CHAPTER 4

Structure of the Atom / Particle nature of matter

- 4.0 Elements and Atoms throughout the ages
- 4.1 The plum pudding / raisin cake atom model of J.J. Thomson
- 4.2 Rutherford Scattering / Planetary model of the atom?
- 4.3 The instability of the classic "solar system" model of atoms
- 3.3 Line spectra of elements, Balmer's numerology and Rydberg's equation and constant
- 4.4 The Bohr Model of the Hydrogen Atom; Sommerfeld fine structure constant
- 4.5.1 Successes
- 4.5.2 Failures
- 4.6 Shell structure of atoms, characteristic X-Ray Spectra, Moseley's fit and it's support of Bohr's model
- 4.7. There are also Auger electrons, not only characteristic X-rays
- 4.8. quantum jumps in physics and how the general public misunderstands the concept

Various Greek (and Indian) philosophers had only a few elements, concept of an atom that is indivisible smallest unit of any form of matter

Various atoms and molecules as depicted in John Dalton's "A New System of Chemical Philosophy" (1808).

Law of constant proportion in chemical reactions, atoms must exist for chemical book keeping reasons

2H₂ + O₂ -> 2H₂O



Faraday, 1838:



Electrolysis of molten NaCl.

Atoms have "electrical constituents"

common salt (NaCl). Faraday found that if 96,500 C of charge (1 faraday) is passed through such a molten solution, 23.0 g of Na will deposit on the cathode and 35.5 g of chlorine gas will bubble off the anode (Fig. 4.2). In this case, exactly 1 gram atomic weight or mole of each element is released because both are monovalent. For divalent and trivalent elements, exactly $\frac{1}{2}$ and $\frac{1}{3}$ of a mole, respectively, would be released. As expected, doubling the

quantity of charge passed doubles the mass of the neutral element liberated. Faraday's results may be given in equation form as

$$m = \frac{(q) \,(\text{molar mass})}{(96,500 \text{ C}) \,(\text{valence})} \tag{4.1}$$
 Faraday's law of electrolysis

where m is the mass of the liberated substance in grams, q is the total charge passed in coulombs, the molar mass is in grams, and the valence is dimensionless.

John Joseph Thomson, 1897

Electrons are negatively charged particles that can be "pulled out" of any metal by a strong electric field (the "thingies" pulled out are all identical and have a charge to mass ratio about 2,000 times larger than hydrogen ions (which we now know to be protons)





Deflection of negative particles by an electric field.

So atoms cannot be indivisible, if not indivisible, they must have some internal structure that is responsible for the physical and chemical properties of the atoms of the various elements

Previous chapter

There is also radioactivity (from 1896 onwards): electrons and other particles, e.g. alpha particles, (we now know nuclei of He, two protons + two neutrons) come out of the atoms of certain radioactive elements



end of the second part of this course, nuclear physics

Einstein's PhD thesis and the related 1905 paper, atoms must exist for physical reasons

ANNALEN PHYSIK.

BEORÜNDET UND FORTORFÜHRT DURCH F. A. C. GREN, L. W. GILBERT, J. C. POGGENDORFF, G. UND E. WIEDEMANN.

VIERTE FOLGE.

BAND 19. DEE GANZEN REIHE 324. BAND

KURATORIUM: F. KOHLRAUSCH, M. PLANCK, G. QUINCKE, W. C. RONTGEN, E. WARBURG.

UNTER MITWIRKUNG DEB DEUTSCHEIN PHYSIKALISCHEIN GESELLSCHAFT UD INSESONDERE VON M. PLANCK

HERACSGEGEBEN VON

PAUL DRUDE.

MIT FÜNF FIGURENTAFELN.



LEIPZIG, 1906. VERLAG VON JOHANN AMBROSIUS BARTH.

 Berichtigung zu meiner Arbeit: ,, Eine neue Bestimmung der Moleküldimensionen⁽¹⁾; von A. Einstein.

> *ibid* vol. **34**, pp. 591-592, 1911

3. Eine neue Bestimmung der Moleküldimensionen; von A. Einstein.

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Die ältesten Bestimmungen der wahren Größe der Moleküle hat die kinetische Theorie der Gase ermöglicht, während die an Flüssigkeiten beobachteten physikalischen Phänomene bis jetzt zur Bestimmung der Molekülgrößen nicht gedient haben. Es liegt dies ohne Zweifel an den bisher unüberwindlichen Schwierigkeiten, welche der Entwickelung einer ins einzelne gehenden molekularkinetischen Theorie der Flüssigkeiten entgegenstehen. In dieser Arbeit soll nun gezeigt werden, daß man die Größe der Moleküle des gelösten Stoffs in einer nicht dissoziierten verdünnten Lösung aus der inneren Reibung der Lösung und des reinen Lösungsmittels und aus der Diffusion des gelösten Stoffes im Lösungsmittel ermitteln kann, wenn das Volumen eines Moleküls des gelösten Stoffs groß ist gegen das Volumen eines Moleküls des Lösungsmittels. Ein derartiges gelöstes Molekül wird sich nämlich bezüglich seiner Beweglichkeit im Lösungsmittel und bezüglich seiner Beeinflussung der inneren Reibung des letzteren annähernd wie ein im Lösungsmittel suspendierter fester Körper verhalten, und es wird erlaubt sein, auf die Bewegung des Lösungsmittels in unmittelbarer Nähe eines Moleküls die hydrodynamischen Gleichungen anzuwenden, in welchen die Flüssigkeit als homogen betrachtet, eine molekulare Struktur derselben also nicht berücksichtigt wird. Als Form der festen Körper, welche die gelösten Moleküle darstellen sollen, wählen wir die Kugelform.

