Einstein and the quantum

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We review here the main contributions of Einstein to the quantum theory. To put them in perspective, we first give an account of physics as it was before him. It is followed by a brief account of the problem of black body radiation which provided the context for Planck to introduce the idea of quantum. Einstein’s revolutionary paper of 1905 on light-quantum hypothesis is then described as well as an application of this idea to the photoelectric effect. We next take up a discussion of Einstein’s other contributions to old quantum theory. These include (i) his theory of specific heat of solids, which was the first application of quantum theory to matter, (ii) his discovery of wave-particle duality for light and (iii) Einstein’s A and B coefficients relating to the probabilities of emission and absorption of light by atomic systems and his discovery of radiation stimulated emission of light which provides the basis for laser action. We then describe Einstein’s contribution to quantum statistics, viz. Bose–Einstein statistics and his prediction of Bose–Einstein condensation of a boson gas. Einstein played a pivotal role in the discovery of quantum mechanics and this is briefly mentioned. After 1925 Einstein contributed mainly to the foundations of quantum mechanics. We choose to discuss here (i) his ensemble (or statistical) interpretation of quantum mechanics and (ii) the discovery of Einstein–Podolsky–Rosen (EPR) correlations and the EPR theorem on the conflict between Einstein-locality and the completeness of the formalism of quantum mechanics. We end with some comments on later developments.

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1. Physics before Einstein

ALBERT Einstein (1879–1955) is one of the two founders of quantum theory along with Max Planck. Planck introduced the ‘quantum’ of energy in his investigations of black body radiation in 1900. He was followed by the young Einstein who proposed the ‘light quantum hypothesis’ in 1905. Albert Einstein sent his revolutionary ‘light quantum’ paper for publication on 17 March 1905 to Annalen der Physik. He was twenty-six years of age and it was his first paper on quantum theory. He had published five papers earlier during 1901–1904 in the same journal. Those dealt with capillarity and statistical mechanics. The major frontier areas of research in physics then were thermodynamics and electrodynamics. The main conceptions about the physical universe prevalent in physics of that time were as follows.

1.1. Newton’s mechanical conception

The earliest of these was that of a ‘mechanical universe’ given by Isaac Newton in his magnum opus Principia in 1687. The physical universe in it was regarded as composed of discrete point-particle endowed with masses. They moved with time along well defined trajectories, in the fixed arena of a three-dimensional Euclidean space, under the influence of mutual forces. The trajectories could be deterministically calculated by using Newton’s three laws of motion provided one knew the forces involved and also the initial position and velocities of all the particles. The forces involved were of the ‘action at a distance’ type. Newton also discovered the universal attractive force of gravitation which acts between any two mass points and falls off as the square of the interparticle distance. Astronomy was thereby brought into the fold of physics unlike the case in Aristotelian physics of ancients.

It was known that there exist other forces such as magnetic forces, electric forces, chemical affinity, etc. It was part of post-Newtonian programme of research to determine their laws. The force law between two ‘magnetic poles’ was determined by John Mitchell in 1750, while that between two electric charges was conjectured theoretically by Joseph Priestley, the discoverer of oxygen, in 1769 and experimentally verified in the unpublished work of Henry Cavendish done in 1771. It was, however, published first, based on his own work, by Charles Coulomb in 1785 and is now known as Coulomb’s Law. Alessandro Volta used electric currents, produced by his Voltaic pile, to dissociate a number of substances, e.g. water into hydrogen and oxygen. After this work it was a clear possibility that the forces responsible for chemical binding may be reducible to electrical forces. Matter could consist entirely of electrically charged mass points.

1.2. Light as waves

Newton was also inclined to view light also to be discrete stream of particles, ‘light-corpuscles’. Christian Huygens
communicated his researches on light to members of French Academy in 1678, and published in 1690 as ‘Tracté de la Lumière’, wherein he advanced the notion that light is a wave phenomenon. The wave theory of light got strong boost from the discoveries of interference of light in 1801 by Thomas Young, and by the studies of Augustin Fresnel on diffraction of light beginning in 1815. As a result the wave theory of light was firmly established. It was inconceivable, in those days, to have a wave motion without a medium for it to propagate, so a ‘luminiferous aether’ was postulated for its propagation.

1.3. Energetics program

We just saw that light had proved refractory to being accommodated within Newton’s mechanical conception of the universe. In thermodynamics, it was easy to see that the first law of thermodynamics, which refers to the law of energy conservation, could be easily interpreted within Newtonian framework. However it did not look possible to interpret the second law of thermodynamics, dealing with increasing entropy, within it. Ludwig Boltzmann’s H-theorem was an attempt towards this goal during 1842–1877 using his kinetic theory of gases. This attempt attracted strong criticism from Ernst Zermelo and others. Georg Helm and Ludwig Ostwald, supported by Ernst Mach, therefore denied the reality of atoms and suggested that energy is the most fundamental concept and the whole program of physics should be reduced to a ‘generalized thermodynamics’. This program, ‘Energetics’, was subscribed to by a small but strongly vocal and influential minority. In fact Einstein’s work on Brownian motion in 1905 played a crucial role in its fall.

1.4. Electromagnetic conception of the universe

Michael Faraday introduced the concept of continuous fields, like electric and magnetic fields, defined over the whole space–time, in contrast to discrete particles. He did this in order to have a deeper understanding of his law of electromagnetic induction in eighteen thirties. These fields are produced by electric charges, and electric currents produced by these charges in motion. They then interact with other electric charges elsewhere. There is no ‘action at a distance’ but every interaction is a local interaction. Faraday quoted the old saying ‘matter cannot act where it is not’ in a letter to Richard Taylor in 1844. Faraday also thought the gravitational force, which appears to act at a distance between two masses, could also be understood as a local interaction by the introduction of a gravitational field.

Clerk Maxwell’s equations for electric and magnetic fields, given in 1864, unified these two disparate entities into a coherent single entity ‘electromagnetic field’. Maxwell, synthesized the earlier known discoveries of Coulomb’s law, Gauss’ laws of magnetic induction, Oersted’s work on production of magnetic fields by electric current, and Faraday’s laws of electromagnetic induction into one set of equations using the field concept. He also appended a new element, now called ‘Maxwell’s displacement current’, to this synthesis.

