1 Lecture 1: The beginnings of quantum physics

1. The Stern-Gerlach experiment
2. Atomic clocks
3. Planck (1900), blackbody radiation, and $E = \hbar\omega$
4. Photoelectric effect
5. Electron diffraction through crystals, de Broglie (1924), and $p = \hbar k$
6. The Bohr atom

2 Lecture 2: The Bohr atom (1913) and the Schrödinger equation (1925)

2.1 The Bohr atom

The Bohr atom assumes the usual electrostatic attraction between an electron and a proton,

$$\mathbf{F} = -\frac{ke^2}{r^2}\hat{\mathbf{r}}$$

Then, for an electron in a circular orbit,

$$\mathbf{a} = -\frac{v^2}{r}\hat{\mathbf{r}}$$

To these classical elements, Bohr added a quantization rule: the angular momentum must be a multiple of Planck's reduced constant,

$$L = mvr = n\hbar$$

Combining the classical elements, we have a relationship between the radius and velocity of circular orbits,

$$\frac{ke^2}{r^2} = \frac{mv^2}{r}$$

Solving for the velocity, we have

$$v = \sqrt{\frac{ke^2}{mr}}$$

Then according to the Bohr quantization rule,

$$\begin{aligned} n\hbar &= mvr \\ &= \sqrt{mrke^2} \end{aligned}$$

or, solving for r,

$$r_n = \frac{n^2\hbar^2}{mke^2}$$

The total energy of the electron is

$$\begin{aligned} E &= \frac{1}{2}mv^2 - \frac{ke^2}{r} \\ &= -\frac{ke^2}{2r} \\ &= -\frac{mk^2e^4}{2n^2\hbar^2} \\ &= -\frac{13.6eV}{n^2} \end{aligned}$$

This means that the energy of an electron that moves between two orbits will change by

$$\begin{aligned} E &= \frac{1}{2}mv^2 - \frac{ke^2}{r} \\ &= -\frac{ke^2}{2r} \\ &= -\frac{mk^2e^4}{2n^2\hbar^2} \\ \Delta E &= -13.6\left(\frac{1}{n^2} - \frac{1}{m^2}\right) eV \end{aligned}$$

If this energy is given off in the form of a photon satisfying the Planck relation, then the frequency of the emitted light will be

$$\omega = \frac{\Delta E}{\hbar}$$

A formula of this form had already been determined experimentally, and was now explained by the Bohr model.

2.2 The Schrödinger equation

The Bohr model restricts the electron to circular motion in a plane, and gives incorrect values of total angular momentum for the electrons. A fuller picture was required, and is provided by writing a 3-dimensional wave equation for the electron.

We may use the deBroglie wavelength and the Planck relation, together with the relativistic relationship between energy and momentum, to derive a suitable equation. We have:

$$\begin{aligned} E &= \hbar\omega \\ \mathbf{p} &= \hbar\mathbf{k} \end{aligned}$$

The 4-momentum of a particle is given by

$$\begin{aligned} p^\alpha &= mu^\alpha \\ &= m\gamma\left(c, \mathbf{v}\right) \\ &= \left(\frac{E}{c}, \mathbf{p}\right) \end{aligned}$$

and the norm of this equation is

$$\begin{aligned} \eta_{\alpha\beta}p^\alpha p^\beta &= p^\alpha p_\alpha \\ &= -\left(p^0\right)^2 + \mathbf{p}^2 \\ &= -\frac{E^2}{c^2} + \mathbf{p}^2 \end{aligned}$$

On the other hand, we have

$$\begin{aligned} \eta_{\alpha\beta}p^\alpha p^\beta &= m^2 u^\alpha u_\alpha \\ &= -m^2c^2 \end{aligned}$$

Equating these,

$$\begin{aligned} -\frac{E^2}{c^2} + \mathbf{p}^2 &= -m^2c^2 \\ E^2 &= \mathbf{p}^2c^2 + m^2c^4 \end{aligned}$$

Now suppose the electron is described by a plane wave,

$$\psi = Ae^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}$$

Then we may recover the wave number and frequency by differentiation,

$$\begin{aligned} \boldsymbol{\nabla}^2\psi &= \boldsymbol{\nabla}^2\left[Ae^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}\right] \\ &= -\mathbf{k}^2\psi \\ \frac{\partial^2}{\partial t^2}\psi &= \frac{\partial^2}{\partial t^2}\left[Ae^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}\right] \\ &= -\omega^2\psi \end{aligned}$$

Multiplying each derivative by $i\hbar$, we have the energy and momentum,

$$\begin{aligned} (i\hbar\boldsymbol{\nabla})^2\psi &= \hbar^2\mathbf{k}^2\psi \\ &= \mathbf{p}^2\psi \\ \left(i\hbar\frac{\partial}{\partial t}\right)^2\psi &= \hbar^2\omega^2\psi \\ &= E^2\psi \end{aligned}$$

