Rethinking Matter

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Professor David Kaiser, 5 October 2020
**“Old Quantum Theory”** (~ 1900 – 1924*)

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* dates are approximate! As we will see, physicists debated and revisited each of these topics over a span of years.
Atomic Structure

By the 1880s, matter seemed to be well understood: chemical elements consisting of physical atoms.

The mid-1890s, however, brought rapid changes. Aided by new instruments like cloud chambers, fluorescent screens, and photographic techniques, researchers identified several new types of radiation.
Things Fall Apart

1896: radioactivity

Pierre and Marie Curie in their Paris laboratory, early 1900s

1897: cathode rays

Laboratory (Cambridge University), ca. 1897

The new findings suggested that atoms can fall apart, and that they have internal structure. Hence they are not really “atoms”! (The ancient Greek word “atom” means “indivisible.”)

By 1900, researchers had identified at least three distinct types of new radiations. They had different properties — some were easily deflected by magnetic fields, others could ‘fog’ photographic plates — so researchers assigned them different names: $\alpha$, $\beta$, $\gamma$, ...

International sensation, then as now...

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Ernest Rutherford grew up in New Zealand and won a fellowship to study at Cambridge University. He studied under J. J. Thomson at the Cavendish laboratory in the 1890s, just as Thomson was conducting his cathode-ray experiments.

Rutherford became fascinated by radioactivity, and identified α rays in the decays of uranium. He also introduced the concept of a “half-life”: the time during which the radioactivity of a sample would fall by half.
Rutherford-Geiger ionization chamber, 1908
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A chamber is filled with an inert gas. When radiation enters, it will ionize atoms within the tube. Given the applied voltage, the ions will flow toward the anode, completing the circuit. Distinct “pulses” or counts can then be identified.

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Using a new ionization chamber (developed with Hans Geiger, now known as a “Geiger counter”), Rutherford determined in 1908 that α particles carry twice the electric charge (and have the opposite sign) compared to Thomson’s β particles.
Rutherford and his group at Manchester University (UK) quickly turned α particles into a tool to investigate atomic structure. Beginning in 1909, they directed α particles from a radon source toward a thin gold foil. They surrounded the foil with a fluorescent screen, which would flash when struck by an α particle. (Researchers needed to sit in a darkened room and let their eyes adjust, so they could count flashes.)

Most of the time, the α particles passed through with no deflection or only a small deflection $\theta$.

But on rare occasions — about 1 out of every $10^5$ events — the α particle would scatter by a large angle $\theta$. 
Rutherford and his group at Manchester University (UK) quickly turned $\alpha$ particles into a tool to investigate atomic structure. Beginning in 1909, they directed $\alpha$ particles from a radon source toward a thin gold foil. They surrounded the foil with a fluorescent screen, which would flash when struck by an $\alpha$ particle. (Researchers needed to sit in a darkened room and let their eyes adjust, so they could count flashes.)

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Rutherford Scattering

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\[ \text{Schematic of 1909-1911 Rutherford-Geiger scattering experiments.} \]

\[ \text{Rutherford: “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch artillery shell at a piece of tissue paper and it came back and hit you.”} \]
Rutherford (1911) argued that this scattering pattern only made sense if \textit{most of the atom’s mass} were concentrated in a dense “nucleus” in the center: the atom was \textit{mostly empty space}.

The nucleus (like the $\alpha$ particles) must have \textit{positive charge}, while the lightweight “electrons,” with \textit{negative charge} (identified as Thomson’s $\beta$ particles), circled around the nucleus.
By 1911, Rutherford had introduced a ‘solar system’ model of atomic structure. But this led to new questions:

Electrons would be constantly accelerated as they moved around the nucleus. According to Maxwell’s electromagnetic work, accelerated charges should radiate. Where is all that light?

Even more important: the electrons should lose energy as they radiated. So why didn’t electrons quickly crash into the nucleus? Why is matter stable at all?
Questions?
Bohr Model

*Niels Bohr* was a young Danish physicist, who was a postdoc in Rutherford’s group between 1911-1913. He was fascinated by the new Rutherford model of atomic structure, but also puzzled by the question of the stability of matter.

Bohr aimed to account for atomic structure from first principles, with a goal of accounting for all the elements of the periodic table.