A brilliant windfall from the Maxwell’s equations was the prediction of the existence of transverse electromagnetic waves with a constant velocity (now denoted by the letter c). The velocity c agreed with the known velocity of light. It was therefore natural for Maxwell to propose ‘electromagnetic wave theory’ of light. The subject of optics thus became a branch of electromagnetic theory. The luminiferous aether was identified as the aether for electromagnetic fields as well.

The tantalising possibility, the electromagnetic conception of the universe, arose now. Could it be that even point charged particles can be viewed as arising from the aether? The mass of an electron could be entirely due to its electromagnetic energy. If so, the ‘electromagnetic aether’ would be the sole ontological entity in terms of which one would be able to understand the whole nature.

1.5. Two clouds on the horizon

In a lecture delivered in April 1900 before the Royal Institution, Lord Kelvin talked about two ‘Nineteenth century clouds over the dynamical theory of heat and light’. It was such a rare case of penetrating insight into the nature of physics that one is left admiring it even now. It is the resolution of these two ‘clouds’ that gave rise to the two revolutions in twentieth century physics. One of these clouds referred to the continued unsuccessful attempts to detect the motion of the earth through aether and its resolution was achieved by Einstein’s special theory of relativity (1905). We shall not be dealing with this any further here. The other cloud referred to the failure of the equipartition theorem in classical statistical mechanics. Its resolution required the second revolution, associated with the quantum.

2. The problem of blackbody radiation: From Kirchhoff to Planck

Max Planck, in 1900, was first to introduce the quantum ideas in physics and he did this in the context of blackbody radiation. We now discuss the early history of this problem for providing the setting of his work.

2.1. Kirchhoff

All heated bodies emit and absorb radiation energy. The emissivity $e(\lambda, T)$ of a body, for the radiation with wave length $\lambda$, depends on the nature of body and its tempera-
ture $T$. It is the same for its absorptivity $a(\lambda, T)$. Using consideration of thermodynamics equilibrium, it was shown by Gustav Kirchhoff of Berlin, in 1859, that the ratio of emissivity $e(\lambda, T)$ to its absorptivity $a(\lambda, T)$ is independent of the nature of the heated body, i.e.

$$e(\lambda, T) = E(\lambda, T)a(\lambda, T),$$

where $E(\lambda, T)$ is a universal function of only the wavelength $\lambda$ of the radiation and its temperature $T$.

If we define, following Kirchhoff, a perfect blackbody as one whose absorptivity is equal to unity, i.e. perfect absorption, then the universal function $E(\lambda, T)$ can be identified with the emissivity of a perfect blackbody. He also showed that the radiation inside a heated cavity which is opaque and maintained at temperature $T$, behaves like blackbody radiation. One can therefore experimentally study the blackbody radiation by using the radiation issuing out a cavity through a small hole.

2.2. Boltzmann

Ludwig Boltzmann, in 1884, using Maxwell’s electromagnetic theory showed that

$$E(\lambda, T) = (c/8\pi)\rho(v, T),$$

where $\rho(v, T)$ is the energy density of radiation at frequency $v$ and temperature $T$. ($c$ = velocity of light in vacuum, $v$ = frequency of the radiation = $c/\lambda$). He further showed using thermodynamics consideration, together with Maxwell’s relation $P = \frac{1}{3}u$ between pressure $P$ and energy density $u$ of the radiation, that the total radiant energy per unit volume is proportional to $T^4$, i.e.

$$\int_0^\infty dv \rho(v, T) = \sigma T^4,$$

where $\sigma$ is called Stefan–Boltzmann constant. Josef Stefan had conjectured the truth of this law on the basis of his experimental work in 1879 for all heated bodies, though it is strictly true only for a blackbody.

2.3. Wien

Further progress was made by William Wien in 1894, when he studied the thermodynamics of extremely slow, i.e. adiabatic, contraction of the cavity on the blackbody radiation contained in it. From these he concluded that

$$\rho(v, T) = v^2 f(v/T).$$

This is known as ‘Wien’s displacement law’. We have thus reduced the problem of determining $\rho(v, T)$, a function of two variables $v$ and $T$, to that of determining a function $f(v/T)$ of a single variable $(v/T)$. This is as far as one can go on the basis of purely thermodynamic considerations.

To give a representation of the experimental data Wien also proposed a form for this function

$$\rho(v, T) = av^b e^{-v/bT},$$

which we shall refer to as Wien’s radiation law. In this $a$ and $b$ are numerical coefficients to be fixed from the data.

2.4. Rayleigh–Jeans

In June 1900, Lord Rayleigh decided to apply equipartition theorem of Maxwell–Boltzmann to the problem of radiation and derived

$$\rho(v, T) = c_v \nu^2(T).$$

He did not calculate at that time the numerical coefficient $c_v$, which he did in May 1905. He however, made a mistake of a factor of 8 which was corrected by James Jeans in June 1905. With the numerical factor included we have

$$\rho(v, T) = \frac{8\pi \nu^2}{c^3} kT,$$

which is known as Rayleigh–Jeans’ radiation law. Here $k$ is the Boltzmann constant. Rayleigh felt that this is a limiting form of $\rho(v, T)$ for $v/T \to 0$. Note that if this law was correct for all $v$, then it would lead to ultraviolet catastrophe. The total energy would be infinite.

2.5. Planck

Max Planck succeeded to the chair of Kirchhoff at Berlin in 1889. He was naturally drawn to the problem of determining the universal function $\rho(v, T)$ introduced by his predecessor. As he said ‘The so-called normal energy distribution represents something absolute, and since the search for absolutes has always appeared to me to be the highest form of research, I applied myself vigorously to its solution’. He argued that since the universal $\rho(v, T)$ does not depend on the nature of the material of walls, its determination would be facilitated if one assumes a simple model for it. He proposed to regard the wall to be made of Hertzian oscillators, each one capable of emitting or absorbing radiation of only a single frequency $v$. He then showed, using electromagnetic theory, i.e.

