Contents

Chapter 1

Introduction

1.1 The History of Quantum Mechanics

In the 18^{th} century Newton formulated a paradigm consisting of three simple laws for the motion of masses that has guided subsequent physical research with great success. In doing so he postulated a preferred, or inertial, space which has the property that for an observer in this space a particle subject to no net external force moves with constant, uniform velocity. If there is a net force the particle has an acceleration proportional to the force an inversely proportional to its mass(this is basically the definition of mass). With these rules the understanding of motion was reduced to the determination of forces. Newton himself formulated a simple and universal law for the gravitational force. In doing so he asserted that the laws of physics are the same in the entire universe. Physicists next turned their attention to the forces associated with electricity and magnetism. They also developed deeper and more subtle formulations of Newtonian mechanics, giving rise to the concepts of energy and momentum conservation and their connection to the structure of space and time. By the end of the 19^{th} century, the phenomena of electricity, magnetism and light were unified into a marvelous system described by Maxwell's equations. The forces of nature had been reduced to two, gravitation and electromagnetism. In view of what had been learned about electromagnetism, it seemed fairly clear that Newton's Law of Gravity was probably a simple surface view of a much deeper problem, one that Einstein addressed early in the 20^{th} century with the General Theory of Relativity. It appeared that physics was well on its way to a complete picture of the universe in terms of two fundamental forces.

A fundamental feature of the Newtonian view was that space and time were continuous concepts into which the physical world was embedded. The motions of all the mass particles were completely determined by the forces of interaction. The only limit on our ability to predict the behavior of all the constituents of the universe was the sheer magnitude of its size and the number of constituents. Some people thought that physics was complete – all that was left was to work out methods for solving problems of greater and greater complexity. Around the end of the 19^{th} century a variety of puzzling observations casting serious doubt on the completeness of the Newtonian view of nature began to emerge. The desire to understand these observations led to a profound change in our world-view, the development of quantum theory. A lesson that could be drawn from this experience is that we should be skeptical of claims that there is nothing more to be learned.

1.1.1 Properties of Atoms

During the 19^{th} century, primarily through the work of chemists plus a few physicists (notably Michael Faraday), the idea of atoms became established as a solid working hypothesis to explain the rules of chemical combinations. Although not directly observable, the atoms explained a large variety of phenomena. On the other hand, the hypothesis led to many questions which could not be answered within the framework of Newtonian mechanics. Some of the successes and difficulties are reviewed in this section.

Using the hypothesis of the atom, some bulk properties of materials and rules for proportions involved in chemical reactions could be explained. From the incompressibility of solids and liquids and from Avogadro's number the size and mass of the atoms could be estimated (some details will be given later). The atoms were all about the same size (of the order of a few Angstroms) from lightest to heaviest. Why were they this particular size and why were they about the same size? How did an atom of one element differ from the atom of another?

At temperatures near the condensation point gases are typically 1000 times less dense than solids, which means the inter-atomic distances are only about 10 atomic diameters, and yet the atoms in a gas move almost independently of each other (one of the properties of an ideal gas). This is hard to understand with classical ideas.

Electric charge was clearly an important property of microscopic matter. The atoms could be induced to emit light by passing electrical discharges through gases. The interaction with electrical currents implied that the atoms contained electrical charge that could absorb energy. (1) If the atoms were neutral and made of charged material, what was their structure? (2)

Why were the emissions from excited atoms in the form of discrete wavelengths of electromagnetic radiation? The Rydberg-Ritz formula for the wavelengths of light emitted by excited atoms was totally at odds with the classical ideas of excited systems.

As the physics of atoms was explored more deeply, more questions arose. Before the construction of the quantum theory, satisfactory answers were not available. Atomic physics provided the motivation for the development of quantum mechanics, and in this course we shall make extensive use of the atom to illustrate its methods. With appropriate modifications to make the theory relativistic and to quantize the force fields as well as the particles of nature, the theory has been extended with success down to the smallest distances that so far have been probed. Quantum mechanics is the basis for our understanding of all atomic and sub-atomic physics.

1.1.2 The discovery of the electron

In 1897 J.J. Thomson[1] published the results of his studies of the particles emitted from the cathode in a cathode ray tubes (CRT). The CRT is a relatively simple device consisting a cathode and an anode sealed inside a glass tube from which most of the air is removed. A high voltage between the electrodes results in the emission of electrons from the anode. The particles can be detected by the glow of fluorescent material painted on the anode end of the glass tube. Thomson hypothesized that the anode was emitting charged particles.

Thomson arranged to pass the particles through a region of electric and magnetic fields, perpendicular to each other and perpendicular to the path of the particles. The electric and magnetic forces could then be balanced to achieve zero deflection of the beam. Only with the electric field, E, a particle with charge q and mass m experiences an acceleration:

$$a = \frac{e}{m} E$$

If the length of the field region is l, the transverse velocity imparted to the particle is,

$$v_T = \frac{q}{m} \frac{El}{v}$$

and the change of direction of the beam as it comes out of the field region is

$$\tan\theta = \frac{v_T}{v} = \frac{q}{m} \frac{El}{v^2}$$

[1] J.J. Thomson, *Phil. Mag.* **44**, 293 (1897).

In order to determine v, the magnetic field, B is turned on and increased until Coulomb force qE and Lorentz force qvB balance each other:

$$v = \frac{E}{B}$$

and,

$$\frac{q}{m} = \frac{E}{B^2 l} \tan\theta$$

With his apparatus Thomson showed the cathode rays behaved like charged particles with a charge to mass ratio of $q/m = -1.7588 \times 10^{11}$ C/kg. He showed that this number was the same for all choices of cathode material. Thomson used some estimates of the mass to infer roughly the value of the charge. The fact that all the particles had identical values for q/m is a strong indication that they all have the same mass and the same charge. He deduced from this work that the particles were an intrinsic part of the structure of the atom, and called them electrons. For more information about Thomson's work see

www.aip.org/history/electron/jjhome.htm

Planck was able to infer from an analysis of thermal radiation that the charge of the cathode ray particles was $q = -1.6 \times 10^{-19}$ C. With this value the mass of the particles is $m = 9.1 \times 10^{-31}$ kg. For comparison, the mass of the hydrogen atom is about 2000 times larger. In 1909 Millikan[2] carried out his famous oil-drop experiment. The oil drops were vastly more massive than the electron mass, and the mass M of an individual droplet could be determined from its terminal velocity as it fell in the earth's gravitational field. The acceleration of a droplet with charge q and mass M in an applied electric field is given by

$$a = \frac{qE}{M}$$

From a measurement of a, the charge q could be easily determined. He found that the charge in all cases was an integer multiple of a fundamental unit of charge, the charge of an electron. With the electronic charge known it became possible to combine it with the results of Faraday's experiments on the charge per gram-atom to determine a precise value for Avogadro's number, the number of atoms in a mole of a substance. From this the atomic masses could immediately be calculated. The liquid and solid form of materials have nearly the same density, and are nearly incompressible. It

[2] R.A. Millikan, *Phys. Rev.* Vol. II, Series II, 109 (1913).

is reasonable to assume that in these forms matter consists of tightly packed spheres, whose size can be determined from Avogadro's number.

For more on the work of Millikan see

http://www.aip.org/history/gap/Millikan/Millikan.html

1.1.3 Difficulties associated with electromagnetic radiation

- More and more experimental phenomena associated with electromagnetic radiation appeared that could not be reconciled with classical theory and the electromagnetic field as described by Maxwell's equations.

  – Black-body radiation law - classical theory clearly wrong, since it predicted an infinite rate of radiation from a body whose temperature was not absolute zero. Rayleigh and Jeans applied the well-established idea of equipartition of the energy to the standing waves in a cavity to obtain the frequency distribution of the energy emitted through a small hole in the cavity (an excellent approximation to a black body). However, their derivation predicted that the energy distribution is proportional to the square of the frequency, $dP = \alpha\nu^2 d\nu$, so that the emitted energy would be infinite. This problem was called the ultra-violet catastrophe and classical ideas could provide no answer as to why the high-frequency modes shouldn't share in the thermal energy of the system.

  – In 1900 Planck[3] published an empirical formula designed to agree with the Rayleigh-Jeans law at low frequencies, but with a free parameter that would cut off the radiation at high frequencies. He could then adjust the parameter to get the best fit to the high frequency part of the measured black-body distributions. Planck's formula is:

$$f(\nu)\ d\nu = \frac{8\pi\nu^2}{c^3}\left(\frac{h\nu}{e^{h\nu/kT}-1}\right)\ d\nu \tag{1.1}$$

  where T is the absolute temperature of the radiator and $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant from the classical theory of thermodynamics. At low frequencies, $h\nu << kT$, this

[3] M. Planck, *Verh. d. D. Phys. Ges.* **2**, 237 (1900).

takes the form:

$$f(\nu) \to \frac{8\pi\nu^2}{c^3}\left(\frac{h\nu}{h\nu/kT}\right) = \frac{8\pi kT\nu^2}{c^3} \tag{1.2}$$

which is the function obtained by Rayleigh and Jeans. The constant, h disappears so the low frequency behavior is independent of its value. At high frequencies $\nu \to \infty$:

$$f(\nu) \ \to \frac{8\pi\nu^2}{c^3}\left(h\nu e^{-h\nu/kT}\right) \to \ 0 \tag{1.3}$$

When he was told that with a single choice of h the formula fit experimental distributions at many different temperatures far better than any empirical formula had a right to, Planck tried to find a derivation. He succeeded in deriving it rigorously from the principles of classical statistical mechanics and thermodynamics, but only by assuming that the radiating oscillators in hot bodies emitted electromagnetic radiation only in quanta of E=hν, where $h = 6.626 \times 10^{-34}$ J/s, and ν is the frequency. Classically, the notion that an oscillator can only emit radiation in units of $h\nu$ makes no sense, and one should let $h \to 0$. If we let $h \to 0$ we get the Rayleigh-Jeans formula with its obviously incorrect high frequency behavior.

