

## **Lecture #2: Wave Nature of the Electron and the Internal Structure of an Atom**

Last time: Surprise — Light acts as a particle

1. Photoelectric effect, especially  $e^-_{KE}$  vs. frequency,  $\nu$ .  
Light as packets of energy, called “photons”,  $E = h\nu$ .
2. Compton scattering

Light as having both KE (scalar) and  $p$  (linear momentum: vector).  
Billiard-like scattering of photon by  $e^-$

Today:

1. Another surprise — wave character of  $e^-$   
compare diffraction of X-ray and  $e^-$  by same Al foil

$$\text{measure } \lambda_{e^-} = \frac{h}{p_{e^-}}$$

deBroglie postulated, for all objects considered to be particles (e.g.  $e^-$ ),

$$\text{that } \lambda = \frac{h}{p}$$

2. Internal structure of matter: observed to be mostly empty space! Another surprise!

In order to fill space, Rutherford postulated “planetary atom”

\* radiative collapse (a fatal flaw)

Bohr model

\* postulated quantized (and conserved) angular momentum,  $\ell = n\hbar$

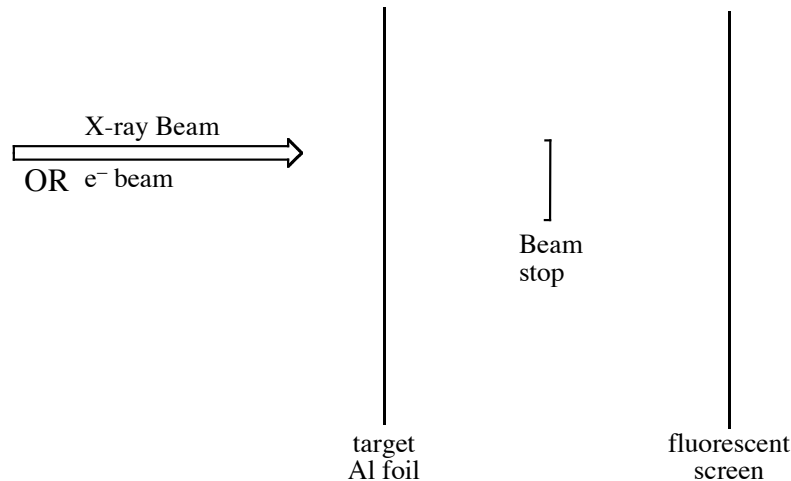
\* “Explained” line spectrum of H

\* radiative collapse “avoided” — sort of!

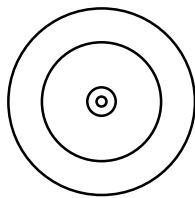
de Broglie

\* postulated integer # of  $\lambda$  around Bohr orbit to prevent self-annihilation of the  $e^-$  by destructive interference

X-ray and  $e^-$  diffraction off of Al foil  
 Davisson and Germer 1927



Use known lattice spacings in Al as a ruler to measure  $\lambda$  of  $e^-$   
 See Figure 1.13 in McQuarrie, page 30.



Obtain bull's eye "diffraction" pattern for *both* X-ray and  $e^-$ .

Closely-spaced pairs of rings come from scattering off nearest and second nearest neighbor atoms. A ring results from constructive interference between waves scattered by pairs of atoms. Paths to screen differ by *integer #* of wave lengths.

Can choose  $\lambda$  of X-rays (measured in separate experiment).

Can control  $p$  (momentum) of  $e^-$ :  $E_{e^-} = q_{e^-} V = \frac{p^2}{2m_{e^-}}$ ,  $p_{e^-} = [2m_{e^-} q_{e^-} V]^{1/2}$ .

$p_{e^-}$  is determined by choice of  $V$  (volts).

When the ring patterns match,  $e^-$  must have the same  $\lambda$  as the X-rays ( $\lambda_{x\text{-ray}} = \lambda_{e^-}$ ).

This is a way to measure  $\lambda_{e^-}$ . We find that it is  $\lambda_{e^-} = \frac{h}{p_{e^-}}$ .