Substituting these operators,

$$\begin{aligned} p_\alpha = \left(-\frac{E}{c}, \mathbf{p}\right) &= -i\hbar\left(\frac{1}{c}\frac{\partial}{\partial t}, \boldsymbol{\nabla}\right) \\ &= -i\hbar\frac{\partial}{\partial x^\alpha} \end{aligned}$$

into the energy-momentum relation,

$$\begin{aligned} E^2 &= \mathbf{p}^2c^2 + m^2c^4 \\ \left(i\hbar\frac{\partial}{\partial t}\right)^2 &= (i\hbar\boldsymbol{\nabla})^2c^2 + m^2c^4 \end{aligned}$$

and allowing this operator relationship to act on a "wave function", ψ,

$$\begin{aligned} -\hbar^2\frac{\partial^2\psi}{\partial t^2} &= -\hbar^2c^2\boldsymbol{\nabla}^2\psi + m^2c^4\psi \\ -\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} + \boldsymbol{\nabla}^2\psi &= \frac{m^2c^2}{\hbar^2}\psi \end{aligned}$$

The differential operator

$$\begin{aligned} \Box &\equiv -\frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \boldsymbol{\nabla}^2 \\ &= \eta^{\alpha\beta}\frac{\partial}{\partial x^\alpha}\frac{\partial}{\partial x^\beta} \end{aligned}$$

is the spacetime generalization of the Laplacian, $\nabla^2 = \delta^{ij}\frac{\partial}{\partial x^i}\frac{\partial}{\partial x^j}$. The time dependence makes it a wave operator, but because of the Planck and deBroglie relationships, it also describes particle-like energy and momentum. Indeed, the plane-wave solutions may be written as

$$\psi = Ae^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{x}-Et)}$$

The wave equation we have written,

$$\Box\psi = \frac{m^2c^2}{\hbar^2}\psi$$

is called the Klein-Gordon equation. It first appears in Schrödinger's notes in 1925 before being published the next year first by Oskar Klein and Walter Gordon, but also the same year by Vladimir Fock, Johann Kudar, Théophile de Donder and Frans-H. van den Dungen, and Louis de Broglie. It is the obvious relativistic generalization of the Schrödinger equation but fails to describe electron spin. Additionally, because the equation is second order in time derivatives, it requires both initial position and velocity specifications, and this is forbidden by the uncertainty principle. Finally, the equation leads to negative probability states.

In 1925, Schrödinger took a different approach. The problems arising from the second order time derivatives may be avoided by first solving for the energy, then taking a non-relativistic approximation. We may then also add a potential to the energy

$$\begin{aligned} E &= \sqrt{\mathbf{p}^2c^2 + m^2c^4} + V \\ &= mc^2\sqrt{1 + \frac{\mathbf{p}^2}{m^2c^2}} + V \end{aligned}$$

For $v \ll c$ we may expand $\sqrt{1 + \frac{\mathbf{p}^2}{m^2c^2}}$ in a Taylor series,

$$\begin{aligned} \sqrt{1 + \frac{\mathbf{p}^2}{m^2c^2}} &= 1 + \frac{\mathbf{p}^2}{2m^2c^2} + \cdots \\ &\approx 1 + \frac{\mathbf{p}^2}{2m^2c^2} \end{aligned}$$

so the non-relativistic version is

$$E = mc^2\left(1 + \frac{\mathbf{p}^2}{2m^2c^2}\right) + V$$

Making the same operator substitutions that led us to the Klein-Gordon equation, and allowing it to operate on a function, ϕ, gives

$$i\hbar\frac{\partial\phi}{\partial t} = mc^2\phi - \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\phi + V\phi$$

The constant mass term may be removed by the replacement

$$\phi = \psi e^{-\frac{i}{\hbar}mc^2t}$$

Then we find

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\left(\psi e^{-\frac{i}{\hbar}mc^2t}\right) &= mc^2\psi e^{-\frac{i}{\hbar}mc^2t} - \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\left(\psi e^{-\frac{i}{\hbar}mc^2t}\right) + V\psi e^{-\frac{i}{\hbar}mc^2t} \\ i\hbar\left(\frac{\partial\psi}{\partial t}e^{-\frac{i}{\hbar}mc^2t} - \frac{i}{\hbar}mc^2\psi e^{-\frac{i}{\hbar}mc^2t}\right) &= \left(mc^2\psi - \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi + V\psi\right)e^{-\frac{i}{\hbar}mc^2t} \end{aligned}$$

resulting in the familiar form of the Schrödinger equation,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\psi + V\psi$$

2.3 The Pauli equation

Although this equation also fails to describe the electron spin, Pauli generalized the Schrödinger equation in 1927. The resulting Pauli equation applies to a 2-component *spinor* and, when the potential for the electromagnetic field is included using the Pauli matrices, allows for the correct description of non-relativistic spin, including the Stern-Gerlach results. If we let

$$\Psi = \begin{pmatrix} \psi_1(\mathbf{x},t) \\ \psi_2(\mathbf{x},t) \end{pmatrix}$$

and $(\varphi, \mathbf{A})$ be the scalar and vector potentials of electrodynamics, then the Pauli equation is