Jeans argued that even though the formula agreed with observation, it had to be wrong since it was logically necessary to set $h = 0$. He argued that some other mechanism was responsible for the high-frequency cut-off (he suggested that the supposition that matter is in equilibrium with the ether must be erroneous for high frequencies).

Planck's derivation did not require quantization of electromagnetic radiation, only quantization of the electromagnetic oscillators.

- 1905-1907: Einstein decided to apply Planck's hypothesis on the restrictions for emission of radiation more generally. He made the intellectual leap from quantized operators to quantization of the radiation itself. In particular he applied the idea of quantized absorption and emission to the photo-electric effect and Stoke's law of fluorescence. It had been demonstrated that when light is absorbed on a clean metal surface, electrons can be emitted from the surface. However, it was found that the wave-length of the light must be shorter than some minimum value characteristic of the metal and the cleanliness of the surface. No matter how intense the light no electrons were emitted if the wavelength was too long. It was also found that the energy of the emitted electrons depended only on the wavelength of the light (shorter wavelength, more energy) and not on the intensity of the light. Only the number of emitted electrons depended on the intensity of the light. Einstein[4] solved the puzzle with the simple formula:

$$E_e = h\nu - W = \frac{hc}{\lambda} - W \tag{1.4}$$

where W was a constant for any particular surface, and interpreted to be the energy needed to overcome the attractive barrier binding the surface electrons to the metal.

In 1909 Einstein concluded that light itself consists of quantized units of energy. These packets of energy came to be called photons.

In 1927 Beams and Lawrence demonstrated that no time was required for light to deposit enough energy for the electrons to emerge from the surface. Even at very low light intensity they showed that electrons could emerge within a nanosecond from the time that light was first shone on the surface.

- Compton Scattering. More evidence for the particle like nature of light was provided by experiments that showed that x-rays scattered from electrons obeyed the kinematics for the scattering of particles. Treating the light as particles with energy $h\nu$ and momentum $p = \frac{h\nu}{c}$, it was shown that the total momentum and energy of the system consisting of an x-ray and the electron were conserved by the collision.

1.1.4 The Rutherford-Bohr Atom

- After his discovery of the electron as a constituent of matter Thomson created a model of the neutral atom. This model was designed to make the atom electrically neutral and to account for the fact that the mass of the electron was much smaller than the mass of the atom. Thomson's atom consisted of a uniform distribution of some unknown positively charged material with negative electrons embedded in it. It was sometimes called the "plum-pudding" model. A watermelon might

[4] A. Einstein, *Ann. der Phys.* **20**, 199 (1906).

be a better analogy. This model enjoyed considerable popularity until it was discredited by the first experiment to make a real study of the structure of the atom.

- In 1911 Rutherford and his assistants carried out one of the classic experiments of physics (the prototype of a large fraction of all the studies carried out in the 20th century on the properties of the microscopic world) Rutherford had already proved that the alpha particles emitted by certain heavy radio-active elements were doubly-charged ionized helium atoms[5]. For a given element the alpha particles are mono-energetic, with an energy of several MeV. Using slits to collimate the mono-energetic alpha particles emitted from a radioactive source, the beam of alpha particles was directed at a thin gold foil. A fluorescent detector was used to observe the alpha's emerging on the other side of the foil at various angles to the beam direction.

  Let us see what we can expect from this experiment based on the Thomson model of the atom. First Let us assume that the gold atoms are uniformly charged spheres of radius R and positive charge Q, we will consider the effects of the electrons later. The electric field inside the atom at a distance r from the center of the sphere is determined by Gauss' law to be

$$\Phi_E = \oint \mathbf{E} \cdot d\mathbf{A} = \frac{q_{in}}{\epsilon_0}, \tag{1.5}$$

$$q_{in} = Q\tfrac{r^3}{R^3} \tag{1.6}$$

$$\Rightarrow E4\pi r^2 = \tfrac{Qr^3}{\epsilon_0 R^3}, \tag{1.7}$$

$$\Rightarrow E = \tfrac{1}{4\pi\epsilon_0} Q \tfrac{r}{R^3} \tag{1.8}$$

  Outside the atom electric field would be that of a point charge of magnitude Q.

  So the potential seen by an alpha particle of charge q is:

$$V(r) = k_e \frac{qQ}{r} \qquad \text{outside;} \tag{1.9}$$

$$V(r) = k_e \left[\frac{3qQ}{2R} - \frac{qQr^2}{2R^2}\right] \qquad \text{inside;} \tag{1.10}$$

  Thus the maximum potential energy of the alpha particle as it passes by an atom would be about $k_e\frac{3qQ}{2R}$. Using the atomic radius of the

[5] E. Rutherford and T. Royds, *Phil. Mag.* **17**, 281 (1909).

order of an Angstrom, this is about 3 keV. Note that the presence of the electrons would reduce this potential energy even further as they shield the electric field due to the positive charge distribution. Since the kinetic energy of the alpha particles used was of the order of several MeV, Rutherford expected the alpha particles to plow through the gold atoms with hardly any deflection in their direction of motion. Instead, they found that a surprising number of the alpha particles were deflected through large angles, occasionally almost directly backward. To explain these observations Rutherford proposed a different model of the atom, [6] in which nearly all the mass and the positive charge were concentrated at a point. Knowing the charge and mass and assuming that the alpha particles and the positive charge interacted according to Coulomb's law, he was able to calculate the orbits they would follow. Since Coulomb's law is an inverse square law, the orbits are the same as for gravitational attraction: the trajectories are parabolas. Assuming that the alpha particle beam was uniformly distributed over some cross section much larger than the atomic size, Rutherford could calculate the fraction of alpha particles deflected into any given angular range. The calculations were in excellent agreement with the experimental observations. For a readable and detailed account of a long string of detailed experiments carried out by Geiger and Marsden, see their published paper[7].

Thomson's plum-pudding model was ruled out by this experiment, and the Rutherford model looked like a serious replacement. In this model all of the mass of the atom is concentrated in a very small region which carries a positive charge Ze where Z is the atomic number of the atom. The negative charge needed to neutralize the atom can be attributed to Z electrons, whose mass is very small relative to the atomic mass. The electrons circulate around the positive charge much like planets around the sun. The radius of the largest orbit determines the size of the atom. For all atoms, the electron farthest from the center of the atom sees the nuclear charge screened by the inner electrons. The effective charge binding the outermost electron is then just one unit of charge [Ze-(Z-1)e]. It follows that the orbital radius of the outer most electron is the same for all atoms, so that all atoms would be about the same size.

[6]E. Rutherford, *Phil. Mag* **21**, 669(1911).
[7]Geiger and Marsden, *Phil. Mag.*, Ser. 6, Vol. 25, No. 148, April, 1913.

Rutherford's planetary model however had some significant problems in the framework of classical E&M. The circulating electrons are accelerated toward the center of the atom and in classical E&M accelerated electrons radiate electromagnetic energy. As they lose energy from radiation they will spiral into the nucleus and combine with its positive charge, reducing the atom to Thomson's model. If one could find some mechanism to prevent the fall into the nucleus, then the spiraling in of electrons with extra energy would account for the electromagnetic radiation from excited atoms. However the classical theory predicts emission of a continuous distribution of electromagnetic frequencies, not the discrete frequencies actually emitted by excited atoms. Rutherford's model explained the alpha particle scattering experiment, but it couldn't account for the stability of unexcited atoms or for the discreteness in the wavelengths emitted by excited atoms..

- In 1912 Niels Bohr, who had recently received his Ph.D. and was looking for a place to pursue his post-doctoral work, came to Rutherford's laboratory. Starting with Rutherford's concept of the atom, he began trying to develop a mathematical model for Rutherford's atom. At a seminar he happened to hear for the first time about Rydberg's empirical formula for the wavelengths emitted from the excited hydrogen atom. Apparently this resulted in an epiphany tying together ideas that he had tried in his efforts to make an atomic model. A year after arriving, he proposed his famous model of the atom [8]. According to this model electrons circled the positive nucleus, bound by the Coulomb force, in circular orbits whose angular momenta were quantized. As a result, the allowed energies of the atom were also quantized. The lowest energy orbit had one unit of angular momentum and was stable against losing energy. The atom could be excited only to one of the discrete allowed energy states and the de-excitation could occur only by a jump to a lower energy level with simultaneous emission of a photon with energy $E = h\nu$ equal to the difference in the energies of the two levels. The angular momentum quantization condition was related to some ideas from classical Hamiltonian mechanics, but in fact had no compelling basis. It simply seemed to work. The discrete changes in energy allowed by the model agreed perfectly with the Rydberg formula for the hydrogen atom.

  We will give a brief derivation of the Bohr model after we discuss the

[8] N. Bohr, *Phil. Mag.* **26**, 1; 476; 857 (1913).

contribution of de Broglie.

- 1912-1923 - Over the next decade, which included the major disruption of World War I, the Bohr model was generalized, and refined, and built into a complex system of postulates and empirical rules now known as the *old quantum theory.* It was very successful in describing the systematics of atomic spectra, but it lacked any dynamical capabilities, and clearly was not the real theory. It also had many striking failures and inconsistencies. For instance, it could not account for the fact that the ground state of the hydrogen atom had zero angular momentum, it could not accommodate non-circular orbits, etc. Following World War I, revolutions occurred throughout the world. There are suggestions that this revolutionary spirit led to the revolutionary developments that occurred over a very short period beginning in 1923.

1.2 The Development of Quantum Mechanics

- 1923-25 - Louis de Broglie[9] proposed that particles should all be assigned a wave-length $\lambda = h/p$. We can derive this rather simply by using Planck's condition, $E = h\nu$, and the classical result that the energy associated with a particle moving with the velocity of light is $p = E/c$. Then, $p = h\nu/c = h/\lambda$. De Broglie used a more complex derivation based on the assumption that light quanta themselves had mass, (very small). He assigned to the quantum in its rest frame a frequency $E_0 = m_0c^2 = h\nu_0$ and then used the laws of special relativity to transform this frequency to some other frame in which their momentum was not zero, and then obtained the relation between wavelength and momentum in this frame. He then hypothesized that the rule could be applied to all particles. (In modern physics, we generally assume that the photon mass is zero. What does experiment have to say about this assumption?)

