

§10. A PREVIEW OF QUANTUM MECHANICS

At the end of the 19th century, theories of matter and energy based on the classical concept of continuity were being replaced by theories based on discontinuities. These theories were being put forth in several fields of science including: physics, biology and geology.

In the field of physics, this transitions to discontinuity can be seen in the writings of Helmholtz and his comments on Faraday's Law of Electrodynamics:

Now the most startling result of Faraday's Laws is perhaps this: if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into elementary portions which behave like atoms of electricity.

Although it would be a great leap to conclude that Helmholtz foresaw the quantum nature of the electric charge — the electron — the concept of an *indivisible* unit of mater has been part of physics since Newton.

The theories of physics put forth at the end of the 19th century did not however provide a uniform and constant picture of nature. Although the common *popular science* impression is that scientist believed that a combination of thermodynamics, electromagnetism and classical mechanics could account for the known physical phenomena — such was not the case. Clausius, Maxwell and Boltzman presented an ambiguous description of the kinetic theory of gases. The theories of the structure of matter and atoms cam under attack for several reasons. Both technical and philosophical changes were taking place. Movement away from mechanistic models of the atom toward an empirical or phenomenological theories were lead by Boltzman and his statistical theory of thermodynamics.

§10.1. DOMINATION OF MODERN QUANTUM MECHANICS

Modern physics is dominated by Quantum Mechanics and the application of Quantum Field Theory. The majority of the experimental activities take place in the fields of High Energy Physics (HEP) and related fields. The research funding and the academic programs are focused on the frontiers of size and energy. However, in the beginning of the 20th century the physical world was described by the laws of classical (or Newtonian) mechanics — the physics of every day life. Experiments

were conducted in which the results could be comprehended on a human scale, in size, energy and funding.

Before proceeding with a more detailed description of quantum mechanics and its origins, the physical aspects the quantum theory needs some explanation. At the macroscopic scale of matter there are two broad types of classical physics: *Waves* and *Particles*. Particles are considered localized phenomena which transport mass and energy as they move. Waves are de-localized phenomena which carry energy, but not mass, as they move [Auya95], [Kim91].

In quantum mechanics the distinction between particles and waves is less clear. Particles can exhibit wave-like behavior and waves can exhibit particle-like behavior. It is important to understand the *-likeness* aspects of these behavior's. Whether an *object* is a particle or a wave can not be clearly defined — only its behavior in the presence of some measuring device or interaction with other objects can be described. The blurring of the distinction between particle and wave causes serious problems when a *visualization* of the behavior is desired. Electrons can create wave-like diffraction patterns, while the electromagnetic radiation of light can interact with matter in a particle-like manner.

At the turn of the century the axioms of Newtonian physics provided a description of the dynamics of point masses — planetary motion, the motion of rigid bodies, the elastic properties of solids, hydrodynamics and acoustics [Schw92]. In classical mechanics the position and momentum of a particle can be *measured* with arbitrary accuracy. With the additional of Maxwell's electrodynamics, classical physics was nearly complete.

Specific quantum phenomena began to be discovered which challenged to classical theories. In chronological order, these *major* phenomena are: blackbody radiation (1900), the photoelectric effect (1905), line spectra of hydrogen (1913), the Compton effect (1923), the diffraction of particle beams (1927), the Ramsauer effect (1927) and the tunnel effect (1928) [Spey94].^[1] As each of these phenomena was explored further,

¹ Each of these effects and the experiments that confirmed them has been performed numerous times and have become the *stock in trade* of University physics. The following is a brief summary of each *selected* effect:

- (1) Blackbody radiation — is described in more details in §10.2.1. This quantum effect occurs when the intensity of electromagnetic radiation is plotted as a function of frequency. The plot does not adhere to the principals of thermodynamics. As shorter wavelengths are examined, the predicted spectral intensity should increase without limit. The thermodynamic equation

$I = (8\pi kT)/\lambda^4$ (the Rayleigh–Jeans equation) fails to predict the measured results.. Max Planck *solved* the problem with the equation $I = (8\pi ch)/(\lambda^5 (e^{ch/\lambda kT} - 1))$. The result is the radiated energy is quantized — see §10.21. for further details.

- (2) Photoelectric Effect — after Planck’s equation was accepted by the community, Albert Einstein publishes a paper describing the photoelectric effect. When weak *red* light is shone onto a surface of cesium, electrons are emitted. The brighter the light the more electrons are emitted. These electrons travel at a velocity *slower* than normal electrons. If a *blue* light (shorter wavelength) is used, electrons are emitted from the cesium surface — but they are traveling at a higher velocity. The brighter the blue light, the more electrons are emitted at this higher velocity. If a very long wave length light is used (infrared) no electrons are emitted no matter what the intensity. The classical description of this effect states that the incident light would be absorbed over the entire surface of the cesium and require some amount of time to raise the energy level of *all* the cesium atoms in order to cause electrons to be emitted — contrary to the observed results. By using Planck’s theory that the emitted energy of a black body is quantized, Einstein made the reverse conjecture — the incident electromagnetic field is quantized — behaving as a group of *particles* colliding with atoms of cesium [Eisn05b]. Einstein’s equations of the interaction is the light with the atoms of cesium is $E = h/\lambda$. Using this *model*, only the cesium atoms struck by the particles of light (which is called the photon but had not been named yet), emitted electrons. The energy of the incident photon gave rise to a proportional energy electron. The higher the energy of the photon — the shorter its wavelength — the higher the energy of the emitted electron. The photoelectric effect laid the groundwork for the *complementarity* principal in which the particle nature of light complements the wave nature. Einstein’s description of the photoelectric effect was *heuristic*, simple in its mathematical formulation and fit the known experimental data. The theoretical formulation was verified in 1916 by Robert Millikan [Mill16].
- (3) Line Series — the description of the emission lines of hydrogen can be described by the Ritz formula $f = R(1/4 - 1/n^2)$. Other spectral lines shapes are given in §10.2.
- (4) Compton Effect — the Compton effect occurs when X-rays are scattered by electrons. In the classical description of the effect using Maxwell’ equations, the wavelength of the scattered light should be the same as the incident light. Arthur Holly Compton (1892–1962) observed that X-rays were *shifted* to a lower frequency when scattered from a collection of electrons. If the incident X-rays are considered as quanta of the electromagnetic field, with an energy of $E = h/\lambda$, then the collision between the electron and the X-ray photon can transfer energy to the electron. Since momentum must be conserved, the incident photon gives up energy during the collision and is scattered at a lower energy, thus a longer wavelength.
- (5) Diffraction of Particle Beams — if the complimentary principal is applied to beams of particles, then wave-like behaviors can be observed. This symmetry between particle and wave is predicted by Louis-Victor Pierre Raymond de Broglie (1892–1987). De Broglie stated that the *wavelength* is a particle is $\lambda = h/mv$. This idea

quantum theory and the experimental techniques used to verify the theory grew. With this growth came the understanding that the Newtonian view of nature was seriously flawed.

Three *principals* of quantum theory of nature were developed:

- (1) The Correspondence Principal — the quantum mechanical description and the classical description of a phenomena are equivalent when Planck's constant becomes zero, that is $\hbar \rightarrow 0$.
- (2) The Complementarily Principal [Holt70] — in which both the wave and particle view of an effect produced similar results.
- (3) The Uncertainty Principal — which describes the hidden interdependence between pairs of measurements.

§10.2. EARLY QUANTUM THEORY

In 1900 the wave theory of light, built on Maxwell's electromagnetic theory and the description of the motion of particles, based on Newton's laws of motion went unchallenged. Two developments in the early 1900's served to upset forever the certainty of these theories.

On December 14th, 1900, Max Planck (1858–1947) presented a paper [Plan01], [Segr80] to the Berlin Academy of Science which stated that under certain ideal conditions energy radiated from a hot body was distributed in a characteristic manner, which could only be explained by assuming the electromagnetic radiation was emitted by the body in discrete amounts called *quanta* (Latin for *how much*) [Crea86], [Waer68].

Prior to this momentous announcement, the 19th century produced many discoveries which lead to the formulation of quantum mechanics.

was developed in de Broglie's Ph.D. thesis and was verified when a beam of electrons was defracted by gratings — as if they were *waves* — electron waves [d'Broh24], [d'Brog46], [d'Brog53].

- (6) Ramsauer Effect — when a beam of electrons travels through a gas, this gas becomes *transparent*. If the electrons are considered as *waves* and are projected through the gas at *just the right* velocity (slow electrons), the incident electrons *resonant* with the atoms of gas and are not scattered. Rather they *tunnel* through unimpeded.
- (7) Tunnel Effect — the *tunneling* observed in the Ramsauer effect can take place in other instances. If the position and momentum of a particle are described by a wave equation, then the particles can have a finite probability of passing through a potential barrier that would be forbidden in classical physics. The description of this behavior involves the use of Schrödinger's equation in which both the particle and wave nature of matter are required to describe the effect.