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left[\boldsymbol{\sigma}\cdot(i\hbar\boldsymbol{\nabla} - e\mathbf{A})\right]^2\Psi + e\varphi\Psi$$

for a spin-$\frac{1}{2}$ particle with charge e. Here, the Pauli matrices are given by

$$\begin{aligned} \boldsymbol{\sigma} &= (\sigma_x, \sigma_y, \sigma_z) \\ &= \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right) \end{aligned}$$

and the quantity $\left[\boldsymbol{\sigma}\cdot(i\hbar\boldsymbol{\nabla} - e\mathbf{A})\right]^2$ works out as

$$\begin{aligned} \left[\boldsymbol{\sigma}\cdot(i\hbar\boldsymbol{\nabla} - e\mathbf{A})\right]^2 &= \left(i\hbar\sigma_i\frac{\partial}{\partial x^i} - e\sigma_i A_i\right)^2 \\ &= \left(i\hbar\sigma_i\frac{\partial}{\partial x^i} - e\sigma_i A_i\right)\left(i\hbar\sigma_j\frac{\partial}{\partial x^j} - e\sigma_j A_j\right) \\ &= -\hbar^2\sigma_j\sigma_i\frac{\partial^2}{\partial x^i\partial x^j} - i\hbar\sigma_i\frac{\partial}{\partial x^i}e\sigma_j A_j - i\hbar e\sigma_i\sigma_j A_i\frac{\partial}{\partial x^j} + e^2\sigma_i\sigma_j A_i A_j \end{aligned}$$

From the exercises we know that

$$\sigma_j\sigma_i = \delta_{ij}1 + i\varepsilon_{jik}\sigma_k$$

Then, because $\varepsilon_{jik} = -\varepsilon_{ijk}$ while both $\frac{\partial^2}{\partial x^i\partial x^j} = \frac{\partial^2}{\partial x^j\partial x^i}$ and $A_iA_j = A_jA_i$ are symmetric, we have (remembering that the derivatives must also act on a function),

$$\begin{aligned} \left[\boldsymbol{\sigma}\cdot(i\hbar\boldsymbol{\nabla} - e\mathbf{A})\right]^2\Phi &= -\hbar^2\sigma_j\sigma_i\frac{\partial^2\Phi}{\partial x^i\partial x^j} - i\hbar\sigma_i\frac{\partial}{\partial x^i}\left(e\sigma_j A_j\Phi\right) - i\hbar e\sigma_i\sigma_j A_i\frac{\partial\Phi}{\partial x^j} + e^2\sigma_i\sigma_j A_i A_j\Phi \\ &= -\hbar^2\nabla^2 - i\hbar e\sigma_i\sigma_j\left(\frac{\partial A_j}{\partial x^i}\Phi + A_j\frac{\partial\Phi}{\partial x^i}\right) - i\hbar e\sigma_i\sigma_j A_i\frac{\partial\Phi}{\partial x^j} + e^2\mathbf{A}^2\Phi \\ &= -\hbar^2\nabla^2\Phi - i\hbar e\left(\delta_{ij}1 + i\varepsilon_{ijk}\sigma_k\right)\left(\frac{\partial A_j}{\partial x^i}\Phi + A_j\frac{\partial\Phi}{\partial x^i}\right) - i\hbar e\left(\delta_{ij}1 + i\varepsilon_{ijk}\sigma_k\right)A_i\frac{\partial\Phi}{\partial x^j} + e^2\mathbf{A}^2\Phi \\ &= -\hbar^2\nabla^2\Phi - i\hbar e\left(\left(\nabla\cdot\mathbf{A}\right)\Phi + \mathbf{A}\cdot\nabla\Phi\right) \\ &\quad + e\hbar\sigma_k\left(\left(\boldsymbol{\nabla}\times\mathbf{A}\right)\Phi + \left(\mathbf{A}\times\boldsymbol{\nabla}\Phi\right)\right) - i\hbar e\mathbf{A}\cdot\boldsymbol{\nabla}\Phi + e\hbar\left(\mathbf{A}\times\boldsymbol{\nabla}\Phi\right)\cdot\boldsymbol{\sigma} + e^2\mathbf{A}^2\Phi \\ &= -\hbar^2\nabla^2\Phi + e\hbar\mathbf{B}\cdot\boldsymbol{\sigma}\Phi - i\hbar e\left(\nabla\cdot\mathbf{A}\right)\Phi \\ &\quad - 2i\hbar e\mathbf{A}\cdot\boldsymbol{\nabla}\Phi + 2e\hbar\left(\mathbf{A}\times\boldsymbol{\nabla}\Phi\right)\cdot\boldsymbol{\sigma} + e^2\mathbf{A}^2\Phi \end{aligned}$$