  Then de Broglie argued that the circumference of the orbits must be an integral number of electron wavelengths (to prevent the wave from canceling itself out after many orbits. This condition is identical to the Bohr quantization condition.

- 1925 - W. Heisenberg[10] published a famous paper "On the quantum

[9] L. de Broglie, *Ann. der Phys.* **10**, 22(1925).
[10] W. Heisenberg, "Uber die quantentheorentische Umdeutung kinematischer und mechanischer Beziehungen", *Zeit. fur Phys.* (1925).

theoretical interpretation of kinematical and mechanical relations". He based his theory on the idea that classical concepts such as velocity and location of the electrons in the atom were not measurable, and should be replaced with relations between observable quantities. The idea that physical theories must be restricted to concepts that are measurable (at least in principle) was a revolutionary step. Quantities that can in principle, even if not in practice, be measured are called "observables". He invented the algebraic rules that defined and connected the physical observables as he went along. In September of 1925 Max Born and Pasqual Jordan pointed out that Heisenberg's rules were the rules of matrix algebra.

- Subsequent direct experimental evidence of the wave properties of electrons and other particles.
  - 1926- Elsasser suggested that the wave nature of matter might be tested by allowing a beam of electrons to fall on a crystalline solid, the atoms of which would act like a three-dimensional array of diffracting centers. Davisson and Germer[11] at Bell Labs got into this business following a fortuitous accident that led to their observation of diffraction of electrons by crystals. The patterns could be completely explained in terms of optical diffraction by the regular pattern of atoms in the crystal.
  - The electron microscope
  - Wave properties of neutrons, protons, etc. have all been demonstrated over the years.

- 1926 -

  Once at the end of a colloquium I heard Debye saying something like: " Schrödinger, you are not working right now on very important problems...why don't you tell us some time about that thesis of de Broglie, which seems to have attracted some attention?" So, in one of the next colloquia, Schrödinger gave a beautifully clear account of how de Broglie associated a wave with a particle, and how he could obtain the quantization rules ... by demanding that an integer number of waves should be fitted along a stationary orbit. When he had finished, Debye casually remarked that he thought this way of talking was rather childish... To deal properly with waves, one had to have a wave equation.

[11] see Richard K. Gehrenbeck, *Physics Today*, **31**, #1, 34 (1978).

Felix Bloch, in his Address to the American Physical Society (1976), as quoted in "An Introduction to Quantum Physics", by A.P. French and E.F. Taylor.

Before discussing how this remark motivated Schrödinger to carry out his famous work, we first ask, what is this exposition of the Bohr model? Using the model developed by Rutherford, Bohr assumed that the electrons(charge=-e) circled the nucleus(charge=+e) in planetary-like orbits, moving under the influence of the Coulomb central force. Equating the required centripetal force for a circular orbit to the Coulomb force:

$$\frac{mv^2}{r} = \frac{ke^2}{r^2}, \qquad mv^2 = \frac{ke^2}{r} \tag{1.11}$$

Using de Broglie:

$$\lambda = h/p = h/(mv) \tag{1.12}$$

Requiring that the circumference of the orbit be an integral number of such wavelengths:

$$2\pi r = nh/(mv) \tag{1.13}$$

Defining $\hbar = \frac{h}{2\pi}$:

$$v = \frac{n\hbar}{mr}, \qquad mvr = n\hbar \text{ (Bohr's quantization condition)} \tag{1.14}$$

By direct substitution into Eq. 1.11:

$$m\left(\frac{n\hbar}{mr}\right)^2 = \frac{ke^2}{r} \tag{1.15}$$

$$\frac{n^2\hbar^2}{mr} = ke^2 \tag{1.16}$$

$$r = \frac{n^2\hbar^2}{kme^2} \tag{1.17}$$

From this value for r we can also solve for v:

$$v = \frac{n\hbar}{mr} = \frac{n\hbar}{m}\frac{kme^2}{n^2\hbar^2} = \frac{ke^2}{n\hbar} \tag{1.18}$$

The energy of the electron is given by:

$$E = \frac{1}{2}mv^2 + V(r) = \frac{1}{2}mv^2 - \frac{ke^2}{r} \tag{1.19}$$

Using Eq. 1.11:

$$E = \frac{ke^2}{2r} - \frac{ke^2}{r} = -\frac{ke^2}{2r} \tag{1.20}$$

Substituting in r from Eq. 1.17, we obtain an infinite number of allowed energies, E_n:

$$E_n = -\frac{ke^2}{2}\frac{kme^2}{n^2\hbar^2} = -\frac{k^2me^4}{2\hbar^2}\frac{1}{n^2} \tag{1.21}$$

In the MKS system of units:

$$k = \frac{1}{4\pi\epsilon_0}$$

$$E_n = -\frac{me^4}{32\hbar^2\epsilon_0^2}\frac{1}{n^2} \tag{1.22}$$

The energies of the electron are restricted to a series of negative values, with the lowest energy, or ground state, obtained by setting $n = 1$. The ground state energy is:

$$E_1 = -\frac{me^4}{32\pi^2\hbar^2\epsilon_0^2} = -13.7 \text{ eV} \tag{1.23}$$

If the atom is excited to states of higher energies, it will decay to a lower energy state, emitting energy in the form of light, with allowed frequencies given by $h\nu_{if} = E_i - E_f$.

$$h\nu_{if} = h\frac{c}{\lambda} = \frac{me^4}{32\pi^2\hbar^2\epsilon_0^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

The allowed wavelengths are in agreement with Rydberg's formula. A simple examination of the energy-level diagram reveals the Ritz combination law. The mechanisms for excitation and decay could not be determined from this simple model, but the spectral frequencies agreed very well with the observed atomic spectra.

Summary of the Bohr model:

$$\hbar = 1.05 \times 10^{-34} \text{ J s}, \qquad m = 9.122 \times 10^{-31} \text{ kg}, \qquad e = 1.6 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.85 \times 10^{-11} \text{ C}^2/\text{Nm}^2, \qquad \text{k} = \frac{1}{4\pi\epsilon_0} = 8.99 \times 10^9 \text{ Nm}^2/\text{C}^2$$

$$E_n = -\frac{me^4}{32\hbar^2\epsilon_0^2}\frac{1}{n^2} = -\frac{13.7}{n^2}\text{ eV}$$

$$r_n = \frac{n^2\hbar^2}{kme^2} = .525n^2 \times 10^{-10}\text{ m}$$

Apparently Debye's remark set Schrödinger off to develop an equation for de Broglie's waves, and in January, 1926 he published[12] his wave-function in a paper on "quantization as an eigenvalue problem". In this paper he introduced his postulates on how to make the transition from classical mechanics to quantum mechanics, applied his equation to the hydrogen atom, and solved the equation in much the same manner that we will use. One month later in February, 1926, he showed that the perturbation theories of classical mechanics could be extended to quantum mechanics. In March, 1926, he showed the equivalence between his theory and Heisenberg's.

- 1927 - Heisenberg's formulation of the Uncertainty Principle. This is in effect the basic feature of quantum mechanics.
- These theories were non-relativistic. The "fine structure" splitting of atomic spectral lines had already been a problem for the old quantum mechanics, and in October, 1925, two Dutch physicists, G.E. Uhlenbeck and S. Goudsmit, using the old theory, explained the splitting in terms of an intrinsic angular momentum of the electron, or spin.
- 1927 - Pauli presented a formal theory for electron spin, using matrix notation.
- The theory was being applied to everything in sight. Then in
- 1928 - P. A. M. Dirac[13] published an article on"The Quantum Theory of the ELectron", which reconciled quantum mechanics with special relativity, showed that the spin of the electron was a natural consequence of the theory, and predicted the existence of anti-electrons, or positrons.

All of this fantastic achievement occurred over a period of only 3 years. During the 1930's a vast array of techniques for the solution of problem in atomic physics were developed, testing the quantum theory in myriad

[12]E. Schrödinger, "Quantisierung als Eigenwert Problem", *Ann. der Phys.*, (1926).
[13]P.A.M. Dirac, *Proc. Roy. Soc.*, **117**, 610 (1928).

ways. Methods for the solution of problems involving the electromagnetic force and radiation were developed. Following an interruption by World War II, more precise experiments revealed atomic features that the quantum theory could not account for. The most famous was the measurement of the *hyper-fine splitting* of levels in atomic hydrogen, measured by Willis Lamb. In the late 1940's and early 1950's Schwinger, Feynman and Tomonaga developed methods for quantizing the electromagnetic field itself, known as Quantum Electro-Dynamics (QED). The methods are inherently based on perturbation theory, and so far the theory has not been contradicted by any experiment.

In the 1970's the weak interaction was unified with QED. Then quantum chromodynamics (QCD) was developed following the model of the field theory for QED, and introducing a new kind of charge, color, a new set of field quanta, the gluons, and a group of color charge carriers, the quarks.

1.3 The Schrödinger Equation

According to Newton's law, the motion of a particle of mass m in one dimension is governed by the law:

$$m\frac{d\mathbf{v}}{dt} = \mathbf{F}(\mathbf{r}) \tag{1.24}$$

You have learned that for *conservative forces*, the force can be written as the gradient of a function of position, called the potential, so that:

$$m\frac{d\mathbf{v}}{dt} = -\vec{\nabla}V \tag{1.25}$$

We can integrate this over the path $\mathbf{s}$ taken by the particle between positions P_1 and P_2:

$$\int_{P_1}^{P_2}\left[m\frac{d\mathbf{v}}{dt} + \vec{\nabla}V\right]\cdot d\mathbf{s} = 0 \tag{1.26}$$

Noting that

$$\mathbf{v} = \frac{d\mathbf{s}}{dt},$$

we can write:

$$m\frac{d\mathbf{v}}{dt}\cdot d\mathbf{s} = m\frac{d\mathbf{v}}{dt}\cdot\frac{d\mathbf{s}}{dt}dt = m\mathbf{v}\cdot\frac{d\mathbf{v}}{dt}dt = \frac{1}{2}\frac{d(mv^2)}{dt}dt \tag{1.27}$$

Integrating over the path followed between two successive points:

$$\frac{1}{2}mv^2 + V(\mathbf{r}) = E \tag{1.28}$$

where E is a constant of the motion. Defining the first term as kinetic energy, the second as potential energy and E as total energy we obtain the law of conservation of energy for conservative forces. The solution of this equation along with initial conditions on position and velocity completely determines the motion of the particle for all earlier and later times.