The achievements that lead to the joining of electricity and magnetism has been presented in the previous sections. The development of the mathematical foundation of theoretical mechanics and the confirmation of the laws of the conservation and transformation of energy lead to the belief that the description of the laws of nature were in their final stages. This situation was illustrated by the experience of Max Planck. After completing the defense of doctoral thesis, he wrote to his teacher and mentor Philip Jolly asking his advise on a career in theoretical physics [Heil86]. Jolly replied that

... theoretical physics is practically finished, the differential equations have all been solved. All that is left is to consider individual special cases...

In August of the same year, David Hilbert (1862–1943) presented his famous 23 problems before the Second International Congress of Mathematicians. ^[2] The sixth problem pertained to axiomation in physics.

² Hilbert presented a talk titled “Mathematical Problems,” in which he outlines the future of mathematics [Reid69]. The significance of mathematics and the role it played in the mind of Hilbert was presented through a set of *problems*. Only 10 of the 23 problems were given during the talk. The full list of problems appeared in *L'enseignement mathématique*, Volume 2, 1900, pp. 349–355. They are:

- (1) Cantor’s problem of the cardinal number of the continuum.
- (2) The compatibility of the arithmetical axioms.
- (3) The equality of the volumes of two terrahedra of equal bases and equal altitudes.
- (4) The problem of the straight line as the shortest distance between two points.
- (5) Lie’s concept of a continuous group of transformations without the assumption of the differentiability of the functions defining the group.
- (6) The mathematical treatment of the axioms of physics.
- (7) The irrationality and the transcendence of certain numbers.
- (8) Problems of prime numbers (including the Riemann hypothesis).
- (9) The proof of the most general law of the reciprocity in any number field.
- (10) The determination of the solvability of a Diophantine equation.
- (11) The problem of quadratic forms with any algebraic numerical coefficients.
- (12) The extension of Kronecker’s theorem of Abelian fields to any algebraic realm of rationality.
- (13) The proof of the impossibility of the solution of the general equation of the 7th degree by means of functions of only two arguments.
- (14) The proof of the faintness of certain complete systems of functions.
- (15) A rigorous foundation of Schubert’s enumerative calculus.

Hilbert proposed that a finite number of initial axioms should be formulated so that all the results needed for a complete description of the physical picture of nature could be obtained by purely logical means [Wigh76].

Events would soon follow to dispel these illusions. At the end of the 19th century a number of discoveries were made which could not be described within the framework of existing theories. These included: X-rays, the dependence of the mass of an electron on its velocity, the photoelectric effect and radioactivity.

§10.3. EXPERIMENTAL NECESSITY FOR THE QUANTUM THEORY OF RADIATION

By the end of the 19th century, experiments that established that the radiation spectra of free atoms consisted of sets of discrete lines, or line spectra, which formed order groups or series. In 1885 Johann Jakob Balmer (1825–1898) ^[3] discovered that atomic hydrogen emits radiation frequencies which can be described by,

$$\omega_n = 2\pi cR \left(\frac{1}{4} - \frac{1}{n^2} \right), \quad (10.1)$$

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- (16) The problem of the topology of algebraic curves and surfaces.
 - (17) The expression of definite forms by squares.
 - (18) The building up of space form congruent polyhedra.
 - (19) The determination of whether the solutions of “regular” problems in the calculus of variations are necessary analytic.
 - (20) The general problem of boundary values.
 - (21) The proof of the existence of linear differential equations having a prescribed monodromic group.
 - (22) Uniformization of analytic relations by means of automorphic functions.
 - (23) The further development of the methods of the calculus of variations.

³ Balmer was a Swiss mathematician and physicist who developed the first formulation of spectroscopic data. Other workers in the field had attempted to establish a mechanical acoustical relationships between the spectral lines of an element. Balmer found his formula for hydrogen by empirical means and used it to predict other spectral lines series that were subsequently confirmed experimentally.

where n are integral numbers 3,4,5, ..., c is the velocity of light in a vacuum and R is the Ryberg constant, where $R=1.097\times 10^7 m^{-1}$.^[4] This formula was derived by Balmer and is called the Balmer series whose frequencies fall in the visible region of the electromagnetic spectrum, with the first Balmer lines having a wavelength of 6563Å, with the next two lines falling in the blue and violet regions of the visible spectrum. Additional series were discovered for hydrogen, atoms which fell in the infrared region of the spectrum. The regularity of these new series, which were similar in structure to the Balmer series, which resulted in the generalized expression,

$$\omega_n = 2\pi cR\left(\frac{1}{k^2} - \frac{1}{n^2}\right), \quad (10.2)$$

where k fixes the series such that $k=1$ gives the Lyman (Therdore Lyman (1874–1919)) series (ultraviolet), $k=2$ gives the Balmer series and $k=3$ gives the Paschne (Friedrich Paschne (1865–1947)) series (infrared), $k=4$ gives the Brackett series (F. S. Brackett) and $k=5$ gives the Pfund series.^[5] The regularity of the structure was also observed in the spectrum of other atoms, which lead to more generalizations. One such theory was proposed by Ritz in 1908. Ritz's combination principal stated that if the formula of a series was given and the constants of the formulas known, then newly discovered spectral lines could be obtained from known spectral lines.

§10.3.1. Black Body Radiation

The black body experiments performed during the same time produced results inconsistent with the thermodynamic description of the equilibrium of radiation with matter [Plan14]. If the radiation emitted by the heated body is completely enclosed by matter as a given temperature, it will be in a temperature equilibrium with its surroundings, but independent of the actual surrounding material. This radiation is called *black body*, since the frequency distribution of the radiation is same as

⁴ Janne (John) Robert Ryberg (1854–1919) described the spectra of periodic elements in a paper submitted to the Swedish Academy of Sciences in 1889, titled "Recherches sur la consitution des spectres d'émission des éléments."

⁵ Recently, hydrogen-like atoms in highly excited states up to $k=100$ have been observed. They are called Ryberg atoms and their diameter is approximately 10^5 times larger than the diameter of a ground state hydrogen atom [Litt79].

that radiated or absorbed by a completely black or completely absorbing material body at that temperature.

The reason that the spectral distribution of the radiated energy is independent of the radiating material can be deduced from classical thermodynamic theory, but the distribution of the radiated frequencies must be measured to confirm the theory. The original measurements were expected to produce results based on the electromagnetic theory of light. If the electromagnetic field inside the enclosed volume can be described by an infinite number of normal coordinates, then the statistics of such a system can express the average energy as a function of the temperature.

During the experimental observation of thermal radiation, the intensity of the radiation, per unit frequency interval, rises from zero at very low frequencies to a maximum value whose position and magnitude depend on the temperature of the body, then falls again, approaching zero at very high frequencies. The drop in intensity in the high frequency region was in conflict with the theoretical results obtained by Lord Rayleigh. This conflict was based on the equipartition theorem derived from classical mechanics and of the wave theory of light. In the theory of the atom developed by Lenard and Rutherford, the atom was composed of a positive *nucleus* surrounded by negative *electrons*. The hydrogen atom is the simplest consisting of one electron and one proton in its nucleus. The electron is held by the nucleus by the electrical force of the proton. If this *binding* force were purely electrical, there was a theorem that states that a system of electrical charges cannot be in a stable equilibrium. This forced Rutherford to propose that the electron moved around the nucleus in such a way that the centrifugal force balanced the electrical force.

At room temperature the atoms or molecules of a gas undergo 100,000,000 collisions per second. If the ordinary laws of mechanics are applied to this gas there would be a slight change in the orbit of the electron with each collision. These changes would accumulate over time and the system would collapse in a few seconds. Since this is not the case, there must be some other principal at work other than the laws of classical mechanics [Born26].

In order to illustrate the *black body* nature of radiation, the electromagnetic waves emitted by an oscillating electron can be examined. If this electron were placed in free space, the radiated energy would escape to infinity. The electron would continually lose energy and eventually stop radiating. If however, the electron were placed inside a container whose walls were perfect reflectors, a different behavior would result.

As the radiation is reflected from the wall it would strike the electron causing it to be re-accelerated. In this way, the electron is bathed in its own radiation. This radiation is absorbed and re-emitted through the process of *scattering*. Since the electron obeys Kirchoff's Law, it acts as both a radiator and an absorber with equal results. Once equilibrium has been reached between the emission and absorption of radiation, the cavity attains a constant *temperature*, with the energy density uniformly filling the cavity. If a small hole is placed in the cavity, the radiating energy has the characteristic of a *black body*.

In such a system, the energy per degree of freedom (per mode of oscillation) is given by,

$$U = \frac{1}{2} kT, \quad (10.3)$$

where $k = 1.381 \times 10^{-23}$ joules is Boltzman's constant and T is the temperature in degrees Kelvin. The modes of oscillation in the cavity are simply standing waves. The total electromagnetic energy can be determined by calculating the total number of modes of oscillation. The electric field of the n^{th} mode is given by,

$$E_n(z, t) = A_n \sin\left(\frac{n\pi z}{L}\right) \cos(\omega_n t), \quad (10.4)$$

whose frequency is given by,

$$\omega_n = \frac{n\pi}{L} c, \quad n = 1, 2, 3, \dots \quad (10.5)$$

where L is the dimension of the cavity. By rewriting Eq. (10.5) in terms of a wavelength, $\lambda_n = 2L/n$, it can be seen that in order to fit a standing wave the dimension L must equal an integral number of half waves.