$$\rho(v, T) = \frac{8\pi \nu^2}{c^3} \bar{E}(v, T),$$

where $\bar{E}(v, T)$ is the average energy of the Hertzian oscillator of frequency $v$ at temperature $T$. He had this result on 18 May 1899.
Earlier experimental work by Friedrich Paschen on blackbody radiation had shown that Wien’s radiation law fitted the data well as it was known in 1897 for $\lambda = 1–8 \mu$ and $T = 400–1600$ K. Later work by Otto Lummer and Ernst Pringsheim, in the region $\lambda = 12–18 \mu$ and $T = 300–1650$ K, had however revealed the deviations from Wien’s radiation law in February 1900. On 19 October 1900 Kurlbaum announced the measurements done with Rubens for even higher wavelength region, $\lambda = 30–60 \mu$ and $T = 200–1500$ K. Planck then gave his radiation law as a discussion remark to this announcement. In modern notation, (first done in 1906), it reads as

$$\rho(\nu, T) = \frac{8\pi c^2 \nu^2}{h^3} \frac{\nu}{e^{\hbar \nu / kT} - 1},$$

where $h$ is now known as Planck’s constant. This suggested radiation law fitted the data perfectly. Note also that it reduces to (i) Rayleigh–Jean’s law for $\nu T \to 0$ and (ii) has the same form as Wien’s radiation law for $\nu T \to \infty$ and (iii) provides the ‘correct’ interpolation formula between the two regions. At this stage it was a purely empirical formula without any derivation. He then got busy looking for one.

Planck, when he began his research career was inclined to ‘energetics’ school and believed in the deterministic significance, unlike what was advocated by Boltzmann who took the probabilistic view, of entropy. In Boltzmann’s view the entropy $S$ of a configuration was related to its thermodynamic probability $W$, i.e.

$$S = k \ln W.$$ 

Planck, as an ‘act of desperation’, was forced to use Boltzmann’s view to derive his formula. In order to calculate thermodynamic probability for a configuration of $N$ oscillators, with total energy $U_N =NU$ and entropy $S_N = NS$, he assumed that $U_N$ is made up of finite energy elements $\varepsilon$, i.e. $U_N = Pe$, and worked out the total number of possible ways $W_N$ of distributing $P$ energy elements $\varepsilon$ among $N$ oscillators. He obtained

$$W_N = \frac{(N + P - 1)!}{P!(N - 1)!}.$$ 

The thermodynamic probability $W$ was taken proportional to $W_N$. This leads to

$$S = \frac{S_N}{N} = k \left[ \left(1 + \frac{U}{\varepsilon} \right) \ln \left(1 + \frac{U}{\varepsilon} \right) - \frac{U}{\varepsilon} \ln \frac{U}{\varepsilon} \right].$$

On using $\frac{\partial S}{\partial U} = \frac{1}{T}$, we obtain

$$\bar{E}(\nu, T) = \frac{\varepsilon}{e^{\hbar \nu / kT} - 1};$$

which on using Wien’s displacement law, leads to (in modern notation)

$$\varepsilon = h\nu.$$ 

Planck presented this derivation of his radiation law on 14 December 1900 to German Physical Society and this can be taken as the birth date of quantum theory. The really new element was his assumption that the Hertzian oscillators with frequency $\nu$ can emit or absorb radiation in the units of $\varepsilon = h\nu$. Planck, however, did not realize the revolutionary nature of his procedure. As he said, ‘this was purely a formal assumption and I really did not give it much thought except that, no matter what the cost, I must bring about a positive result’.

3. Einstein’s light quantum paper

3.1. Light quantum hypothesis

Albert Einstein was the first person to have a clear realization that Planck’s introduction of energy quanta was a revolutionary step and thus one which would have larger significance for physics than just for the problem of blackbody radiation. In 1905, Einstein’s annus mirabilis, he published his light quantum paper.

Einstein starts in this paper by first noting that the unambiguous prediction of electrodynamics and equipartition theorem for the material oscillators is that given by the radiation law, now called Rayleigh–Jeans law’. He is, in fact, the first person to derive this law from classical physics correctly as his work was done before Jeans obtained the proper numerical constant in it. As such, Abram Pais, even feels that it would be more proper to call it Rayleigh–Einstein–Jean’s law’. Since this radiation law does not agree with experiments, and theoretically suffers from ‘ultraviolet catastrophe’ (i.e. infinite total energy), it leads to a clear failure of classical physics. Something in classical physics has to yield.

In his search for the cause of failure, Einstein is motivated by his dissatisfaction with asymmetrical treatment of matter and radiation in classical physics. As we saw earlier, matter is discrete and particulate while the radiation is continuous and wave-field like in classical physics. He wondered whether the failure of the classical radiation theory was in not treating radiation also as discrete and particulate. He thus proposes his hypothesis of ‘light quantum’. Of course he is well aware of the enormous success which wave theory of light had in dealing with the phenomenon of interference, diffraction, etc. of light. About this aspect he comments ‘The wave theory, operating with continuous spatial functions, has proved to be correct in representing purely optical phenomena and will probably not be replaced by any other theory. One must, however, keep in mind that the optical observations are concerned
with temporal mean values and not with instantaneous values, and it is possible, in spite of the complete experimental verification of the theory of reflection, refraction, diffraction, dispersion and so on that the theory of light which operates with continuous spatial functions may lead to contradictions with observations if we apply it to the phenomenon of generation and transformation of light.

Einstein then proceeds to show that an analysis of ‘experimental’ Wien’s radiation law, valid in ‘nonclassical’ regime of large $v/T$, gives an indication of the particle nature. For this purpose he does an elaborate calculation of the probability $p$ that the monochromatic radiation of frequency $v$, occupying a volume $V_0$, could all be found later in a volume $V$. He finds this, on using Wien’s radiation law, to be given by

$$p = (V/V_0)^n$$

with $n = E/(hv)$,

(in modern notation), where $E$ is the total energy. This is of the same form as that of a gas of $n$ particles. From this remarkable similarity in the two results, he concludes ‘Monochromatic radiation of small energy density behaves, as long as Wien’s radiation law is valid, for thermodynamic considerations, as if it consisted of mutually independent energy quanta of magnitude $Rb\nu/N$. (The quantity $Rb\nu/N$ is now denoted by $hv$). This was the introduction of Einstein by light quanta hypothesis.