He began by considering electrostatic repulsion and magnetic effects among electrons in *multi-electron atoms and molecules*, seeking equilibrium configurations. Perhaps such balanced configurations could account for why matter was stable.
Bohr Model

When that proved cumbersome, he turned to the simplest case of a hydrogen atom, with a single electron. Again for simplicity, he considered a circular orbit. By balancing the forces, he could solve for the electron’s velocity. In these expressions, both $v$ and $r$ were continuous variables.

Next he imposed a new “quantum condition,” that the electron’s orbital angular momentum could only take specific values. He was inspired by Planck and (especially) Einstein, who had emphasized discreteness at a scale set by Planck’s constant $\hbar$.

Now Bohr had two expressions for $v$; equating them, he could solve for $r$. The allowable radii for electron orbits were now discrete:

\[
r = \frac{n^2 \hbar^2}{me^2} = n^2 a_0
\]

“Bohr radius”: $a_0 \equiv \frac{\hbar^2}{me^2} = 5.3 \times 10^{-11}$ m
Again starting with classical expressions, Bohr next calculated the energy of an electron in such an orbit:

\[ E = \frac{1}{2}mv^2 - \frac{e^2}{r} \]

(substitute \( v^2 = \frac{e^2}{mr} \)):

\[ E = -\frac{1}{2} \frac{e^2}{r} \]

(substitute \( r = n^2 a_0 \)):

\[ E = -\frac{1}{2} \frac{e^2}{n^2 a_0} \]

(use definition of \( a_0 \)):

\[ E = -\frac{1}{2} \frac{me^4}{\hbar^2 n^2} \]
\[ \Delta E = E_2 - E_1 = \frac{1}{2} \frac{me^4}{\hbar^2} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (\text{for } n_2 > n_1) \]

Now Bohr got excited! Balmer spectrum from excited hydrogen atoms:

Bohr proposed: light would be emitted whenever an electron jumped from an “excited” orbit to a lower-energy orbit: \( \Delta E = h\nu \), or:

\[ \nu = R \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \text{Johann Balmer, 1885} \]
Bohr Model

Bohr was reluctant to publish his new ideas, because he had only treated hydrogen atoms; his goal had been to account for the stability and structure of all the atoms of the periodic table! Happily, Rutherford convinced Bohr to publish anyway (1913).

Central to Bohr’s explanation was the new “quantum condition” \( J = n\hbar \), which restricted electrons to discrete orbits \( r = n^2a_0 \); only for those choices of \( r \) would the atom remain stable. Bohr had neither derived nor explained the origin of his proposed “quantum condition,” but by using it he had been able to reproduce the Balmer spectrum for hydrogen.

The question still remained: why didn’t this discreteness appear in ordinary experience? Bohr worked out the “correspondence principle”: in the limit of large quantum numbers, \( n >> 1 \), quantum systems should reproduce classical behavior.
Bohr’s Correspondence Principle

According to Maxwell’s electrodynamics, $\nu_{\text{radiation}}$ should be equal to $\nu_{\text{mechanical}}$, the frequency of the mechanical motion of the moving charge:

$\nu_{\text{mechanical}} = \frac{1}{T} = \frac{v}{2\pi r}$

(use $v^2 = \frac{e^2}{mr}$): $\nu_{\text{mechanical}} = \frac{1}{2\pi} \frac{e}{\sqrt{mr^3}}$

According to Bohr’s atomic model, $\nu_{\text{radiation}}$ is given by the energy difference between discrete electron orbits:

$\nu_{\text{radiation}} = \frac{me^4}{4\pi\hbar^3} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$ (use definition of $a_0$)

(consider $n_2 = n_1 + \Delta n$, $\Delta n \ll n_1$):

$\nu_{\text{radiation}} = \frac{e^2}{2\hbar a_0} \frac{\Delta n}{n_1} \left( 1 + O[(\Delta n/n_1)^2] \right)$

$\nu_{\text{radiation}} = \left( \frac{e^2}{\hbar a_0} \frac{\Delta n}{n_1^3} \right) \left( \frac{2\pi\sqrt{m} r^{3/2}}{e} \right)$

$(\text{use } r = n_1^2 a_0 = \frac{n_1^2 \hbar^2}{me^2})$

$\frac{\nu_{\text{radiation}}}{\nu_{\text{mechanical}}} = \Delta n \rightarrow 1$

for transitions between neighboring states $n_1$ and $n_2 = n_1 + 1$, for $n_1 \gg 1$. 

