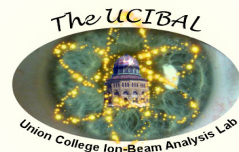


Materials Analysis with fast ions using the 1.1MV tandem electrostatic Pelletron Particle Accelerator at Union College



Introduction to Ion Beam Analysis

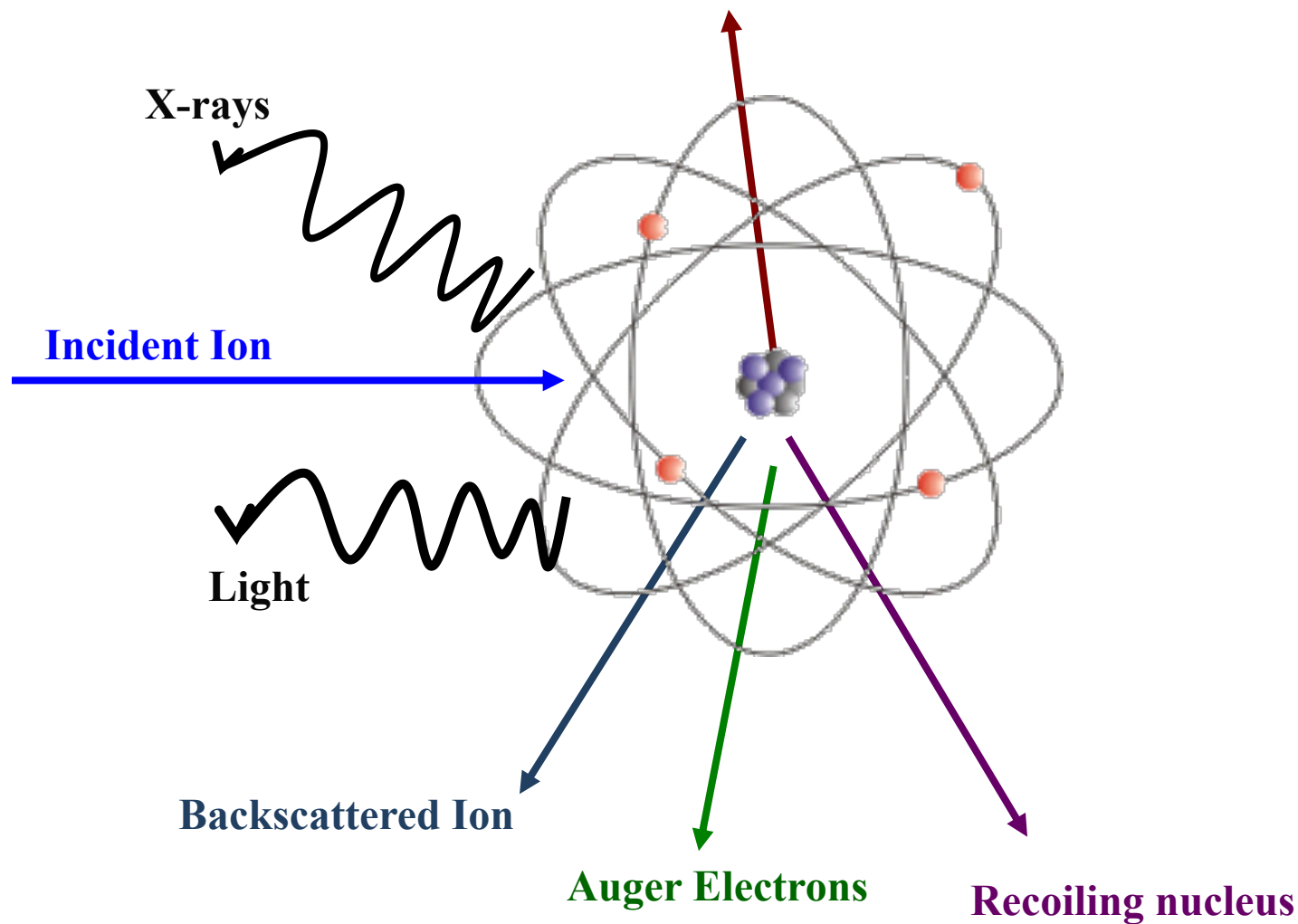
→ Ion –Target Interaction

- Elastic Atomic Collisions
 - Very low energies, typically a few keV
 - Surface composition and structure
 - Ion Scattering spectrometry (ISS)
- Inelastic Atomic Collisions
 - Ionization of target atoms
 - Characteristic x-ray emission
 - Particle Induced X-Ray Emission (*PIXE*)
 - Detection of elements with $Z > 6$
- Elastic Nuclear Collisions
 - Rutherford Backscattering (*RBS*)
 - Mainly for $Z > Z_{ion}$ (usually He^{++})
 - Elastic Recoil Detection Analysis (*ERDA*)
 - Mainly for $Z < Z_{ion}$ (only H in this case)
- Inelastic Nuclear Collisions
 - Nuclear Reactions can occur
 - Nuclear Reaction Analysis (NRA)
 - Gamma ray production (*PIGE*)

