Postulates of Quantum Mechanics

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1 Inadequacy of Classical Mechanics and Origin of Quantum Mechanics

At the end of the nineteenth century, physics consisted essentially of classical mechanics, the theory of electromagnetism, and thermodynamics. Classical mechanics was used to predict the dynamics of material bodies, and Maxwell's electromagnetism provided the proper framework to study radiation; matter and radiation were described in terms of particles and waves, respectively. As for the interactions between matter and radiation, they were well explained by the Lorentz force or by thermodynamics. The overwhelming success of classical physics— classical mechanics, classical theory of electromagnetism, and thermodynamics—made people believe that the ultimate description of nature had been achieved. It seemed that all known physical phenomena could be explained within the framework of the general theories of matter and radiation.

At the turn of the twentieth century, however, classical physics, which had been quite unassailable, was seriously challenged on two major fronts:

- **Relativistic domain:** Einstein's 1905 theory of relativity showed that the validity of Newtonian mechanics ceases at very high speeds (i.e., at speeds comparable to that of light).
- **Microscopic domain:** As soon as new experimental techniques were developed to the point of probing atomic and subatomic structures, it turned out that classical physics fails miserably in providing the proper explanation for several newly discovered phenomena. It thus became evident that the validity of classical physics ceases at the microscopic level and that new concepts had to be invoked to describe, for instance, the structure of atoms and molecules and how light interacts with them.

The failure of classical physics to explain several microscopic phenomena—such as black- body radiation, the photoelectric effect, atomic stability, and atomic spectroscopy—had cleared the way for seeking new ideas outside its purview.

The first real breakthrough came in 1900 when Max Planck introduced the concept of the quantum of energy. In his efforts to explain the phenomenon of blackbody radiation, he succeeded in reproducing the experimental results only after postulating that the energy exchange between radiation and its surroundings takes place in discrete, or quantized, amounts. He argued that the energy exchange between an electromagnetic wave of frequency ν and matter occurs only in integer multiples of $h\nu$, which he called the energy of a quantum, where h is a fundamental constant called Planck's constant. The quantization of electromagnetic radiation turned out to be an idea with far-reaching consequences.

Planck's idea, which gave an accurate explanation of blackbody radiation, prompted new thinking and triggered an avalanche of new discoveries that yielded solutions to the most outstanding problems of the time.

In 1905 Einstein provided a powerful consolidation to Planck's quantum concept. In trying to understand the photoelectric effect, Einstein recognized that Planck's idea of the quantization of the electromagnetic waves must be valid for light as well. So, following Planck's approach, he posited that light itself is made of discrete bits of energy (or tiny particles), called photons, each of energy $h\nu$, ν being the frequency of the light. The introduction of the photon concept enabled Einstein to give an elegantly accurate explanation to the photoelectric problem, which had been waiting for a solution ever since its first experimental observation by Hertz in 1887.

Another seminal breakthrough was due to Niels Bohr. Right after Rutherford's experimental discovery of the atomic nucleus in 1911, and combining Rutherford's atomic model, Planck's quantum concept, and Einstein's photons, Bohr introduced in 1913 his model of the hydrogen atom. In this work, he argued that atoms can be found only in discrete states of energy and that the interaction of atoms with radiation, i.e., the emission or absorption of radiation by atoms, takes place only in discrete amounts of hF because it results from transitions of the atom between its various discrete energy states. This work provided a satisfactory explanation to several outstanding problems such as atomic stability and atomic spectroscopy. Then in 1923 Compton made an important discovery that gave the most conclusive confirmation for the corpuscular aspect of light. By scattering X-rays with electrons, he confirmed that the X-ray photons behave like particles with momenta $h\nu/c$; ν is the frequency of the X-rays.

This series of breakthroughs—due to Planck, Einstein, Bohr, and Compton—gave both the theoretical foundations as well as the conclusive experimental confirmation for the particle aspect of waves; that is, the concept that waves exhibit particle behavior at the microscopic scale. At this scale, classical physics fails not only quantitatively but even qualitatively and conceptually.

As if things were not bad enough for classical physics, de Broglie introduced in 1923 an- other powerful new concept that classical physics could not reconcile: he postulated that not only does radiation exhibit particle-like behavior but, conversely, material particles themselves display wave-like behavior. This concept was confirmed experimentally in 1927 by Davisson and Germer; they showed that interference patterns, a property of waves, can be obtained with material particles such as electrons.