Fortunately, in the atomic world, the fundamental forces are all conservative, so we represent them with a potential. However, rather than writing an equation for the position $x(t)$ of a particle, Schrödinger started from de Broglie's idea that a particle could be represented in some sense by a wave, $\Psi(x,t)$, whose wave-length was related to its momentum. Classically a variety of equations to represent the spatial and time dependence of waves had been well studied These equations are typified by a linear relationship between partial derivatives with respect to space and time. Schrödinger found a specific, and somewhat unusual, equation that he could solve with classical methods for boundary value problems to obtain the energy levels of the hydrogen atom. In one dimension Scrhödinger's equation is:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{1.29}$$

where m is the mass of the particle and $V(x,t)$ is the potential energy. In addition to the mass, the equation includes a variant of Planck's constant as a scale factor:

$$\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34} \text{ J s} \tag{1.30}$$

The three-dimensional generalization is straight-forward. We simply add second derivatives with respect to y and z and replace $V(x,t)$ by $V(\vec{r},t)$. Before long we will see the relationship between the Schrödinger Equation and the classical equation for conservation of energy.

In comparison to the classical wave equation that you have studied, the Schrödinger Equation has two unusual features. (1) The imaginary number $i = \sqrt{-1}$ implies that the solutions are intrinsically complex. (2) The equation contains a first-order time derivative rather than the usual second order time derivative. Given an appropriate set of initial conditions at $t = 0$, as well as boundary conditions, we can solve the differential equation for later times.

Free particle solution – separation of variables

Now suppose we examine this equation a bit more in light of de Broglie's hypothesis. Let us consider a free particle ($V = 0$), so classically, at least, its momentum should be constant. Then the Schrödinger Equation becomes:

$$\frac{-\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{1.31}$$

We can try to obtain a solution in the form $\psi(x,t) = f(x)g(t)$. Then:

$$\frac{-\hbar^2}{2m}g(t)\frac{d^2f(x)}{dx^2} = i\hbar f(x)\frac{dg(t)}{dt} \tag{1.32}$$

If we move all the constants to the rhs and divide by the product fg:

$$\frac{1}{f}\frac{d^2f(x)}{dx^2} = -i\frac{2m}{\hbar}\frac{1}{g}\frac{dg(t)}{dt} \tag{1.33}$$

The left side doesn't depend on time, and the right side doesn't depend on x, and this can only be true for all times and places if both sides are equal to a constant. Let us then write:

$$\frac{1}{f}\frac{d^2f(x)}{dx^2} = -k^2, \qquad -i\frac{2m}{\hbar g}\frac{dg(t)}{dt} = -k^2 \tag{1.34}$$

Concentrating on the first equation:

$$\frac{d^2f(x)}{dx^2} + k^2 f = 0 \tag{1.35}$$

The general solution can be written:

$$f(x) = A\sin(kx+\phi) \tag{1.36}$$

The second equation is a first order differential equation:

$$\frac{dg(t)}{dt} = \frac{\hbar k^2}{2im}g = -i\frac{\hbar k^2}{2m}g \tag{1.37}$$

Its solution contains one arbitrary constant:

$$g(t) = Be^{-i\hbar\frac{k^2}{2m}t} \tag{1.38}$$

Combining the two solutions, the solution to the Schrödinger Equation is:

$$\Psi(x,t) = A\sin(kx+\phi)e^{-i\hbar\frac{k^2}{2m}t} \tag{1.39}$$

with A, ϕ and k free to be given any values. At a fixed time, the solution is sinusoidal in x, with a wave-length:

$$\lambda = 2\pi/k \tag{1.40}$$

Using deBroglie's hypothesis, $\lambda = h/p$, so:

$$h/p = 2\pi/k \tag{1.41}$$

which tells us that if the wave is to represent a particle of momentum p we must choose k to be:

$$k = \frac{p}{\hbar} \tag{1.42}$$

The time dependent function can be written as:

$$g(t) = e^{-\frac{i\hbar p^2}{2m\hbar^2}t} = e^{-\frac{ip^2}{2m\hbar}t} \tag{1.43}$$

But, classically:

$$p^2/2m = E \tag{1.44}$$

where E is the kinetic energy of the particle so that:

$$g(t) = e^{-i\frac{E}{\hbar}t} \tag{1.45}$$

We can now write the solution of Schrödinger Equation as:

$$\Psi(x,t) = A\sin\left(\frac{p}{\hbar}x + \phi\right)e^{-i\frac{E}{\hbar}t} \tag{1.46}$$

At any given time, this is a sinusoidal wave extending over the entire x axis, with a wavelength $\lambda = h/p$. Thus, we are tempted to say that this is the wave representing a particle with momentum p. Where is the particle? The wave seems to be everywhere. Is the particle everywhere? What is the significance of the time dependence?

Let us define:

$$\omega \equiv \frac{E}{\hbar} \tag{1.47}$$

so that the time-dependent part is:

$$e^{-i\omega t} = \cos(\omega t) - i\sin(\omega t) \tag{1.48}$$

Except for the complication that it has both real and imaginary parts, this time dependent function represents an oscillation with angular frequency, ω. Because Planck's constant is so small, this frequency is enormous for ordinary macroscopic energies. For energies comparable to the ground state energy of the hydrogen atom, we obtain:

$$\omega = 13.7 \cdot 1.6 \times 10^{-19}/1.05 \times 10^{-34} = 2.09 \times 10^{16}\ \mathrm{s}^{-1} \tag{1.49}$$

The corresponding frequency and wave-length are:

$$\nu = \frac{\omega}{2\pi} = 3.32 \times 10^{15} \text{ Hz}, \quad \lambda = 904 \times 10^{-10}\text{m} \tag{1.50}$$

This wave-length would be emitted if an electron should fall directly from a very high excited state to the ground state of hydrogen. The wavelength of visible light ranges from $4000 - 7200 \times 10^{-10}$ m, so it is in the ultra-violet part of the electromagnetic spectrum. The unit of 10^{-10} m is called the *Angstrom*, and is roughly the diameter of an atom. It is more common now to use the unit $1\text{m}\mu = 10^{-9}$ m.

Comparison to non-dispersive wave equation

A more familiar wave equation is the one for waves on a string, or for a plane light-wave, which has the form:

$$\frac{\partial^2\psi}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} = 0 \tag{1.51}$$

where v is a constant that depends on the density of the string and its tension. For an electromagnetic wave in free space, v is the velocity of light, c. This equation can be solved by using any function $f(u)$ where $u = x \pm vt$. The solutions are in the form of a function that propagates uniformly along the x axis with velocity, $\mp v$. As a special case, we can use a harmonic solution:

$$u = A\sin\left(k(x - vt)\right) = A\sin\left(kx - \omega t\right) \tag{1.52}$$

This represents a sine wave of angular frequency $\omega = kv$, with wave-length $\lambda = 2\pi/k$. The sine wave propagates to the right with *wave-velocity*, $v_w = v$. The wave-velocity is independent of the frequency, and the wave-equation is said to be non-dispersive.

The *wave-velocity* is also frequently called the *phase velocity*.

General solution of S.E. for a free particle

The solution to the Schrödinger Equation that we obtained by separation of variables is not in itself the most general sort of solution. We could make a more general one by adding a second solution, e.g. the cosine function, where the additive constant could be imaginary as well as real. The trouble with our solution is that it does not represent a traveling wave, and it would be a nuisance to combine two independent stationary waves to obtain a traveling wave when there is a simpler way to proceed. We can write the solution in the simple form:

$$\Psi(x,t) = Ae^{\frac{i}{\hbar}(px-Et)} = Ae^{\frac{i}{\hbar}px}e^{-\frac{i}{\hbar}Et} \tag{1.53}$$

where A can be a complex number. To prove that this is a solution simply insert its derivatives into the Schrödinger Equation . The wave-length associated with this wave is

$$\lambda = \frac{2\pi\hbar}{p}$$

The period of the wave is

$$T = \frac{2\pi\hbar}{E} = \frac{h}{E}$$

and the frequency is

$$\nu = \frac{E}{h}$$

The wave-velocity for this function is obviously:

$$v_w = E/p = \frac{mv^2}{2mv} = \frac{v}{2} \tag{1.54}$$

We make two observations about this result. 1) the wave velocity depends on the particle momentum, which is reasonable, 2) however, it seems odd that the wave velocity is half the particle velocity. The meaning of the wave velocity of an infinite wave is perhaps not so clear. The theory of Fourier transforms provides a procedure to combine unconfined waves of different frequencies as a linear sum to form a wave packet confined to a small region in space. In this way we could construct a function to represent a localized particle. However, it is known that the more tightly we localize the packet the greater the range in frequencies(and hence, momenta) that we must use to construct it. A localized particle would be described by waves with a range of frequencies, and therefore, according to de Broglie, a range of momenta, which is certainly not a classical concept. There is yet another problem. Since the different waves in the combination have different wave velocities the packet would spread out in time. The Schrödinger Equation is necessarily *dispersive.* Localized packets will spread out as time progresses. Before we worry about this problem any more deeply, it is time to give a precise meaning to the wave-function.

1.4 Interpretation of the Wave Function

Although we will see that the application of the Schrödinger Equation to the hydrogen atom doesn't actually require any precise interpretation of the wave-function, we could hardly be satisfied without trying to give it some physical interpretation. Moreover, there will be many other applications (such as the description of a free particle) in which the interpretation of the wave function will play a role.

