Origins of Quantum Mechanics
- Dimensional analysis
- Line spectra of atoms
- Bohr’s atom
- Sommerfeld-Wilson quantization
- Wave-particle duality
- Heisenberg’s uncertainty principle
Seated (left to right): Erwin Schrödinger, Irène Joliot-Curie, Niels Bohr, Abram Ioffe, Marie Curie, Paul Langevin, Owen Willans Richardson, Lord Ernest Rutherford, Théophile de Donder, Maurice de Broglie, Louis de Broglie, Lise Meitner, James Chadwick.

So far in this class, we’ve learned these constants, in some sense parameters of the universe:

- $e$, the electron charge;
- $m_e$, the electron mass;
- $h$, Planck’s constant.

Can we derive a length scale from these units? Let’s say

$$l_{\text{natural}} = m_e^\alpha (e^2)^\beta h^\gamma.$$ 

Remember that $e^2$ has units

$$F \cdot l^2 = \frac{m l^3}{l^2}$$

and $h$ has units

$$h = E \cdot t = \frac{m l^2}{t}.$$

We can plug these in:

$$l_{\text{natural}} = m^\alpha \cdot (m l^3 t^{-2})^\beta \cdot (m l^2 t^{-1})^\gamma.$$

We want the units on the right to multiply out to $l$, so:

\begin{align*}
\alpha + \beta + \gamma &= 0 \quad (4.1) \\
3\beta + 2\gamma &= 1 \quad (4.2) \\
-2\beta - \gamma &= 0 \quad (4.3) \\
&= (4.4)
\end{align*}

Solving this (details omitted) gives us $(\alpha, \beta, \gamma) = (-1, -1, 2)$. Thus, the “natural” unit length derived from these constants is

$$l_{\text{natural}} = m_e^{-1} (e^2)^{-1} h^2 = \frac{h^2}{m_e e^2} = (2\pi)^2 \cdot 0.528\text{Å}.$$

It turns out that 0.528Å is the radius of a hydrogen atom. This isn’t a coincidence! We’ll see the constant...
Balmer-Rydberg-Ritz formula

When hydrogen in glass tube is excited by 5,000 V discharge
4 lines are observed in visible part of emission spectrum
- red @ 656.3 nm
- blue-green @ 486.1 nm
- blue violet @ 434.1 nm
- violet @ 410.2 nm

Explanation
Balmer’s empirical formula

\[ \lambda = 364.56 \frac{n^2}{(n^2 - 4)} \text{ nm} \quad n = 3, 4, 5, \ldots \]  \hspace{1cm} (1)

Generalized by Rydberg and Ritz
to accommodate newly discovered spectral lines in UV and IR

\[ \frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{for} \quad n_2 > n_1 \]  \hspace{1cm} (2)
is the magnitude of $E_n$ with $n = 1$. It is called the ground state. It is convenient to plot these allowed energies of the stationary states as in Figure 4-16. Such a plot is called an energy-level diagram. Various series of transitions between the stationary states are indicated in this diagram by vertical arrows drawn between the levels. The frequency of light emitted in one of these transitions is the energy difference divided by $h$ according to Bohr’s frequency condition, Equation 4-15. The energy required to remove the electron from the atom, 13.6 eV, is called the ionization energy, or binding energy, of the electron.

$E_n = -\frac{13.6}{n^2}$ eV,

Where $n$ is an integer. The dashed line shown for each series is the series limit, corresponding to the energy that would be radiated by an electron at rest far from the nucleus ($E_f$) for that series. The horizontal spacing between the transitions shown for each series is proportional to the wavelength spacing between the lines of the spectrum. (b) The spectral lines corresponding to the transitions shown for the three series. Notice the regularities within each series, particularly the short-wavelength limit and the successively smaller separation between adjacent lines as the limit is approached. The wavelength scale in the diagram is not linear.
Rydberg constant

- For hydrogen \( R_H = 1.096776 \times 10^7 \text{ m}^{-1} \)

- Balmer series of spectral lines in visible region correspond to \( n_1 = 2 \) and \( n_2 = 3, 4, 5, 6 \)

- Lines with \( n_1 = 1 \) in ultraviolet make up Lyman series

- Line with \( n_2 = 2 \) designated Lyman alpha has longest wavelength in this series: \( \lambda = 121.57 \text{ nm} \)

- For very heavy elements \( R_\infty = 1.097373 \times 10^7 \text{ m}^{-1} \)
Thomson’s atom

- Many attempts were made to construct atom model that yielded Balmer-Rydberg-Ritz formula.