In our lab we have the ability to do *PIXE*, *PIGE*, *RBS* & *ERDA*

Introduction: Ion –Target Interaction

Nuclear Reactions producing n , γ -rays, ions

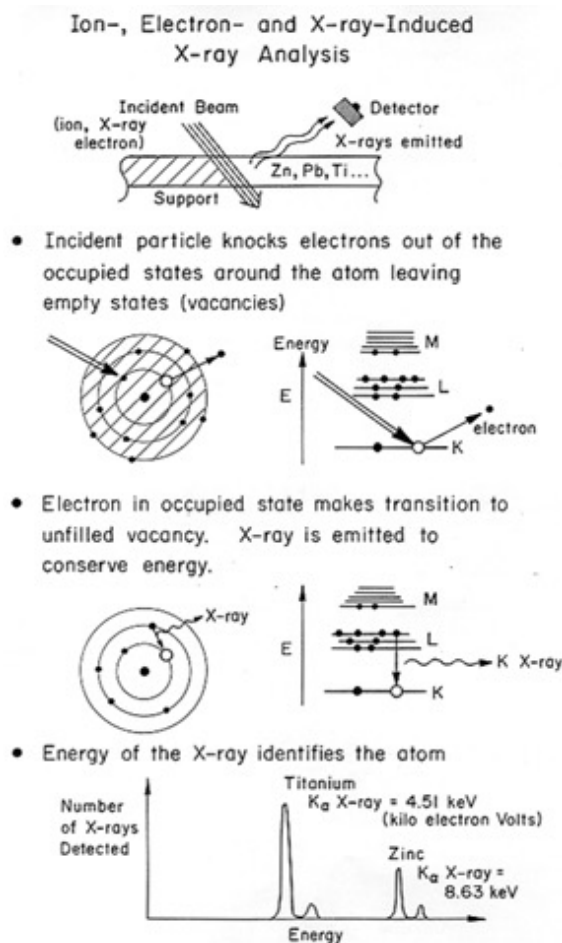


Proton Induced X-ray Emission Spectroscopy

PIXE

- First observation by Chadwick (the discover of the neutron) (Phil. Mag. 24 (1912) 54)
- X-ray emission induced by charged particles from a radioactive source. We're going to produce protons on our accelerator and shoot them at a target to produce x-rays.
- Moseley in 1913: the x-ray energy scales with Z^2
- First application T.B. Johansson et al, Nucl. Instr. Meth. B 84 (1970) 141
- 2024: most widely used technique in materials analysis, atmospheric aerosols, archaeology, paleontology, archaeometry, criminology, biology, geology, environmental sciences.....

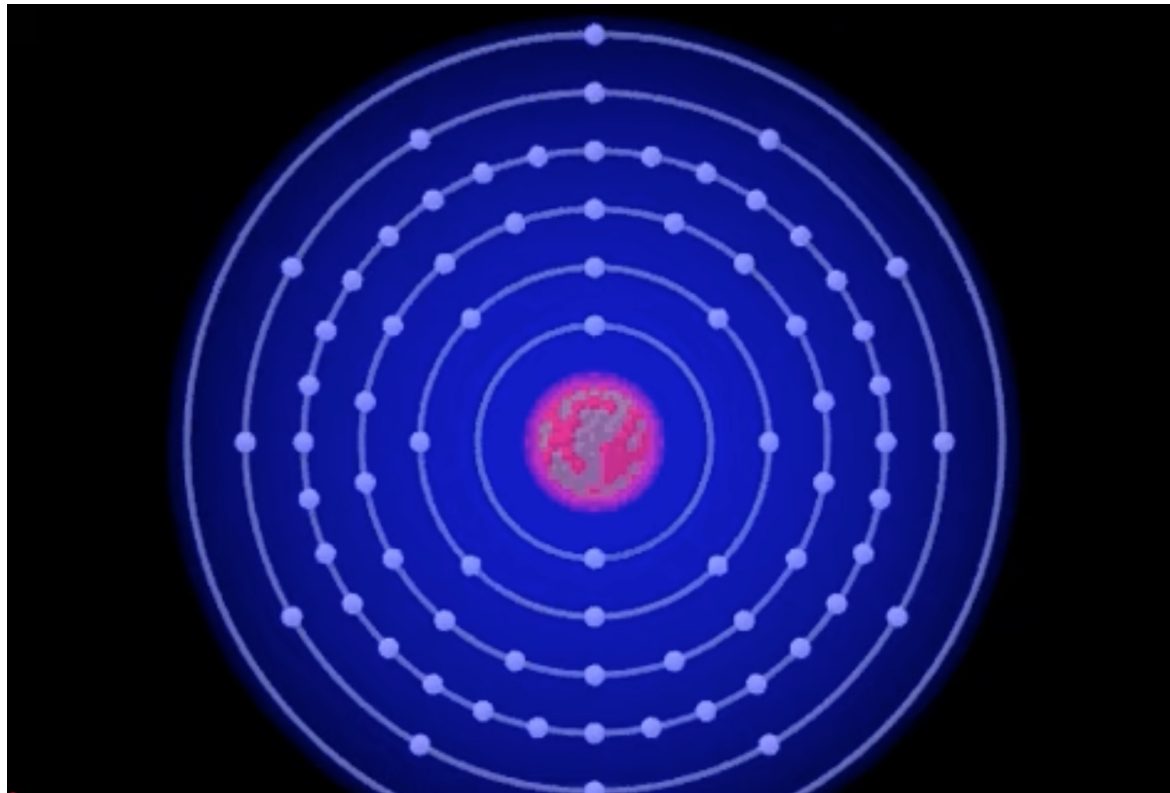
PIXE: The Basics



Jones, C.C., Emeritus Professor of Physics, Union College, Lecture Notes

- Incident proton interacts with electrons in the material ejecting electrons.
- This creates a vacancy in a shell that is usually filled with an electron from a higher orbit.
- For the electron to fill this vacancy it needs to lose energy.
- The energy difference is the difference from where the electron is currently to where it wants to go, and this is typically on the order of several keV and higher.
- When the electron transitions an x-ray photon of that energy difference is emitted and the spectrum of all x-ray photons are plotted and identified.