In the light quantum picture of Einstein ‘in the propagation of a light ray emitted from a point source, the energy is not distributed continuously over ever-increasing volumes of space, but consists of a finite number of energy quanta localized at points of space that move without dividing, and can be absorbed or generated as complete units’. He then went on to apply the light quantum hypothesis to other phenomena involving the generation and transformation of light. The most important of these was his treatment of photoelectric effect. They also involved his successful application to elucidating the Stokes’ rule in photoluminescence and to the ionization of a gas by ultraviolet light.

3.2. The photoelectric effect

In 1887 Heinrich Hertz observed that the ultraviolet light incident on metals can cause electric sparks. In 1899 J. J. Thomson established that the sparks are due to emission of the electrons. Phillip Lenard showed in 1902 that this phenomenon, now called the Photoelectric effect, showed ‘not the slightest dependence on the light intensity’ even when it was varied even a thousandfold. He also made a qualitative observation that photoelectron energies increased with the increasing light frequency. The observations of Lenard were hard to explain on the basis of electromagnetic wave theory of light. The wave theory would predict an increase in photoelectron energy with increasing incident light intensity and no effect due to increase of frequency of incident light.

On the Einstein’s light quantum picture, a light quantum, with energy $hv$, on colliding with an electron in the metal, gives its entire energy to it. An electron from the interior of a metal has to do some work, $W$, to escape from the interior to the surface. We therefore get the Einstein photoelectric equation, for the energy of the electron $E$.

$$E = hv - W.$$ Of course electron may lose some energy to other atoms before escaping to the surface, so this expression gives only the maximum of photo-electron energy which would be observed. One can see that Einstein’s light quantum picture explains quite naturally the intensity independence of photoelectron energies and gives a precise quantitative prediction for its dependence on incident light frequency. It also predicts that no photoelectrons would be observed if $v < v_0$ where $hv_0 = W$. The effect of increasing light intensity should be an increase in the number of emitted electrons and not on their energy. Abram Pais has called this equation as the second coming of the Planck’s constant.

Robert A. Millikan spent some ten years testing Einstein equation and he did the most exacting experiments. He summarized his conclusions as well as his personal dislike of light quantum concept, as follows: ‘Einstein’s photoelectric equation … appears in every case to predict exactly the observed results … yet the semi-corpuscular theory by which Einstein arrived at his equations seems at present wholly untenable’ (1915) and ‘the bold, not to say reckless hypothesis of electromagnetic light corpuscle’ (1916).

3.3. Envoi

Einstein’s light quantum paper, which was titled ‘Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Geschichtspunkt’ (on a heuristic point of view concerning the generation and transformation of light), was completed on 7 March 1905 and appeared in Annalen der Physik, 1905, 17, 132–148 and was received by them on 18 March 1905.

It was thus his first paper during his annum mirabilis during which he also wrote papers on Brownian motion, special theory of relativity, and $E = mc^2$. Though in public mind he is associated indissolubly with relativity, with relativity as his most revolutionary contribution, Einstein himself regarded his light quantum paper among his papers written in 1905 as the ‘most revolutionary’. The opinion of the recent historians of science is tending to agree with Einstein about it. He was awarded Nobel prize for 1921 in Physics for this paper which was announced in November 1922. Paraphenetically his Nobel Lecture is on relativity theory.
Einstein’s light-quantum is now known as ‘photon’, a name given by G. N. Lewis as late as 1926. Though Einstein talked about photon energy $E = h\nu$, it is curious that he introduced the concept of photon momentum $\mathbf{p}$ with magnitude $1\mathbf{p} = h\nu/c$ only in 1917. As we have seen, even Millikan did not believe in photon concept in 1915–16 despite his having spent years on experimental work confirming it. In 1923, the kinematics of the Compton effect was worked out on the basis of it being an elastic electron–photon scattering by A. H. Compton. After that it was generally accepted by physicists that light sometimes behaves as a photon.

4. Contributions to the old quantum theory

4.1. Specific heat of solids

Both Planck in 1900, and Einstein 1905 used the quantum theory to understand problems of radiation. Einstein in 1907 was first to apply it to the problems of matter. This was the problem of specific heat of solids.

In 1879 Pierre Dulong and Alexis Petit, as a result of their joint experimental work on a number of metals and sulphur at room temperature, noted that all of them have almost the same specific heat $C_v$ at constant volume, with a value of 6 calories per mol per K, i.e. $C_v = 3R$. Here $R$ is universal gas constant. When other solids were investigated, especially carbon, the deviations were found from the Dulong–Petit Rule. In early 1870’s Friedrich Weber conjectured and then verified that $C_v$ approaches the value $3R$ even for those cases at higher temperature, i.e. $C_v = 3R$ is only an asymptotic result. Theoretically Ludwig Boltzmann applied energy equipartition theorem to a three-dimensional lattice crystal and showed that $C_v = 3R$. However, the generality of the theorem left no scope for any deviations from this result within classical physics. There were similar problems which arose in the application of energy equipartition theorem for gases. As Lord Rayleigh noted in 1900 ‘What would appear to be wanted is some escape from the destructive simplicity of the general conclusions (following from energy equipartition theorem)’. As we have noted earlier Lord Kelvin regarded this problem as one of the clouds on the horizon of classical physics.

Einstein was first to realize that a use of equipartition theorem of classical statistics leads to Rayleigh–Jeans radiation law which was only asymptotically correct for large temperature. To get the correct Planck’s radiation law one had to use quantum theory. It was therefore natural for him to try the same remedy to the problem of specific heat of solids. Besides he was always inclined to a symmetrical treatment of radiation and matter.

Einstein assumed a simple model of the solid. It is that of three-dimensional crystal lattice where all the atoms on the lattice oscillate harmonically and independently and with the same frequency. For a solid with $N$ atoms we thus have a system of $3N$ harmonic oscillators of frequency $\nu$. We thus have using the earlier expression, used in deriving Planck’s expression for the average energy of an oscillator of frequency $\nu$, and in thermal equilibrium at temperature $T$, we get for the total energy $U$ of the solid,

$$U = 3N \frac{h\nu}{e^{h\nu/kT} - 1}.$$

This leads to Einstein’s expression for specific heat for his model

$$C_v = 3R \frac{\xi^2 e^\xi}{(e^\xi - 1)^2} \text{, } \xi = \frac{h\nu}{kT}.$$

It has the desirable feature that for $\xi$ small, i.e. large $T$, we get the Dulong–Petit result, i.e.

$$C_v \rightarrow 3R \text{ as } \xi \rightarrow 0,$$

which is the classical equipartion result. It provides one parameter, i.e. $\nu$, formula for the specific heat of a solid. The deviations from Dulong–Petit value are also in broad agreement with the experimental data. The model of solid assumed is too simplistic in that only a single frequency is assumed for all the oscillations. It was improved by Peter Debye in 1912, and a more exact treatment of atomic oscillations was given by Max Born and Theodore von Kármán in 1912–1913.