The interpretation of the wave-function has been the subject of a lot of debate, and is probably not fully resolved yet in everyone's mind. We would probably agree that if the wave function is large in a region A and negligible elsewhere, it is reasonable to expect the particle to be located in A. Since experiments measure real numbers, for example, the position of the particle, we require that any physical information associated with the complex wave function must be real. An important real quantity associated with a complex number is its magnitude. A complex number can be represented by its magnitude and a phase angle whose tangent is the ratio of the imaginary and real parts. For example we can write the constant A for our free particle solution as:

$$A = A_0 e^{i\phi} = A_0 \cos\phi + iA_0 \sin\phi = \Re\{A\} + i\Im\{A\} \tag{1.55}$$

where A_0 and ϕ are real. The free particle solution is then:

$$\Psi(x,t) = A_0 e^{i(\frac{px-Et}{\hbar}+\phi)} = A_0 e^{i\theta(x,t)} \tag{1.56}$$

This is a function with a constant magnitude and a phase dependent on space and time. The function is equally important everywhere in space.

The usual interpretation of the wave-function is due to Max Born: **The magnitude squared of the wave function is the probability distribution for measurement of the position of a particle**. Quantitatively, the probability that a measurement of the particle's position at time t will yield a value between x and $x + dx$ is:

$$P(x,t)dx = |\Psi(x,t)|^2 \, dx \tag{1.57}$$

This is known as the *statistical interpretation*, implying that the most we can learn from the wave function is a probability, not an exact prediction that we are used to obtaining from Newtonian mechanics. Unless the value of $\Psi(x,t) = 0$ for some choice of x and t there is always a chance that we might find the particle there when we look for it.

For our free-particle, the probability distribution is:

$$P(x)dx = A_0^2 \, dx \tag{1.58}$$

The particle is equally likely to be anywhere. The probability that it is in any particular finite region of space out of an infinite number of such finite regions must be zero. Clearly, there are some mathematical difficulties associated with the solution of a free particle.

If we accept the probability interpretation there are still some interesting questions. Suppose we do make a measurement of the position at time t, and find it at $x = X$. Ok, I know where it is now, where was it an infinitesimal time before.

Some possible answers:

1. It was at X or at least within an infinitesimal distance of X.

2. It wasn't anywhere, since its position hadn't yet been measured.

3. It's an ill-defined question. If the answer is not subject to experimental verification there is no reason to give an answer.

Einstein favored the first answer. The particle was at X, but we simply didn't know it until we made the measurement. This leads to the question of why the theory doesn't contain this information explicitly. Proponents argued that the theory must be incomplete, due to our ignorance or limited imagination, and that there must be some additional variables (hidden variables) that should be included in the theory. The fact that we are too stupid to find them doesn't mean they don't exist.

Over the years, through the forceful arguments of Bohr the second answer became the favored one. This is called the *Copenhagen interpretation.* According to this interpretation the act of measurement forces the particle to be somewhere, but before that it was nowhere, or anywhere. Once on an evening walk, Einstein after looking at the moon, said do you really believe the moon is not there until somebody looks at it? We probably all think it is there, but perhaps one should be careful about applying quantum mechanics to a macroscopic object containing the order of 10^{30} particles.

The third answer is sort of a cop-out, but it is not totally without merit.

In 1964, John Bell showed that the answer could in fact be provided by experiment. It makes a difference in the probabilities if the particle has a definite (but unknown) position before the experiment is done. The experiments have been done, and apparently support position 2.

This leads us to another obvious question: After I measure the position of the particle, suppose I measure it again a very short time later. Will I get the same answer as from the first experiment? Well, if I didn't, the position measured in the first experiment doesn't have much meaning. In fact, a repeated measurement does give the same answer, provided one doesn't wait so long that the particle has moved on. So what is the wave function that is to be used for calculating the probability distribution for the second measurement. It must be totally different than before the measurement, since now it must give 100% probability of finding the particle at X at time $t = 0$. We describe this change of the wave function to what is basically a delta function at $t = 0$ as the *collapse of the wave function*, brought about by the measurement. As time passes after the measurement the wave function whose initial state is a delta function will evolve according to the Schrödinger Equation and over time become more spread out, and our knowledge of the position that will be revealed by another measurement decreases steadily as time passes. This spreading out of the wave-function is inherent in the dispersive nature of the Schrödinger Equation

1.5 Elements of Probability Theory

Since probability will play a central role in the interpretation of quantum mechanical calculations, it is a good idea to review the basic ideas of probability theory. We can begin with a treatment of the probability behavior of discretely distributed quantities, such as the number of pennies which will be found with heads up if we dump a can full of them onto a table, or the number to be found on the upward face of a die thrown onto a table.

1.5.1 Discrete variables

Most probable result: the value of j for which the probability is maximum.

Median: The value of j for which half the cases lie below and half lie above.

Average or mean: The average value of many measurements on an identically prepared system:

$$\langle j \rangle = \sum_{j=0}^{\infty} j P(j) \quad , \quad P(j) = \frac{N(j)}{\sum_{k=0}^{\infty} N(k)} \tag{1.59}$$

In q.m. we use the name **expectation value** for this quantity.

Variance or standard deviation: the average of the squared difference between a case and the mean value:

$$S.D. \equiv \sigma^2 = \sum_j (j - \langle j \rangle)^2 P(j) \tag{1.60}$$

Most probable value: the value of j that appears the most number of times in the set $\{j_i\}$. If no value appears more than once then there is no most probable value. However, in that case you might make the bins in j bigger so that several cases appear in the same bin.

Useful relation for the standard deviation:

$$\sigma^2 = \sum_j (j - \langle j \rangle)^2 P(j) = \sum_i \left[j^2 - 2j\langle j \rangle + \langle j \rangle^2\right] P(j)$$

$$\begin{aligned}
\sigma^2 &= \left[\sum_j j^2 - 2\sum_j \langle j \rangle j + \sum_j \langle j \rangle^2\right] P(j) \\
&= \sum_j j^2 P(j) - 2\langle j \rangle \sum_j j P(j) + \langle j \rangle^2 \sum_j P(j) \\
&= \langle j^2 \rangle - 2\langle j \rangle^2 + \langle j \rangle^2 \\
\sigma^2 &= \langle j^2 \rangle - \langle j \rangle^2
\end{aligned} \tag{1.61}$$

Since σ^2 cannot be negative, it follows that $\langle j^2 \rangle \geq \langle j \rangle^2$,

Example: Distribution of grades on a quiz. Let g be a possible grade, and let N_g be the number of students with the grade g.

Grade (g)	Number of cases(N_g)	g^2	$N_g\,g$	$N_g\,g^2$
5	1	25	5	25
6	2	36	12	72
7	6	49	42	294
8	7	64	56	448
9	4	81	36	324
10	1	100	10	100
sums	21		161	1263

Table 1.1: Distribution of grades on a quiz

There are a total of $N = 21$ students.

Most probable value: the grade g obtained by the largest number of students $= 8$.

Median value: $= 7\frac{1.5}{7} = 7.2$

Mean:

$$\langle g \rangle = \frac{\sum_g N_g g}{N} = 161/21 = 7.66$$

Standard deviation:

$$\langle g^2 \rangle = \frac{\sum_g N_g g^2}{N} = 1263/21 = 60.1$$

$$\sigma^2 = 60.1 - 7.66^2 = 1.41, \qquad \sigma = 1.2$$

Continuous distributions: Let $\rho(x)$ be a function that expresses the distribution of probabilities. Its maximum value is the most probable value. However, for continuous distributions, the chance of getting one particular value of x is 0. We must look in the neighborhood of x. The smaller the neighborhood the less chance we will have of getting the value. The probability that a value between x and $x + dx$ will be obtained is:

$$\rho(x)\ dx \tag{1.62}$$

The probability of obtaining a value between a and b is:

$$P_{ab} = \int_a^b \rho(x)\ dx \tag{1.63}$$

The probability that some value is obtained must be 1, so the probability distribution must have the property:

$$\int_{-\infty}^{\infty} \rho(x)\ dx = 1 \tag{1.64}$$

This is called the normalization condition for probability distributions.

The mean value of a continuous distribution is given by:

$$\langle x \rangle = \sum_i x_i P_i = \sum_i\ x_i \rho(x_i)\ dx \to \int_{-\infty}^{\infty}\ x\rho(x)\ dx \tag{1.65}$$

Likewise,

$$\langle x^2 \rangle = \int_{-\infty}^{\infty}\ x^2 \rho(x)\ dx$$

and:

$$\sigma^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2\ \rho(x)\ dx = \langle x^2 \rangle - \langle x \rangle^2 \tag{1.66}$$

Gaussian Distribution: The Gaussian distribution plays an important role in the distribution of statistical quantities. It appears frequently in Quantum Mechanics, so it is very important to be familiar with it:

$$\rho(z) = Ae^{-\alpha(z-z_0)^2} \tag{1.67}$$

Let us first find the area under this function (using Gauss's method):

$$I = A \int_{-\infty}^{\infty} e^{-\alpha(z-z_0)^2}\ dz \tag{1.68}$$

Let:
$$I/A = \int_{-\infty}^{\infty} e^{-\alpha(z-z_0)^2}\ dz \tag{1.69}$$
Change variables, $z - z_0 = x$, so that $dz = dx$. Then:
$$I/A = \int_{-\infty}^{\infty} e^{-\alpha x^2}\ dx \tag{1.70}$$
We can write:
$$(I/A)^2 = \int_{-\infty}^{\infty} e^{-\alpha x^2}\ dx \int_{-\infty}^{\infty} e^{-\alpha y^2}\ dy \tag{1.71}$$
$$(I/A)^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\ e^{-\alpha(x^2+y^2)} \tag{1.72}$$
Now change to polar coordinates:
$$(I/A)^2 = \int_0^{\infty}\int_0^{2\pi} e^{-\alpha r^2}\ r\ dr\ d\phi = 2\pi \int_0^{\infty} e^{-\alpha r^2}\ r\ dr \tag{1.73}$$
Change variables $u = r^2$, so that $du = 2r\ dr$:
$$(I/A)^2 = \pi \int_0^{\infty} e^{-\alpha u}\ du = \frac{\pi}{\alpha} \tag{1.74}$$
Thus, we obtain:
$$I = A\sqrt{\frac{\pi}{\alpha}} \tag{1.75}$$
Usually, the function is tabulated with A chosen to make the integral equal to unity. Then:
$$A = \sqrt{\frac{\alpha}{\pi}} \tag{1.76}$$
We can easily shift the center of the Gaussian by writing:
$$\rho(x) = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(x-x_0)^2} \tag{1.77}$$
In this case the most probable value is $x = x_0$. Since the function is symmetric about x_0, the median is also $x = x_0$