§ 1. Über die Beeinflussung der Bewegung einer Flüssigkeit durch eine sehr kleine in derselben suspendierte Kugel.

Es liege eine inkompressible homogene Flüssigkeit mit dem Reibungskoeffizienten k der Betrachtung zugrunde, deren Geschwindigkeitskomponenten u, v, w als Funktionen der Koordinaten x, y, z und der Zeit gegeben seien. Von einem beliebigen Punkt x_0 , y_0 , z_0 aus denken wir uns die Funktionen u, v, w als Funktionen von $x - x_0$, $y - y_0$, $z - z_0$ nach

Vor einigen Wochen teilte mir Hr. Bacelin, der auf Veranlassung von Hrn. Perrin eine Experimentaluntersuchung über die Viskosität von Suspensionen ausführte, brieflich mit, daß der Viskositätskoeffizient von Suspensionen nach seinen Resultaten erheblich größer sei, als der in § 2 meiner Arbeit entwickelten Formel entspricht. Ich ersuchte deshalb Hrn. Hopf, meine Rechnungen nachzuprüfen, und er fand in der Tat einen Rechenfehler, der das Resultat erheblich fälscht. Diesen Fehler will ich im folgenden berichtigen.

also start of quantitative nanoscience

Wir wollen die Rechnung für wässerige Zuckerlösung durchführen. Nach den oben mitgeteilten Angaben über die innere Reibung der Zuckerlösung folgt zunächst für 20°C.:

 $NP^{3} = 200$.

Nach Versuchen von Graham (berechnet von Stefan) ist der Diffusionskoeffizient von Zucker in Wasser bei 9,5°C. 0,384, wenn der Tag als Zeiteinheit gewählt wird. Die Zähigkeit des Wassers bei 9,5° ist 0,0135. Wir wollen diese Daten in unsere Formel für den Diffusionskoeffizienten einsetzen, trotzdem sie an 10 proz. Lösungen gewonnen sind und eine genaue Gültigkeit unserer Formel bei so hohen Konzentrationen nicht zu erwarten ist. Wir erhalten

 $NP = 2,08.10^{16}$.

Aus den für NP^3 und NP gefundenen Werten folgt, wenn wir die Verschiedenheit von P bei $9,5^{\circ}$ und 20° vernachlässigen,

 $P = 9,9 \cdot 10^{-8} \text{ cm},$ $N = 2,1 \cdot 10^{23}.$

Der für N gefundene Wert stimmt der Größenordnung nach mit den durch andere Methoden gefundenen Werten für diese Größe befriedigend überein.

Bern, den 30. April 1905.

(Eingegangen 19. August 1905.)

A. Einstein, "Eine neue Bestimmung der Moleküldimensionen", *Annalen der Physik*, vol. **19**, pp. 289-306, 1906

Legt man die berichtigte Formel zugrunde, so erhält man für das Volumen von 1 g in Wasser gelöstem Zucker statt des in § 3 angegebenen Wertes 2,45 cm³ den Wert 0,98, also einen vom Volumen 0,61 von 1 g festem Zucker erheblich weniger abweichenden Wert. Endlich erhält man aus der inneren Reibung und Diffusion von verdünnten Zuckerlösungen statt des im Anhange jener Arbeit angegebenen Wertes $N = 4,15 \cdot 10^{23}$ für die Anzahl der Moleküle im Grammolekül den Wert $6,56 \cdot 10^{23}$.

Zürich, Januar 1911.

(Eingegangen 21. Januar 1911.)

Big questions: What is the true nature of atoms?

What is their internal structure that is responsible for the chemical and physical properties of the atoms of the various chemical elements, expanded to molecules and condensed matter

Smaller questions (the answers to which will help with the big questions above:

How come there are characteristic emission and absorption spectra for all of the elements?

How come there are characteristic X-ray emission spectra for the elements (there are of course also characteristic X-ray absorption spectra – not part of this course, there are also characteristic γ -ray absorptions and emissions, end of the second part of this course, nuclear physics)

How come ...



Thomson's Atomic Model

Thomson's "plum-pudding" model of the atom had the positive charges spread uniformly throughout a sphere the size of the atom, with electrons embedded in the uniform background.



 In Thomson's view, when the atom was heated, the electrons could vibrate about their equilibrium positions, thus producing electromagnetic radiation.