Planck attributed the discrepancy to the breakdown of the equipartition theorem when applied to high frequency oscillations and made the suggestion that, if the vibrating matter particles which emit radiation have motions restricted to certain discrete energy values there would be a departure from the laws of the classical statistical mechanics, that was required to describe to experimental facts.^[6] That is, the emission

⁶ The German physicist Max Karl Ernst Ludwig Planck (1858–1947) found an empirical formula that described the dependency of the intensity of radiation on temperature and wavelength. Planck assumed that the radiation escaping from a *black body* (which may be realized in practice as the radiation escaping a heated cavity through a

and absorption of radiation always takes place in discrete portions of energy quanta, $h\nu$, where ν is the frequency of the emitted or absorbed radiation [Born26].

This remarkable development is best demonstrated by the photoelectric effect, which had been discovered by Heinrich Hertz in 1886–87, in which the kinetic energy of the photon emitted is given by $mv^2/2 = h\nu$. This equation, proposed by Einstein, was proved experimentally by Robert A. Millikan (1868–1953) provided the first evidence of the existence of the *quantum*.^[7]

The acceptance of Planck's theory meant a revolution in physics since it was incompatible with both Newtonian mechanics and the electromagnetic theory of light. This proposal was verified in short order by Heinrich Reubens, when he compared his experimental results with Planck's formula [Bagg92]. The explanation of this behavior however was unknown to Planck and Reubens.

In 1905 Albert Einstein observed that Planck's assumption regarding the energy radiated by a *black body* $\epsilon = h\nu$, followed closely his predictions of the behavior of light...

small hole) originated in oscillations in the wall of the cavity. According to classical physics an oscillator may have any value for its total energy. Planck made the assumption that the oscillations occur only at discrete values of the total energy. By using statistical arguments, Planck derived the radiation density law, as a function of temperature, $\nu_\nu(T) = (8\pi h\nu^3) / (c^3 (e^{h\nu/kT} - 1))$. This derivation *came about* by dividing the total energy of each oscillator into equal values, then letting these values become infinitely small. Using a standard calculus technique, these values were *integrated* to restore the original energy calculation. In Planck's calculation this did not work. He found that in order to make the integration fit the experimental data the infinitesimal values of the oscillator energy could not be vanishingly small, but had to have a finite value — meaning their sum, or the total energy of the oscillator, could only have particular energy values [Bagg92], [Serg80], [Kuhn78], [Klei66].

An important point should be made here. The units of Planck's constant are the same as the units of *action*, energy–seconds. The idea of action will be developed in later sections with Lagrangian and Hamiltonian dynamics. Hamilton's are a method of finding the minimum value of a given equation. Neils Bohr won the Nobel Prize for the insight that when calculating the orbits of electrons, Planck's constant should be used in place of the Hamiltonian action variables.

⁷ R. A. Millikan developed a method to determine the value of the fundamental unit of electrical charge. In 1923 Millikan received the Nobel Prize for his work as well as the measurement of Planck's constant to an accuracy greater than previously possible [Nobe65]. Millikan's paper, with G. Winchester [Mill07] describes the photo–electric effect that was theorized by Einstein and Planck, which Millikan called the *Planck–Einstein light unit theory* [Mill50], [Mill68].

... monochromatic radiation ... behaves ... as if it consists of mutually independent energy quanta of magnitude $[\hbar\nu]$ then this suggests an inquiry as to whether the laws of the generation and Conservation of light are also constituted as if light were to consist of energy quanta of this kind. [Eins05].^[8]

Planck was unwilling to accept so radical a theory and spent much of his time in a fruitless attempt to save the wave theory of light by a modification of his original energy–level assumptions.

In 1909 Einstein showed how the fluctuations of the blackbody radiation confined in a volume V could be written as the sum of two terms – one describing the quantum properties of the radiation and the other describing the wave properties of the radiation [Eisn09]. The mean square fluctuations of the black body energy is given by,

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E \rangle h\nu + \frac{c^3 \langle E \rangle^2}{8\pi\nu^2 d\nu V}. \quad (10.6)$$

In another paper [Eisn19], Einstein described the probability transition rates of atoms which experience induced emission and absorption as well as spontaneous emission. The emission transition rate $dW_{mm}/dt = N_m (\rho B_{mm} + A_{mm})$, the absorption rate $dW_{mm}/dt = N_n \rho B_{nm}$ and spontaneous rate A_{mm} , where N_n is the number of oscillators on the energy level E_n and ρ is the radiation energy per unit volume in the frequency interval $\nu \rightarrow \nu + d\nu$.

This two expressions can be used to derive Planck's Law. The A and B coefficients are related by,

$$A_{mm} = B_{nm} \frac{8\pi h\nu^3}{c^3}. \quad (10.7)$$

⁸ The concept of *photons* as the quanta of light was proposed by Gilbert. N. Lewis (1875–1946), a physical chemist at the University of California, Berkeley, in 1926 [Lewi26], [Sutt92]. Lewis speculated the light consists of...

...a new kind of atom ... uncreatable and indestructible (for which) I ... propose the name photon [Pas82].

Nearly 90 years after Einstein's observations, it is difficult to imagine just how revolutionary his ideas were. The ideas of the quanta were not readily accepted by most physicists of the time, but the mounting experimental evidence eventually convinced the world of the need for the quantum hypothesis.

It was not until Neils Bohr (1885–1962) united the Rutherford nuclear model of the atom with the energy–level hypothesis to formulate his theory of the structure and spectrum of hydrogen, that the quantum theory of the atom was accepted as a fact of nature.^[9]

Bohr showed in 1918 that the transition probabilities were associated with the electric dipole moments of the radiation oscillators given,

$$A_{mm} = \frac{(2\pi)^4 v^3}{3hc^3} |P_{mm}|^2, \quad (10.8)$$

where P_{mm} is the Fourier coefficients of the dipole moment. This result was valid only for large quantum numbers – large numbers of oscillators. In the summer of 1925 Jordan made use of Heisenberg’s matrix mechanics to construct a theory of the radiated electromagnetic field [Born25]. Jordan showed that the black body radiation could be properly described if the oscillators had an energy of,

$$E = \left(n + \frac{1}{2}\right) h\nu. \quad (10.9)$$

§10.4. STATES OF A MECHANICAL SYSTEM

The underlying structure of the theory of quantum mechanics is based on the representation of the *states* of a system by a one–to–one correspondence with vectors in a suitably chosen linear vector space.^[10]

⁹ Bohr was 28 years old when he published his first paper on the theory of the hydrogen spectrum. Einstein had already written his initial paper on the corpuscular theory of light at the age of 26. Heisenberg was 24 years old when he laid the foundation of matrix mechanics. Dirac and Jordan write their papers at 24 and 23. All of these efforts as well as many others in the field of quantum mechanics focus attention on youth as one of the ingredients of scientific discovery.

When Bohr went from Cambridge to Manchester University in march of 1912 on a visit to Rutherford’s laboratory, he was unaware of the regularities of the hydrogen spectrum lines. He did not learn of the Balmer series until the beginning of 1913, a few weeks before submitting his paper to *Philosophical Magazine* [Bohr13]. The starting point for Bohr’s atomic model was instead Rutherford’s experimental discovery of the existence of the nucleus and the contradiction of the observed stability of atoms that cam about if the laws of classical electrodynamics were applied to the Rutherford model of the atom.

¹⁰ The concept of *state* is one of the most subtle and controversial concepts in quantum mechanics. In classical mechanics the word state is used to refer to the coordinates and momenta of an individual system, and early on it was supposed that the quantum state description would also refer to attributes of an individual system. However,

The measurement of the attributes of these states are described in terms of operations on these vectors. These *operations* are assumed to be linear. The operation of an operator on a vector is intended to describe a *physical* operation on the system. The result of the operation (measurement) of an attribute (dynamical variable) is an eigenvalue of the linear operator representing the dynamical variable. The state in which the dynamical variable has that value is represented by the corresponding eigenvector.

In quantum theory, quantities like position and momentum cannot have definite numerical values. Heisenberg's *uncertainty principle* states that the product of the uncertainty in coordinate position and the uncertainty in momentum is given by: $\Delta x \Delta p_x \approx \hbar$, where $\hbar = 1.054572 \times 10^{-34} \text{ kgms}^{-1}$ is Planck's constant [Heis30]. A similar

the assumption that a quantum state is a property of an individual physical system leads to contradictions and must be abandoned [Wign73], [Heal79], [Shim74], [Redh87].

The quantum state description may be taken to refer to an ensemble of similarly prepared systems. One of the earliest advocates of the ensemble interpretations was Einstein. His view is concisely expressed as follows [Eins49]:

The attempt to conceive the quantum-theoretical description as the complete description of the individual systems leads to unnatural theoretical interpretations, which become immediately unnecessary if one accepts the interpretation that the description refers to ensembles of systems and not individual systems.

