Henry Moseley X-Ray Activity

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 By measuring the Ka and La x-ray lines characteristic of 38 elements in 1913-1914, Henry Moseley was able to make a powerful argument that the atomic number of an element in the periodic table was equal to the number of positive electric charges in the atomic nucleus of the element. This is something we now take for granted. Before Moseley’s work, the atomic number was seen by many as an ordering number from light to heavy atoms with no obvious significance. When Mendeleev first constructed the periodic table of elements in 1869 (with a revision in 1871), he ordered the elements from lowest to highest atomic mass with several gaps and occasional swaps, *e. g*. cobalt and nickel, to make sure that elements in columns had similar chemical properties.

 Antonius van der Broek suggested, based on Geiger and Marsden’s data of Rutherford scattering of a-particles by metal foils, that the atomic number of an element, rather than atomic mass, is an indicator of the element’s positive nuclear charge ((*Nature*, **92** (1913), 372 f.). Moseley set out to examine this suggestion. His evidence from measurements of the characteristic K and L x-ray wavelengths of 38 elements convinced scientists of the truth of this idea.

Use the data in the Excel spreadsheet “Henry Moseley Data-stu.xlsx” for the calculations below.

**Part A**

1. For the 10 elements in **Part A**, calculate wavelengths *l*2 and *l*3 of the second and third order Ka Bragg spectra from Moseley’s angle measurements. See “Henry Moseley Data-tch.xlsx”.

2. State conclusions you draw from a comparison of the of the two wavelength values.
(Moseley used the *l*3 value in his calculations because it was the brighter of the two orders of the Ka line, scattered at a greater angle, and had less measurement uncertainty.)

The wavelength values *l*2 and *l*3 are almost the same. This indicates that the identification of the lines as different orders of the same spectral line is justified.

3. Calculate wavelength uncertainties that result from Moseley’s 0.1° angle uncertainty.

See the calculations in the spreadsheet “Henry Moseley Data-unc.xlsx”.

4. a. As a check on Moseley’s measurement, calculate the energy of the x-ray photons corresponding to the *l*3 wavelength values.

See “Henry Moseley Data-tch.xlsx”.

b. Look up, and enter in the spreadsheet, the modern measured value of the Ka photon energies from the Lawrence Berkeley Lab X-ray Data Booklet <https://xdb.lbl.gov>.
[Click the element symbol in the Periodic Table icon on the website opening page.]

See “Henry Moseley Data-tch.xlsx”.

c. What is the largest fractional difference (LBL – Moseley)/LBL?

See “Henry Moseley Data-tch.xlsx”. The largest fractional difference is 0.65 %.

5. Shortly before Moseley’s work, in 1913 Niels Bohr developed a semi-classical theory for the wavelengths of radiation emitted by single electron atoms. Wavelengths (*l*) emitted in transitions between energy state *n*2 and energy state *n*1 for a single electron with negligible mass (*m*e) orbiting an atom with nuclear mass *M* are given by $\frac{1}{λ}=RZ^{2}\left(\frac{1}{n\_{1}^{2}}-\frac{1}{n\_{2}^{2}}\right)$ , where
*R* = Rydberg constant, *Z* =number of positive nuclear charges. The Rydberg constant is
 $R=\frac{q\_{e}^{4}m\_{e}}{8ϵ\_{0}^{2}h^{3}c}=0.010973732 nm^{-1}$,where
 *q*e = elementary charge = 1.602176634 x 10-19 C, *m*e = 9.1093837015 x 10-31 kg,
 *e*0 = 8.854187817 x 10-12 F m-1, *h* = 6.62607015 x 10-34 J s, *c* = 299792458 m s-1.

a. Show that the units of the Rydberg constant are [length]-1.

UNITS for R: [C]4[kg][F m-1]-2[J s]-3[m/s]-1 = C4 kg (C/V)-2 m2 J-3 s-3 m-1 s
 = C2 kg V-2 m J-3 s-2 = C2 kg (J/C)2 m J-3 s-2 = kg J-1 m s-2
 = kg (kg m2/s2)-1 m s-2 = m-1 QED

b. Calculate the Rydberg constant from the fundamental constants given above to verify the value quoted.

 The calculation gives the expected value.

6. Make an argument that Moseley’s Q values for the Ka lines should be a good proxy for (Z *-* 1).

Comparison of Moseley’s Q value for the Ka line with the atomic number (*Z*) for an element indicates that Q is very nearly (Z-1). We now know that the innermost electron shell (n=1) of elements (except hydrogen with only one electron) contains two spherically symmetric electron distributions. The Ka line results when one of those electrons is ejected and an electron from the n=2 shell drops into that vacant place. That electron experiences an effective central charge of about (Z-1) during the transition due to the shielding of the nucleus by the remaining n=1 electron.