A preliminary formulation of the third law of thermodynamics was given by Walter Nernst in December 1905 according to which the entropy of a system goes to zero at $T = 0$. Einstein’s specific heat expression has the property that $C_v \rightarrow 0$ as $T \rightarrow 0$ and provides the first example of a model which is consistent with Nernst’s heat theorem, as was noted by Nernst in 1910.

4.2. Wave–particle duality

In 1905 Einstein had used phenomenological Wien’s radiation law to argue the particle nature of light. In 1909 he used Planck’s radiation law to argue that light has both a particle and a wave aspect. For this purpose he calculated an expression for mean of square of energy fluctuations $\langle \epsilon^2(v, T) \rangle$ in the frequency interval $\nu$ and $\nu + d\nu$. From general thermodynamic considerations, we have

$$\langle \epsilon^2(v, T) \rangle = kT^2 \frac{\partial^2 \rho(v, T)}{\partial T^2}.$$

in a subvolume $v$.

If we calculate this quantity using Rayleigh–Jeans radiation law $\rho = \rho_{R,J}(v, T)$, we obtain
\[ \langle \varepsilon^2(v, T) \rangle_{R,J} = \frac{e^2}{8 \pi v} P_{R,J}^2 \mathrm{d}v. \]

Note that Rayleigh–Jeans derivation is based on wave picture of light. If on the other hand we calculate this quantity using Wien’s radiation law, \( P = P_{\text{Wien}}(v, T) \), we obtain

\[ \langle \varepsilon^2(v, T) \rangle_{\text{Wien}} = h v P_{\text{Wien}} \mathrm{d}v. \]

As we know Wien’s radiation law support a particle picture of light.

We now use the correct Planck’s law of radiation \( P = P_{\text{Planck}}(v, T) \) and obtain

\[ \langle \varepsilon^2(v, T) \rangle_{\text{Planck}} = h v P_{\text{Planck}} \mathrm{d}v + \frac{c^2}{8 \pi v^2} P_{\text{Planck}} \mathrm{d}v. \]

It is a very suggestive expression. The first term is of the form we get using Wien’s law and supporting the particle picture light, while the second term has the same form as that given by Rayleigh–Jeans law which uses a wave picture of light. We also know that the contribution to the mean square fluctuations arising from independent causes are additive. This radiation has both wave and particle aspects. This was the first appearance in physics of wave-particle duality, here for light radiation.

Einstein was quite prophetic in his remarks on the implications of these results. He says ‘it is my opinion that the next phase in the development of theoretical physics will bring us a theory of light which can be interpreted as a kind of fusion of the wave and emission theory ... wave structure and quantum structure ... are not to be considered as mutually incompatible .... We will have to modify our current theories, not to abandon them completely’.

4.3. Einstein’s A and B coefficients and the discovery of stimulated emission of light

In 1916–1917 Einstein gave a new and wonderful derivation of Planck’s radiation law which provides a lot of new insights. As he wrote to his friend Michel Besso, in 1916, ‘A splendid light has dawned on me about the absorption and emission of radiation’.

He considers the thermodynamic equilibrium of a system comprising a gas of ‘molecules’ and radiation. The ‘molecules’ here refers to any material system which is interacting with radiation. Let the energy levels of the ‘molecules’ be denoted by \( E_m \) and let the number of ‘molecules’ be given by \( N_m \) when they occupy the energy level \( E_m \).

Consider two of these levels \( E_2 \) and \( E_1 \) with \( E_2 > E_1 \) and consider the transitions from level 2 to level 1 and the reverse. Einstein postulates that the number of transitions, in time \( t \), in the ‘molecules’ for the higher state \( E_2 \) to the lower state \( E_1 \) consists of two components. One of these due to spontaneous jumps from \( E_2 \) to \( E_1 \). The number of transition, however, is given by the term \( A_{21} N_t \mathrm{d}t \). Here the coefficient \( A_{21} \) is related to the intrinsic probability of this jump and does not depend on the radiation density. The second of these is due to stimulated emission of radiation. The number of transitions is here taken to be given by the term \( B_{21} N_t \mathrm{d}t \) and is taken proportional to the radiation density \( \rho \). Here the coefficient \( B_{21} \) is related to the probability of this process. The presence of radiation will also induce transitions from the lower level 1 to higher level 2. The number of these transitions is taken to \( B_{12} N_t \mathrm{d}t \) and is again taken proportional to the radiation density \( \rho \). The coefficient \( B_{12} \) again is related to the probability of this process. The \( A_{ij} \)’s and \( B_{ij} \)’s are called Einstein’s A and B coefficients.

In equilibrium the number of transitions from level 1 to level 2 must be same as the number of transitions from level 2 to level 1. We therefore get the relation

\[ N_{21}(A_{21} + B_{21}\rho) = N_{12}B_{12}\rho. \]

or

\[ \rho = \frac{(A_{21}/B_{21})}{B_{12}N_{21}/N_{12}} - 1. \]

Following Boltzmann, we have

\[ N_m = p_m e^{-E_m/kT}, \]

where \( p_m \) is the relevant weight factor, and using it, we get

\[ \rho = \frac{(A_{21}/B_{21})}{B_{12}P_2/B_{21}P_1} e^{(E_1 - E_2)/kT} - 1. \]

From Wien’s displacement we conclude that

\[ E_2 - E_1 = h\nu, \]

a relation given by Bohr in 1913. These transitions must involve emission or absorption of radiation of frequency \( v \). Further for large temperatures, i.e. \( T \to \infty \), the \( \rho \) must reduce to Rayleigh–Jeans’s law. This is possible only if we have

\[ \frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}, \]

\[ p_2 B_{12} = p_1 B_{21}. \]

Through this analysis we have got insights into the probabilities of transitions and correct quantitative relations.
between them. A calculation of these was not possible until full apparatus of quantum electrodynamics was in place which came much later, only in 1927.