Mean:
$$\langle x\rangle = \int_{-\infty}^{\infty} x\rho(x)\ dx = \int (x-x_0)\rho(x)\ dx + x_0 \int \rho(x)\ dx$$

Change variables, $x - x_0 = u$, so that $dx = du$. Then:

$$\langle x \rangle = \int_{-\infty}^{\infty} ue^{-\alpha u^2}\, du + x_0 = x_0$$

The most probable value, the median and the mean are the same for the Gaussian distribution.

$$\langle x^2 \rangle = \int x^2 \rho(x)\, dx \tag{1.78}$$

Changing variables, $x - x_0 = u$, so that $x^2 = u^2 + 2ux_0 + x_0^2$. Then:

$$\langle x^2 \rangle = A\int_{-\infty}^{\infty} u^2 e^{-\alpha u^2}\, du + 2x_0 A\int_{-\infty}^{\infty} ue^{-\alpha u^2}\, du + x_0^2 A\int_{-\infty}^{\infty} e^{-\alpha u^2}\, du \tag{1.79}$$

Integrating by parts, this reduces to:

$$\langle x^2 \rangle = \frac{1}{2\alpha}\int_{-\infty}^{\infty} Ae^{-\alpha u^2}\, du + x_0^2 = \frac{1}{2\alpha} + x_0^2 \tag{1.80}$$

Standard deviation:

$$\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{2\alpha} + x_0^2 - x_0^2 = \frac{1}{2\alpha} \tag{1.81}$$

Thus, we can replace α with:

$$\alpha = \frac{1}{2\sigma^2} \tag{1.82}$$

thereby obtaining the standard form for the Gaussian distribution:

$$\rho(x) = \sqrt{\frac{1}{2\pi\sigma^2}}\, e^{-\frac{(x-\langle x \rangle)^2}{2\sigma^2}} \tag{1.83}$$

which explicitly displays the mean, median and standard deviation.

At the mean value of x

$$\rho(\langle x \rangle) = \sqrt{\frac{1}{2\pi\sigma^2}}$$

At one s.d. from the mean value, $x - \langle x \rangle = \pm\sigma$,

$$\rho(\sigma) = \sqrt{\frac{1}{2\pi\sigma^2}}\, e^{-\frac{1}{2}} = \rho(\langle x \rangle)e^{-\frac{1}{2}} = 0.6065\rho(\langle x \rangle)$$

The probability that a value lies more than 1 s.d. on either side of the mean is $\approx 1/3$. The probability that a value lies more than 2 s.d. on either side of the mean is $\approx 5\%$. The probability that a value lies more than 3 s.d. on either side of the mean is $\approx 1\%$.

1.6 Normalization

The probability interpretation of the wave-function requires that it be normalized, i.e.:

$$\int_{-\infty}^{\infty} P(x,t)dx = 1 \tag{1.84}$$

so:

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \; dx = 1 \tag{1.85}$$

The Schrödinger Equation is homogeneous, so if $\Psi(x,t)$ is a solution then so is $A\Psi(x,t)$ where A is any constant (it can be complex). Thus, we can normalize the wave function by multiplying the solution by a suitable constant. However, if the normalization integral is infinite, the wave-function is not normalizable and must be rejected as a non-physical solution of the Schrödinger Equation . For example, consider our solution for a particle of pure momentum, p:

$$\Psi(x,t) = Ae^{i(px-Et)/\hbar} \tag{1.86}$$

$$P(x,t) = |A|^2 \int_{-\infty}^{\infty} dx = \infty \tag{1.87}$$

This function is not normalizable and cannot represent a real particle. We will however make use of it later, with special caveats about its normalization.

Is the normalization preserved in time?

$$N = \int_{-\infty}^{\infty} \; P(x,t) \; dx \tag{1.88}$$

$$\frac{dN}{dt} = \int_{-\infty}^{\infty} \; \frac{\partial P(x,t)}{\partial t} \; dx \tag{1.89}$$

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial \Psi^*}{\partial t}\Psi + \Psi^*\frac{\partial \Psi}{\partial t} \tag{1.90}$$

We can use the Schrödinger Equation to write the time derivatives in terms of spatial derivatives:

$$\Psi^*\frac{\partial \Psi}{\partial t} = \frac{i\hbar}{2m}\Psi^*\frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar}V\Psi^*\Psi \tag{1.91}$$

$$\frac{\partial \Psi^*}{\partial t}\Psi = -\frac{i\hbar}{2m}\frac{\partial^2 \Psi^*}{\partial x^2}\Psi + \frac{i}{\hbar}V\Psi^*\Psi \tag{1.92}$$

Adding these

$$\frac{\partial P}{\partial t} = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi = \frac{i\hbar}{2m}\left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2}\Psi\right)$$

$$= \frac{\partial}{\partial x}\frac{i\hbar}{2m}\left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x}\Psi\right) = -\frac{\partial J(x,t)}{\partial x} \tag{1.93}$$

where we have defined a function, J, as:

$$J(x,t) \equiv \frac{i\hbar}{2m}\left(\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x}\right) \tag{1.94}$$

Now that the integrand has been reduced to a perfect derivative in x it is trivial to do the integration:

$$\frac{dN}{dt} = \int_{-\infty}^{\infty} \frac{\partial P}{\partial t}\, dx = [J(x,t)]_{-\infty}^{\infty} \tag{1.95}$$

For the wave-function to be normalizable, it must vanish at x = infinity and so too must $J(x,t)$, so that $\frac{dN}{dt} = 0$. The normalization condition is time-independent.

1.6.1 Probability Current

What is the significance of the function $J(x,t)$ that we defined above? Suppose we evaluate the probability for finding the particle in some finite region, $a \leq x \leq b$:

$$P_{ab}(t) = \int_x^b P(x,t)\; dx \tag{1.96}$$

The rate of change of P_{ab} with time is:

$$\frac{dP_{ab}}{dt} = \int_a^b \frac{\partial P(x,t)}{\partial t}\, dx = -\int \frac{\partial J(x,t)}{\partial x}\, dx = J(a,t) - J(b,t) \tag{1.97}$$

The rate of change in the probability of finding the particle in the interval $[a,b]$ is the difference between the values of the function $J(x,t)$ at the two end-points at time t. We interpret $J(x,t)$ as the rate of flow of probability at the point (x,t), i.e. it is a probability current. If the current at a exceeds the current at b there is a net flow into the interval $[a,b]$ and this net flow is exactly equal to the change in the probability for finding the particle in the interval $a \leq x \leq b$. This is a consequence of the fact that probability integrated over all space is conserved, and it can increase in one region only by a flow into this region accompanied by a flow out of some other region.

Equation 1.93 is usually written as:

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0 \tag{1.98}$$

This is the formal mathematical statement of conservation. P is the probability density and J is the probability current. The equation appears in many fields of physics, where-ever conserved quantities are involved. For instance there is an identical statement for electrical charge density and current. Later on we shall generalize this equation to three dimensions.

1.7 Velocity and Momentum

It may not be immediately obvious how the wave-function represents the velocity of a particle. If the wave function is well localized with a small width and its shape does not change rapidly with time, we would probably not quarrel with defining the velocity as the rate of change of the expectation value of position with time. Starting from:

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi(x,t)|^2 \, dx \tag{1.99}$$

we define the velocity as:

$$\langle v \rangle \equiv \frac{d\langle x \rangle}{dt} = \int x \frac{\partial}{\partial t} |\Psi(x,t)|^2 \, dx = \int x \frac{\partial P(x,t)}{\partial t} \, dx = -\int x \frac{\partial J}{\partial x} \, dx \tag{1.100}$$

Now:

$$x \frac{\partial J}{\partial x} = \frac{\partial (xJ)}{\partial x} - J \tag{1.101}$$

Integrating the first term and using the vanishing of the wave-function at the limits, we are left with:

$$\langle v \rangle = \int J(x,t) \, dx = -\frac{i\hbar}{2m} \int \left[\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right] dx \tag{1.102}$$

Replacing

$$\frac{\partial \Psi^*}{\partial x} \Psi = \frac{\partial (\Psi^* \Psi)}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x}$$

The first term integrates to 0, so that:

$$\langle v \rangle = -\frac{i\hbar}{m} \int \Psi^* \frac{\partial \Psi}{\partial x} \, dx \tag{1.103}$$

This is the expectation value of a measurement of "velocity". Usually we work with momentum instead:

$$\langle p \rangle = m\langle v \rangle = -i\hbar \int \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) \; dx = \int \Psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi \; dx \qquad (1.104)$$

Using this form, we can also write:

$$\langle x \rangle = \int \Psi^*(x,t) \;\; (x \; \Psi(x,t)) \;\; dx, \qquad \langle p \rangle = \int \Psi^* \, (p\Psi) \; dx \qquad (1.105)$$

Here we treat x and $p = \frac{\hbar}{i}\frac{\partial}{\partial x}$ as operators, and note that their expectation values are obtained by sandwiching them between the wave function and its complex conjugate and integrating over the entire space. An operator is simply an instruction for changing a function. It could be a number, a function of x, a set of derivatives, an integration, or something even more exotic. As something more exotic, one might consider the operator, $1/p$, or $1/\sqrt{p^2+a}$.

Expectation values of other dynamical variables

What about other dynamical variables? All of them can be written in terms of position and momentum.