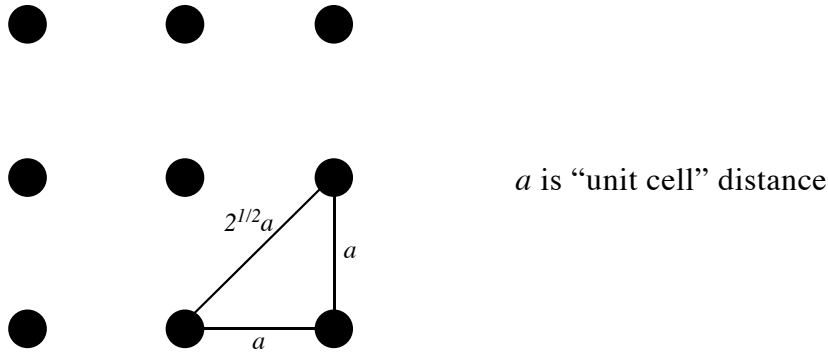
small  $p$ , large  $\lambda$

large  $p$ , small  $\lambda$

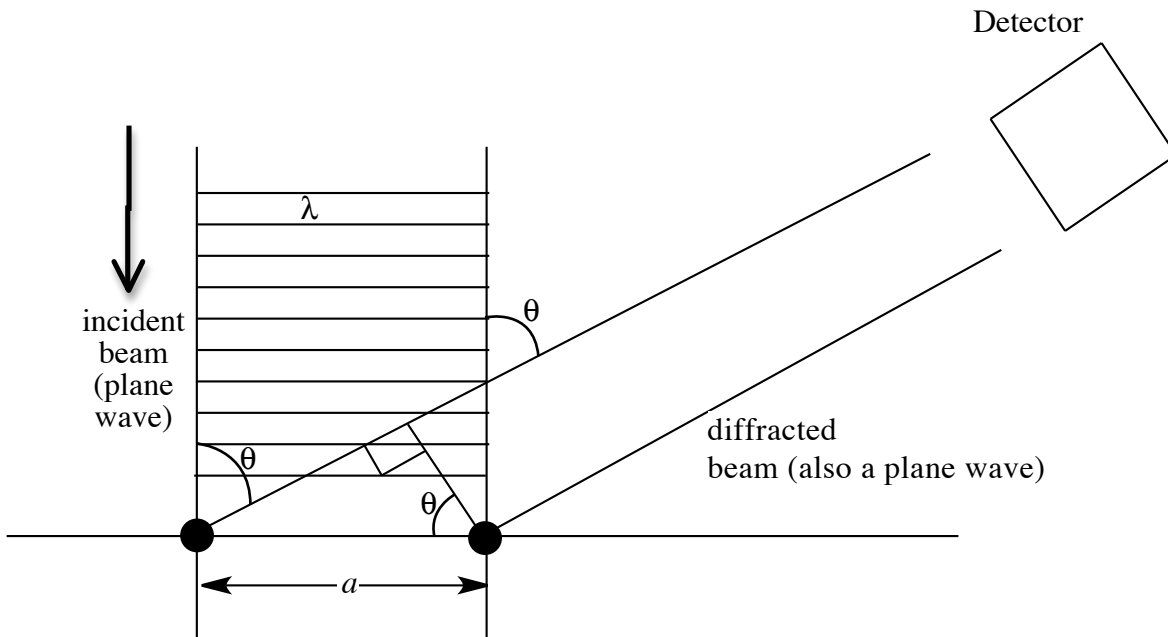
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### Non-Lecture

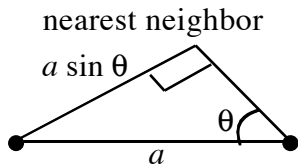
How does diffraction work?



See page 59 of Karplus and Porter.



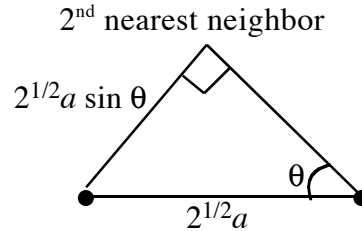
Get *constructive* interference from scattering off of 2 atoms separated by  $a$  when the angle  $\theta$  between incident and detected radiation is such that the 2 paths differ by  $n\lambda$ . ( $n$  is an integer, the "order")



$$n\lambda = a \sin \theta$$

1<sup>st</sup> order when  $n = 1$

$$\theta_n = \sin^{-1} \left( \frac{n\lambda}{a} \right)$$



$$n\lambda = 2^{1/2} a \sin \theta$$

1<sup>st</sup> order when  $n = 1$

$$\theta_n = \sin^{-1} \left( \frac{n\lambda}{2^{1/2} a} \right)$$

Suppose  $\lambda = a/2$

<u>nearest neighbor</u>	<u>2<sup>nd</sup> nearest neighbor</u>
$\theta_n = \sin^{-1}\left(\frac{n}{2}\right)$	$\theta_n = \sin^{-1}\left(\frac{n}{2^{3/2}}\right)$
$n = 1 \quad \theta_1 = 0.52$	$\theta_1 = 0.36$
$n = 2 \quad \theta_2 = 1.57$	$\theta_2 = 0.79$
...	...