The concept of stimulated emission, given by the coefficient $B_{21}$, was introduced by Einstein here for the first time. He was forced to this step, since otherwise he would have been led to Wien’s radiation law by these considerations and not to the correct Planck’s law. This concept is of fundamental importance in the theory of lasers.

5. Quantum statistics: Bose and Einstein

The last great contribution to quantum theory, before the advent of quantum mechanics, by Einstein was to develop quantum statistics for a system of material particles. Here the original idea was due to the Indian physicist Satyendra Nath Bose from Dacca University and was given in the context of radiation theory. Einstein extended it to matter. As such this quantum statistical method is known as Bose statistics or Bose–Einstein statistics. All integral spin particles in the nature have been found to obey these statistics and are called ‘bosons’. All half-odd integer spin particles obey Fermi–Dirac statistics, which was given later in 1926 and are called ‘Fermions’.

5.1. Bose

On 4 June 1924, Bose sent a short paper to Einstein containing a new derivation of Planck’s law. It was accompanied by a very unusual request to translate it into German and get it published in Zeitsschrift für Physik, if he found it worthwhile. Bose explained his chutzpah in doing it by saying ‘Though a complete stranger to you, I do not feel any hesitation in making such a request, because we are all your pupils though profiting only by your teachings through your writings’. He also mentioned that he ‘was the one who translated your paper on Generalized Relativity’ when the first ever English translation of the relativity papers of Einstein was published by the Calcutta University in 1920. We also know now, through William Blanpied, that this paper had earlier been rejected for publication by the Philosophical Magazine.

Bose noted ‘since it’s (Planck’s law’s) publication in 1901, many methods for deriving this law have been proposed … In all cases it appears to me that the derivations have not been sufficiently justified from a logical point of view. As opposed to these, the light quantum combined with statistical mechanics (as formulated to meet the needs of the quantum) appears sufficient for the derivation of the law independent of the classical theory’.

Bose’s idea was to regard the blackbody radiation as a free photon gas and then treat it by the method of statistical mechanics. This was his strategy to derive Planck’s radiation law in a logically consistent manner.

Now photons of frequency $\nu$ have energy $h\nu$ and a momentum, with magnitude $p = h\nu/c$, on the light quantum hypothesis of Einstein. A straightforward calculation of the phase space volume element leads to the factor $4\pi p^2 dp V$, where $V$ is the volume of the gas. Bose multiplied it by a further factor of 2, in order to take into account the two polarization states of the light, to obtain $8\pi p^2 dp V$. If we now divide it by a factor $h^3$, following Planck’s proposal of 1913 ‘that phase space cells have a volume $h^3$’, we obtain for the number of phase space cells in this phase space volume element $8\pi p^2 dp V = h^3$. This leads to, using $p = h\nu/c$, the first factor $8\pi \nu^2 \nu^2 c^3$ in the Planck’s radiation law. Bose has thus shown that the number $A^S$ of the phase space cells between radiation frequency $\nu'$ and $\nu + d\nu$ to be given by

$$A^S = \frac{8\pi \nu^2 \nu^2 c}{c^3},$$

in a novel way. Note that Bose obtained this factor here, unlike Planck, without making any use of the electromagnetic theory. Bose emphasized this aspect of his derivation in his letter to Einstein.

If Bose had proceeded further and used the statistical methods of Boltzmann, at this stage, he would have obtained Wien’s law and not the desired Planck’s law. He, however, chose to interpret $A^S$, not as the number of ‘particles’ but as number of ‘cells’, which played the role of ‘particles’ in Boltzmann’s counting. This procedure then leads to Planck’s law. This is equivalent to treating photons as indistinguishable in contrast to classical Boltzmann statistics where particles are identical but distinguishable. To give a simple example if we have to distribute two identical balls, which are distinguishable, by being coloured red and blue, into three containers, there are nine possible different configurations and probability of each one is 1/9 (Boltzmann counting). On the other hand if two identical balls are not distinguishable, as we are colour blind, then there are only six possible different configurations. This is so since the red ball in one container and blue ball in the other container are indistinguishable from the configuration in which we interchange the two balls. The probability of each distinct configuration flow is now 1/6 (Bose counting).

5.2. Einstein

Einstein immediately saw the importance of Bose’s work and got it published in Zeitschrift für Physik after translating it into German together with an appreciative note. Not only that, in view of his predilection to treat radiation and matter on the same footing, he extended it immediately to a gas of material particles during 1924–1925. For a photon gas there is no constraint of holding the total number of photons fixed but for material particles, let us say ‘atoms’, we have also a new constraint to hold the total number fixed. This introduced another parameter,
chemical potential, which has to be determined using this constraint. Bose had not commented on the indistinguishable aspect in his paper. To bring this aspect out, Einstein also rewrote the Bose's formula for the total number of configuration in the form it is normally found in textbooks.

We have seen that Einstein's model of solids was the first known example in which Nernst's theorem was valid. The case of Bose-Einstein gas, which Einstein worked out, provides first model of a gas for which Nernst's theorem holds.

Einstein also studied the fluctuations for the ideal Bose-Einstein gas, as he had done earlier for radiation. On calculating the mean square fluctuation \((\Delta n)^2\) for the number \(n(\varepsilon)\) of atoms having energy between \(\varepsilon\) and \(\varepsilon + d\varepsilon\), he found it to consist again of two terms

\[
(\Delta n)^2 = n(\varepsilon) + \frac{n^2(\varepsilon)}{Z(\varepsilon)},
\]

where \(Z(\varepsilon)\) is the number of particle states in the energy interval \(\varepsilon\) and \(\varepsilon + d\varepsilon\). The first term is the expected one for particles.

For an interpretation of the second term, which implies a wave aspect for matter, Einstein suggested that this is due to wave nature of atoms as postulated by Louis de Broglie in his recent doctoral thesis of 1924. Einstein was aware of this thesis as Pierre Langevin had sent him a copy for his opinion, and it was only Einstein's favourable comments on it which made Langevin accept de Broglie's thesis. Einstein also suggested associating a scalar field with these waves.