Criticisms of the *ensemble* interpretation have often resulted from a confusion of the ensemble, which is the virtual infinite set of similarly prepared systems, with a concrete sequence or assembly of similar systems. These criticisms may be alleviated by a slightly more abstract interpretation in which a state of identified with the preparation *procedure* itself. *State* is then an abbreviation for *state preparation procedure*.

In quantum mechanics the *state* of the system is usually taken to mean a mathematical object such as a wave function, state vector or density operator. Due to the underlying complexities involved in the description of the quantum mechanical process it is important to further distinguish between the *dynamical state* of the system and its *quantum state* [Heal89]. The role of the quantum state is to generate probabilities concerning the possible outcomes of a measurement performed on the system. The dynamical state is usually identified with a quantum variable, position, momentum, spin at some instant. Using these *weak definitions* a quantum system always has a dynamical state. There is however no general connection between a system quantum state and dynamical state [d'Esp71].

By identifying the *state* concept directly with a set of probability distributions, this approach makes clear the fact that the interpretation of quantum mechanics is dependent on choosing a suitable interpretation of probability and the probability density function.

uncertainty can occur for the product of time and energy $\Delta t \Delta E \approx \hbar$.^[11] Planck's constant is so minute that its effect on the *macroscopic* world can be ignored. In the *microscopic* world of atoms \hbar places a significant role in the description of the nature.

The *uncertainty* principle, although quite foreign in the realm of classical physics results from the *Correspondence Principle*^[12] which states that any quantum mechanical theory must provide proper *classical* results when the action per cycle of the system is large compared to Planck's constant [Dirac25].

It is agayans the process of nature.

— Geoffrey Chaucer (1343–1400), *The Frankeleyn's Tale* [Chau94]

¹¹ Although the *time–energy* uncertainty given by $\Delta t \Delta E \approx \hbar$ is given as an extension of the *position–momentum* uncertainty in many quantum mechanics texts. This relation can not be directly derived from the original *position–momentum* relation $\Delta x \Delta p \approx \hbar$ [Eber73]. The first problem is that the time variable t is not an operator associated with an observable characterizing the particle, but is a parameter. Secondly the energy E is not a generalized canonical conjugate of time t . These *difficulties* can be overcome by considering the *time–energy* uncertainty relation in light of the *wave* nature of matter. In this description, the *dispersion* of the wave packet represents the quantum mechanical particle traveling through space. Consider a one–dimensional matter wave described by the function $f(x)$ whose uncertainty (dispersion) of x is given by $\Delta x = \left(f, [x - (f, xf)]^2 \right)^{1/2}$ where $(f, Af) = \int f^* A f dx$. Using the Fourier transform $f(x) \rightarrow g(k)$ the theorem provided by Heisenberg in [Heis30] states that the minimum product of the dispersions $\Delta x \cdot \Delta k$ can be obtained if $f(x) = 1/\sqrt{2\pi} e^{-x^2/(\Delta x)^2}$ is a Gaussian distribution, which results in $g(k) = 1/\sqrt{2\pi} e^{-k^2/(\Delta k)^2}$ also being a Gaussian distribution, where Δx and Δk are identical with the dispersions defined by the original expression. Their product is $\Delta x \cdot \Delta k = 1/2$ which is independent of the *meaning* of the two values x and k . By identifying x with a coordinate and k with the inverse of the de Broglie wave length so that $k = 2\pi/\lambda$ the usual uncertainty relation between position and momentum can be derived. Using the standard parameters for the Fourier transform t and ω a similar expression can be formed by substituting x by t and k by ω to give $\Delta t \cdot \Delta \omega = 1/2$ or $\Delta t \cdot \Delta E = \hbar/2$ [Rays77].

¹² The traditional correspondence principle implies the Bohr Correspondence Principle as a statement that for large quantum numbers, quantum mechanical laws must reduce to their classical counterparts. In this monograph the correspondence principle will imply additionally that operators are assigned to physical quantities. The details of this statement will be developed later, but for now this implies momentum is given by $p \rightarrow (\hbar/i)\nabla$ and energy is given by $E \rightarrow (i\hbar)\partial/\partial t$ [Jord75].

Instead of *certain* values of a measurable component, quantum theory provides probabilities for the measurable value, derived from the *Wave Equation* ψ which describes the measurable component.^[13] The wave equation states the probability of finding a particle at a certain position, given its momentum. In this way ψ is something that varies from point to point in the same manner as a *field* varies from point to point. The result of this approach is that particles become interchangeable with waves and fields become interchangeable with propagating particles.

§10.5. QUANTUM MECHANICS OF ELECTROMAGNETIC FIELDS

In quantum mechanics, the fields generated by the electric charge are subjected to the uncertainties of Werner Karl H. Heisenberg's (1906–1976) principle. In classical physics, fields are associated with forces. In quantum physics, fields are associated with particles.^[14] For particle fields and their associated force, the range of the force is related to the mass of the particle *carrying* the force. In order for the particle to have an effect, it has to travel over a distance \hbar/m_0c . Because the electromagnetic force is *long range* or possibly infinite, a particle of zero mass is need to carry the electromagnetic force. The Heisenberg uncertainty principle provides for the suspension of the conservation of energy for the duration Δt , by an

¹³ The concept of a wave equation originated with Einstein's 1905 theory of the photoelectric effect in which particles — photons — of energy $h\nu$ and momentum h/λ are associated with electromagnetic radiation of frequency ν and wavelength λ . In 1923 Louis de Broglie suggested a particle of momentum p should be associated with a wave of wavelength $\lambda = h/p$ [D'brog24]. It was William Hamilton in the early nineteenth century (1828–1837) that noted a formal similarity between the description of a light ray in optics and the motion of a particle in classical mechanics.

¹⁴ The term particle here refers to elementary particles. In the *standard model* all known particles belong to three classes:

- (1) Leptons — are point like particles with no detectable spatial extent. The six known leptons are the electron, muon, tauon and their corresponding neutrinos.
- (2) Hadrons — are particles believed to be composed of quarks. Hundreds of hadrons have been observed, with the most important being the proton and the neutron.
- (3) Bosons — are *exchange* or *gauge* particles. These particles are the carriers of force, with the photon carrying the electromagnetic force, the intermediate vector bosons carrying the weak force, the gluon carrying the strong force and the graviton carrying the gravitational force. The electromagnetic and weak forces were united in the late 1970's into the electroweak, which predicts a massive boson which has yet to be detected — the Higgs boson.

amount ΔE , where $\Delta t \cdot \Delta E \cong \hbar$. This value is the Compton (Arthur Holly Compton (1892–1962)) wavelength of a particle representing the electromagnetic force — such a particle is the photon.

In quantum mechanical terms charge — the electrostatic unit — is available only in units of $\hbar c$. Coulomb's law given in Eq. (2.2), is then given as,

$$\mathbf{F} = \alpha \hbar c \frac{e_1 e_2}{\mathbf{r}^2}. \quad (10.10)$$

The quantized charge and the resulting quantized field are represented by a quantum particle of spin 1 — the photon. Particles that correspond to the constituents of matter — particles of spin $\frac{1}{2}$ — and particles that correspond to force — particles of spin 1 can both be represented by quantized field equations.^[15]

The electromagnetic field equations are introduced into the realm of quantum mechanics through the potential field equation Eq. (4.22) and Eq. (4.23). The electromagnetic force was derived from the vector potential \mathbf{A} , where,

$$\mathbf{B} = \nabla \times \mathbf{A}. \quad (10.11)$$

With the scalar potential $\phi = 0$ and gauge condition $\nabla \cdot \mathbf{A} = 0$, the \mathbf{E} and \mathbf{B} fields are given as,

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}, \quad (10.12)$$

and

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad (10.13)$$

resulting in,

¹⁵ The concept of *intrinsic* spin was introduced in 1925 by the Dutch physicists Samuel Abraham Goudsmit (1902–1978) and George Eugene Uhlenbeck (1900–1988) [Gard90], [Pais86] and was confirmed experimentally, even though the property was not fully understood at the time. In 1928 P. A. M. Dirac made progress in the explanation of spin when he combined special relativity with the understanding of angular momentum. Twenty years later Wolfgang Pauli earned a Nobel Prize, in 1989, for *exclusion principle*. This principle forbids two particles with spin $\frac{1}{2}$ (fermions) from being too close to each other when they are in the same state — that is they both have the same spin orientation. Pauli's exclusion principle explains the patterns in the periodic table of elements which in turn explains most of chemistry. It explains why electrons in atoms maintain their orbital positions, which explains the stability of matter.

$$\nabla^2 \mathbf{A} - \frac{1}{c} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0, \quad (10.14)$$

which is the traveling wave equation given in terms of the vector potential \mathbf{A} , where \mathbf{A} satisfies the transverse condition $\nabla \cdot \mathbf{A} = 0$. According to Eq. (10.14) if \mathbf{A} and $\partial \mathbf{A} / \partial t$ are given as functions of position at $t = t_0$ the electromagnetic field is completely determined as a function of time. With no charges or currents present in the volume, a single vector potential \mathbf{A} is sufficient to describe the electromagnetic radiation within the volume. Although this expression has been stated elsewhere in this monograph, its meaning is now important in the quantum mechanical behavior of the radiation field.