- It was known that:
  - atom was about $10^{-10}$ m in diameter
  - it contained electrons much lighter than the atom
  - it was electrically neutral

- Thomson hypothesis: electrons embedded in fluid that contained most of atom mass and had enough positive charge to make atom electrically neutral.

- He then searched for configurations that were stable and had normal modes of vibration corresponding to known frequencies of spectral lines.

- One difficulty with all such models is that electrostatic forces alone cannot produce stable equilibrium.
Rutherford’s atom

Atom ⚛ positively-charged nucleus
around which much lighter negatively-charged electrons circulate
(much like planets in the Solar system)

Contradiction with classical electromagnetic theory
accelerating electron should radiate away its energy

Hydrogen atom should exist for no longer than $5 \times 10^{-11}$ s
Bohr’s atom

- Attraction between two opposite charges \( \mathbf{F} \) Coulomb’s law

\[
\mathbf{F} = \frac{e^2}{r^2} \hat{r} \quad \text{(Gaussian – cgs units)}
\]  

(3)

- Since Coulomb attraction is central force (dependent only on \( r \))

\[
|\mathbf{F}| = -\frac{dV(r)}{dr}
\]  

(4)

- For mutual potential energy of proton and electron

\[
V(r) = -\frac{e^2}{r}
\]  

(5)

- Bohr considered electron in circular orbit of radius \( r \) around proton

- To remain in this orbit \( \Rightarrow \) electron needs centripetal acceleration

\[
a = \frac{v^2}{r}
\]  

(6)
Bohr’s atom (cont’d)

- Using (4) and (6) in Newton’s second law

\[ \frac{e^2}{r^2} = \frac{m_e v^2}{r} \]  

(7)

- Assume \( m_p \) is infinite so that proton’s position remains fixed
  (actually \( m_p \approx 1836m_e \))

- Energy of hydrogen atom is sum of kinetic and potential energies

\[ E = K + V = \frac{1}{2} m_e v^2 - \frac{e^2}{r} \]  

(8)

- Using (7)

\[ K = -\frac{1}{2} V \quad \text{and} \quad E = \frac{1}{2} V = -K \]  

(9)

- Energy of bound atom is negative
  since it is lower than energy of separated electron and proton
  which is taken to be zero
Bohr’s atom (cont’d)

- For further progress, restriction on values of \( r \) or \( v \)
- Angular momentum \( \vec{L} = \vec{r} \times \vec{p} \)
- Since \( \vec{p} \) is perpendicular to \( \vec{r} \), \( L = rp = mevr \)
- Using (9), \( r = \frac{L^2}{me^2} \)
Bohr’s atom

Bohr’s quantization

- Introduce angular momentum quantization
  
  \[ L = n\hbar \quad \text{with} \quad n = 1, 2, \cdots \]  
  (10)

  excluding \( n = 0 \) electron would then not be in circular orbit

- Allowed orbital radii
  
  \[ r_n = n^2 a_0 \]

  (Bohr radius \( a_0 \equiv \frac{\hbar^2}{m_e e^2} = 5.29 \times 10^{-11} \text{ m} \approx 0.529 \text{ Å} \))

- Corresponding energy
  
  \[ E_n = -\frac{e^2}{2a_0 n^2} = -\frac{m_e e^4}{2\hbar^2 n^2}, \quad n = 1, 2 \cdots \]

- Balmer-Rydberg-Ritz formula
  
  \[
  \frac{hc}{\lambda} = E_{n_2} - E_{n_1} = \frac{2\pi^2 m_e e^4}{\hbar^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)
  \]  
  (11)

\[
\mathcal{R} = \frac{2\pi m_e e^4}{\hbar^3 c} \approx 1.09737 \times 10^7 \text{ m}^{-1}
\]

- Slight discrepancy with experimental value for hydrogen
  due to finite proton mass
Figure 3: Emission Spectrum of Hydrogen. Image Source: Wikipedia.

