP-TEK.
5 H. Moseley, Philosophical Magazine Series 6, 1024 (1914).
6 H. Moseley, Philosophical Magazine Series 6, 703 (1914).
7 N. Bohr, Philosophical Magazine, (1913).
8 X-ray Physics Lab Manual, MIT Department of Physics (2014).
9 V. Chechev and N. Kuzmenko, “Table de radionuclides, 133ba,” (2016).
10 The Hall China Company, “Color history,” https://fiestafactorydirect.com/pages/color-history, [Retrieved 2018-09-04].
11 The Homer Laughlin China Co, “Radiation in ceramic glazes, 2011-03-16,” https://web.archive.org/web/20120401000958/http://www.hlchina.com/gmastatement.html Archived 2014-04-16 at the Wayback Machine, [Retrieved 2018-09-40].