Fundamental Quantum Theory

Atomic Theory

Contrast

- Atoms (ατοµος) are indivisible and immutable.

- Size and shape (and weight) of atoms determines properties of chemicals, materials, etc.

20th century understanding of the structure of the atom (protons, neutrons, electrons):
Electrons interact with nuclei and each other. The rules for these interactions are conceptually simple, but:

- it is mathematically very difficult to model these interactions, and
- the physical behavior that results can be counterintuitive.

If we understand electrons, we understand chemistry.

The time-dependent Schrödinger equation:

\[-\frac{\hbar^2}{2m} \nabla^2 \psi(r, t) + V(r) \psi(r, t) = i\hbar \frac{\partial \psi(r, t)}{\partial t}\]
Atomic Spectra

Atomic spectra consist of a small (or potentially large) number of sharp, discrete lines, observed in emission or absorption:

What types of physics result in discretization?

Atomic spectrum of hydrogen

There are lines at 656 nm, 486 nm, 434 nm, 410 nm, 397 nm, and 389 nm, \ldots 365 nm. Balmer equation:

\[ \nu = \text{constant} \times \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \]

with \( n = 3, 4, 5, \ldots \)
Rydberg equation:

\[ \frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

For the ultraviolet \( n_1 = 1 \) and \( n_2 = 2, 3, 4, \ldots \), and for the IR, \( n_1 = 3 \) and \( n_2 = 4, 5, 6, \ldots \).

The hydrogen atom must have wavelike properties that result in the enumerability of lines in the atomic spectrum.

**Waves and Particles**

Double-slit experiment with particles (very simple behavior):
Major difference between particles and waves is *interference*:

Very broadly speaking, a free electron usually behaves in a more particle-like fashion, while an electron confined—to pass through a slit, bounce of a surface, move closely around a nucleus—behaves in a much more wavelike way.

**Wave Equations**

Classical wave equation for a plucked, uniformly tensioned string:
\[ F = T \left( \frac{\partial y}{\partial x}\bigg|_{x+dx} - \frac{\partial y}{\partial x}\bigg|_x \right) \]

or

\[ F = T \frac{\partial^2 y}{\partial x^2} \, dx \]

Using Newton’s second law:

\[ F = ma \]

gives us

\[ F = ma \]

\[ F = \lambda dxdx \]

\[ T \frac{\partial^2 y}{\partial x^2} = \lambda dx \frac{\partial^2 y}{\partial t^2} \]

\[ T \frac{\partial^2 y}{\partial x^2} = \lambda \frac{\partial^2 y}{\partial t^2} \]

Standing modes:

as well as more complex behavior:

Characteristic of all wave equations is the relationship between the shape of the wave and its change in time: the proportionality of an \( x \) derivative to a \( t \) derivative.
The Schrödinger Wave Equation

The Schrödinger Wave Equation:

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t}\]

with

\[h = 6.626 \times 10^{-34} \text{ J s}\]

and

\[\hbar = \frac{h}{2\pi}\]

also, \(i\) is the root of \(-1:\)

\[i = \sqrt{-1}\]

Finally, \(\psi(x, t)\) is the wavefunction.

Again, curvature is related to rate of change (characteristic of all wave equations).

Classically, + and − signs, while they may have physical meaning for waves (peaks and troughs), are also a way to keep track of interference.
In quantum mechanics, the signs and the $i$s have no meaning in and of themselves, but they are critical for explaining quantum interference.