Although Bohr's model for the atom produced results that agree well with experimental spectroscopy, it was criticized for lacking the ingredients of a theory. Like the "quantization" scheme introduced by Planck in 1900, the postulates and assumptions adopted by Bohr in 1913 were quite arbitrary and do not follow from the first principles of a theory. It was the dissatisfaction with the arbitrary nature of Planck's idea and Bohr's postulates as well as the need to fit them within the context of a consistent theory that had prompted Heisenberg and Schrodinger to search for the theoretical foundation underlying these new ideas. By 1925 their efforts paid off: they skillfully welded the various experimental findings as well as Bohr's postulates into a refined theory: quantum mechanics. In addition to providing an accurate reproduction of the existing experimental data, this theory turned out to possess an astonishingly reliable prediction power which enabled it to explore and unravel many uncharted areas of the microphysical world. This new theory had put an end to twenty five years (1900–1925) of patchwork which was dominated by the ideas of Planck and Bohr and which later became known as the old quantum theory.

2 Formulations of Quantum Mechanics

Historically, there were two independent formulations of quantum mechanics. The first formulation, called *matrix mechanics*, was developed by Heisenberg (1925) to describe atomic structure starting from the observed spectral lines. Inspired by Planck's quantization of waves and by Bohr's model of the hydrogen atom, Heisenberg founded his theory on the notion that the only allowed values of energy exchange between microphysical systems are those that are discrete: quanta. Expressing dynamical quantities such as energy, position, momentum and angular momentum in terms of matrices, he obtained an eigenvalue problem that describes the dynamics of microscopic systems; the diagonalization of the Hamiltonian matrix yields the energy spectrum and the state vectors of the system. Matrix mechanics was very successful in accounting for the discrete quanta of light emitted and absorbed by atoms.

The second formulation, called *wave mechanics*, was due to Schrödinger (1926); it is a generalization of the de Broglie postulate. This method, more intuitive than matrix mechanics, describes the dynamics of microscopic matter by means of a *wave equation*, called the *Schrödinger equation*; instead of the matrix eigenvalue problem of Heisenberg, Schrödinger obtained a differential equation. The solutions of this equation yield the energy spectrum and the wave function of the system under consideration. In 1927 Max Born proposed his probabilistic interpretation of wave mechanics: he took the square moduli of the wave functions that are solutions to the Schrödinger equation and he interpreted them as *probability densities*.

These two ostensibly different formulations—Schrödinger's *wave* formulation and Heisenberg's *matrix* approach—were shown to be equivalent. Dirac then suggested a more general formulation of quantum mechanics which deals with abstract objects such as kets (state vectors), bras, and operators. The representation of Dirac's formalism in a *continuous basis*—the position or momentum representations—gives back Schrödinger's wave mechanics. As for Heisenberg's matrix formulation, it can be obtained by representing Dirac's formalism in a *discrete basis*. In this context, the approaches of Schrödinger and Heisenberg represent, respectively, the wave formulation and the matrix formulation of the general theory of quantum mechanics.

Combining special relativity with quantum mechanics, Dirac derived in 1928 an equation which describes the motion of electrons. This equation, known as Dirac's equation, predicted the existence of an antiparticle, the positron, which has similar properties, but opposite charge, with the electron; the positron was discovered in 1932, four years after its prediction by quan- tum mechanics. In summary, quantum mechanics is the theory that describes the dynamics of matter at the microscopic scale. Fine! But is it that important to learn? This is no less than an otiose question, for quantum mechanics is the only valid framework for describing the microphysical world. It is vital for understanding the physics of solids, lasers, semiconductor and superconductor devices, plasmas, etc. In short, quantum mechanics is the founding basis of all modern physics: solid state, molecular, atomic, nuclear, and particle physics, optics, thermodynamics, statistical mechanics, and so on. Not only that, it is also considered to be the foundation of chemistry and biology.

3 Formalism of Quantum Mechanics

The formalism of quantum mechanics is based on a number of postulates. These postulates are in turn based on a wide range of experimental observations; the underlying physical ideas of these experimental observations have been briefly mentioned in section 1. In this section we present a formal discussion of these postulates, and how they can be used to extract quantitative information about microphysical systems.

These postulates cannot be derived; they result from experiment. They represent the minimal set of assumptions needed to develop the theory of quantum mechanics. But how does one find out about the validity of these postulates? Their validity cannot be determined directly; only an indirect inferential statement is possible. For this, one has to turn to the theory built upon these postulates: if the theory works, the postulates will be valid; otherwise they will make no sense. Quantum theory not only works, but works extremely well, and this represents its experimental justification. It has a very penetrating qualitative as well as quantitative pre- diction power; this prediction power has been verified by a rich collection of experiments. So the accurate prediction power of quantum theory gives irrefutable evidence to the validity of the postulates upon which the theory is built.