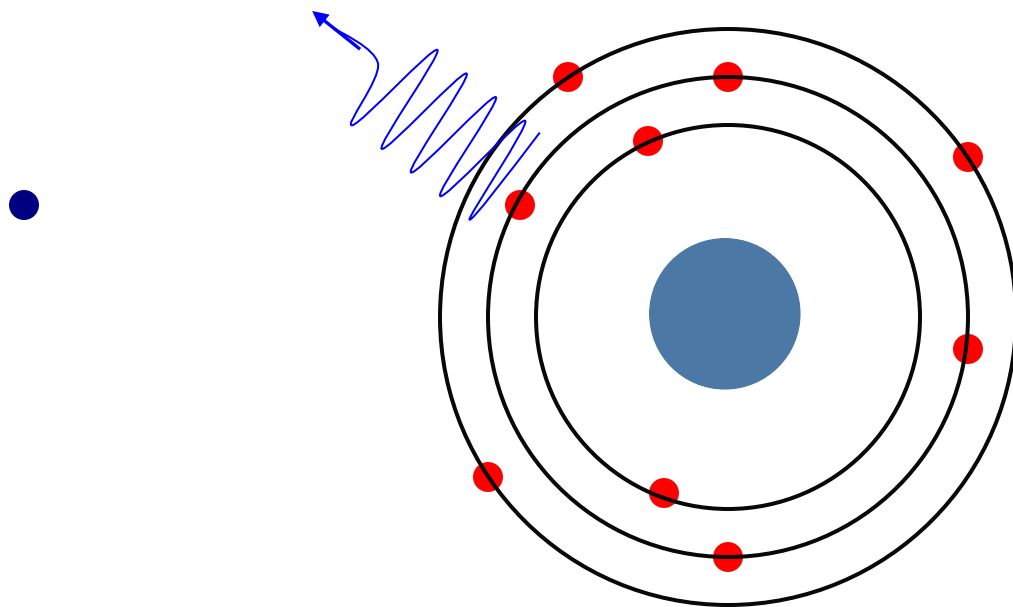
An Illustration of the *PIXE* process



K_{α} transition in an atom

The incident proton ejects an electron from the $n = 1$ orbital and creates a vacancy in the $n = 1$ orbital. An electron from the $n = 2$ orbital de-excites to fill the vacancy created in the $n = 1$ orbital and emitting an x-ray in the process that we can detect.

An Illustration of the *PIXE* process



L_{α} transition in an atom

The incident proton ejects an electron from the $n = 2$ orbital and creates a vacancy in the $n = 2$ orbital. An electron from the $n = 3$ orbital de-excites to fill the vacancy created in the $n = 2$ orbital and emitting an x-ray in the process that we can detect.

PIXE: The Basics

- For an incident proton energy of 1 – 4 MeV, elements with atomic numbers up to about 50 (Sn) are generally determined through their *K shell* X-rays (typically K_{α} line).
- Heavier elements (greater than $Z = 50$) are measured through their *L shell* X rays because the beam energy is not enough to eject the tightly bound *K shell* electrons.
- The concentration of a particular element is deduced from the intensity of the measured x-ray line together with parameters obtained either theoretically and/or experimentally.