4.5 Wilson-Sommerfield Quantization

4.5.1 Quantize All the Things!

So far we've discussed two kinds of quantization:

- Quantization of EM energy for a harmonic oscillator into lumps $h \Delta \ell$ led to understanding of blackbody radiation;
- Quantization of angular momentum $L$ led to the Bohr atom.

The natural question arising from this is: what else can we quantize?

Wilson and Sommerfield proposed a general rule: if we integrate variables with respect to their conjugate variables in a closed action, we get a multiple of $\hbar$:

$$I_p \cdot dq = n\hbar,$$

if $p, q$ are conjugate, and the integral is over one cycle.

4.5.2 Case Study: Position and Momentum

Position $x$ and momentum $p_x$ are conjugate. Consider a harmonic oscillator, oscillating in the $x$ direction. The potential energy of this oscillator is quadratic in $x$.

Let's say the oscillator has energy $E$ and amplitude $x_{\text{max}}$. Then

$$E = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 = \frac{1}{2}kx_{\text{max}}^2.$$
Hydrogen-like ions systems

- Generalization for single electron orbiting nucleus
  
  \((Z = 1 \text{ for hydrogen}, \ Z = 2 \text{ for He}^+, \ Z = 3 \text{ for Li}^{++})\)

- Coulomb potential generalizes to

  \[ V(r) = -\frac{Ze^2}{r} \]  
  \( (12) \)

- Radius of orbit becomes

  \[ r_n = \frac{n^2a_0}{Z} \]  
  \( (13) \)

- Energy becomes

  \[ E_n = -\frac{Z^2e^2}{2a_0n^2} \]  
  \( (14) \)
Quantize all the things!

- So far we’ve discussed two kinds of quantization:
  - Quantization of EM energy for a harmonic oscillator into lumps $h$ led to understanding of blackbody radiation
  - Quantization of angular momentum $L$ led to the Bohr atom

- The natural question arising from this is: what else can we quantize?

- Wilson and Sommerfeld proposed general rule:
  If we integrate variables with respect to their conjugate variables in a closed action $\oint p\,dq = nh$

\[ \oint p\,dq = nh \]

if $p, q$ are conjugate and the integral is over one cycle
Generalized Bohr’s formula for allowed elliptical orbits

\[ \oint p \, dr = n\hbar \quad \text{with} \quad n = 1, 2, \ldots \]

Applying rule to conjugate variables \( L, \theta \) gives us:

\[ \oint L \cdot d\theta = 2\pi L = n\hbar = \frac{n\hbar}{2\pi} = n\hbar \]
de Broglie wavelength

- In view of particle properties for light waves – photons – de Broglie ventured to consider reverse phenomenon
- Assign wave properties to matter:
  To every particle with mass $m$ and momentum $\vec{p}$ associate
  \[
  \lambda = \frac{h}{|\vec{p}|} \quad (16)
  \]
- Assignment of energy and momentum to matter in (reversed) analogy to photons
  \[
  E = \hbar\omega \quad \text{and} \quad |\vec{p}| = \hbar|\vec{k}| = \frac{h}{\lambda} \quad (17)
  \]
Light waves \( \rightarrow \) Young’s double slit experiment

- Monochromatic light from a single concentrated source illuminates a barrier containing two small openings
- Light emerging from two slits is projected onto distant screen
- Distinctly \( \rightarrow \) we observe light deviates from straight-line path and enters region that would otherwise be shadowed
\[ d \ll L \land \lambda \ll d \Rightarrow \theta \approx \sin \theta \approx \tan \theta \Rightarrow \delta / d \approx y / L \]
Interference

- Bright fringes measured from $O$ are

$$y_{\text{bright}} = \frac{\lambda L}{d} m$$

$m = 0, \pm 1, \pm 2, \cdots$ (18)

$m$ is order number
when $\delta = m\lambda$ constructive interference

- Dark fringes measured from $O$ are

$$y_{\text{dark}} = \frac{\lambda L}{d} (m + \frac{1}{2})$$

$m = 0, \pm 1, \pm 2, \cdots$ (19)

when $\delta$ is odd multiple of $\lambda/2$ two waves arriving at point $P$ are out of phase by $\pi$ and give rise to destructive interference
Parallel beam of neutrons falls on double-slit