5.3. Bose–Einstein condensation

A free boson gas undergoes a phase transition below a critical temperature \(T_{BE}\). A macroscopic fraction of the atoms condense into lowest energy state. This phase transition is not due to interparticle attractive interaction but is simply a manifestation of the tendency of bosons to stick together. This was again a first solvable model for a phase-transition.

Despite lot of efforts it was not possible to experimentally test this prediction of Bose–Einstein until quite late. It was finally observed only in 1995. The Nobel Prize in Physics for the year 2001 was awarded to Eric Cornell, Carl Wieman and Wolfgang Ketterle for this discovery.

6. Foundations of quantum mechanics

6.1. Discovery of quantum mechanics

After a quarter century of long and fruitful interaction between the old quantum theory and the experimental work on atomic systems and radiation, this heroic period came to an end in 1925 with the discovery of quantum mechanics. It was discovered in two different mathematical formulations, viz. first as matrix mechanics and a little later as wave mechanics.

Werner Heisenberg discovered matrix mechanics during April–June 1925. A complete formulation was achieved by Max Born, Werner Heisenberg and Pascual Jordan in October 1925. After the mathematical formalism was in place, the problems of its interpretation arose. At Copenhagen, Niels Bohr and Heisenberg and others devoted their full attention to this talk. The resulting interpretation, called 'The Copenhagen Interpretation of Quantum Mechanics', was to dominate the physics, despite some other contenders, for a long time. Heisenberg proposed his famous 'uncertainty principle' in February 1927 in this connection. In this work he was strongly influenced by a conversation he had with Einstein in 1926 at Berlin. Heisenberg acknowledged to Einstein the role which relativity with its analysis of physical observation had played in his own discovery of matrix mechanics. His motivation in formulating it had been to rid the theory of physical unobservables. Einstein differed and said 'it is nonsense even if I had said so ... on principle it is quite wrong to try founding a theory on observables alone ... It is the theory which decides what is observable'.

The second formulation, wave mechanics, was published during the first half of 1926, as a series of four papers 'Quantization as an Eigenvalue problem' in Annalen der Physik by Erwin Schrödinger. He was led to study the papers of de Broglie, wherein he suggested that matter should also exhibit a wave nature, through a study of Einstein's papers on Bose–Einstein gas. He preferred a wave theory treatment to the photon treatment of Bose and avoid new statistics. As he said 'That means nothing else but taking seriously the de Broglie–Einstein wave theory of moving particles' in a paper on Bose–Einstein gas theory. His next step was to make the idea of matter-waves more precise by writing a wave equation for them. This is the famous Schrödinger wave equation for matter waves resulting in the birth of wave mechanics. As Schrödinger acknowledged 'I have recently shown that the Einstein gas theory can be founded on the consideration of standing waves which obey the dispersion law of de Broglie ... The above considerations about the atom could have been presented as a generalization of these considerations'. As Pais says 'Thus Einstein was not only one of three fathers of the quantum theory but also the sole godfather of wave mechanics'. The three fathers alluded to here are Planck, Einstein and Bohr.

The mathematical equivalence of these two formulations was soon established by Schrödinger and Carl Eckart in 1927.

After the discovery of quantum mechanics the focus of Einstein shifted from applications of quantum theory to various physical phenomena to the problems of under-
standing what the new mechanics mean. With his deep commitment to the reality of an objective world Einstein was not in tune with the Copenhagen interpretation.

6.2. Discussions at Solvay Conferences

The fifth Solvay Conference was held at Brussels in October 1927. It was in this meeting that the claim of completeness of quantum mechanics as a physical theory was put forward first. In this connection Einstein discussed the example of single hole diffraction of the electron in order to illustrate two contrasting points of view:

(i) ‘the de Broglie–Schrödinger waves do not correspond to a single electron but to a cloud of electrons extended in space. The theory does not give any information about the individual processes’, and

(ii) ‘the theory has the presentations to be a complete theory of individual processes’.

The first viewpoint is what is now known as statistical or ensemble interpretation of quantum mechanics if we clarify the phrase ‘a cloud of electrons’ to refer to an ensemble of single electron systems rather than to a many electron system. This is the view which Einstein held in his later work. He was thus the originator of ‘The statistical or ensemble interpretation of quantum mechanics’. This view was also subscribed to by many others including Karl Popper and Blokhintsev. It is essentially the minimalist interpretation of quantum mechanics.

The second viewpoint is the one upheld by the Copenhagen School and very many others and may be termed as the maximalist interpretation. Here a pure state provides the fullest description of an individual system, e.g. an electron.

The setup envisaged by Einstein was as follows: Consider a small hole in an opaque screen and let an electron beam fall on it from the left side. Let it be surrounded by another screen, on the right side, a hemispherical photographic plate. From quantum mechanics the probability of an electron hitting at any point of the photographic is uniform. In the actual experiment the electron will be found to have been recorded at a single definite point on the plate. As Einstein noted, one has to ‘presuppose a very peculiar mechanism of action at a distance which would prevent the wave function, continuously distributed over space from acting at two places of the screen simultaneously ... if one works exclusively with Schrödinger waves, the second interpretation of \( \psi \) in my opinion implies a contradiction with the relativity principle’. Here Einstein is worried about, what we now call ‘the collapse of the wave function’ postulate and its consistency with special theory of relativity. Einstein therefore opted for the statistical interpretation of quantum mechanics. A detailed discussion of this interpretation would be out of place here.

Apart from the formal discussion remark of Einstein noted above there were also lots of informal discussions between him and Niels Bohr. In these discussions Einstein generally tried to evade or violate Heisenberg’s uncertainty relations for individual processes by imagining various possible experimental setups and Bohr constantly trying to find the reason as to why they would not work. The uncertainties involved were taken to be due to errors involved in the simultaneous measurement of position–momentum or energy–time pairs. These discussions continued also at Solvay Conference held at 1930. These dialogues are quite famous and Niels Bohr wrote an elegant account of them later. It is generally agreed that in these discussions Bohr was successful in convincing Einstein that it was not possible to evade the uncertainty principle. However later developments, such as the realistic model have shown that these discussions are somewhat irrelevant to the problem of interpretation of quantum mechanics.