PERIODIC TABLE OF ELEMENTS

<div><div>1</div><div>H</div><div>Hydrogen</div><div>1s¹</div></div>																		<div><div>2</div><div>He</div><div>Helium</div><div>1s²</div></div>																																																																																																																																																																																																																																																																																																																	
<div><div>3</div><div>Li</div><div>Lithium</div><div>[He] 2s¹</div></div>																		<div><div>4</div><div>Be</div><div>Beryllium</div><div>[He] 2s²</div></div>																		<div><div>5</div><div>B</div><div>Boron</div><div>[He] 2s² 2p¹</div></div>																		<div><div>6</div><div>C</div><div>Carbon</div><div>[He] 2s² 2p²</div></div>																		<div><div>7</div><div>N</div><div>Nitrogen</div><div>[He] 2s² 2p³</div></div>																		<div><div>8</div><div>O</div><div>Oxygen</div><div>[He] 2s² 2p⁴</div></div>																		<div><div>9</div><div>F</div><div>Fluorine</div><div>[He] 2s² 2p⁵</div></div>																		<div><div>10</div><div>Ne</div><div>Neon</div><div>[He] 2s² 2p⁶</div></div>																																																																																																																																																																																																					
<div><div>11</div><div>Na</div><div>Sodium</div><div>[Ne] 3s¹</div></div>																		<div><div>12</div><div>Mg</div><div>Magnesium</div><div>[Ne] 3s²</div></div>																		<div><div>13</div><div>Al</div><div>Aluminum</div><div>[Ne] 3s² 3p¹</div></div>																		<div><div>14</div><div>Si</div><div>Silicon</div><div>[Ne] 3s² 3p²</div></div>																		<div><div>15</div><div>P</div><div>Phosphorus</div><div>[Ne] 3s² 3p³</div></div>																		<div><div>16</div><div>S</div><div>Sulfur</div><div>[Ne] 3s² 3p⁴</div></div>																		<div><div>17</div><div>Cl</div><div>Chlorine</div><div>[Ne] 3s² 3p⁵</div></div>																		<div><div>18</div><div>Ar</div><div>Argon</div><div>[Ne] 3s² 3p⁶</div></div>																																																																																																																																																																																																					
<div><div>19</div><div>K</div><div>Potassium</div><div>[Ar] 4s¹</div></div>																		<div><div>20</div><div>Ca</div><div>Calcium</div><div>[Ar] 4s²</div></div>																		<div><div>21</div><div>Sc</div><div>Scandium</div><div>[Ar] 3d¹ 4s²</div></div>																		<div><div>22</div><div>Ti</div><div>Titanium</div><div>[Ar] 3d² 4s²</div></div>																		<div><div>23</div><div>V</div><div>Vanadium</div><div>[Ar] 3d³ 4s²</div></div>																		<div><div>24</div><div>Cr</div><div>Chromium</div><div>[Ar] 3d⁵ 4s¹</div></div>																		<div><div>25</div><div>Mn</div><div>Manganese</div><div>[Ar] 3d⁵ 4s²</div></div>																		<div><div>26</div><div>Fe</div><div>Iron</div><div>[Ar] 3d⁶ 4s²</div></div>																		<div><div>27</div><div>Co</div><div>Cobalt</div><div>[Ar] 3d⁷ 4s²</div></div>																		<div><div>28</div><div>Ni</div><div>Nickel</div><div>[Ar] 3d⁸ 4s²</div></div>																		<div><div>29</div><div>Cu</div><div>Copper</div><div>[Ar] 3d¹⁰ 4s¹</div></div>																		<div><div>30</div><div>Zn</div><div>Zinc</div><div>[Ar] 3d¹⁰ 4s²</div></div>																		<div><div>31</div><div>Ga</div><div>Gallium</div><div>[Ar] 3d¹⁰ 4s² 4p¹</div></div>																		<div><div>32</div><div>Ge</div><div>Germanium</div><div>[Ar] 3d¹⁰ 4s² 4p²</div></div>																		<div><div>33</div><div>As</div><div>Arsenic</div><div>[Ar] 3d¹⁰ 4s² 4p³</div></div>																		<div><div>34</div><div>Se</div><div>Selenium</div><div>[Ar] 3d¹⁰ 4s² 4p⁴</div></div>																		<div><div>35</div><div>Br</div><div>Bromine</div><div>[Ar] 3d¹⁰ 4s² 4p⁵</div></div>																		<div><div>36</div><div>Kr</div><div>Krypton</div><div>[Ar] 3d¹⁰ 4s² 4p⁶</div></div>																	
<div><div>37</div><div>Rb</div><div>Rubidium</div><div>[Kr] 5s¹</div></div>																		<div><div>38</div><div>Sr</div><div>Strontium</div><div>[Kr] 5s²</div></div>																		<div><div>39</div><div>Y</div><div>Yttrium</div><div>[Kr] 4d¹ 5s²</div></div>																		<div><div>40</div><div>Zr</div><div>Zirconium</div><div>[Kr] 4d² 5s²</div></div>																		<div><div>41</div><div>Nb</div><div>Niobium</div><div>[Kr] 4d⁴ 5s¹</div></div>																		<div><div>42</div><div>Mo</div><div>Molybdenum</div><div>[Kr] 4d⁵ 5s¹</div></div>																		<div><div>43</div><div>Tc</div><div>Technetium</div><div>[Kr] 4d⁵ 5s²</div></div>																		<div><div>44</div><div>Ru</div><div>Ruthenium</div><div>[Kr] 4d⁷ 5s¹</div></div>																		<div><div>45</div><div>Rh</div><div>Rhodium</div><div>[Kr] 4d⁸ 5s¹</div></div>																		<div><div>46</div><div>Pd</div><div>Palladium</div><div>[Kr] 4d¹⁰</div></div>																		<div><div>47</div><div>Ag</div><div>Silver</div><div>[Kr] 4d¹⁰ 5s¹</div></div>																		<div><div>48</div><div>Cd</div><div>Cadmium</div><div>[Kr] 4d¹⁰ 5s²</div></div>																		<div><div>49</div><div>In</div><div>Indium</div><div>[Kr] 4d¹⁰ 5s² 5p¹</div></div>																		<div><div>50</div><div>Sn</div><div>Tin</div><div>[Kr] 4d¹⁰ 5s² 5p²</div></div>																		<div><div>51</div><div>Sb</div><div>Antimony</div><div>[Kr] 4d¹⁰ 5s² 5p³</div></div>																		<div><div>52</div><div>Te</div><div>Tellurium</div><div>[Kr] 4d¹⁰ 5s² 5p⁴</div></div>																		<div><div>53</div><div>I</div><div>Iodine</div><div>[Kr] 4d¹⁰ 5s² 5p⁵</div></div>																		<div><div>54</div><div>Xe</div><div>Xenon</div><div>[Kr] 4d¹⁰ 5s² 5p⁶</div></div>																	
<div><div>55</div><div>Cs</div><div>Cesium</div><div>[Xe] 6s¹</div></div>																		<div><div>56</div><div>Ba</div><div>Barium</div><div>[Xe] 6s²</div></div>																		<div><div>57</div><div>La</div><div>Lanthanum</div><div>[Xe] 5d¹ 6s²</div></div>																		<div><div>58</div><div>Ce</div><div>Cerium</div><div>[Xe] 4f¹ 5d¹ 6s²</div></div>																		<div><div>59</div><div>Pr</div><div>Praseodymium</div><div>[Xe] 4f³ 6s²</div></div>																		<div><div>60</div><div>Nd</div><div>Neodymium</div><div>[Xe] 4f⁴ 6s²</div></div>																		<div><div>61</div><div>Pm</div><div>Promethium</div><div>[Xe] 4f⁵ 6s²</div></div>																		<div><div>62</div><div>Sm</div><div>Samarium</div><div>[Xe] 4f⁶ 6s²</div></div>																		<div><div>63</div><div>Eu</div><div>Europium</div><div>[Xe] 4f⁷ 6s²</div></div>																		<div><div>64</div><div>Gd</div><div>Gadolinium</div><div>[Xe] 4f⁷ 5d¹ 6s²</div></div>																		<div><div>65</div><div>Tb</div><div>Terbium</div><div>[Xe] 4f⁹ 6s²</div></div>																		<div><div>66</div><div>Dy</div><div>Dysprosium</div><div>[Xe] 4f¹⁰ 6s²</div></div>																		<div><div>67</div><div>Ho</div><div>Holmium</div><div>[Xe] 4f¹¹ 6s²</div></div>																		<div><div>68</div><div>Er</div><div>Erbium</div><div>[Xe] 4f¹² 6s²</div></div>																		<div><div>69</div><div>Tm</div><div>Thulium</div><div>[Xe] 4f¹³ 6s²</div></div>																		<div><div>70</div><div>Yb</div><div>Ytterbium</div><div>[Xe] 4f¹⁴ 6s²</div></div>																		<div><div>71</div><div>Lu</div><div>Lutetium</div><div>[Xe] 4f¹⁴ 5d¹ 6s²</div></div>																																			
<div><div>72</div><div>Hf</div><div>Hafnium</div><div>[Xe] 4f¹⁴ 5d² 6s²</div></div>																		<div><div>73</div><div>Ta</div><div>Tantalum</div><div>[Xe] 4f¹⁴ 5d³ 6s²</div></div>																		<div><div>74</div><div>W</div><div>Tungsten</div><div>[Xe] 4f¹⁴ 5d⁴ 6s²</div></div>																		<div><div>75</div><div>Re</div><div>Rhenium</div><div>[Xe] 4f¹⁴ 5d⁵ 6s²</div></div>																		<div><div>76</div><div>Os</div><div>Osmium</div><div>[Xe] 4f¹⁴ 5d⁶ 6s²</div></div>																		<div><div>77</div><div>Ir</div><div>Iridium</div><div>[Xe] 4f¹⁴ 5d⁷ 6s²</div></div>																		<div><div>78</div><div>Pt</div><div>Platinum</div><div>[Xe] 4f¹⁴ 5d⁹ 6s¹</div></div>																		<div><div>79</div><div>Au</div><div>Gold</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s¹</div></div>																		<div><div>80</div><div>Hg</div><div>Mercury</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s²</div></div>																		<div><div>81</div><div>Tl</div><div>Thallium</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p¹</div></div>																		<div><div>82</div><div>Pb</div><div>Lead</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p²</div></div>																		<div><div>83</div><div>Bi</div><div>Bismuth</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p³</div></div>																		<div><div>84</div><div>Po</div><div>Polonium</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p⁴</div></div>																		<div><div>85</div><div>At</div><div>Astatine</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p⁵</div></div>																		<div><div>86</div><div>Rn</div><div>Radon</div><div>[Xe] 4f¹⁴ 5d¹⁰ 6s² 6p⁶</div></div>																																																																							
<div><div>87</div><div>Fr</div><div>Francium</div><div>[Rn] 7s¹</div></div>																		<div><div>88</div><div>Ra</div><div>Radium</div><div>[Rn] 7s²</div></div>																		<div><div>89</div><div>Ac</div><div>Actinium</div><div>[Rn] 6d¹ 7s²</div></div>																		<div><div>90</div><div>Th</div><div>Thorium</div><div>[Rn] 6d² 7s²</div></div>																		<div><div>91</div><div>Pa</div><div>Protactinium</div><div>[Rn] 5f² 6d¹ 7s²</div></div>																		<div><div>92</div><div>U</div><div>Uranium</div><div>[Rn] 5f³ 6d¹ 7s²</div></div>																		<div><div>93</div><div>Np</div><div>Neptunium</div><div>[Rn] 5f⁴ 6d¹ 7s²</div></div>																		<div><div>94</div><div>Pu</div><div>Plutonium</div><div>[Rn] 5f⁶ 7s²</div></div>																		<div><div>95</div><div>Am</div><div>Americium</div><div>[Rn] 5f⁷ 7s²</div></div>																		<div><div>96</div><div>Cm</div><div>Curium</div><div>[Rn] 5f⁷ 6d¹ 7s²</div></div>																		<div><div>97</div><div>Bk</div><div>Berkelium</div><div>[Rn] 5f⁹ 7s²</div></div>																		<div><div>98</div><div>Cf</div><div>Californium</div><div>[Rn] 5f¹⁰ 7s²</div></div>																		<div><div>99</div><div>Es</div><div>Einsteinium</div><div>[Rn] 5f¹¹ 7s²</div></div>																		<div><div>100</div><div>Fm</div><div>Fermium</div><div>[Rn] 5f¹² 7s²</div></div>																		<div><div>101</div><div>Md</div><div>Mendelevium</div><div>[Rn] 5f¹³ 7s²</div></div>																		<div><div>102</div><div>No</div><div>Nobelium</div><div>[Rn] 5f¹⁴ 7s²</div></div>																		<div><div>103</div><div>Lr</div><div>Lawrencium</div><div>[Rn] 5f¹⁴ 6d¹ 7s²</div></div>																																			