Angular momentum: Classically, the angular momentum of a particle is defined as:

$$\vec{L} = \vec{r} \times \vec{p} = m\vec{r} \times \vec{v} = (xp_y - yp_x)\hat{k} + (yp_z - zp_y)\hat{\imath} + (zp_x - xp_z)\hat{\imath} \quad (1.106)$$

To calculate $\langle L_z \rangle$:

$$\langle L_z \rangle = \int \Psi^* L_z \Psi \; dx \; dy \; dz = \int \Psi^* \frac{\hbar}{i} \left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right] \Psi \; dx \; dy \; dz \quad (1.107)$$

General theorem for expectation value We make the conjecture, without proof, that for any dynamical quantity, $\mathcal{O}$, that is a function of position and momentum, its expectation value in three dimensions is given by:

$$\langle \mathcal{O}(\vec{r}.\vec{p}) \rangle = \int \Psi^* \;\; \left[\mathcal{O}(x, y, z, \frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z})\Psi \right] \; d\tau \qquad (1.108)$$

Kinetic, potential and total energy,

$$T = p^2/2m \qquad (1.109)$$

In one dimension:

$$\mathcal{T} = p_x^2/2m = \frac{1}{2m}\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right]\left[\frac{\hbar}{i}\frac{\partial}{\partial x}\right] = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{1.110}$$

The expectation value of the kinetic energy is:

$$\langle \mathcal{T} \rangle = \frac{-\hbar^2}{2m}\int \Psi^*(x,t)\frac{\partial^2 \Psi(x,t)}{\partial x^2}\ dx \tag{1.111}$$

Since the potential depends only on x:

$$\langle V \rangle = \int \Psi^* V(x) \Psi\ dx \tag{1.112}$$

Note that this is not generally the same as $V(\langle x \rangle)$, unless the uncertainty in x is negligible. For instance, if the particle is subject to a spring force:

$$V(x) = \frac{1}{2}k(x - x_0)^2 \tag{1.113}$$

From symmetry,

$$\langle x \rangle = x_0$$

$$\langle V(x) \rangle = \frac{1}{2}k\langle (x-x_0)^2 \rangle = \frac{1}{2}k\left(\langle x^2 \rangle - 2x_0\langle x \rangle + x_0^2\right) = \frac{1}{2}k\left(\langle x^2 \rangle - \langle x \rangle^2\right)$$

$$\langle V(x) \rangle = \frac{1}{2}k\sigma_x^2 = V(\langle x \rangle \pm \sigma_x)$$

In terms of operators, we can write the Schrödinger Equation as:

$$\frac{1}{2m}p^2\Psi + V\Psi = i\hbar\frac{\partial}{\partial t}\Psi \tag{1.114}$$

or:

$$(\mathcal{T} + V)\Psi = \mathcal{H}\Psi \tag{1.115}$$

where we have introduced the total energy operator:

$$\mathcal{H} = i\hbar\frac{\partial}{\partial t} \tag{1.116}$$

In this form the Schrödinger Equation looks like the classical statement that $E = T + V$, where all three quantities have been turned into operators acting on the wave-function. The expectation value of the total energy is:

$$\langle \mathcal{H} \rangle = \int \Psi^*\ \mathcal{H}\ \Psi\ dx = i\hbar\int \Psi^*\frac{\partial \Psi}{\partial t}\ dx \tag{1.117}$$

The operator $\mathcal{H}$ is called the **Hamiltonian**. Hamiltonian's elegant formulation of classical mechanics provides a natural bridge between classical and quantum mechanics.

1.8 The Uncertainty Principle

We have mentioned several times that waves do not in general have precisely located positions in space. However, in geometrical optics it is possible to construct bundles of waves that behave very much like particles following well-defined trajectories. It is also possible to construct very short pulses of light that travel through space much like a single particle. These bundles or wave-packets, are linear combinations of waves with different wave-lengths. The localization of the wave packet is only approximately point-like and does not have unique wave-length. The more we try to localize the wave motion, the greater the spread in wave lengths that is required. The more pure we make the frequency the more spread-out in space the packet becomes. Since for de Broglie waves, the wave length is

$$\lambda = h/p$$

a spread in wave-lengths is a spread in momentum. We will show that the standard deviations in x and p are related by the inequality,

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}$$

This is the famous Heisenberg uncertainty principle, first published by him in 1927. It is the fundamental basis of quantum mechanics, and serves as the starting point for the algebraic formulation initiated by Heisenberg, a formulation that makes no reference at all to waves.

It is important to observe that the Uncertainty Principle provides a lower limit on the combined uncertainty in momentum and position represented by the wave-function of a particle. It is easy to prepare quantum states for which the product of uncertainties is larger than the lower limit. The lower limit is the best that can be achieved.

1.8.1 Example - A Gaussian wave-packet

Using the method of Fourier transforms, the following normalized function arises rather naturally as the solution of the Schrödinger Equation for a localized free particle Schrödinger Equation with momentum in one dimension for all times,

$$\Psi(x,t) = \left[(2\pi\sigma_0^2)^{1/2}\left(1 + \frac{i\hbar t}{2m\sigma_0^2}\right)\right]^{-1/2}$$

$$\times \exp\left[\frac{-(x - p_0 t/m)^2}{4\sigma_0^2(1 + i\hbar t/(2m\sigma_0^2))}\right] \times \exp\left[\frac{ip_0}{\hbar}\left(x - \frac{p_0 t}{2m}\right)\right] \qquad (1.118)$$

To verify that this is a solution calculate the partial derivatives with respect to x and t and substitute them into the free-particle Schrödinger Equation .

The function has been chosen to satisfy the following initial conditions ($t = 0$): (1) the probability distribution in space is Gaussian, centered at $x = x_0$ with a width σ_0, and (2) the distribution in momentum is also Gaussian, centered at $p = p_0$ with $\sigma_p = \hbar/(2\sigma_0)$.

We can check this by substituting $t = 0$:

$$\psi(x,0) = e^{ip_0x/\hbar}\frac{e^{-x^2/4\sigma_0^2}}{\left(2\pi\sigma_0^2\right)^{1/4}} \tag{1.119}$$

The probability distribution at $t = 0$ is:

$$P(x,0) = |\psi^*\psi| = \frac{e^{-x^2/2\sigma_0^2}}{\left(2\pi\sigma_0^2\right)^{1/2}} \tag{1.120}$$

which is the familiar normalized Gaussian distribution with $\langle x\rangle = 0$ and where $\sigma_x = \sigma_0$ is the s.d. in x. To calculate the expectation value for the momentum at $t = 0$, first calculate the spatial derivative of the wave function, eqn. 1.118

$$\frac{\partial}{\partial x}\Psi = \left[\frac{ip_0}{\hbar} - \frac{x}{2\sigma_0^2}\right]\Psi$$

so

$$p\Psi = \frac{\hbar}{i}\frac{\partial\Psi}{\partial x} = \left[p_0 + i\hbar\frac{x}{2\sigma_0^2}\right]\Psi$$

From this equation we can read off that:

$$\langle p\rangle = p_0 + i\hbar\frac{\langle x\rangle}{2\sigma_0^2} = p_0 \tag{1.121}$$

To calculate $\langle p^2\rangle$ at time $t = 0$:

$$p^2\Psi = -\hbar^2\frac{\partial^2\Psi}{\partial x^2} = -\hbar^2\left(\left[\frac{ip_0}{\hbar} - \frac{x}{2\sigma_0^2}\right]^2 - \frac{1}{2\sigma_0^2}\right)\Psi \tag{1.122}$$

$$p^2\Psi = -\hbar^2\left(-\frac{p_0^2}{\hbar^2} - 2\frac{ip_0x}{2\hbar\sigma_0^2} + \frac{x^2}{4\sigma_0^4} - \frac{1}{2\sigma_0^2}\right)\Psi \tag{1.123}$$

$$p^2\Psi = \left(p_0^2 + 2\frac{i\hbar p_0x}{2\sigma_0^2} - \frac{\hbar^2x^2}{4\sigma_0^4} + \frac{\hbar^2}{2\sigma_0^2}\right)\Psi \tag{1.124}$$

With this result, we immediately obtain without any integrations:

$$\langle p^2\rangle = p_0^2 + 2\frac{i\hbar p_0\langle x\rangle}{2\sigma_0^2} - \frac{\hbar^2\langle x^2\rangle}{4\sigma_0^4} + \frac{\hbar^2}{2\sigma_0^2} = p_0^2 - \frac{\hbar^2\langle x^2\rangle}{4\sigma_0^4} + \frac{\hbar^2}{2\sigma_0^2} \tag{1.125}$$

Recalling that $\langle x^2\rangle = \sigma_x^2 = \sigma_0^2$:

$$\sigma_p^2 = \langle p^2\rangle - \langle p\rangle^2 = \frac{\hbar^2}{4\sigma_x^2} \tag{1.126}$$

so:

$$\sigma_p\sigma_x = \frac{\hbar}{2} \tag{1.127}$$

At $t = 0$ the wave function satisfies the minimum uncertainty allowed by the Heisenberg Uncertainty Principle.