That is the dough or pudding in the plum pudding? the plums/raisins are the electrons

What to do? Rutherford's idea: shoot small but highly energetic probes at atoms, see what happens,

Still done in particle physics today, also Rutherford managed to transform one type of atom into another by shooting at them with α -particles



Figure 4-3 Thomson's model of the atom: (a) A sphere of positive charge with electrons embedded in it so that the net charge would normally be zero. The atom shown would have been phosphorus. (b) An α particle scattered by such an atom would have a scattering angle θ much smaller than 1°.

That is what physicists do, take things apart, figure out what its "internal structure" is, how it works on the basis of this structure

Rutherford himself: "In Science there is only physics, anything else is stamp collecting." Various versions: "The only real science is physics,

everything else is stamp collecting."

the atom. The accidental chain of events and the clever capitalization on the accidental discoveries leading up to Rutherford's monumental nuclear theory of the atom are nowhere better described than in Rutherford's own essay summarizing the development of the theory of atomic structure:

... I would like to use this example to show how you often stumble upon facts by accident. In the early days I had observed the scattering of α -particles, and Dr. Geiger in my laboratory had examined it in detail. He found, in thin pieces of heavy metal, that the scattering was usually small, of the order of one degree. One day Geiger came to me and said, "Don't you think that young Marsden, whom I am training in radioactive methods, ought to begin a small research?" Now I had thought that, too, so I said, "Why not let him see if any α -particles can be scattered through a large angle?" I may tell you in confidence that I did not believe that they would be, since we knew that the α -particle was a very fast, massive particle, with a great deal of energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings the chance of an α -particle's being scattered backwards was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying, "We have been able to get some of the α -particles coming backwards...." It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that this scattering backwards must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive center carrying a charge. I worked out mathematically what laws the scattering should obey, and I found that the number of particles scattered through a given angle should be proportional to the thickness of the scattering foil, the square of the nuclear charge, and inversely proportional to the fourth power of the velocity. These deductions were later verified by Geiger and Marsden in a series of beautiful experiments.⁷

Experiments of Geiger and Marsden

- Rutherford conceived a new technique for investigating the structure of matter by scattering α particles from atoms.
- Marsden and Geiger showed that a few α particles were scattered from thin goldleaf targets at backward angles greater than 90°.



Figure 4.10 A schematic view of Rutherford's *α* scattering apparatus.



Figure 4-4 Schematic diagram of the apparatus used by Geiger and Marsden to test Rutherford's atomic model. (*a*) The beam of α particles is defined by the small hole *D* in the shield surrounding the radioactive source *R* of ²¹⁴Bi (called RaC in Rutherford's day). The α beam strikes an ultrathin gold foil *F* (about 2000 atoms thick), and the α particles are individually scattered through various angles. Those scattering at the angle θ shown strike a small screen *S* coated with a scintillator, i.e., a material that emits tiny flashes of light (scintillations) when struck by an α particle. The scintillations were viewed by the observer through a small microscope *M*. The scintillation screen–microscope combination could be rotated about the center of the foil. The region traversed by the α beam is evacuated. The experiment consisted of counting the number of scintillations as a function of θ . (*b*) A diagram of the actual apparatus as it appeared in Geiger and Marsden's paper describing the results. The letter key is the same as in (*a*). [*Part* (*b*) from *H*. *Geiger and E. Marsden*, *Philosophical Review*, 25, 507 (1913).]



No experiments for Z = 60(Neodymium) as it is rare and cannot easily be beaten into very thin foils as the crystal structure is hexagonal closepacked, but Ag (Z = 47) and Au, Cu, and Al all can, because they are cubic densest packed

Figure 4.12 Comparison of theory and experiment for α particle scattering from a silver foil. (*From E. Rutherford, J. Chadwick, and J. Ellis,* Radiations from Radioactive Substances, *Cambridge, Cambridge University Press, 1951.*)



Figure 4-9 (a) Geiger and Marsden's data for α scattering from thin gold and silver foils. The graph is a log-log plot to show the data over several orders of magnitude. Note that scattering angle increases downward along the vertical axis. (b) Geiger and Marsden also measured the dependence of ΔN on t predicted by Equation 4-6 for foils made from a wide range of elements, this being an equally critical test. Results for four of the elements used are shown.

4.2: Rutherford Scattering

- Scattering experiments help us study matter too small to be observed directly.
- There is a relationship between the impact parameter b and the z' axis scattering angle θ . $\phi = 0$ Positive ϕ VO When *b* is small, Z1e \rightarrow r gets small. Z9e \rightarrow Coulomb force gets large. Scatterer $\rightarrow \theta$ can be large and the particle can be repelled backward. $b = \frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K} \cot \frac{\theta}{2} \quad \text{where } K = m v_0^2 / 2$ Z_1 and Z_2 are the repulsive charges in units

of the elemental charge e

Rutherford Scattering

Impact parameter b gets expanded into a circular area πb_0^2 which is called cross section.



cross section $\sigma = \pi b^2$ enters into relation for **probability** for a particle being scattered by a nucleus

$$=\pi nt \left(\frac{Z_1 Z_2 e^2}{8\pi\varepsilon_0 K}\right)^2 \cot^2 \frac{\theta}{2}$$

with n number of scattering nuclei per unit area and t thickness of the target foil