The 1<sup>st</sup>-order ring for the *second-nearest* neighbor ( $\theta_1 = 0.36$ ) is of smaller diameter than that for the *nearest* neighbor (0.52).

The angular separation between ring pairs ( $\theta_1$  vs.  $\theta_2$ ) is larger in second-order. [This reminds you that a grating operated in second-order gives higher spectral resolution than in first-order.]

Different ring patterns (spacings and relative intensities) are observed for different lattice structures:

simple cubic	SC
face-centered cubic	FCC
body-centered cubic	BCC
hexagonal close packed	HCP

Can use “powder pattern” to assign unit cell type and to determine the unit cell distances. Why is it called a powder pattern?

#### END of NON-LECTURE

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So we can measure  $a$  using X-rays of known  $\lambda$ .

We can then measure  $\lambda$  of  $e^-$  for measured value of  $p$  (measured in a separate experiment).

Find *empirically* that

$$\lambda_{e^-} = h/p.$$

Einstein (1906 special relativity) showed, for light

$$p = \frac{E}{c} = \frac{h\nu}{\lambda\nu} = \frac{h}{\lambda}.$$

DeBroglie, in his 1924 Ph.D. Thesis, postulated that if  $p = \frac{h}{\lambda}$  for light, then the same formula would give  $\lambda$  for “particles”. Was this just a lucky guess or a deep insight?

Example calculation and a paradox

For an  $e^-$ , if  $\lambda = 1\text{\AA}$ , then  $v = ?$   $E = ?$  Typical diameter of an atom is  $\sim 1\text{\AA}$ . What  $E$  or  $v$  of an orbiting electron would be required for an  $e^-$  to “live inside” an atom?

$$\lambda = 10^{-10} \text{ m} = \frac{h}{p} = \frac{6.6 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.1 \times 10^{-31} \text{ kg})(v[\text{m/s}])}. \text{ Thus, for } \lambda = 1\text{\AA}, \text{ we predict}$$

$$v = 7.25 \times 10^6 \text{ m/s} \quad 2.4\% \text{ of } c \quad (\text{speed of light}).$$

$$E = \frac{1}{2}mv^2 = 2.4 \times 10^{-17} \text{ J} = (6.242 \times 10^{18} \text{ eV/J})(2.4 \times 10^{-17} \text{ J}) \text{ (units conversion)}$$

$$= 149 \text{ eV} \quad 10 \times \text{ typical ionization energy!}$$

(Energy required to remove one  $e^-$  from a gas phase atom or molecule.)

Paradox: How can an  $e^-$  fit inside of an atom?

Typical diameter of an atom is  $\sim 1\text{\AA}$ .

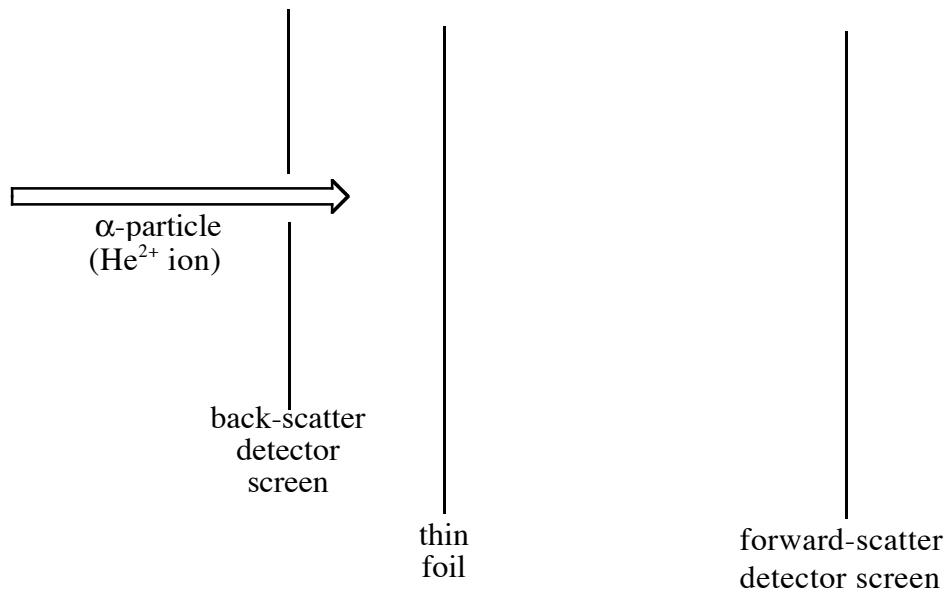
Typical binding energy of an  $e^-$  to a +1 charged nucleus is  $\approx 15\text{eV}$ .