- Neutron detector capable of detecting individual neutrons
- Detector registers discrete particles localized in space and time
- This can be achieved if the neutron source is weak enough

- neutron kinetic energy $2.4 \times 10^{-4}$ eV
- de Broglie wavelength $1.85$ nm
- center-to-center distance between two slits $d = 126 \mu$m
Estimating spacing \((y_{n+1} - y_n) \approx 75 \mu m\)

\[
\lambda = \frac{d (y_{n+1} - y_n)}{D} = 1.89 \text{ nm}
\]
Heisenberg’s Uncertainty Principle

\[ \Delta x \Delta p \geq \frac{\hbar}{4\pi} = \frac{\hbar}{2} \]

The more accurately you know the position (i.e., the smaller \( \Delta x \) is), the less accurately you know the momentum (i.e., the larger \( \Delta p \) is); and vice versa.
Heisenberg realised that ...

- In the world of very small particles, one cannot measure any property of a particle without interacting with it in some way.

- This introduces an unavoidable uncertainty into the result.

- One can never measure all the properties exactly.
Measuring Position and Momentum of an Electron

- Shine light on electron and detect reflected light using a microscope

- Minimum uncertainty in position is given by the wavelength of the light

- So to determine the position accurately, it is necessary to use light with a short wavelength
Measuring Position and Momentum of an Electron

- By Planck’s law $E = \frac{hc}{\lambda}$, a photon with a short wavelength has a large energy.
- Thus, it would impart a large ‘kick’ to the electron.
- But to determine its momentum accurately, electron must only be given a small kick.
- This means using light of long wavelength.
Light Microscopes

- Suppose the positions and speeds of all particles in the universe are measured to sufficient accuracy at a particular instant in time.
- It is possible to predict the motions of every particle at any time in the future (or in the past for that matter).

“The intelligent being knowing, at a given instant of time, all forces acting in nature, as well as the momentary positions of all things of which the universe consists, would be able to comprehend the motions of the largest bodies of the world and those of the smallest atoms in one single formula, provided it were sufficiently powerful to subject all the data to analysis; to it, nothing would be uncertain, both future and past would be present before its eyes.”

Pierre Simon Laplace
θ₁ \angle angle between central maximum and first minimum
- for \( m = 1 \angle \sin \theta_1 = \lambda / d 
- neutron striking screen at outer edge of central maximum
  must have component of momentum \( p_y \) as well as a component \( p_x \)
- from the geometry \angle components are related by \( p_y / p_x = \tan \theta_1 \)
- use approximation \( \tan \theta_1 = \theta_1 \) and \( p_y = p_x \theta_1 \)
Heisenberg’s uncertainty principle

- All in all
  \[ p_y = p_x \frac{\lambda}{d} \quad (21) \]

- Neutrons striking detector within central maximum
  i.e. angles between \((-\lambda/d, +\lambda/d)\)
  have \(y\)-momentum-component spread over \((-p_x \lambda/d, +p_x \lambda/d)\)

- Symmetry of interference pattern shows \(\langle p_y \rangle = 0\)

- There will be an **uncertainty** \(\Delta p_y\) at least as great as \(p_x \lambda/d\)

  \[ \Delta p_y \geq p_x \frac{\lambda}{d} \quad (22) \]

- The narrower the separation between slits \(d\)
  the broader is the interference pattern
  and the greater is the uncertainty in \(p_y\)

- Using de Broglie relation \(\lambda = h/p_x\) and simplifying

  \[ \Delta p_y \geq p_x \frac{h}{p_x d} = \frac{h}{d} \quad (23) \]
Heisenberg’s uncertainty principle (cont’d)

What does this all mean?

- $d \equiv \Delta y$ represents uncertainty in $y$-component of neutron position as it passes through the double-slit gap. (We don’t know where in gap each neutron passes through)

- Both $y$-position and $y$-momentum-component have uncertainties related by
  \[
  \Delta p_y \Delta y \geq h \quad (24)
  \]

- We reduce $\Delta p_y$ only by reducing width of interference pattern. To do this increase $d$ which increases position uncertainty $\Delta y$

- Conversely, we decrease position uncertainty by narrowing double-slit gap. Interference pattern broadens and corresponding momentum uncertainty increases.
Bibliography