Anything within a cross section area will be scattered to angles larger than θ_0

Rutherford Scattering Equation

In actual experiment a detector is positioned from θ to $\theta + d\theta$ that corresponds to incident particles between *b* and *b* + *db*.



no *h* in these equations, so there are just the correct classical treatment of particles

• The number of particles scattered per unit area is

4.16
$$N(\theta) = \frac{N_i nt}{16} \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z_1^2 Z_2^2}{r^2 K^2 \sin^4(\theta/2)}$$

Where N_i is total number of incident particles, K again kinetic energy, r the angular widths of the detector



Figure 4-13 (a) If the α particle does not penetrate the nuclear charge, the nucleus can be considered a point charge located at the center. (b) If the particle has enough energy to penetrate the nucleus, the Rutherford scattering law does not hold but would require modification to account for that portion of the nuclear charge "behind" the penetrating α particle. Shooting with the toughest bullets at the weakest target, Rutherford's scattering theory broke down, this means the underlying assumptions are no longer valid, from that one can determine the size of the nucleus, still done today for other particles in particl accelerators



Figure 4-14 Data from Rutherford's group showing observed α scattering at a large fixed angle versus values of r_d computed from Equation 4-11 for various kinetic energies.

EXAMPLE 4.5 Estimate of the Radius of the Aluminum Nucleus

In 1919, Rutherford was able to show a breakdown in Equation 4.16 for 7.7-MeV α particles scattered at large angles from aluminum nuclei (Z = 13). Estimate the radius of the aluminum nucleus from these facts.

Solution Rutherford's scattering formula is no longer valid when α particles begin to penetrate or touch the nucleus. When the α particle is very far from the aluminum nucleus, its kinetic energy is 7.7 MeV. This is also the total energy of the system (α particle plus aluminum nucleus), because the aluminum nucleus is at rest and the potential energy is zero for an infinite separation of particles. When the α particle is at the point of closest approach to the aluminum nucleus in a head-on collision, its kinetic energy is zero and it is at a distance d_{\min} .

which we may take to be the radius of the aluminum nucleus. At this point, the kinetic energy of the system is zero and the total energy is just the potential energy of the system. Applying conservation of energy gives

$$K_{\alpha}$$
 = potential energy at closest approach = $\frac{k(Ze)(2e)}{d_{\min}}$

.

. . .

or

$$d_{\min} = k \frac{2Ze^2}{K_{\alpha}}$$

$$= \frac{2(13) (1.60 \times 10^{-19} \text{ C})^2 (8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2)}{(7.7 \times 10^6 \text{ eV}) (1.60 \times 10^{-19} \text{ J/eV})}$$

$$= 4.9 \times 10^{-15} \text{ m}$$

Order of magnitude correct ! Atoms are on the order of 1 to 3 Å (10⁻¹⁰ m)

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1908 Nobel prize in **chemistry** to Ernest Rutherford (later Lord Rutherford of Nelson after the town where he was born in New Zealand) and the physical chemist Frederic Soddy, both at McGill University in Canada

for the radioactive transmutation of chemical elements

$^{14}N + \alpha \rightarrow \frac{17O}{P} + p$. 1917-1919 but that stable isotope of oxygen was not identified until the 1930s

the alchemists' dreams realized about 100 years ago, Glenn Seaborg has produced several thousand atoms of gold from bismuth, but at a big net financial loss.

"If your experiment needs statistics, you ought to have done a better experiment."

"All science is either physics or stamp collecting"

"The energy produced by the breaking down of the atom is a very poor kind of thing. Anyone who expects a source of power from the transformation of these atoms is talking moonshine." -1933

"An alleged scientific discovery has no merit unless it can be explained to a barmaid."





Rutherford's Atomic Model

 Rutherford proposed that an atom has a positively charged core (nucleus) surrounded by the negative electrons.



There is no positively charged dough or pudding in the plum pudding/raisin cake, only raisins, empty space, and a core

4.3: The classical/solar system Atomic Model is doomed

Let's consider atoms as a quasi sun/planet model (only one planet so that it is just a two body problem.

The force balance of circular orbits for an electron "going around" a stationary nucleolus



where v is the tangential velocity of the electron.

Circular motion is accelerated, accelerated charges need to radiate energy off according to Maxwell, loosing kinetic energy



Other weaknesses:

- (1) gravity in the solar system is attractive, if there is more than one electron in an atom, they will repel each other.
- (2) most importantly: if two solar system atom models were to "collide", they would form a "molecule model", but when that "molecule model" is broken up, there is no physics that would ensure that the two original "solar system atom models" would be obtained again.