Now let us see how this wave function evolves with time. Returning to the time dependent function, eqn. 1.118, let us write it as

$$\Psi(x,t) = \frac{A}{\sqrt{s}}e^{-\frac{(x-vt)^2}{4s}}e^{\frac{ip_0}{\hbar}\left(x-\frac{vt}{2}\right)} = N(t)e^{-\frac{(x-vt)^2}{4s}}e^{\frac{ip_0}{\hbar}\left(x-\frac{vt}{2}\right)}$$

where

$$s \equiv \sigma_0^2 + \frac{i\hbar t}{2m}$$
$$A \equiv (2\pi\sigma_0^2)^{-1/4}\sigma_0$$
$$v \equiv \frac{p_0 t}{m}$$

and where $N(t)$ is the normalization factor. The complex conjugate of the wave function is

$$\Psi(x,t)^* = N^* e^{-\frac{(x-vt)^2}{4s^*}}e^{\frac{-ip_0}{\hbar}\left(x-\frac{vt}{2}\right)}$$

Their product provides the probability distribution,

$$P(x,t) = \Psi^*\Psi = |N|^2 e^{-\frac{(x-vt)^2}{4}\left(\frac{1}{s}+\frac{1}{s^*}\right)} = |N|^2(t)e^{-\frac{(x-vt)^2}{2\sigma_x(t)^2}}$$

The probability distribution is a Gaussian for any time centered at

$$\langle x(t)\rangle = vt$$

The standard deviation in the spatial distribution is given by $\sigma_x(t)$, which is given by

$$\frac{1}{\sigma_x(t)^2} = \frac{1}{2}\left(\frac{1}{s} + \frac{1}{s^*}\right) = \frac{s+s^*}{2ss^*}$$

$$\sigma_x^2 = \frac{2ss^*}{s+s^*}$$

Now

$$s + s^* = 2\sigma_0^2$$

and

$$ss^* = \sigma_0^4 + \frac{\hbar^2 t^2}{4m^2}$$

so

$$\sigma_x^2 = \frac{\sigma_0^4 + \frac{\hbar^2 t^2}{4m^2}}{\sigma_0^2} = \sigma_0^2\left(1 + \frac{\hbar^2 t^2}{4m^2\sigma_0^4}\right)$$

$$\sigma_x(t) = \sigma_0\sqrt{1 + \frac{\hbar^2 t^2}{4m^2\sigma_0^4}}$$

The wave-packet spreads out as time increases, and the particle becomes less and less localized. The tighter the initial localization, i.e. the smaller the value of σ_0, the more rapidly the wave function spreads out.

It is straight-forward to show that the momentum distribution is constant in time: $\langle p(t)\rangle = p_0$ and $\sigma_p(t) = \sigma_p(t=0)$. We need the derivatives of the wave-function;

$$\frac{\partial\Psi}{\partial x} = -\left[\frac{x-vt}{2s} - \frac{ip_0}{\hbar}\right]\Psi$$

$$\frac{\partial^2\Psi}{\partial x^2} = \left(\left[\frac{x-vt}{2s} - \frac{ip_0}{\hbar}\right]^2 - \frac{1}{2s}\right)\Psi$$

$$\frac{\partial^2\Psi}{\partial x^2} = \left(\frac{x^2 - 2xvt + v^2t^2}{4s^2} - \frac{ip_0(x-vt)}{\hbar s} - \frac{p_0^2}{\hbar^2} - \frac{1}{2s}\right)\Psi$$

It follows that

$$\langle p\rangle = -\frac{\hbar}{i}\left[\frac{\langle x\rangle - vt}{2s} - \frac{ip_0}{\hbar}\right] = -\frac{\hbar}{i}\left[-\frac{ip_0}{\hbar}\right] = p_0$$

and

$$\langle p^2\rangle = -\hbar^2\left(\frac{\langle x^2\rangle - 2vt\langle x\rangle + v^2t^2}{4s^2} - \frac{ip_0(\langle x\rangle - vt)}{\hbar s} - \frac{p_0^2}{\hbar^2} - \frac{1}{2s}\right)$$

Using $\langle x\rangle = vt$, this reduces to

$$\langle p^2\rangle = -\hbar^2\left(\frac{\langle x^2\rangle - 2\langle x\rangle^2 + \langle x\rangle^2}{4s^2} - \frac{1}{2s}\right) + p_0^2$$

so that

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2 == -\hbar^2 \left(\frac{\langle x^2 \rangle - \langle x \rangle^2}{4s^2} - \frac{1}{2s} \right) = \frac{\hbar^2}{2s} \left(1 - \frac{\sigma_x^2}{2s} \right)$$

$$= \frac{\hbar^2}{2s} \left(1 - \frac{2ss^*}{2s(s+s^*)} \right) = \frac{\hbar^2}{2s} \left(1 - \frac{s^*}{(s+s^*)} \right) = \frac{\hbar^2}{2s} \left(\frac{s}{(s+s^*)} \right) = \frac{\hbar^2}{2(s+s^*)}$$

$$\sigma_p^2 = \frac{\hbar^2}{4\sigma_0^2}$$

so

$$\sigma_p(t) = \sigma_p(t=0)$$

The expectation value of the momentum and its standard deviation remain constant. The product of the two uncertainties grows with time. A **free** particle that satisfies the minimum requirement of the uncertainty principle at time $t = 0$ will not do so for later times.

1.9 Appendix

1.9.1 High Points in the History of Quantum Physics

- 19^{th} century: Existence of atoms firmly established. Chemistry, Faraday.
- 1897: Discovery of the electron by J.J. Thomson
- 1900: Planck's formula for the spectrum of blackbody radiation.
- 1905-1907: Einstein's theory of the photo-electric effect and Stoke's law of fluorescence.
- 1909: Einstein concluded that light consists of quantized units of energy
- 1909: Millikan oil-drop experiment:
- 1911: Rutherford's α particle scattering experiments
- 1912: Bohr's mathematical formulation of the Bohr-Rutherford model of the atom.
- 1912-1923: Refinements and applications of the Bohr model.
- 1923-25: Louis de Broglie's assignment of wave-length to particles.

$$\lambda = \frac{h}{p}$$

- 1925: W. Heisenberg,"Uber die quantentheorentische Umdeutung kinematischer und mechanischer Beziehungen" in Zeitschrift für Physik ("On the quantum theoretical interpretation of kinematical and mechanical relations").
- September, 1925: Max Born and Pasqual Jordan pointed out that Heisenberg's rules were the rules of matrix algebra.
- 1926: Schrödinger wave equation
  - January: "Quantisierung als Eigenwert Problem" Annalen der Physik, Jan. 1926.
  - February: he showed that the perturbation theories of classical mechanics could be extended to quantum mechanics.

- March: he showed the equivalence between his theory and Heisenberg's.

- 1926: Elsasser suggested testing the wave nature of matter by crystalline diffraction of electrons. Experimentally demonstrated by Davisson and Germer.

- 1928: P. A. M. Dirac, "The Quantum Theory of the ELectron", Proc. Roy. Soc., 117, 610(1928). Relativistic wave equation of the electron. Explained the spin of the electron and predicted the existence of its anti-particle, the positron.

- 1948: Lamb and Retherford found an energy level shift in the hydrogen atom that resulted in a transition emitting microwave radiation. The shift was not explained by the Dirac equation. The effect came to be called the "Lamb Shift".

- 1948-1955: Lamb Shift explained by quantization of the electromagnetic field (Quantum Electro-Dynamics (QED)). The theory was developed by Schwinger, Feynman and Tomonaga.

- 1970's: Unification of the weak interaction with QED. Development of chromodynamics (QCD) field theory, incorporating quarks, gluons and color charge.

The function given by Eq. 1.118 can be written as

$$\Psi(x,t) = \frac{A}{\sqrt{\sigma^2}} e^{\frac{-(x-vt)^2}{4\sigma^2}} e^{\frac{ip_0}{\hbar}\left(x-\frac{vt}{2}\right)}$$

where

$$\sigma^2 = \sigma_0^2 + \frac{i\hbar t}{2m}$$

$$A = (2\pi\sigma_0^2)^{-1/4}\sigma_0$$

Differentiating with respect to x,

$$\frac{1}{\Psi}\frac{\partial\Psi}{\partial x} = -\frac{x-vt}{2\sigma^2} + \frac{ip_0}{\hbar}$$

$$\frac{1}{\Psi}\frac{\partial^2\Psi}{\partial x^2} = -\frac{1}{2\sigma^2} + \left(\frac{x-vt}{2\sigma^2} - \frac{ip_0}{\hbar}\right)^2$$

Differentiating with respect to t,

$$\frac{1}{\Psi}\frac{\partial\Psi}{\partial t} = -\frac{1}{2\sigma^2}\frac{\partial\sigma^2}{\partial t} + \frac{v(x-vt)}{2\sigma^2} - \frac{ip_0 v}{2\hbar} + \frac{(x-vt)^2}{4\sigma^4}\frac{\partial\sigma^2}{\partial t}$$

Using

$$\frac{\partial\sigma^2}{\partial t} = \frac{i\hbar}{2m}$$

$$\frac{1}{\Psi}\frac{\partial\Psi}{\partial t} = -\frac{1}{2\sigma^2}\frac{i\hbar}{2m} + \frac{v(x-vt)}{2\sigma^2} - \frac{iE}{\hbar} + \frac{(x-vt)^2}{4\sigma^4}\frac{i\hbar}{2m}$$

Setting $v = p/m$ in the second term,

$$= -\frac{1}{2\sigma^2}\frac{i\hbar}{2m} + \frac{p(x-vt)}{2m\sigma^2} - \frac{iE}{\hbar} + \frac{(x-vt)^2}{4\sigma^4}\frac{i\hbar}{2m}$$

$$= \frac{i\hbar}{2m}\left[-\frac{1}{2\sigma^2} + \frac{p(x-vt)}{i\hbar\sigma^2} + \left(\frac{(x-vt)}{2\sigma^2}\right)^2\right] - \frac{iE}{\hbar}$$

Completing the square in the bracketed term,,

$$= \frac{i\hbar}{2m}\left[-\frac{1}{2\sigma^2} + \left(\frac{(x-vt)}{2\sigma^2} - \frac{ip}{\hbar}\right)^2 + \frac{p^2}{\hbar^2}\right] - \frac{iE}{\hbar}$$

$$= \frac{i\hbar}{2m}\left[-\frac{1}{2\sigma^2} + \left(\frac{x-vt}{2\sigma^2} - \frac{ip}{\hbar}\right)^2\right]$$

so

$$\frac{1}{\Psi}\frac{\partial\Psi}{\partial t} = \frac{i\hbar}{2m}\frac{1}{\Psi}\frac{\partial^2\Psi}{\partial^2 x}$$

Multiply through by $i\hbar\Psi$,

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial^2 x}$$

which is the Schrödinger Equation for a free particle.