§10.6. PRELIMINARIES TO QUANTIZING THE RADIATION FIELD

Quantizing the electromagnetic field is the central problem addressed in this section. In performing this quantization care must be taken to deal with the gauge arbitrariness and the redundancy of the vector scalar potentials.^[16] The approach used here is *heuristic* in nature and is developed with *hind sight*. This heuristic is augmented with the Lagrangian formalisms by defining the conjugate dynamical variables of the system and an expression for the *energy* of the system in terms of the Hamiltonian in the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$.

This approach consists of showing that the equations of classical electrodynamics, the Maxwell–Lorentz equations, can be thought of as Lagrange's equations of motion. Canonical quantization of the system can then be achieved by associating each pair of *generalized coordinates* and *canonical conjugate momentum* variables with the *annihilation* and *creation* operators used in the quantum electrodynamics description of radiation [Heit54].

¹⁶ Several approaches are available to *quantize* the electromagnetic field. By showing that the electromagnetic field and a set of particles is formally equivalent to a set of mutually interacting particles and oscillators the Lagrangian method of canonical variables can be used. This approach will quantize the system by associating the momentum and position of particles with commuting *operators* and replacing the *normal mode* variables of the field oscillators with *annihilation* and *creation* operators. All physical quantities of the classical electromagnetic theory become operators acting on the quantum states of the system.

§10.6.1. *Vector Potential Expanded as a Fourier Series*

The vector potential found in Eq. (10.14) is a function defined at all points in space and time. If this vector potential field equation is to be described in quantum mechanical terms, the number of variables needed becomes infinite. However, it is possible to choose an *innumerable* set of variables if the radiation field is enclosed in a volume of size $K = d^3k$. The exact form the boundaries of the enclosing volume are not needed, since the radiation equations can be described properly if the fields on one side of the volume are the same as they are on the other.

Each component of the vector potential can then be expressed as a component of a Fourier series. This new set of variables will represent the vector potential in *Fourier* space rather than *xyz* coordinate space. In this new volume some boundary conditions on the surface of the volume can be satisfied such that \mathbf{A} and its derivatives have the same values on two opposite planes of the volume — \mathbf{A} is periodic on the volume surface, and d^3k is considered large compared to the material system under analysis. For convenience $d^3k = 1$ will be used in this monograph.

Fourier's theorem [Korn92] states that, any function of x real or complex, defined within the limits $-\pi \leq x \leq \pi$, that has only a finite number of discontinuities, can be expanded in the Fourier series,

$$f(x) = \sum_{k=0}^{\infty} a_k \cos(kx) + \sum_{k=0}^{\infty} b_k \sin(kx), \quad (10.15)$$

by using,

$$e^{ix} \equiv \cos x + i \sin x, \quad (10.16)$$

so that,

$$f(x) = \sum_{n=-\infty}^{\infty} a_n e^{inKx}, \quad (10.17)$$

with the Fourier coefficients,

$$a_k = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{+\pi} f(x) e^{-ikx} dx, \quad (10.18)$$

and,

$$a_k^* = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{+\pi} f(x)e^{ikx} dx = a_{-k}. \quad [17] \quad (10.19)$$

The vector potential field can be converted from a continuous expression to a discrete expression using the Fourier series expansion. This is done by assuming the potential field is a periodic non degenerate dynamical system of k degrees of freedom, defined by equations connecting the coordinates and their time differential coefficients. Each coordinate can be expanded in the form of a multiple Fourier series in the time t , giving,

$$\mathbf{A} = \sum_{\mathbf{k}} \left(\mathbf{a}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \mathbf{a}_{\mathbf{k}}^* e^{-i\mathbf{k}\cdot\mathbf{r}} \right) \quad (10.20)$$

explicitly indicating that \mathbf{A} is *real* and where the coefficients $\mathbf{a}_{\mathbf{k}}$ are vector functions of time such that $\mathbf{a}_{\mathbf{k}} \approx e^{-i\omega t}$ with $\omega \equiv \omega_{\mathbf{k}} = |\mathbf{k}|$. [18] Since the vectors

¹⁷ The term $1/\sqrt{2\pi}$ is inserted for convenience of the Fourier theory and has no particular purpose for this development.

¹⁸ Jean Baptiste Joseph (Baron: conferred by Napoleon in 1808) Fourier (1768–1830) formulated his theorem for complex variations in 1807. The development of Fourier's *trigonometric* series expansion technique was motivated by the description of the heat diffusion between disjoint masses and in special continuous bodies based on the diffusion equation $\nabla^2 v = k \partial v / \partial t$ [Gill72], [Ligh60], [Heri75]. Fourier found that any periodic function could be expressed as a sum of sine functions. The *harmonic analysis* makes the study of sound, heat, light and all periodic phenomena amenable to mathematical treatment.

Fourier's contribution to mathematical physics is best illustrated by his 1822 publication *Théorie Analytique de la Chaleur (Analytical Theory of Heat)* [Four22]. In this work Fourier described his theory of the conduction of heat. In previous theories, heat was seen as the *flow of an imponderable fluid the caloric*, which was responsible for the repulsive force in matter. Fourier formulated his theory on *rational mechanics* using differential equations to characterize the conduction of heat. Fourier's contribution to physics was to describe heat conduction in terms of a mathematical theory independent of any physical behavior.

His description was based on the *effects of heat* on the temperature distribution in materials, not on the way in which the *repulsive power* of heat determined the physical state of the material. Fourier's analytical approach to the study of heat had an important influence on later mathematical descriptions of electromagnetic phenomenon. Fourier stressed the distinction between a mathematical theory and a physical interpretation. This approach allowed *models* of nature to be built using mathematical tools. These models could then be compared with physical reality using experiment — but it was the formulation of the model that moved the study of electromagnetism forward.

The Fourier expansion and subsequent Fourier transform allow time dependent descriptions of Maxwell's equations to be transformed into frequency based descriptions. According to Fourier every wave of the form $f(x - ct)$ can be decomposed into an integral

are functions of time they behave like periodic functions with frequency $\omega = |\mathbf{k}|c$ and the expansion of the field appears as an expansion of propagating plane waves.

The divergence condition $\nabla \cdot \mathbf{A} = 0$ (transversality condition) states that the complex vectors $\mathbf{a}_{\mathbf{k}}$, represented by the Fourier coefficients, are orthogonal to the corresponding wave vectors \mathbf{k} , such that $\mathbf{a}_{\mathbf{k}}(t) \cdot \mathbf{k} = 0$ and $\mathbf{a}_{\mathbf{k}}^*(t) \cdot \mathbf{k} = 0$, which can be verified by taking the divergence of each side of Eq. (10.20) using,

$$\nabla e^{\mathbf{k} \cdot \mathbf{r}} = i\mathbf{k}e^{\mathbf{k} \cdot \mathbf{r}} \quad (10.21)$$

If the vectors $\mathbf{a}_{\mathbf{k}}$ are specified, the field in a volume $d^3k = dk_x dk_y dk_z$ is completely determined. These quantities may be regarded as a discrete set of classical field variables.

It is convenient to include the polarization vectors in the notation for the wave vector, through the following notation. The polarization vectors in Eq. (5.37) can be used to define the wave vector of,

$$\boldsymbol{\varepsilon}_1 \cdot \mathbf{k} = \boldsymbol{\varepsilon}_2 \cdot \mathbf{k} = 0, \quad (10.22)$$

$$\boldsymbol{\varepsilon}_i \cdot \boldsymbol{\varepsilon}_j = \delta_{i,j} \quad (10.23)$$

The Fourier coefficients can now be expanded as,

$$\mathbf{a}_{\mathbf{k}}(t) = \sum_{\lambda=1,2} a_{\mathbf{k}\lambda}(t) \boldsymbol{\varepsilon}_{\mathbf{k}\lambda}. \quad (10.24)$$

For the electric field,

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} = -\sum_{\mathbf{k}} (\dot{\mathbf{a}}_{\mathbf{k}} e^{\mathbf{k} \cdot \mathbf{r}} + \dot{\mathbf{a}}_{\mathbf{k}}^* e^{-\mathbf{k} \cdot \mathbf{r}}) \quad (10.25)$$

or simply,

$$\mathbf{E} = i \sum_{\mathbf{k}} \mathbf{k} (\mathbf{a}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} + \mathbf{a}_{\mathbf{k}}^* e^{-i\mathbf{k} \cdot \mathbf{r}}) \quad (10.26)$$

For the magnetic field,

over such waves: $f(x-ct) = \int_{-\infty}^{+\infty} A(\omega) e^{i\omega(t-x/c)} d\omega$. The coefficient $A(\omega)$ is obtained from $f(x-ct)$ by the Fourier transformation: $A(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} f(x-ct) e^{i\omega(t-x/c)} dt$.

$$\mathbf{B} = \nabla \times \mathbf{A} = i \sum_{\mathbf{k}} (\mathbf{k} \times \mathbf{a}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} - \mathbf{k} \times \mathbf{a}_{\mathbf{k}}^* e^{-i\mathbf{k}\cdot\mathbf{r}}) \quad (10.27)$$