7. a. For a finite mass electron (*m*) orbiting a nuclear mass (*M*), the so-called reduced mass of the electron $μ=\frac{1}{\frac{1}{m}+\frac{1}{M}}=m\left(\frac{1}{1+\frac{m}{M}}\right)$ should be used in Bohr’s theory. Calculate $\left(\frac{1}{1+\frac{m}{M}}\right)$ for calcium to show that this correction is negligible for Moseley’s data.

 $\left(\frac{1}{1+\frac{m\_{e}}{M\_{Ca}}}\right)=\frac{1}{1+\frac{1}{(40.09)(1822)}}=0.99999$

 This is within the uncertainty of Moseley’s data.

b. EXTRA
 Show (on a separate page) why the reduced mass should be used in Bohr’s theory.

 See derivation attached at the end of part B.

**Part B**

If you have time to work with Moseley’s data in **Part B** of the spreadsheet, continue with the following.

8. a. What trend do you see for (*Z* - *Q*) for the Ka lines of the heavier elements?

For the Ka line, (Z-Q goes from slightly more that 1 to slightly less than 1 as Z increases.

 b. Make an argument that the trend is expected.

As Z increases, the probability distribution for the location of the innermost electron is drawn more and more toward the center of the nucleus. So, it shields less and less of the nuclear charge. (This seems plausible to me, but it should be checked with someone with more quantum mechanical insight. – RGD)

9. Make an argument that Moseley’s *Q* value for the La line should be a good proxy for approximately (*Z* – 7).

For the La line, an electron from the n=3 level drops to the n = 2 level. The two n = 1 electrons are most likely near the center of the nucleus and not contributing much to shielding the nuclear charge for the heavy elements for which the La line is measured. One of the eight n=2 level electrons has been ejected. So, the n = 3 electron is shielded by approximately 7 electrons from the nuclear charge. Why does (Z-Q) increase toward 8 with increasing Z? (This seems plausible to me, but it should be checked with someone with more quantum mechanical insight. – RGD)

10. **BONUS**
 Which element did Moseley name incorrectly among his list for La line measurements?

Moseley mislabeled dysprosium (Z = 66) as holmium (Z = 67) in his table.

EXTRA – Derivation of Reduced Mass of the Electron in Bohr’s Theory

Bohr’s theory of single electron atoms is a semi-classical theory with a quantum restriction on angular momentum values for the atom.

First, consider an electron with charge (*e*) and negligible mass (*m*) in a stable circular orbit at radius (*r*e) about an atom nucleus with charge (*Ze*) and mass (*M*>>*m*). Choose a reference frame in which the nucleus is at rest. Assume the electron is kept in its orbit by the electric force between the electron and nucleus. Also, assume the electron does not radiate any energy while it remains in that stable orbit. In his approximation, the center of mass of the system is at the center of the nucleus (assumed to be spherically symmetric), and the nucleus is stationary. Then the centripetal force on the electron is equal to the electric force between the electron and nucleus, or
 $m\frac{v^{2}}{r\_{e}}=\frac{k\_{C}Ze^{2}}{r\_{e}^{2}} ⇒ v^{2}=\frac{k\_{C}Ze^{2}}{mr\_{e}}$ (1)

The energy of the electron-nucleus system is $E=KE+PE=\frac{1}{2}mv^{2}-\frac{k\_{C}Ze^{2}}{r\_{e}}$ ,
where the potential energy is zero at infinite separation between electron and nucleus.

Substituting in the expression for *v*2 from equation (1), we obtain
 $E=-\frac{k\_{C}Ze^{2}}{2r\_{e}}$ (2)

Bohr’s restriction on angular momentum values for the system is
 $mvr\_{e}=nℏ$ , where *n* is an integer and $ℏ=\frac{h}{2π}$ . (3)

From equation (3), $v=\frac{nℏ}{mr\_{e}} and v^{2}=\frac{n^{2}ℏ^{2}}{m^{2}r\_{e}^{2}}$ . (4)

Bohr assumed that an atom with energy *E*j emits a photon with energy *hn*=*hc*/*l* when it transitions to an orbit with smaller radius and lower energy *E*i or symbolically
 $hν=\frac{hc}{λ}=E\_{j}-E\_{i}=-\frac{k\_{C}Ze^{2}}{2r\_{j}}+\frac{k\_{C}Ze^{2}}{2r\_{i}}=\frac{k\_{C}Ze^{2}}{2}\left[\frac{1}{r\_{i}}-\frac{1}{r\_{j}}\right]$ . (5)

Equating the two expressions for *v*2 in (1) and (4) yields an expression for 1/*r*e :
 $\frac{1}{r\_{e}}=\frac{k\_{C}Ze^{2}m}{ℏ^{2}}\left[\frac{1}{n^{2}}\right]$ . (6)

Substituting (6) into (5), we obtain and expression of 1/*l* :

 $\frac{1}{λ}=\frac{k\_{C}^{2}Z^{2}e^{4}m}{2ℏ^{2}hc}\left[\frac{1}{n\_{i}^{2}}-\frac{1}{n\_{j}^{2}}\right]=RZ^{2}\left[\frac{1}{n\_{i}^{2}}-\frac{1}{n\_{j}^{2}}\right]$ , (7)
where $R=\frac{k\_{C}^{2}e^{4}m}{2ℏ^{2}hc}=\frac{e^{4}m}{8ε\_{0}h^{3}c}$ is the Rydberg constant.