Yet we require that, for an  $e^-$  to have small enough  $\lambda$  to “fit inside” an atom, it must have an energy  $10\times$  too large to remain trapped inside the atom. This is a **paradox**.

To “understand” this we must go back to the question: what is the *internal structure* of an atom?

Ernest Rutherford 1911

$\alpha$ -particle ( ${}^4\text{He}^{2+}$ ) scattering off of a metal foil. Experiments by Hans Geiger and Ernest Marsden.



Found that *very few*  $\alpha$ -particles were back-scattered. If atoms were “homogeneous” and we know the # of atoms per area of foil (how would we know this?), we know that most of the  $\alpha$  particles should arrive at the detector screen only weakly deflected. Fraction back-scattered tells us the effective diameter, mass, and charge of each atom, *as seen by an  $\alpha$ -particle*.

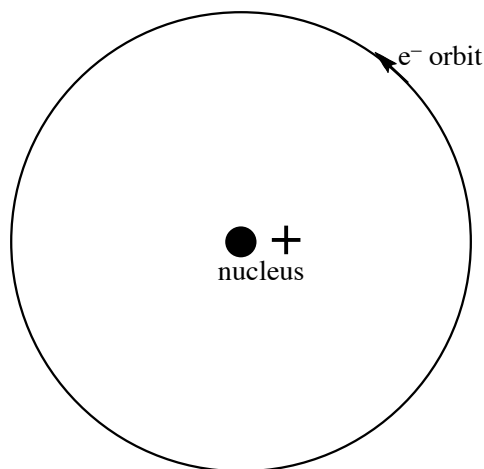
Found the “atomic diameter” determined in this way to be vastly smaller than the distance between atoms (calculated from the measured density of the metal of the foil and its known atomic weight).

The “Jellium” (homogeneous atom) model is ruled out.

Most of mass of atom is localized inside a *very small* diameter “nucleus”. Yet atoms are space filling. [Also, the charge on this “nucleus” is found to be positive and equal to the atomic number of the atom.]

How do we rationalize these two seemingly contradictory facts (space-filling yet most of the mass is confined to nucleus)?

Planetary model of an atom proposed by Rutherford:



Coulomb attraction between nucleus and  $e^-$ :

$$F_{\text{in}} = -\frac{q_{e^-}^2}{4\pi\epsilon_0} \frac{1}{r^2} \quad \boxed{\text{SI units, } \epsilon_0 \text{ is permittivity of free space}} \quad (1)$$

Centrifugal force:

$$F_{\text{out}} = +\frac{m_e v^2}{r} \quad (2)$$

$F_{\text{in}} = -F_{\text{out}}$ , solve for  $v$

$$v = \left[ \frac{q_{e^-}^2}{4\pi\epsilon_0 m_e r} \right]^{1/2} \quad (3)$$

We have found (treating the nucleus as infinitely heavy), for every value of the circular orbit radius,  $r$ , a constant speed,  $v$ , along the orbit.

No quantization of  $r$ ,  $v$ , or  $E$  is required, but small- $r$  must correspond to large- $v$ .

We have an accelerated  $e^-$  charge. Must radiate energy =  $h\nu$  where  $\nu$  is the frequency of the orbital motion. Loses energy. Must move to smaller radius orbit. Orbit frequency increases. Rate of radiation of energy increases. Radiative collapse. Bad! Fatal! Can this contradiction be explained?

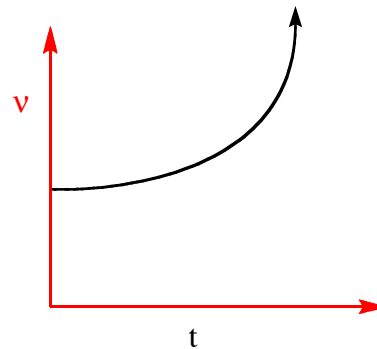
### Non-Lecture

$$\text{circumference} = 2\pi r$$

$$\text{period} = \frac{2\pi r}{v}$$

$$\text{frequency} = \frac{v}{2\pi r} = \left[ \frac{q_e^2}{r\pi\epsilon_0 m_e} \frac{1}{4\pi^2 r^2} \right]^{1/2}$$

small  $r$ , high frequency  
 $e^-$  spirals in toward nucleus.