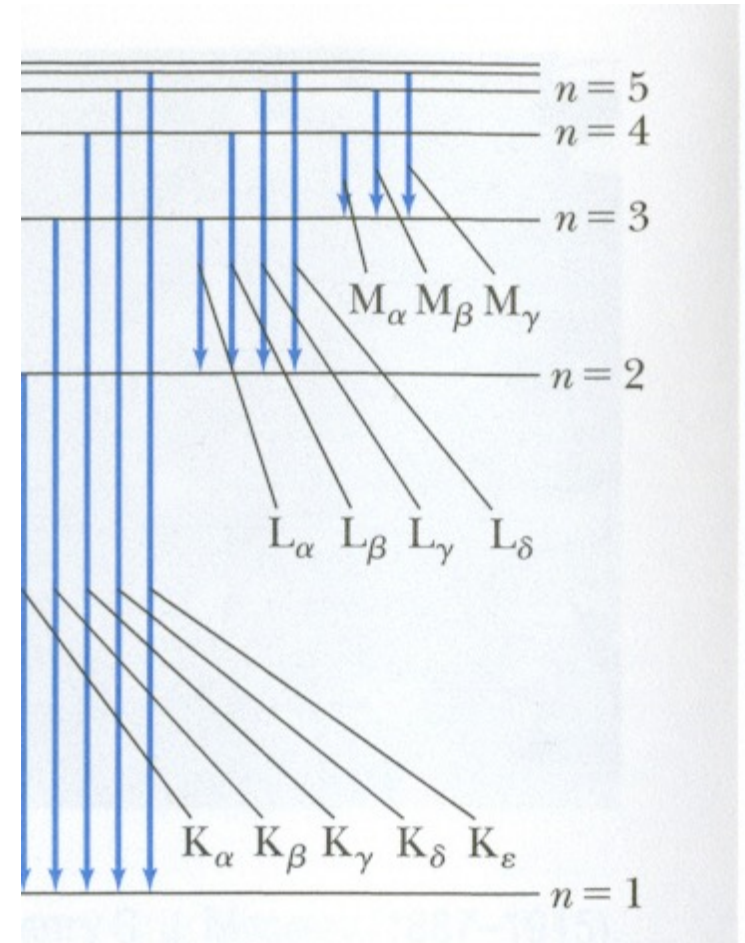


Characteristic X-ray production

- Idea based on the incorrect *Bohr model of the atom*.
- The energy of the photon emitted depends on the energy of the upper state (E_{upper}) and the energy of the lower state (E_{lower}).