Balmer Series – hydrogen is the simplest atom, so theoretical modeling starts there

 In 1885, Johann Balmer found an empirical formula for wavelengths of the emission spectrum for hydrogen in nm within the visible range



A good physical theory for H atom needs to make sense of this empirical result 22

Rydberg Equation

As more scientists discovered emission lines at infrared and ultraviolet wavelengths, the Balmer series equation was extended to the Rydberg equation, actually on the basis of this equation, people went out looking for more lines :

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{k^2} \right) \qquad R_H = 1.096776 \times 10^7 \text{ m}^{-1} \qquad \text{Aside:}$$

Table 3.2 Hyd	rogen Series of Spectral	Lines		$R_H = \frac{1}{m_e} R_\infty$
Discoverer (year)	Wavelength	n	k	$R_{\infty} = \frac{\alpha^2 m_e c}{2 h} =$
Lyman (1916)	Ultraviolet	1	>1	2n 1.09737 $\cdot 10^7 \ m^{-1}$
Balmer (1885)	Visible, ultraviolet	2	>2	m . M
Paschen (1908)	Infrared	3	>3	$\mu = \frac{m_e + M}{m_e + M}$
Brackett (1922)	Infrared	4	>4	with u as reduced
Pfund (1924)	Infrared	5	>5	mass of the elecron, α as fine structure

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Can be applied to isotopes of hydrogen by modifying R slightly

constant, and M

mass of the nucleus

4.4: The Bohr Model of the Hydrogen Atom

Niels Bohr's general assumptions:

- 1) "Stationary states" (orbiting electron does not radiate energy) exist in the hydrogen atom.
- 2) $\Delta E = E_{\text{initial}} E_{\text{final}} = hf$
- 3) Classical laws of physics do not apply to transitions between stationary states, the electron just "jumps" makes a "quantum leap"
- 4) Angular momentum is quantized in units of ${}^{\text{h}}\!/_{2\pi}$, in the future simply called h-bar \hbar
- 5) Correspondence principle, at very high quantum numbers (the indices in (2)) binding energies become so low that transitions between stationary states can be achieved without us noticing their discrete quantum nature, energy changes seem to be continuous again
- Nota Bene: All of these assumptions are consistent with the assumption that the electron is a classical particle, as supported by J.J. Thomson's experiments and the rest of classical physics except for the Maxwell equations





Figure 4.23 The first three Bohr orbits for hydrogen.

$$r_n = \frac{4\pi\varepsilon_0 n^2\hbar^2}{me^2} \equiv n^2 a_0$$

radius of the hydrogen atom for stationary states, n = 1, 2, 3, ...

The smallest diameter of the hydrogen atom is two times the Bohr radius $\approx 1 \text{ Å} = 0.1 \text{ nm}$

n = 1 gives its lowest energy state (called the "ground" state), there is formally no E₀
 since quantum numbers start with 1 and are positive integers

$$E_n = -\frac{ke^2}{2a_0} \left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3,$$

. . .

But some books may call it E_0 nevertheless, E_1 is also called 1 Rydberg \approx 13.6 eV, needs to be divided by h and c in order to get the Rydberg constant in m⁻¹

Transitions in the Hydrogen Atom



Lyman series

The atom will remain in the excited state for a short time before emitting a photon and returning to a lower stationary state. Most hydrogen atoms exist in n = 1 at room temperature.

Balmer series (of formula fame)

When sunlight passes through the atmosphere, hydrogen atoms in water vapor absorb certain wavelengths (visible), seen as dark lines in absorption spectrum.

If the material is very dilute there are discrete spectra: Ångstrom (~ 1860)

last chapter, we learned that emission and absorption lines are at the same wavelength

Continuous Spectrum



Very dense material, i.e. hot "black body", big-bang background radiation, sun if one does not look too carefully

There is *typically* more emission lines than absorption lines, because there are many more possible transitions to go back to lower state from a multitude of excited states

Absorption lines are fewer in number because there are naturally only a small numbers of atoms in exited states



If highly excitated due to high tension, there are many different transitions downwards, so typically more emission lines than absorption lines

- Spectroscopy can be done very precisely, in fact so precisely that isotopes of hydrogen, were discovered that way, Deuterium as early as 1932, later on also Tritium)
- Much depends on the quality of the grating ...spectroscopic measurements can be very precise, one can distinguish between isotopes of hydrogen



Figure 4.19 Kirchhoff's experiment explaining the Fraunhofer D-lines. The D-lines darken noticeably when sodium vapor is introduced between the slit and the prism.

Absorption spectra, light of certain wavelengths is taken out of the "quasi black-body spectrum" of the sun, the glass prism provides a limited dispersion so that the emission lines from the excited atoms in the sun are not readily visible

It is typically only transition from the ground state to higher states that are missing in the otherwise continuous spectrum from the sun, so it is only a few No need for special relativity / Fine Structure Constant

The electron's velocity in the Bohr model:

For any state, n = 1, 2, ...
$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{e^2}{4\pi\varepsilon_0\hbar}$$

- $v_1 = 2.2 \times 10^6$ m/s ~ less than 1% of the speed of light.
- In any other orbit, there is less kinetic energy, i.e. the electron needs to move even slower than that
- There is no need to use special relativity
- The ratio of v_1 to c is known as fine structure constant.

$$\alpha \equiv \frac{v_1}{c} = \frac{\hbar}{ma_0 c} = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137}$$

It is dimension-less, so other creatures in distant galaxies will have it as well (will have the very same numerical value for it) !!