The Fourier expansion expresses the field in terms of a series of discrete parameters — the vector $\mathbf{a}_{\mathbf{k}}$ in place of the continuous parameters given in Eq. (10.20) Because of the orthogonality of the trigonometric functions in the Fourier expansion of the vector potential, the following equation is required:

$$\frac{d^2 \mathbf{a}_{\mathbf{k}}}{dt^2} + k^2 \mathbf{a}_{\mathbf{k}} = 0, \quad (10.28)$$

where k^2 is the square of the length of the vector \mathbf{k} . Each of these variables will be used later in the formulation of the Hamiltonian representation of the radiation field. ^[19]

§10.6.2. Planck's Conclusions Using the Vector Potential

With the vector potential written in terms of $\mathbf{a}_{\mathbf{k}}$, it is possible to transform the expression for the energy stored in the field from an integral over the volume to a sum over the various $\mathbf{a}_{\mathbf{k}}$'s and their time derivatives, giving:

$$W = \frac{1}{2} \int (E^2 + B^2) dv = \frac{V}{16} \sum_{\mathbf{k}} (\dot{\mathbf{a}}_{\mathbf{k}}^2 + K^2 \mathbf{a}_{\mathbf{k}}^2) \quad (10.29)$$

Because of the orthogonality of the trigonometric functions most of the terms in the integral vanish, and the remaining integrate to $V/8$. Since this term contains only the squares of their derivatives, the $\mathbf{a}_{\mathbf{k}}$'s are normal coordinates. Eq. (10.29) is an exact expression for the energy in the field. It contains no assumptions regarding the nature of the field except for the periodicity of the boundary conditions. If there were only one field present, the distribution of energy among the different normal coordinates would remain constant and there would be no approach to an equilibrium distribution.

¹⁹ With the introduction of the Fourier representation of the radiated field, the groundwork has been laid for the quantum mechanical description of electromagnetism that will take place in later sections. An important linguistic change will also take place. The *classical* vocabulary of describing a physical phenomenon as *is* must now be replaced with the provisional statement *acts as though it were* [Baey92]. This change results from the mathematical descriptions of the physical processes that are *counter intuitive* in nature.

However, black body radiation is radiation in equilibrium with matter, and the presence of the matter provides the means by which energy can be transferred from one normal coordinate to another, maintaining the state of equilibrium. This state can be described in statistical terms without reference to the process which created it. According to the equipartition theorem of classical statistical mechanics, when equilibrium is obtained, the average energy associated with each normal vibration is $E = kT$.

Eq. (10.29) demands that each normal coordinate vibrate as a simple harmonic oscillator of frequency $\nu = K/2\pi$. In order to determine the energy of the electromagnetic field as a function of frequency, it is necessary to find how many normal vibrations have frequencies in the range ν to $\nu + d\nu$. This is equivalent to finding the number of vectors \mathbf{k} whose lengths are in the range $2\pi\nu$ and $2\pi(\nu + d\nu)$. The components of the \mathbf{k} 's are restricted by the relation $\mathbf{k} = 2\pi/L(k_1\mathbf{i} + k_2\mathbf{j} + k_3\mathbf{k})$. The length of such a vector is $\sqrt{(k_1^2 + k_2^2 + k_3^2)} = L\nu$. The number of these vectors in a solid angle of 2π and in the range corresponding to $d\nu$ is $2\pi L^3 \nu^2 d\nu$. The total number of coordinates whose frequencies lie between ν and $\nu + d\nu$ is given by:

$$dN = 8\pi V \nu^2 d\nu. \quad (10.30)$$

According to classical statistics, the energy distribution in a black body is then given by:

$$E_\nu d\nu = 8\pi V k T_\nu d\nu. \quad (10.31)$$

This expression is contradicted by experiment in many ways.^[20] Planck found that in order to correct these problems a change in the

²⁰ There are several problems that arise from using classical electromagnetic theory to predict the energy distribution of a black body. If a cavity is heated and the frequency of the radiation being emitted by the cavity through a small hole is measured several problems arise with the predicted results:

- (1) There is an infinite total energy in the radiating cavity. This cannot be immediately disproved experimentally because the total energy is not a directly observable quantity, but it is an undesirable result.
- (2) The radiation in the cavity has an infinite specific heat. This is not possible, since the temperature of the cavity can be raised with a finite amount of energy.
- (3) The specific heat is independent of the temperature and the total energy is proportional to the temperature. This is also not possible since it can be shown thermodynamically that the total energy in the cavity is proportional to the fourth power of the temperature T .

statistical treatment of the radiation was needed. He assumed — quite arbitrarily — that each normal coordinate can vibrate with an amplitude which gives it the energy $nh\nu$, where n is an integer and ν is the frequency of the normal vibration. He also proposed that the probability of an oscillator has the energy $nh\nu$ is proportional to $e^{-nh\nu/kT}$, which is not really different from the assumptions based on classical mechanics. The critical point made by Planck was the assumption that energy came in discrete values and was proportional to the frequency. With these assumptions the average energy in one normal coordinate whose frequency is ν is given by:

$$\frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{-h\nu \frac{d}{dx} \sum_{n=0}^{\infty} e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} = \frac{h\nu}{e^{-nh\nu/kT} - 1} \quad (10.32)$$

From Eq. (10.31) and Eq. (10.32) the energy distribution law is given as:

$$E_{\nu} = 8\pi V \frac{h\nu^3}{e^{h\nu/kT} - 1}. \quad (10.33)$$

This expression is *Planck's Law* and agrees closely with experimental measurements. Through this development Planck's constant h became a famous icon for modern physics and the concept of *quanta* of radiated energy was formed.

§10.7. RADIATION FIELD EXPANSION USING CANONICAL VARIABLES

By adopting the Hamiltonian description of the electromagnetic field, the formulation of the field equations is reduced to finding an appropriate expression for the potential and kinetic energies of the field.

In order to transform the quantities from classical form, stated in terms of the Fourier series expansion of the vector potential, to quantum form, a canonical set of Hamilton equations are generated [Dick60]. Eq. (10.32) expresses the field in terms of a series of discrete variables in place of a series continuous variables.

-
- (4) The energy is concentrated in the high frequencies and the energy per unit frequency range is proportional to the square of the frequency. Experiments show that the energy as a function of frequency has a definite maximum at a frequency which is a function of the temperature.

The *canonical* field variables of the classical field potential developed in the previous section are,

$$Q_n = \frac{1}{\sqrt{4\pi}} (\mathbf{a}_n + \mathbf{a}_n^*), \quad (10.34)$$

and,

$$P_n = \frac{-i\omega}{\sqrt{4\pi}} (\mathbf{a}_n - \mathbf{a}_n^*) = \dot{Q}_n, \quad (10.35)$$

where the canonical variables $Q_{\mathbf{k}}$ are generalized coordinates and $P_{\mathbf{k}}$ are generalized momentum(s).^[21] The field vector potential is now expressed in terms of the canonical variables as,

$$\mathbf{A} = \sqrt{4\pi} \sum_n \left(Q_n \cos \mathbf{k} \cdot \mathbf{r} - \frac{1}{\omega} P_n \sin \mathbf{k} \cdot \mathbf{r} \right). \quad (10.36)$$

The Hamiltonian H can be expressed in terms of the canonical variables $Q_{\mathbf{k}}$ and $P_{\mathbf{k}}$ by calculating the total energy of the electromagnetic field as,

$$\begin{aligned} H &= \frac{1}{2} \int (\mathbf{E}^2 + \mathbf{B}^2) dV, \\ &= \frac{1}{2} \int \left\{ |\nabla \times \mathbf{A}|^2 + \left| (1/c) \frac{\partial \mathbf{A}}{\partial t} \right|^2 \right\} dV. \end{aligned} \quad (10.37)$$

The derivation of the Hamiltonian of the electromagnetic field, shown in Eq. (10.37) is shown in detail in the following section. The method of this derivation is important in that it lays the groundwork for the quantum mechanical representation of the radiation field.

When the field potential \mathbf{A} is expanded in terms of the canonical field variables, the Hamiltonian becomes,

²¹ The operators for the electric and magnetic fields can be obtained by *analogy* with those for a mechanical oscillator. The identification of these operators with the electromagnetic fields should not be regarded as established principles but rather a hypothesis necessary to make the transition from classical mechanics to quantum mechanics.

$$\begin{aligned} H &= \sum_{\mathbf{k}} 2 \left(\frac{\omega}{c} \right) \left\{ \frac{c(\omega Q_{\mathbf{k}} - iP_{\mathbf{k}})}{2\omega} \right\} \left\{ \frac{c(\omega Q_{\mathbf{k}} + iP_{\mathbf{k}})}{2\omega} \right\} \\ &= \frac{1}{2} \sum_{\mathbf{k}} (P_{\mathbf{k}}^2 + \omega^2 Q_{\mathbf{k}}^2). \end{aligned} \quad (10.38)$$

This expression is referred to as an oscillator expansion of the field.^[22] Each vector P_n and Q_n is perpendicular to the wave vector \mathbf{k} and is denoted by $Q_{\mathbf{k},\alpha}$, $P_{\mathbf{k},\alpha}$ giving the Hamiltonian as,

$$H = \sum_{\mathbf{k}} \sum_{\alpha=1,2} \frac{1}{2} (P_{\mathbf{k},\alpha}^2 + \omega^2 Q_{\mathbf{k},\alpha}^2). \quad (10.39)$$

Each term in the above expression corresponds to a traveling wave with a definite wave vector and polarization and has the form of the Hamiltonian for a one-dimensional oscillator. Thus the Hamiltonian is the sum of independent terms, each of which contains only one pairs of quantities $Q_{\mathbf{k},\alpha}$ and $P_{\mathbf{k},\alpha}$.