6.3. Quantum nonseparability and Einstein–Podolsky–Rosen correlations

In quantum mechanics if two systems have once interacted together and later separated, no matter how far, they cannot any more be assigned separate state vectors. Since physical interaction between two very distant systems is negligible, this situation is very counterintuitive. Schrödinger even emphasized this aspect, ‘I would not call that one but rather the characteristic of quantum mechanics’. More technically, this is so for all two-particle systems having a nonseparable wave function. A wave function is regarded as nonseparable, if no matter what choice of basis for single particle wave function is used, it cannot be written as a product of single particle wave functions. Such wave functions are called entangled. The entanglement is a generic feature of two particle wave functions.

In 1935, A. Einstein, B. Podolsky and B. Rosen (EPR) published a paper ‘Can quantum mechanical description of reality be considered complete?’ in Physical Review. It had a rather unusual title for a paper for this journal. In view of this they provided the following two definitions at the beginning of the paper: (1) A necessary condition for the completeness of a theory is that every element of the physical reality must have a counterpart in the physical theory. (2) A sufficient condition to identify an element of reality: ‘If, without in any way disturbing a system, we can predict with certainty (i.e. with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity’.

We now illustrate the use of these definitions for a single-particle system. Let the position and momentum observable of the particle be denoted by \( Q \) and \( P \) respectively. Since in an eigenstate of \( Q \), we can predict with certainty the value of \( Q \), which is given by its eigenvalue in that
eigenstate, it follows that the position \( Q \) of the particle is an element of physical reality (e.p.r.). Similarly the momentum \( P \) is also an e.p.r. The position \( Q \) and the momentum \( P \) however are not simultaneous e.p.r. So at the single particle level there is no problem with quantum mechanics, as far as these definitions of ‘completeness’ and ‘elements of reality’ are concerned.

The interesting new things are, however, encountered when a two-particle system is considered. Let the momenta and position of the two particles be denoted respectively by \( P_1 \) and \( Q_1 \) for the first particle and by \( P_2 \) and \( Q_2 \) for the second particle. Consider now the two-particle system in the eigenstate of the relative-position operator, \( Q_2 - Q_1 \) with eigenvalue \( q_0 \). The relative position \( Q_2 - Q_1 \) can be predicted to have a value \( q_0 \) with probability one in this state and thus qualifies to be an e.p.r. We can also consider an eigenstate of the total momentum operator, \( P_1 + P_2 \), with an eigenvalue \( p_0 \). The total momentum can be predicted to have a value \( p_0 \) with probability one and thus also qualifies to be an e.p.r. Furthermore relative position operator, \( Q_2 - Q_1 \) and total momentum operator, \( P_1 + P_2 \), commute with each other and thus can have a common eigenstate, and thus qualify to be simultaneous elements of physical reality.

We consider the two-particle system in which two particles are flying apart from each other having momenta in opposite directions and are thus having a large spatial separation. The separation will be taken so that no physical signal can reach between them. Let a measurement of position be made on the first particle in the region \( R_1 \) and let the result be \( q_1 \). It follows from standard quantum mechanics that instantaneously the particle 2, which is a spatially far away region \( R_2 \), would be in an eigenstate \( q_0 + q_1 \) of \( Q_2 \). The \( Q_2 \) is thus an e.p.r. The position of second particle gets fixed to the value \( q_0 + q_1 \) despite the fact that no signal can reach from region \( R_1 \) to \( R_2 \) where the second particle is, a ‘spooky action at a distance’ indeed. On the other hand, a measurement of the momentum \( P_1 \) of the first particle, in the region \( R_1 \) can be carried out and let it result in a measured value \( p_1 \). It then follows from the standard quantum mechanics, that the particle 2 in the region \( R_2 \) would be in an eigenstate of its momentum \( P_2 \) with an eigenvalue \( p_0 - p_1 \). The \( P_2 \) is thus also an e.p.r. This, however, leads to a contradiction since \( Q_2 \) and \( P_2 \) cannot be a simultaneous e.p.r. as they do not commute. We quote the resulting conclusion following from this argument as given by Einstein in 1949.

**EPR Theorem:** The following two assertions are not compatible with each other: (1) the description by means of the \( \psi \)-function is complete, (2) the real states of spatially separated objects are independent of each other.

The predilection of Einstein was that the second postulate, now referred to as ‘Einstein locality’ postulate, was true and thus EPR theorem establishes the incompleteness of quantum mechanics.

As Einstein said ‘But on one supposition we should in my opinion, absolutely hold fast: the real factual situation of the system \( S_2 \) is independent of what is done, with system \( S_1 \), which is spatially separated from the former’.

Einstein, Podolsky and Rosen were aware of a way out of the above theorem but they rejected it as unreasonable. As they said ‘Indeed one would not arrive at our conclusion if one insisted that two or more quantities can be regarded as simultaneous elements of reality only when they can be simultaneously measured or predicted. On this point of view, either one or the other, but not both simultaneously, of the quantities \( P \) and \( Q \) can be predicted, they are not simultaneously real. This makes the reality of \( P \) and \( Q \) depend upon the process of measurement carried out on the first system, which does not disturb the second system in any way. No reasonable definition of reality could be expected to permit this’.

6.4. Later developments

David Bohm reformulated the Einstein–Podolsky–Rosen discussion in a much simpler form in terms of two spin-one-half particles in a singlet state in 1951. This reformulation was very useful to John Bell, who in 1964, gave his now famous Bell-inequalities on spin correlation coefficients following from Einstein locality for EPR correlations. These inequalities are experimentally testable. In experiments of increasingly higher precision and sophistication, they have shown agreement with quantum mechanics and a violation of local realism though some loopholes remain. Bell’s work on hidden variable theories and Einstein–Podolsky–Rosen correlations had a profound influence on the field of foundations of quantum mechanics, in that it moved it from a world of sterile philosophical discussions to a world of laboratory experiments.

More recently, EPR correlations and quantum entanglement have been found useful in developing new technologies of quantum information such as quantum cryphography, quantum teleportation. They have ceased to be embarrassments but are seen as useful resources provided by quantum mechanics. There are even hopes of developing quantum computing which would be much more powerful that usual universal Turing machines.

Einstein’s legacy in physics still looms large. Talking about his work Max Born once said ‘In my opinion he would be one of the greatest theoretical physicists of all times even if he had not written a single line of relativity’.

7. Bibliographical notes


![Niels Bohr and Albert Einstein. Photo courtesy of AIP Emilio Segre Archives.](image-url)