 α was actually introduced by Arnold Sommerfeld (nominated 81 times for Nobel prize, didn't win but died in a car accident) in his attempt to explain spectral line doublets by elliptical electron orbits, confirmation of his theory, just fortuitous, as his physics was as wrong as Bohr's discrete Hydrogen Atom Energy levels (after all it's a bound system)

The energies of the stationary states

$$E_n = -\frac{e^2}{8\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2}$$

where $E_0 = E_1 = -13.6$ eV (negative as all binding energies). Ground state energy, also called one Rydberg of energy



• Emission of light occurs when the atom is in an excited state and de-excites to a lower energy state $(n_{\mu} \rightarrow n_{\ell})$.

$$hf = E_u - E_\ell$$

Something negative minus something even more negative is positive, *u* for upper, *l* for lower

where *f* is the frequency of a photon.

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{E_u - E_\ell}{hc} = R_\infty \left(\frac{1}{n_\ell^2} - \frac{1}{n_u^2}\right)$$

 R_{∞} is the **Rydberg constant** for a hypothetical nucleolus that is so heavy that it remains stationary while the electron moves around it, note that R_{∞} is a model concept in accordance to the Bohr's model The electron and hydrogen nucleus actually revolved about their mutual center of mass.



• The electron mass is replaced by its **reduced mass**.

$$\mu_e = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \frac{m_e}{M}}$$

• The Rydberg constant for infinite nuclear mass is replaced by R_H for hydrogen, R_D for deuterium, R_T for tritium.

$$R = \frac{\mu_e}{m_e} R_{\infty} = \frac{1}{1 + \frac{m_e}{M}} R_{\infty} = \frac{\mu_e e^4}{4\pi c \hbar^3 (4\pi \varepsilon_0)^2}$$

See also earlier slide where we used α instead

All three hydrogen isotopes have a slightly different R values in precision experiments, a way to detect these isotopes in the sun by their "signature" on earth

$$R_{\infty} = \frac{e^2}{8\pi\varepsilon_0 a_0 h^2}$$

From Bohr's model

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$$

from Sommerfeld model

$$R_{\infty} = \frac{\alpha^2 m_e c}{2h} =$$

 $1.09737 \cdot 10^7 \ m^{-1}$

BUT Rydberg's constant from high precision experiment R_H , very close but **not exactly the same**, how come?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{k^2} \right) \qquad R_H = 1.096776 \times 10^7 \text{ m}^{-1}$$

To resolve:

$$R_{H} = \frac{\mu_{e}}{m_{e}} R_{\infty} \qquad \mu_{e} = \frac{m_{e} \cdot M}{m_{e} + M}$$

mass of nucleus of one atom of deuterium (2.0141102 u) is less than an isolated proton (1.007825 u and an isolated neutron (1.008665 u) added together (the rest is 2.224 MeV binding energy with negative sign) with µ as reduced electron mass and M as mass of the nucleus, in case of standard hydrogen it's just a proton, in case of deuterium a proton and a neutron (beware binding energy) in case of tritium a proton and two neutrons (again beware of binding energy) how come? **Special relativity says so!**)

Correspondence Principle in general



Need a principle to relate the new modern results with classical ones.



In the limits where classical and quantum theories should agree, the quantum theory must reduce the classical result. That limit is quantum leaps between very lightly bound electron states (very high quantum numbers)

Bohr's Correspondence Principle specific for orbits of hydrogen atom

The frequency of the radiation emitted $f_{\text{classical}}$ is equal to the orbital frequency f_{orb} of the electron around the nucleus.

$$f_{\text{classical}} = f_{\text{orb}} = \frac{\omega}{2\pi} \qquad \qquad f_{\text{classical}} = \frac{1}{2\pi} \left(\frac{e^2}{4\pi\varepsilon_0 mr^3}\right)^{1/2} = \frac{me^4}{4\varepsilon_0^2\hbar^3} \frac{1}{n^3}$$

The frequency of the transition from n + 1 to n is

For

$$f_{\text{Bohr}} = \frac{E_0}{h} \left[\frac{1}{n^2} - \frac{1}{(n+1)^2} \right]$$
$$= \frac{E_0}{h} \left[\frac{n^2 + 2n + 1 - n^2}{n^2 (n+1)^2} \right] = \frac{E_0}{h} \left[\frac{2n + 1}{n^2 (n+1)^2} \right]$$
For very large *n* only,
$$f_{\text{Bohr}} \approx \frac{2nE_0}{hn^4} = \frac{2E_0}{hn^3}$$
Substitute for E_0 :
$$f_{\text{Bohr}} = \frac{me^4}{4\varepsilon_0^2 h^3} \frac{1}{n^3} = f_{\text{classical}}$$

From this idea he actually figured angular momentum needs to be quantized in units of \hbar for the mathematics to work out