$$\Delta E_{photon} = E_{upper} - E_{lower}$$

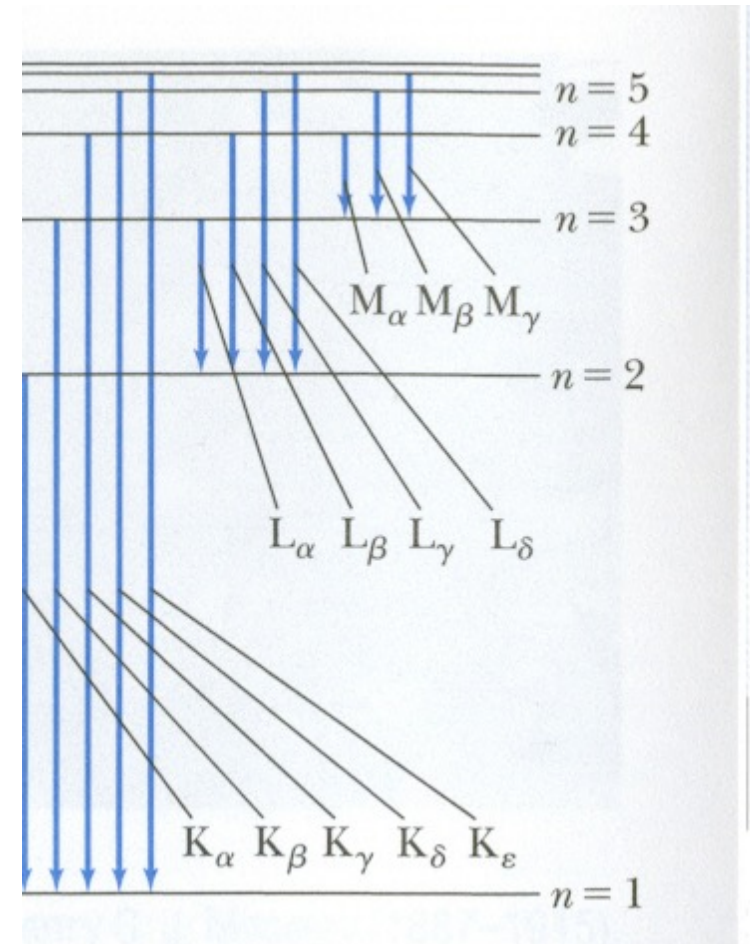
- The n designations correspond to atomic orbitals while the letter designations (K , L , $M...$) correspond to shells in the older spectroscopic notation.
- The actual energies are determined from the Schrodinger equation of quantum mechanics.
- We need to determine a formula for the upper and lower energy states.



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 151(2006).

Characteristic X-ray production

- Further, the letters are used to designate the shell to which the electron is transitioning.
- The Greek letters are used to designate the higher energy transitions and give the value of Δn .
- For example, the α -transition is a lower energy (higher probability) transition than the β -transition (lower probability), which is in turn lower than the γ -transition.
- The K shell transitions are the highest energy transitions possible.



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 151(2006).

Characteristic X-ray production

- Moseley in 1913 empirically determined the relationship between the atomic number and the frequency of the x-ray emitted (or the energy of the x-ray emitted as is how we will use it). Plots like those on the right are called Moseley Plots.

- This is the most fundamental idea behind PIXE.

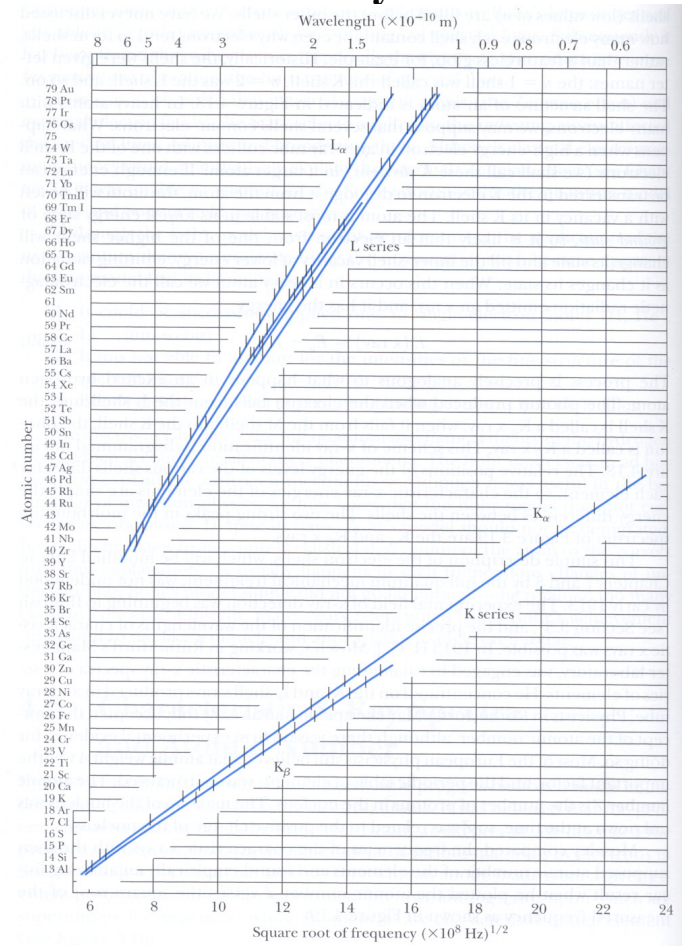
- It shows that for each atomic number (element) there are a characteristic set of x-ray wavelengths and energies emitted.

- Moseley found the relationship to be of the form:

$$Z = a\sqrt{f} + b$$

where a and b are constants from the fitting of a line to the data.