To avoid this fatal flaw, Bohr postulated that electron orbital angular momentum,  $\ell$ , is quantized, and therefore, conserved. Only values of  $|\ell|$  that are integer multiples of  $\hbar = h/2\pi$  are allowed.

$$\vec{\ell} = \vec{r} \times \vec{p} = m_e v r = n\hbar$$

$$v_n = \frac{n\hbar}{m_e r_n} \quad \boxed{\vec{r} \perp \vec{p}} \quad \text{for circular motion} \quad (4)$$

This provides an *artificial answer* to the problem of radiative collapse. Why artificial?

Combine Eqs. (3) and (4) to solve for the orbit radius:

$$r_n = n^2 \frac{\hbar^2 4\pi\epsilon_0}{q_e^2 m_e} = n^2 \underbrace{[0.5292]}_{\text{atomic unit of length}} \text{\AA}$$

Orbit radius,  $r_n$ , gets large as  $|\vec{\ell}|$  (or  $n$ ) increases. Instead, solve for the orbit velocity:

$$v_n = \frac{1}{n} \left[ \frac{q_e^2}{\hbar 4\pi\epsilon_0} \right] = \frac{1}{n} [2.188 \times 10^6] m/s$$

$v$  gets small as  $\ell$  (or  $n$ ) increases. Next, solve for  $\lambda_n$  :

$$p_n = \frac{1}{n} \frac{q_e^2 m_e}{\hbar 4\pi\epsilon_0}$$

$$\lambda_n = \frac{h}{p_n} = n \frac{8\pi^2 \epsilon_0 \hbar^2}{q_e^2 m_e} = \frac{2\pi r_n}{n} = n[3.32] \text{Å}$$

Circumference of  $n^{\text{th}}$  orbit =  $2\pi r_n = n\lambda_n$ ! This is a pleasant surprise. *The  $e^-$  fits inside an atom if its wavelength is arranged along the orbit circumference!* Next, solve for the allowed energy levels:

$$E_n = T(r_n) + V(r_n) = \frac{1}{2} m_e v_n^2 - \frac{q_e^2}{4\pi\epsilon_0} \frac{1}{r_n}$$

$$= \frac{-m_e q_e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2}$$

$\frac{1}{hcR_H}$

Rydberg constant for H

Balmer, from numerical study of the emission lines of H atom, proposed that the frequency of a spectral line is given by  $\frac{1}{h}$  times the difference between energy levels. Transitions between discrete (quantized) energy levels!

$$\begin{array}{c} \text{----- } n' \\ \nu_{n',n} = \frac{E_{n'} - E_n}{h} \\ \text{----- } n \end{array}$$

Turns out that

- \* This energy level formula for the Bohr atom exactly reproduces *all of the energy levels of all  $1e^-$  systems*  $\left( \text{replacing } m_e \text{ by } \mu = \frac{m_e m_{\text{nucleus}}}{m_e + m_{\text{nucleus}}} \approx m_e \right)$
- \* accounts for line spectra if  $\nu_{n,n'} = \frac{E_n - E_{n'}}{h}$
- \* according to Bohr, the lowest possible value of  $\ell$  is  $\ell = 1$  (we will find out later that  $\ell = 0$  is also possible)
- \* does not account for relative intensities of spectral lines, or “radiative lifetimes” of energy levels
- \* does not explain effect of a magnetic field on spectrum



- \* more satisfying to use deBroglie's idea to prevent radiative collapse. But insistence on integer orbital angular momenta [Bohr] and avoidance of destructive interference around a circular orbit [de Broglie] are *both* based on artificial constraints.
- \* if the  $e^-$  is moving on a circular orbit, it must radiate, but is it really moving? WEIRD! But this gives a peek at the resolution of the paradox! What is this peek?

deBroglie: Integer number of  $\lambda$  around orbit circumference is what is required to prevent destructive interference of  $e^-$  with itself. An  $e^-$  should not "disappear".

Seems more fundamental. But we are just making *ad hoc* proposals to explain a fundamental contradiction. *We should not be comfortable with any of this!*

Bohr theory cannot "explain" any spectra other than  $1e^-$  spectra (H,  $He^+$ ,  $Li^{2+}$  ...).

At this stage, the spectrum of the simplest possible  $2e^-$  atom, He, remains a mystery.

What do we do now?

Next Lecture: Discuss wave equation in preparation for Schrödinger Equation, which is a more complete and widely applicable way to deal with these unexpected results.

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5.61 Physical Chemistry  
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