§10.8. SCHRÖDINGER'S EQUATION

During the years 1828–1837, William Rowan Hamilton noted the formal similarity between the decryption of a light ray in the field of optics and the motion of a particle in the presence of the potential field. The basis of the that waves are related to particles started with Fermat in 1657 when he discovered a principle describing the path of a light ray. If a light ray moves between two points A and B in a medium where the index of refraction is a function of the spatial coordinates $n = n(x, y, z)$, then the path the ray takes is determined by the condition that the time of

²² The original concept for the oscillator expansion came in the 1920's when Born, Heisenberg, Jordan and Paulie formulated a quantum description of Einstein's energy description of a dynamical system, $E_n = nh\nu$ [Pais86]. Born, Heisenberg and Jordan [Born25] utilized a one-dimensional model — the energy fluctuations in a segment of a vibrating string with length l and fixed endpoints. The displacement of the string $u(x, t)$ at point x and time t was, $u(x, t) = \sum_{k=1}^{\infty} q_k(t) \sin v_k x$ where $v_k = k \frac{\pi}{l}$, $k=1, 2, \dots$, which reduces to an infinite set of uncoupled oscillators with coordinates $q_k(t)$. The total string energy is then $H = \frac{1}{2} \sum_k (p_k^2 + \omega^2 q_k^2)$, $\omega = 2\pi\nu$ which can be rewritten as, $H = \sum_k (n_k + \frac{1}{2}) h\nu$. This *Hamiltonian* forms the basis of the quantum mechanical description to be developed later.

traversal is a minimum. If the phase velocity of the ray is $u = c/n$, the time of the traversal for the distance ds is given by ds/u . Since the phase velocity can also be given as $u = v\lambda$, where λ is the wavelength. The time for traversal can now be given as,

$$I = \frac{1}{v} \int_A^B \frac{ds}{\lambda}. \quad (10.40)$$

The minimum condition becomes,

$$\delta I = 0 \Rightarrow \delta \int_A^B \frac{1}{\lambda(x, y, z)} ds = 0. \quad (10.41)$$

A similar principal was developed in the section on Hamiltonian mechanics, where the kinetic energy of a particle, T , in motion has the least possible value, such that,

$$\delta \int_A^B T dt = 0, \quad (10.42)$$

which can be restated in terms of the momentum of a particle by the use of $2T dt = mv ds = p ds$, which gives,

$$\delta \int_A^B p ds = 0. \quad (10.43)$$

This formal similarity, described by Hamilton, between the path of a ray of light and the motion of a particle, was the starting point for Prince Victor de Broglie (1892–1987) nearly one hundred years later. ^[23] In 1923 de Broglie [D'brog24] proposed that a particle's momentum p and the energy E of a wave with wavelength λ and frequency ν , could be related as,

$$\lambda = \frac{h}{p} \text{ and } \nu = \frac{E}{h}. \quad (10.44)$$

²³ Prince Louis–Victor de Broglie presented his doctoral thesis “Recherches sur la Theorie des Quants” (“The Theory of Matter Waves”) to his committee at the Sorbonne in 1924. De Broglie's concept of matter waves was beyond the thesis committee's ability to make any critical review. They awarded de Broglie his degree after Einstein commented on his work. De Broglie was awarded the Nobel Prize in 1927 after Clinton Joseph Davidson (1881–1958) and Lester Halbert Germer (1896–1971) verified (in 1927) that electrons can be diffracted by a crystal.

This relationship implies that a particle with a well defined momentum p would experience diffraction, as if it were a wave with a wavelength of $\lambda = h/p$. The experimental verification of de Broglie's ideas came in 1927 when Clinton Joseph Davisson (1881–1958) and Lester Halbert Germer (1896–1971) at Bell Laboratories and Sir George Paget Thompson (1892–1975) in England observed that an electron beam diffracted from the surface of a nickel crystal, just as light is diffracted by a ruled grating.^[24] de Broglie compared the energy and momentum of a particle, $E^2 = m^2 c^4 + p^2 c^2$ with the form of a plane wave, $e^{i(\mathbf{k}\mathbf{r}-\omega t)}$. This concept of a matter wave became the basis of Erwin Schrödinger's (1887–1961) formulation of wave mechanics.^[25] Schrödinger first published his results in a series of papers starting March of 1926 [Darr86].

§10.8.1. *Development of Schrödinger's Equation*

There are actually two Schrödinger equations, one time-dependent and one time-independent. The approach suggested by Schrödinger was to postulate an equation that could vary in both space and time — in a wave-like manner, thus the *wave equation*. There are actually two Schrödinger equations. The time-dependent equation provides a description of the wave function as it *evolves* in time, once the initial conditions are determined. These initial conditions are contained in the *potential* that would be experienced by a particle. All the solutions to the time-dependent wave equation vary over time in a *wave-like* manner, these solutions may be converted into eigenfunctions of a time-independent wave equation multiplied by a time-dependent factor related to the energy of the wave. The simplified (time-independent) solution to the wave

²⁴ This observation won Davisson the Nobel Prize in 1937, [Davi27].

²⁵ Schrödinger *came upon* the wave equation while attending a seminar held jointly by the Eidgenössische Technische Hochschule in Zurich and the University of Zurich. The seminar was lead by a professor at the University of Zurich, Peter Joseph Wiheim Debye, who suggested that Schrödinger present a report on de Broglie's concept of particle waves. During Schrödinger's talk Debye remarked that the proper description of the particle wave required a *wave equation* [Bloc76].

Several weeks later Schrödinger had *formulated* his wave equation and produced four papers in *Annalen der Physik* titled "Quantizierung als Eigenwertproblem," [Blin74], [Schr26]. In three papers Schrödinger derived both the time independent and the time dependent equations and formulated their solutions for the harmonic oscillator. Schrödinger arrived at his equation by using an analog between classical geometric optics and classical particle dynamics.

equation in which the time-independent wave equation is solved, then multiplied by a sinusoidal factor related to the energy. The solutions to the time-independent wave equation are simply the *amplitudes* of the full time-dependent equation. In both cases the wave equation has no physical interpretation. It simply contains information regarding the system to which it refers. The most important characteristic of the wave equation is that the square of its magnitude is a measure of the probability of finding a particle described by the wave function at a given point in space.

The development of Schrödinger's wave equation can be approached using a classical wave equation example. A wave equation can be formulated for a vibrating string can be constructed which can then be extended to the Schrödinger wave equation.^[26] Assume a transverse displacement of a string from its undisplaced position be represented by the function $\psi(x,t)$, where x is the position along the string and t is time. If Newton's equation $F = ma$ is applied to an element of the string, the force arising from the tension of the string, T , will be acting in different directions on the two ends of the string element, dx . The transverse component of the tension force can be approximated by $T \partial\psi/\partial x$ as shown in Figure 1.0. At the point $x + dx$, this tension force can be approximated by $T \partial\psi/\partial x$, but there is a force at the point x of the opposite sign, $-T \partial\psi/\partial x$, where the derivative is computed at the point x . The sum of these forces gives the total transverse force on the string and can be approximately given as, $T(\partial^2\psi/\partial x^2) dx$. This force must equal mass times the acceleration. If μ is the mass per unit length, the mass of an element of the string is then μdx . The acceleration of the string is given by, $\partial^2\psi/\partial t^2$, which results in Newton's equation of motion for the string as,

$$T \frac{\partial^2\psi}{\partial x^2} = \mu \frac{\partial^2\psi}{\partial t^2}, \quad (10.45)$$

which is the wave equation for a vibrating string [Gold51], [Arfk85], [Brau93], [Resn60], [Wall72], [Whit37].

²⁶ This example of a vibrating string re-occurs throughout the history of physics.