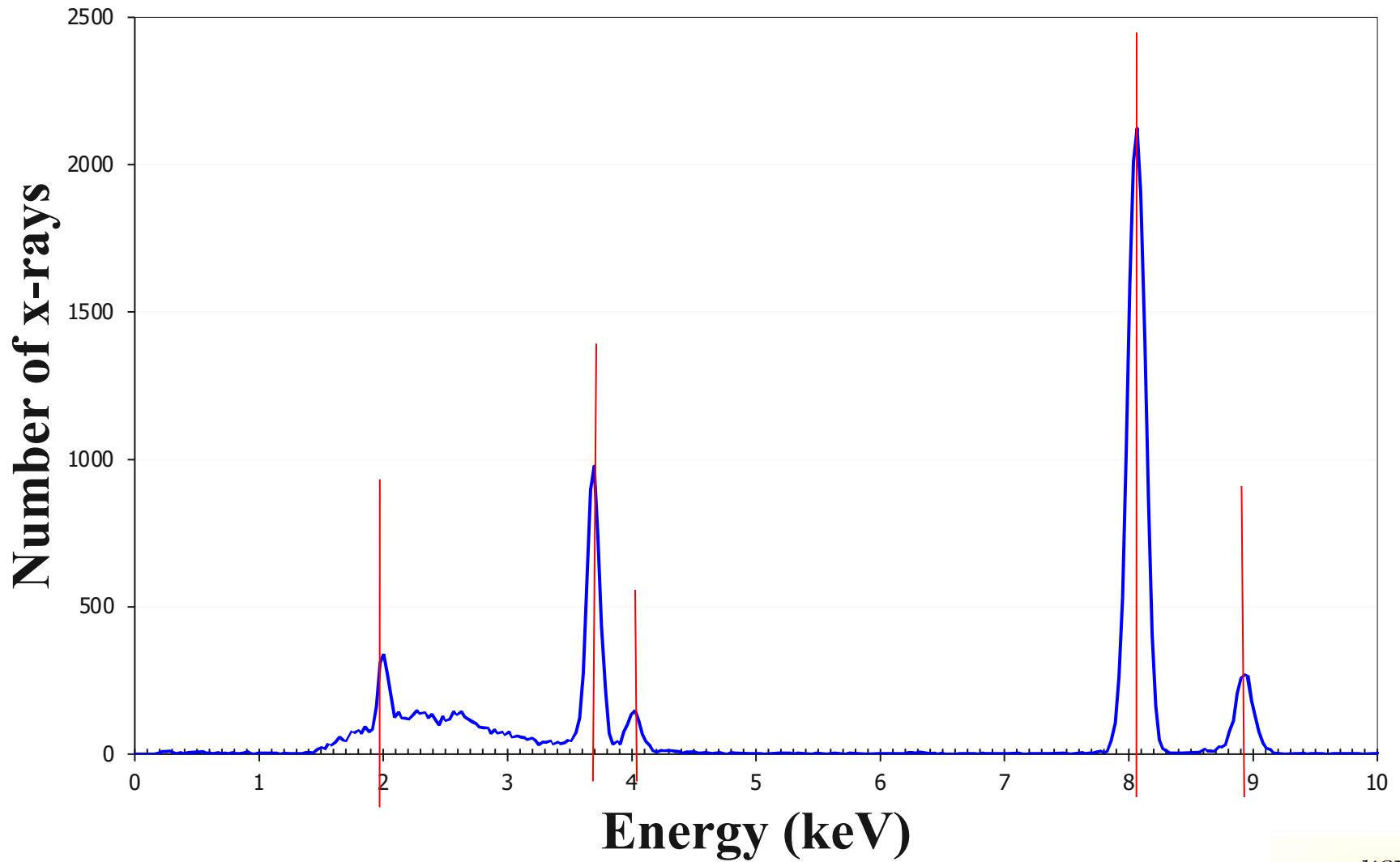
Moseley Plots



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 152(2006).



A typical *PIXE* Spectrum



Characteristic X-ray production

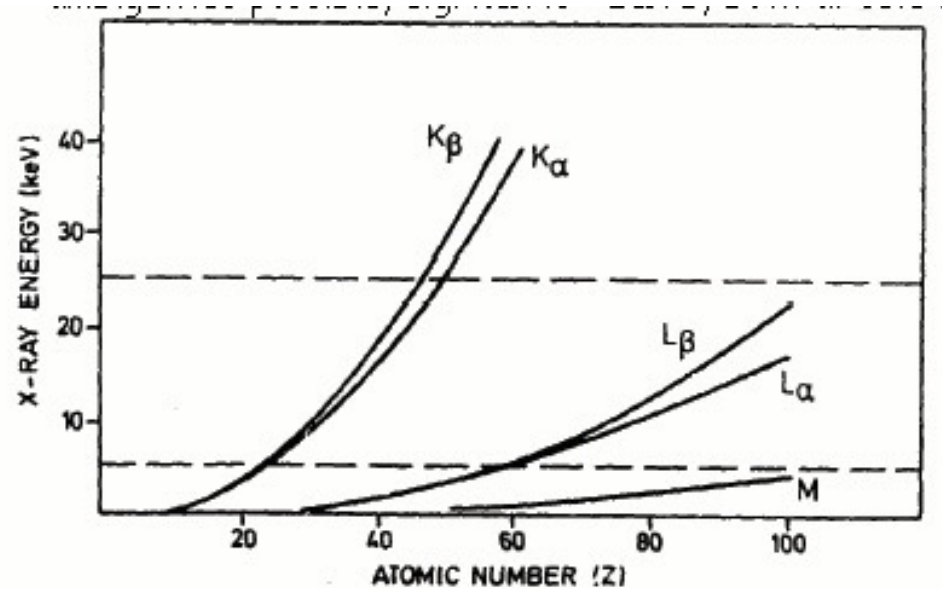
- When a vacancy is created in the K shell ($n = 1$ orbital), an electron in the L shell ($n = 2$ orbital) feels an effective charge of $(Z-1)e^-$. This is due to the Ze^- charge of the nucleus and the e^- remaining in the K shell. Thus, the net force on an L shell electron is towards the K shell and a de-excitation occurs.