Limitations of the Bohr Model

- The Bohr model was a great step towards a quantum theory of matter, explained the spectral lines of hydrogen (and its three isotopes) comprehensively but it had its limitations.
- Works only for single-electron atoms and ions that have a single electron left. Only modification in all equations Ze instead of e, where Z is the number of positive charges in the nucleus
- Could neither account for the intensities nor the fine structure of the spectral lines (they are actually doublets) for hydrogen when atoms were put into magnetic fields (Nobel prize to Lorentz and Zeeman 1902)
- 3) Could not explain the binding of atoms into molecules
- 4) Contained unexplained quantum jumps that's not good physics, just a step in the right direction, i.e. energy and other physical entities such as angular momentum in bound systems need to be quantized

The reason for all of this is that the model is build on the basis of the particle nature of matter.

$$E_n = -\frac{Z^2 E_0}{n^2}$$
$$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

Because we have e^2 in both E_0 and the Rydberg constant

$$R_{\infty} = \frac{e^2}{8\pi\varepsilon_0 a_0 h^2}$$

Unexpected lines in the sun's spectrum were identified to be He+ (which also has isotopes), i.e. different effective mass corrections for R Within the three paper series by Niels Bohr in 1913, idea that electrons in other atoms are arranged in shells with lots of empty space between then, essentially correct



4.6: Characteristic X-Ray Spectra and Atomic Number beyond hydrogen and one electron left ions

Shells have letter names:

```
K shell for n = 1
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```
L shell for n = 2
```

- The atom is most stable in its ground state, most atoms are in their ground state at ambient conditions
 - An electron from higher shells will fill an inner-shell vacancy at lower energy, when that vacancy has been created by any sufficiently energetic process in the first place
- When it occurs in a muti-electron atom, radiation is emitted as an X ray photon.

```
• It has the energy E(x-ray) = E_u - E_{\ell}.
```



- Atomic number Z = number of protons in the nucleus (6 for carbon, 7 for nitrogen)
- Moseley found relationships between the frequencies of the characteristic x-ray and Z.

This holds for the K_{α} x-ray.

$$f_{\rm K_{\alpha}} = \frac{3cR}{4}(Z-1)^2$$

Why is b = 1? There are two electrons in the lowest orbit in all elements except H, one is left and shields the nucleolus if the other is removed



Figure 3.21 (a) A Bragg crystal x-ray spectrometer. The crystal is rotated about an axis through *P*. (b) The x-ray spectrum of a metal target consists of a broad, continuous spectrum plus a number of sharp lines, which are due to the characteristic x-rays. Those shown were obtained when 35-keV electrons bombarded a molybdenum target. Note that 1 pm = 10^{-12} m = 10^{-3} nm.



Figure 4-19 Moseley's plots of the square root of frequency versus Z for characteristic x rays. When an atom is bombarded by high-energy electrons, an inner atomic electron is sometimes knocked out, leaving a vacancy in the inner shell. The K-series x rays are produced by atomic transitions to vacancies in the n = 1 (K) shell, whereas the L series is produced by transitions to the vacancies in the n = 2 (L) shell. [From H. Moseley, Philosophical Magazine (6), 27, 713 (1914)

These curves can be fitted by the empirical equation

$$A^{1/2} = A_n(Z - b)$$
 4-34

where A_n and b are constants for each characteristic x-ray line. One family of lines, called the *K* series, has b = 1 and slightly different values of A_n for each line in the graph. The other family shown in Figure 4-19, called the *L* series, ¹⁷ could be fitted by Equation 4-34 with b = 7.4.

$$K_{\alpha}$$
 and K_{β} , slightly different A_{n}

Now with a generalization of Bohr's H-model, we have a "reasonable" theory of matter (atoms) that can to some extend explain this peculiar behavior !!

Moseley's Empirical Results

• The most intense K α X-ray is produced by transition from n = 2 to n = 1

$$\frac{1}{\lambda_{\rm K}} = R(Z-1)^2 \left(\frac{1}{1^2} - \frac{1}{n^2}\right) = R(Z-1)^2 \left(1 - \frac{1}{n^2}\right)$$

valid for whole K series, R is again Rydberg's constant, as this is a "modified Rydberg equation", which can be explained on the basis of the Bohr-shell-model of multi-electron atoms and the idea of shielding by a single remaining electron in the K shell

- Moseley's research clarified the importance of the electron shells for all the elements (except hydrogen which has only 1 electron) and beyond Mg (Z = 12) for practical reasons.
- For a vacancy in the K shell to be filled by an electron from the L shell (and assuming that two electrons can occupy the K shell at most), the electron that "jumps down" sees the nuclear charge reduced (shielded) by the 1 remaining electron



$$f^{1/2} = A_n(Z - b)$$

$$f = \frac{mk^2 e^4}{4\pi\hbar^3} (Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{n^2}\right) = cR_\infty (Z - 1)^2 \left(1 - \frac{1}{n^2}\right)$$

$$A_n^2 = cR_\infty \left(1 - \frac{1}{n^2}\right)$$

$$\lambda = \frac{c}{f} = \frac{c}{A_n^2 (Z - 1)^2} = \frac{1}{R_\infty (Z - 1)^2 \left(1 - \frac{1}{n^2}\right)}$$

Figure 4-18 A stylized picture of the Bohr circular orbits for n = 1, 2, 3, and 4. The radii $r_n \sim n^2$. In a high-Z element (elements with $Z \ge 12$ emit x rays), electrons are distributed over all the orbits shown. If an electron in the n = 1 orbit is knocked from the atom, e.g., by being hit by a fast electron accelerated by the voltage across an x-ray tube, the vacancy thus produced is filled by an electron of higher energy (i.e., n = 2 or higher). The difference in energy between the two orbits is emitted as a photon, according to the Bohr frequency condition, whose wavelength will be in the x-ray region of the spectrum if Z is large enough.