4 The Basic Postulates of Quantum Mechanics

According to classical mechanics, the state of a particle is specified, at any time t, by two fundamental dynamical variables: the position $\vec{r}(t)$ and the momentum $\vec{p}(t)$. Any other physical quantity, relevant to the system, can be calculated in terms of these two dynamical variables. In addition, knowing these variables at a time t, we can predict, using for instance Hamilton's equations $dx/dt = \partial H/\partial p$, $dp/dt = -\partial H/\partial x$, the values of these variables at any later time t') . The quantum mechanical counterparts to these ideas are specified by postulates, which enable us to understand:

- how a quantum state is described mathematically at a given time t,
- how to calculate the various physical quantities from this quantum state, and
- knowing the system's state at a time t, how to find the state at any later time t) ; that is, how to describe the time evolution of a system.

The answers to these questions are provided by the following set of five postulates.

- **Postulate 1: State of a system**
  The state of any physical system is specified, at each time t, by a state vector $|\psi(t)\rangle$ in a Hilbert space H; $|\psi(t)\rangle$ contains (and serves as the basis to extract) all the needed information about the system. Any superposition of state vectors is also a state vector.

- **Postulate 2: Observables and operators**
  To every physically measurable quantity A, called an observable or dynamical variable, there corresponds a linear Hermitian operator $\hat{A}$ whose eigenvectors form a complete basis.

- **Postulate 3: Measurements and eigenvalues of operators**
  The measurement of an observable A may be represented formally by the action of $\hat{A}$ on a state $|\psi(t)\rangle$. The only possible result of such a measurement is one of the eigenvalues a_n (which are real) of the operator $\hat{A}$. If the result of a measurement of A on a state $|\psi(t)\rangle$ is a_n , the state of the system immediately after the measurement changes to $|\psi_n\rangle$:
  $$\hat{A}|\psi(t)\rangle = a_n|\psi_n\rangle \tag{1}$$
  where $a_n = \langle\psi_n|\psi(t)\rangle$. **Note:** a_n is the component of $|\psi(t)\rangle$ when projected onto the eigen-vector $|\psi_n\rangle$.

- **Postulate 4: Probabilistic outcome of measurements**

  1. **Discrete spectra:** When measuring an observable A of a system in a state $|\psi\rangle$, the probability of obtaining one of the nondegenerate eigenvalues a_n of the corresponding operator $\hat{A}$ is given by
     $$P_n(a_n) = \frac{|\langle\psi_n|\psi\rangle|^2}{\langle\psi|\psi\rangle} = \frac{|a_n|^2}{\langle\psi|\psi\rangle} \tag{2}$$
     where $|\psi_n\rangle$ is the eigenstate of $\hat{A}$ with eigenvalue a_n . If the eigenvalue a_n is m-degenerate, P_n becomes
     $$P_n(a_n) = \frac{\sum_{j=1}^{m}|\langle\psi_n^j|\psi\rangle|^2}{\langle\psi|\psi\rangle} = \frac{\sum_{j=1}^{m}|a_n^{(j)}|^2}{\langle\psi|\psi\rangle} \tag{3}$$
     The act of measurement changes the state of the system from $|\psi\rangle$ to $|\psi_n\rangle$. If the system is already in an eigenstate of $\hat{A}$, a measurement of A yields with certainty the corresponding eigenvalue a_n :$\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$

2. **Continuous spectra:** The relation 2, which is valid for discrete spectra, can be extended to determine the probability density that a measurement of $\hat{A}$ yields a value between a and $a + da$ on a system which is initially in a state $|\psi\rangle$:

$$\frac{dP(a)}{da} = \frac{|\psi(a)|^2}{\langle\psi|\psi\rangle} = \frac{|\psi(a)|^2}{\int_{-\infty}^{+\infty} |\psi(a')|^2 da'} \tag{4}$$

for instance, the probability density for finding a particle between x and $x + dx$ is given by $dP(x)/dx = |\psi(x)|^2/\langle\psi|\psi\rangle$.

- **Postulate 5: Time evolution of a system**
The time evolution of the state vector $|\psi(t)\rangle$ of a system is governed by the time-dependent *Schrödinger equation*

$$i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle, \tag{5}$$

where $\hat{H}$ is the Hamiltonian operator corresponding to the total energy of the system.

Remark: These postulates fall into two categories:

- The first four describe the system at a given time.
- The fifth shows how this description evolves in time.