- The transition energies are given by the Einstein relation

$$\Delta E_{\text{photon}} = E_{x\text{-ray}} = hf \approx -13.57\text{eV} \left(\frac{1}{n_{\text{lower}}^2} - \frac{1}{n_{\text{upper}}^2} \right) Z^2$$

- The x-ray energies go as $(Z - 1)^2$ which produces the parabolic energy curves.
- Notice that if we rearrange the above equation and take a square root, we get the form that Moseley obtained, namely:

$$Z = a\sqrt{f} + b$$



Jones, C.C., Emeritus Professor of Physics, Union College, Lecture Notes

Comments: Derivation of the Bohr Theory

- Energies and wavelengths are based on the Bohr Theory of the atom for an electron orbiting around a nucleus of charge Ze .

$$F_{\text{centripetal}} = F_{\text{electrostatic}} \rightarrow \frac{m_e v_e^2}{r_e} = \frac{Ze^2}{4\pi\epsilon_0 r_e^2} \rightarrow v_e^2 = \frac{Ze^2}{4\pi\epsilon_0 m_e r_e}$$

- Using the fact that the angular momentum of the electron $L = mv_e r_e$, we can write the above as

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 L}$$

- The angular momentum can also be represented as an integer multiple of Planck's constant, or the angular momentum is quantized.

$$L = n\hbar = n \frac{h}{2\pi}$$

- This is a completely non-classical or quantum mechanical result.

- Therefore, the velocities are quantized, meaning they only have certain allowed values.

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar}$$

- Now, returning to angular momentum, we can express the orbital radius in terms of this velocity that we just found.

$$L = n\hbar = mv_n r_n \rightarrow r_n = \frac{n\hbar}{mv_n} = \frac{4\pi\epsilon_0 n^2 \hbar^2}{mZe^2}$$

- The orbital radius is thus also quantized.
- If we have, for example, hydrogen with $Z = 1$, the radius of the 1st orbital, known as the *Bohr radius*, is given as

$$r_1 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

- Substituting the values of the constants gives the value of the Bohr radius

$$r_1 = \frac{4\pi \left(8.85 \times 10^{-12} \frac{C^2}{Nm^2} \right) \left(\frac{6.63 \times 10^{-34} Js}{2\pi} \right)^2}{9.11 \times 10^{-31} kg \times (1.6 \times 10^{-19} C)^2} = 5.31 \times 10^{-11} m$$

- One more thing about orbital radii...

$$r_n = \frac{4\pi\epsilon_0 n^2 \hbar^2}{mZe^2} = n^2 r_1$$

- The radius of the n^{th} orbital can be expressed as an integer multiple of the Bohr radius.
- Now, this is nice and all, but we really want to be able to calculate the energy of individual orbits and then talk about differences in energy levels.
- This will allow us to talk about the x-rays emitted when an electron transitions between an upper orbital and a lower orbital.
- So, how do I calculate the energy of any orbital?
- The energy of an orbit is the sum of the kinetic energy of the electron and a potential energy due to its position with respect to the nucleus.

- The potential energy of a particle of mass m and charge $-e$ a distance r from a heavy nucleus of charge $+Ze$ is given as

$$V_n = -\frac{Ze^2}{4\pi\epsilon_0 r_n}$$

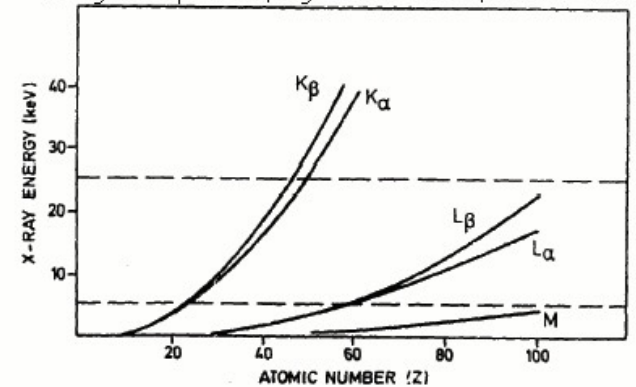
- The energy of the orbit is given as

$$E = \frac{1}{2}mv_n^2 + V_n = \frac{1}{2}m\left(\frac{Ze^2}{4\pi\epsilon_0 n\hbar}\right)^2 - \frac{Ze^2}{4\pi\epsilon_0 \frac{4\pi\epsilon_0 n^2 \hbar^2}{mZe^2}}$$

- Doing the math... $E_n = -\frac{Z^2 me^4}{2(4\pi\epsilon_0)^2 n^2 \hbar^2}$

- And here we are, the energy of the n^{th} orbital for a hydrogen-like (1 electron) atom.

- Notice that the energy is proportional to Z^2 and if you plot the energy versus atomic number, you get parabolic energy curves which is what Moseley obtained.



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The X-ray Energies

- The energies of an emitted x-ray are given as the difference between where the electron originates and where the electron is going to

$$\Delta E = E_{upper} - E_{lower}$$

- So, we have:

$$\Delta E = E_{upper} - E_{lower} = -\frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 n_{upper}^2 \hbar^2} - \left(-\frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 n_{lower}^2 \hbar^2} \right)$$

$$\Delta E = \frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \left(\frac{1}{n_{lower}^2} - \frac{1}{n_{upper}^2} \right) = hf = \frac{hc}{\lambda}$$

$$\rightarrow \Delta E = -13.6\text{eV} \left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2} \right) Z^2$$

- Next, we'll examine this formula and see what it tells us.....
- We'll calculate the K_{α} and K_{β} transition energies of a particular element.
- Then we'll discuss how well our results agree with experiments and look at a *PIXE* spectrum for a single element