9 if generalized Bohr H model would work

 $f = cR_{\infty} \left(\frac{1}{2^2} - \frac{1}{n^2}\right) (Z - 7.4)^2 \quad \text{where } n = 3, 4, 5, \dots \quad \text{Empirically for } L\alpha \text{ series}$ 43 There are also other processes, emission of Auger electrons to reduce an exited atom's energy, again what we detect is quantized energy levels in bound systems, these spectra test the energy of the outermost electrons, so are sensitive to the valence in compounds, ultra clean surfaces, i.e. ultra high vacuum is required



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Summary		
ΤΟΡΙΟ	RELEVANT EQUATIONS AND REMARKS	
1. Atomic spectra	$\frac{1}{\lambda_{mn}} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \qquad n > m$	4-2
	This empirical equation computes the correct wavelengths of observed splines. The Rydberg constant R varies in a regular way from element to	ectral ment.
2. Rutherford scattering		
Impact parameter	$b = \frac{kq_{\alpha}Q}{m_{\alpha}v^2}\cot\frac{\theta}{2}$	4-3
Scattered fraction f	$f = \pi b^2 nt$	4-5
	for a scattering foil with n nuclei/unit volume and thickness t	
Number of scattered alphas observed	$\Delta N = \left(\frac{I_0 A_{\rm sc} nt}{r^2}\right) \left(\frac{kZe^2}{2E_k}\right)^2 \frac{1}{\sin^4 \frac{\theta}{2}}$	4-6
Size of nucleus	$R \approx R_0 A^{0.3333}$ with $R_0 = 1.2 \ 10^{-15}$ m and $A = Z + N$	4-11
3. Bohr model		
Bohr's postulates	 Electrons occupy only certain nonradiating, stable, circular orbits selection by quantization of the angular momentum L. 	ted
	$L = mvr = \frac{nh}{2\pi} = n\hbar$ for integer n	4-17

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Bohr's postulates	1. Electrons occupy only certain nonradiating, stable, circular orbits selected by quantization of the angular momentum <i>L</i> .				
	$L = mvr = \frac{nh}{2\pi} = n\hbar$ for integer n	4-17			
	2. Radiation of frequency f occurs when the electron jumps from an allow orbit of energy E_i to one of lower energy E_f f is given by the frequenc condition	wed y			
	$hf = E_i - E_f$	4-15			
Correspondence principle	In the region of very large quantum numbers classical and quantum calcumust yield the same results.	lations			
Bohr radius	$a_0 = \frac{\hbar^2}{mke^2} = \frac{\hbar}{mc\alpha} = 0.0529 \text{ nm}$	4-19			
Allowed energies	$E_n = -\frac{Z^2 E_0}{n^2}$ for $n = 1, 2, 3,$ also for He ⁺ . Li ⁺⁺	4-20			
	where $E_0 = mk^2 e^2/2\hbar^2 = 13.6 \text{ eV}$ Better to call it E ₁				
Reduced mass	$\mu = \frac{mM}{m+M}$	4-25			
Fine-structure constant	$\alpha = \frac{ke^2}{\hbar c} \approx 1/137$	4-30			
4. X-ray spectra	particularly important for K_{α}				
Moseley equation	$f^{1/2} = A_n(Z - b)$ lines, then b = 1	4-34			
5. Franck-Hertz experiment	Supported Bohr's theory by verifying the quantization of atomic energies in absorption.				

http://www.kokogiak.com/megapenny/fourteen.asp

A real quantum jump would be adding or taking away one penny from such a cube





Costs of Major U.S. Wars

Stephen Daggett Specialist in Defense Policy and Budgets

June 29, 2010

the "war on terror" has cost about \$1 trillion so far (2010), but as wars go that one accounts only for a few % of the annual GDP since 9/11

http://www.fas.or g/sgp/crs/natsec /RS22926.pdf

1,000,000,016,640, one trillion, sixteen thousand six hundred and forty Pennies [one cube measuring 273 x 273 x 273 feet]

http://www.kokogiak.com/megapenny/seventeen.asp

A real quantum jump would be adding or taking away one penny from such a cube



Sure "quantum jumps" in macroeconomic and "bankstering" are not based on the quantum jumps physicists, other natural scientists, and engineers are talking about

1,000,067,088,384,000, One quadrillion, sixty-seven billion, eighty-eight million, three hundred and eighty-four thousand Pennies, [One cube measuring 2,730 x 2,730 feet]



other cubic stacks of pennies, always remember what a quantum jump really is, Francis Scott Fitzgerald to Ernest Hemmingway: *"the rich are different from you and me".*