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Bohr’s Correspondence Principle

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$$\frac{\nu_{\text{radiation}}}{\nu_{\text{mechanical}}} = \left( \frac{\frac{e^2}{\hbar a_0} \frac{\Delta n}{n_1^3}}{2\pi \sqrt{m} r^{3/2}} \right)$$

For large quantum numbers ($n >> 1$), quantum systems do behave like classical ones.

(Use definition of $a_0$): $\nu_{\text{radiation}} = \frac{e^2}{2\hbar a_0} \frac{1}{n_1^2} \left[ \frac{1}{n_2^2} - \frac{1}{n_1^2} \right]$

(Consider $n_2 = n_1 + \Delta n$, $\Delta n \ll n_1$): $\nu_{\text{radiation}} = \frac{e^2}{\hbar a_0} \frac{\Delta n}{n_1^3} \left( 1 + O\left[ (\Delta n/n_1)^2 \right] \right)$

for transitions between neighboring states $n_1$ and $n_2 = n_1 + 1$, for $n_1 >> 1$. 
The Bohr model further developed Rutherford’s model of atomic structure, and successfully accounted for the Balmer spectrum of hydrogen. But several questions remained:

- It only seemed to work for single-electron atoms (H, He⁺, Li⁺⁺).
- Why quantize angular momentum, \( J = n \hbar \)?
- What happened to electrons between stable orbits?
- What determined when an electron would “jump” between orbits?
- How did an electron “know” what energy \( h\nu \) to radiate as light, before landing at a different stable orbit?
- How to account for the relative intensities of spectral lines?
Questions?
de Broglie’s Hypothesis

In his 1924 Ph.D. dissertation, a French aristocrat, Louis de Broglie, offered a hypothesis to account for Bohr’s strange quantum condition, \( J = n\hbar \). He began with Einstein’s work on photons (which had recently been set on a more solid footing, given Arthur Compton’s X-ray scattering results):

\[
p = \frac{E}{c} = \frac{h\nu}{c}
\]

Then de Broglie simply asserted that the same relation should hold for matter:

\[
p = \frac{h}{\lambda}
\]

\[
\lambda = \frac{h}{mv}
\]

For a thrown baseball, \( \lambda_{\text{baseball}} \sim 10^{-32} \text{ m} \), totally unobservable on human scales. But \( \lambda_{\text{electron}} \sim 10^{-11} \text{ m} \sim a_0 \): for an electron, the “waviness” was on the same scale as the electron’s own orbit.

What if stable electron orbits arose from constructive interference of the corresponding waves?

\[
2\pi r = n\lambda
\]

\[
2\pi r = n \left( \frac{h}{mv} \right)
\]

\[
J = mvr = n\hbar
\]
In 1927, Clinton Davisson and Lester Germer, at Bell Labs, found electron scattering results consistent with the concept of de Broglie waves: the scattered intensity showed a distinctive interference pattern.
“Old Quantum Theory”

Between 1900 – 1924, physicists dramatically reassessed their assumptions about light and matter. In contrast with the great triumph of 19th century physics — the wave theory of light — several physicists began to explore discrete or particle-like attributes of light (blackbody radiation, Einstein’s light-quantum hypothesis, and Compton scattering). Meanwhile, de Broglie could only salvage Bohr’s new “quantum condition,” $J = nh$, by suggesting that matter had wave-like properties.

By the early 1920s, each of the successes of the emerging quantum theory seemed to follow a pattern: begin with classical expressions for force or energy, and then append some new, unexplained “quantum condition” ($E = h\nu$ or $J = nh$ or $\lambda = h/p$). Though many of these models could account for (otherwise puzzling) experimental results, it was not clear whether each new model for a given phenomenon was consistent with other (equally ad hoc) models.

Quantum theory seemed to many physicists to have become a disorganized grab-bag of heuristic guesses and disjointed models, united only by their invocation of Planck’s constant $h$ and some sort of conceptual break with 19th century physics.