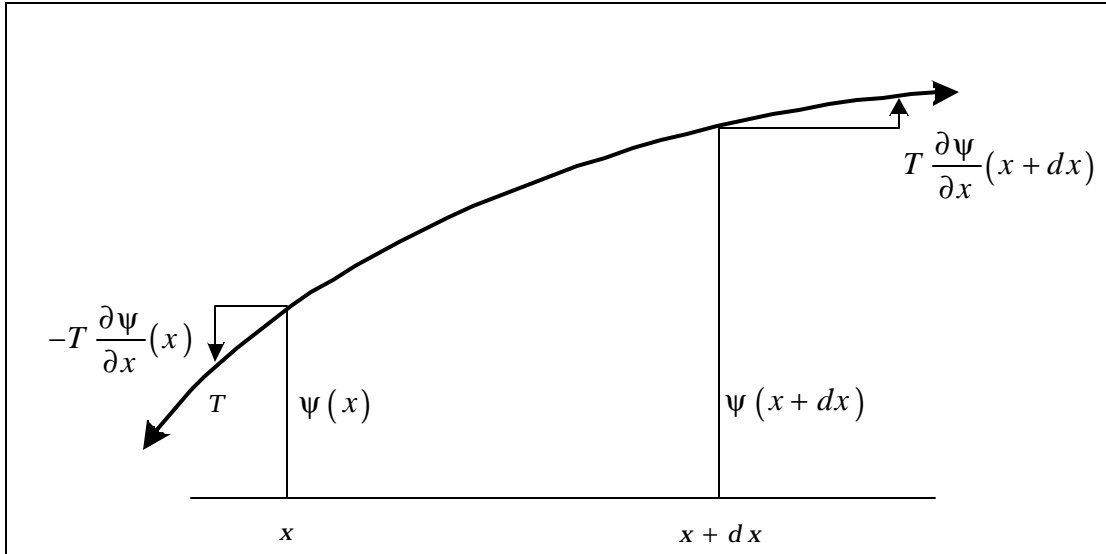


Figure §10.1 — Tensions in an element of a string.

Ordinarily the solutions to this wave equation vary sinusoidally with time so that $\psi = u(x)\sin \omega t$, where $u(x)$ provides a separation of variables of the differential wave equation. In this case $\partial^2 \psi / \partial t^2 = -\omega^2 \psi$, which allows the wave equation to be rewritten in the form which cancels the time dependence,

$$\frac{d^2 u}{dx^2} + \omega^2 \frac{\mu}{T} u = 0, \quad (10.46)$$

which has the solution,

$$u = \sin 2\pi \frac{x}{\lambda}, \quad (10.47)$$

where λ is the wave length of the vibration given by, $2\pi/\lambda = \omega\sqrt{\mu/T}$, which allows the wave equation to be simplified to the form,

$$\frac{d^2 u}{dx^2} + \left(\frac{2\pi}{\lambda}\right)^2 u = 0. \quad (10.48)$$

This is the standard form of a wave equation with the time parameter eliminated. This equation assumes that properties of the string, or in the case of the generalized three dimensional problem, the properties of the vibrating medium do not vary from point to point. In the case where the properties *do* vary with position, the wave length of the solution to the wave equation also vary with position. It is this property that can be used to derive the wave equation for de Broglie waves. Since the wavelength

can be a function of position, it becomes a differential equation whose solution becomes very difficult, which can only be solved in certain special simple cases.

§10.9. FORMULATING SCHRÖDINGER'S WAVE EQUATION

The path taken by Schrödinger in the formulation of the wave equation was quite simple — now that hind sight provides a clear view of the events of the 1920's and 30' [Sopk80]. Given a particle of mass m moving along the x axis subject to a conservative force, $V(x)$. Using the mathematics developed for the vibrating string, the momentum and hence the wave length at every point along the particles path can be described.

The conservation of energy states that the total energy, E , is given by $E = mv^2/2 + V$ or using the momentum representation $E = p^2/2m + V$. The momentum of the traveling particle is then given by,

$$p = \sqrt{2m(E - V)}. \quad (10.49)$$

In de Broglie's postulate the momentum is related to the wavelength of the particle by, $p = h/\lambda$ or $\lambda = h/p$. Replacing the momentum gives, $\lambda = h/\sqrt{2m(E - V)}$. Substituting the expression the wavelength into the wave equation Eq. (10.48) gives,

$$\frac{d^2 u}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) u = 0. \quad (10.50)$$

In order to generalize this expression for three dimensions, the wave equation becomes,

$$\nabla^2 u + \frac{8\pi^2 m}{h^2} (E - V) u = 0. \quad (10.51)$$

§10.10. SCHRÖDINGER'S TIME DEPENDENT EQUATION

The time independent wave equation for the tension in the string developed above, involve the second time derivative. Only by assuming that the function varies sinusoidally with time can time be eliminated from the wave equation. By making use of the Hamilton description of the motion of particles, the bridge to quantum mechanics can be made through a simple mathematical transformation. As developed in the previous section, Hamiltonian function is simply the energy of the system

expressed as a function of the coordinates and momenta. In rectangular coordinates, the Hamiltonian function for a particle of mass m moving in a potential field with energy V , is given by,

$$H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V(x, y, z). \quad (10.52)$$

The law of conservation energy requires that $H = E$, where E is a constant of the system. This relationship determines the momentum as a function of position. Using de Broglie's postulate, the wave length of the particle can now be determined as a function of position.

It was observed by Schrödinger, that the wave equation can be formulated in the following manner. By replacing the momentum variables by differential operators the Hamiltonian can also be transformed into a differential operator. Thus,

$$p_x \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{h}{2\pi i} \frac{\partial}{\partial z}. \quad (10.53)$$

By substituting these expressions into the Hamiltonian, it is changed into a quantity called the Hamiltonian operator,

$$H \rightarrow -\frac{h^2}{8\pi^2 m} \nabla^2 + V. \quad (10.54)$$

Now taking the equation $H = E$ and applying the differential operators to the wave function u , results in a wave equation $Hu = Eu$, which can be expanded to,

$$-\frac{h^2}{8\pi^2 m} \nabla^2 u + Vu = Eu. \quad (10.55)$$

This expression is identical to the Schrödinger equation, which was derived in an intuitive manner. The last substitute for a differential operator can be made using,

$$E \rightarrow -\frac{h}{2\pi i} \frac{\partial}{\partial t}. \quad (10.56)$$

By substituting the energy differential operator into the wave equation and changing the symbol for the wave function to ψ , results in Schrödinger's time dependent equation of,

$$-\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi + V\psi = -\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}, \quad (10.57)$$

which is the form of Schrödinger's equation involving time.

§10.10.1. The General Solution to Schrödinger's Equation

By separating Schrödinger's equation into a function of the spatial coordinates and a function of time, the solution to Schrödinger's equation takes on the form,

$$\psi = u(x, y, z) T(t), \quad (10.58)$$

which results in,

$$\frac{1}{u} \left(-\frac{\hbar^2}{8\pi^2 m} \nabla^2 u + Vu \right) = \frac{1}{T} \left(-\frac{\hbar}{2\pi i} \frac{dT}{dt} \right). \quad (10.59)$$

Schrödinger's equation is known as a homogeneous linear differential equation. The equation is linear because it does not contain ψ or its derivatives in powers higher than the first and it is homogeneous because it does not contain any terms dependent on ψ . Any such differential equation has the property that the sum of any two solutions to the equation is itself a solution. This allows for the general solution to be made up of other solutions, such that,

$$\psi = \sum_i c_i e^{-(2\pi i E_i / \hbar) t} \cdot u_i(x, y, z), \quad (10.60)$$

where c_i is an arbitrary complex constant.

§10.10.2. Semi-Classical Theory of Radiation

In the Hamiltonian formulation of Maxwell's equations, the electromagnetic *fields* themselves become *real* entities, separate from the charges that generate them. The Hamiltonian given in Eq. (10.39) can now be used to describe the quantum mechanical motion of a charged particle. The Schrödinger equation is given in its simplest form as,

$$i\hbar \frac{\partial}{\partial t} \psi = H\psi. \quad (10.61)$$

Assuming a time-independent Hamiltonian, the following separate of the terms of the equation can be made,

$$\psi \Rightarrow \psi e^{-iEt/\hbar}, \quad (10.62)$$

where E is the total energy of the charged particle.

When this charged particle is placed in an electromagnetic field described by the vector potential \mathbf{A} , the Schrödinger equation becomes,

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + \frac{ie\hbar}{mc} \mathbf{A} \cdot \nabla + V \right] \psi. \quad (10.63)$$

Although the motion of the particle is quantized in this description, the electromagnetic field is treated classically, which allows the potential to be specified with complete certainty in space–time by using Maxwell’s equations. This approach results in an correct description of the influence of the external radiation field on the charged particle — absorption and induced emission, but not of the influence of the charged particle on the radiation field — spontaneous emission [Beth64], [Schi68]. The reason for the correct result in the first case lies with the correspondence principal. When the radiation field is quantized it is regarded as a collection of quantized oscillators, with the n^{th} excited state of the oscillator describing n photons in the electromagnetic field. The semi–classical description of the radiation field provides the correct results because the numbers of photons representing the field are very large. The details of this description will be developed in the next chapters.

Because the vector potential \mathbf{A} is linear, the results developed for intense radiation fields will also hold for weak fields, or low values of n . This consideration does not hold for spontaneous emission though. The spontaneous emission of a photon from a accelerated charged particle occurs regardless of the presence of an external electromagnetic field. At least one quantum of radiation must be emitted when the charged particle is accelerated. This effect is not linear in the field and the correspondence principal cannot be extrapolated in a simple way to the emission of one photon. For a satisfactory theory of both the electromagnetic field and the charged particle, the electromagnetic field must be quantized.

We must accept the truth, even if it changes our point of view.

— *George Sand*