(Recall that *k*C = 1/4*pe*0.)

To see the effect of an electron of finite mass and the place of the “reduced mass”
*m* = *m*/(1 +*m*/*M*) in Bohr’s theory, consider an electron with mass (*m*) with charge (*e*) and a nucleus of mass (*M*) with charge (*Ze*) in mutual circular orbits around a common center of mass (CM) located on the line between nucleus and electron. Choose a reference frame in which the CM is at rest. The radius of the electron’s orbit from the CM is designated *r*e. The radius of the nucleus’s orbit from the CM is designated *r*N.

 The CM position is determined by the relation *Mr*N = *mr*e . (8)

 The distance between nucleus and electron is *r* = *r*e + *r*N .

 Consequently, *r* = (1 + *m*/*M*)*r*e . (9)

The orbital period (*T*) of the electron and nucleus are equal. So that:

 $T=\frac{2πr\_{e}}{v\_{e}}=\frac{2πr\_{N}}{v\_{N}}$ , which yields $v\_{N}=\frac{r\_{N}}{r\_{e}}v\_{e}=\frac{m}{M}v\_{e}$ . (10)

As above, we equate the centripetal forces keeping the electron and the nucleus in their circular orbits to the electrical force acting between them:
 $m\frac{v\_{e}^{2}}{r\_{e}}=\frac{k\_{C}Ze^{2}}{r^{2}}$ and $M\frac{v\_{N}^{2}}{r\_{N}}=\frac{k\_{C}Ze^{2}}{r^{2}}$ . (11)

The energy of the electron-nucleus system is now (substituting from equations 11):
 $E=KE+PE=\frac{mv\_{e}^{2}}{2}+\frac{Mv\_{N}^{2}}{2}-\frac{k\_{C}Ze^{2}}{r}=\frac{k\_{C}Ze^{2}r\_{e}}{2r}+\frac{k\_{C}Ze^{2}r\_{N}}{2r}-\frac{k\_{C}Ze^{2}}{r}$

 $E=-\frac{k\_{C}Ze^{2}}{2r}=-\frac{k\_{C}Ze^{2}}{2\left(1+\frac{m}{M}\right)r\_{e}}$ (12)

Bohr’s restriction on angular momentum values for the system is now
 $mv\_{e}r\_{e}+Mv\_{N}r\_{N}=mv\_{e}r\_{e}+M\left(\frac{m}{M}v\_{e}\right)\left(\frac{m}{M}r\_{e}\right)=m\left(1+\frac{m}{M}\right)v\_{e}r\_{e}=nℏ$ , (13)
 where, as before, *n* is an integer.

Again make Bohr ‘s assumption that an atom (energy *E*j) emits a photon (energy *hn*=*hc*/*l*) when its electron transitions to a smaller orbit and lower energy (*E*i):
 $hν=\frac{hc}{λ}=E\_{j}-E\_{i}=-\frac{k\_{C}Ze^{2}}{2\left(1+\frac{m}{M}\right)r\_{j}}+\frac{k\_{C}Ze^{2}}{2\left(1+\frac{m}{M}\right)r\_{i}}=\frac{k\_{C}Ze^{2}}{2\left(1+\frac{m}{M}\right)}\left[\frac{1}{r\_{i}}-\frac{1}{r\_{j}}\right]$ . (14)

Equating expressions for *v*e2 from (11) and (13) yields an expression for 1/*r*e :
 $\frac{1}{r\_{e}}=\frac{k\_{C}Ze^{2}m}{ℏ^{2}}\left[\frac{1}{n^{2}}\right]$ . (15)

Finally, $\frac{1}{λ}=\frac{k\_{C}^{2}Z^{2}e^{4}m}{2\left(1+\frac{m}{M}\right)ℏ^{2}hc}\left[\frac{1}{n\_{i}^{2}}-\frac{1}{n\_{j}^{2}}\right]=\frac{RZ^{2}}{\left(1+\frac{m}{M}\right)}\left[\frac{1}{n\_{i}^{2}}-\frac{1}{n\_{j}^{2}}\right]$ . (16)

Equation 16 is equivalent to equation 7 for an electron with reduced mass *m*.