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Review

A concise history of Einstein's 1905 proposal of the quantum of radiation, *E* = *hν*, and his leadership through the following development to wave mechanics

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ABSTRACT

We employ a novel, three-pronged approach to demonstrate Albert Einstein's bold scientific and personal intuition and leadership, especially concerning the development of the quantum theory. (1) We present some of Einstein's personal history, his four 1905 *Annus Mirabilis* research papers and some thoughts on the nature of his genius. (2) We describe Max Planck's use of Ludwig Boltzmann's notion of a harmonic energy-level discontinuity in his Black-Body Radiation theory, and we examine Einstein's 1905 analysis of the Photoelectric Effect, focusing on his revolutionary proposal of the quantum of radiation, $E = h\nu$. (3) We provide the story of Einstein's tenacious leadership and milestone contributions during the following 20-year journey to Schrödinger's wave mechanics.

KEYWORDS: Einstein, photoelectric effect, photon, quantum mechanics.

1. Introduction

We describe here some aspects of Albert Einstein's personal nature as well as his unique scientific insight, leadership and accomplishments. Our focus is on the quantum theory starting with his profound and revolutionary 1905 suggestion of the quantum of radiation (now called the photon) given by $E = h\nu$. The story then continues through more than 20 years of fundamental work after 1905 by Einstein and others (e.g., P. Debye, K. T. and later A. H. Compton, N. Bohr, R. A. Millikan, S. N. Bose, and L. de Broglie) that eventually led to Schrödinger's wave mechanics.

2. Part 1. Einstein himself

2.1. Setting the stage

The state of physics seemed stable in the late 19th century. Indeed, some people thought physics was complete except for some details. Steam engines, thermodynamics, Carnot, Lord Kelvin, and Maxwell's wave-theory of light were dominant. However, this apparent stability was deceiving. Knowledge of the physical world was growing hand-in-hand with the industrial revolution and the associated growth and research orientation of European universities. Experimental methods of increasing sophistication appeared and led to discovery and characterization of new phenomena, e.g., Atomic/Molecular Spectra, Black-Body Radiation, and the Photoelectric Effect (PE), all of these not understandable within then-existing physical theory. Powerful theoreticians followed Maxwell, including Boltzmann, Clausius, Gibbs, Mach, Planck, and Poincaré, but by the very early 20th century, understanding of things atomic/molecular was in serious disarray.

Into this environment strode a unique mind and personality, Albert Einstein (AE). In 1905 he published four papers that fundamentally changed the practice of physics. The power of these papers was not only in the thought and ideas they presented, but also in Einstein's self-confident boldness in forcefully challenging (sometimes with little but his own intuition as support) the paradigm of beliefs essentially universally accepted by physicists of the day.

2.2. Einstein's *Annus Mirabilis*

Four profoundly original AE papers were published in Annalen der Physik in 1905 and led over succeeding years to a nearly complete reconstruction of microscopic (radiation/atomic/molecular) physics and the introduction of relativity into the theory of moving bodies. He was 26 years old at the time! Later pioneering years occurred in 1915-1917 focused on General Relativity [1, 2] and Quantum Theory [3-5], and in 1924-25 focused on Quantum statistics [6, 7].

The first "Miracle" paper [8] was: (1) *Concerning a Heuristic Point of View Toward the Emission and Transformation of Light* [9], translations of which are available [10, 11]. This paper is a major focus here and builds on AE's earlier work [12-14] on statistical mechanics and electromagnetic radiation. It rationalizes then recent observations of the Photoelectric Effect (PE) by introduction of $E = h\nu$, the quantum of electromagnetic radiation.

The remaining *Annus Mirablis* papers were: (2) *On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular-Kinetic Theory of Heat* [15]. Einstein presents here a statistical treatment of Brownian Motion as resulting from continuous, statistically governed molecular collisions with tiny suspended macroscopic particles and provided compelling evidence for the existence of atoms and molecules. (3) *On the Electrodynamics of Moving Bodies* [16]. This paper is his revelation of Special Relativity. (4) *Does the Inertia of a Body Depend on its Energy Content?* [17] formulates the then unexpected fundamental relation, $E = mc^2$. That is, in processes during which energy and mass are interconverted, the proportionality constant between the change in energy and the change in mass is c^2! Significant follow-up papers were published in 1906 and 1907, including AE's Zurich Ph.D. thesis [18], further work on the quantum [19], and his theory of low-temperature heat capacities [20].

2.3. The PE paper

Einstein here "modestly" introduces [9] the quantum of electromagnetic radiation from a "heuristic" (learning) point of view, "hoping that this approach may turn out to be useful for some researchers in their investigations." However, this paper provides the first explicit modern recognition of the corpuscular aspect of light [21] and the wave-particle duality [22]. It took nearly 20 years despite AE's intense personal and intellectual efforts for the light quantum to be generally accepted [23-25], due largely to the unrelenting resistance of the powerful German theoretician Max Planck [26, 27] and especially the prominent American experimentalist R. A. Millikan [28-32]. Pockets of disbelief continued despite the award of the 1921 Nobel Prize in physics to AE in 1922 citing [33] the "interpretation of the PE and resulting perfection of the quantum theory." The delayed award of the 1921 prize until 1922 perhaps was in deference to the expressed preference in Alfred Noble's will to honor experimental over theoretical work. Ironically, Einstein's 1923 Nobel Lecture [34] focused entirely on his General Theory of Relativity [1, 16], which was not unequivocally observationally verified [35] until 1941.

2.4. The Nature of Einstein's genius

2.4.1. Intellectual aspects

The PE paper [9] exemplifies several aspects of AE's genius. His extraordinary intelligence, focus, clarity of thought, imagination and physical intuition, as well as his work ethic and personal stability, are well known [36]. However, AE also seems to have worked mindfully [37] by being able to objectively observe nature without interference from previous experience and concepts. Mindfulness allows one's thinking to be boldly independent and seems to have been present in all aspects of AE's life and being.

A closely related aspect of AE's intellectual and personal genius was his ability to see, recognize and accept in well-known observations significance that had been overlooked by other physicists, sometimes for many years [22]. Four examples of well-known observations whose significance finally was recognized by AE are:

(1) The equality of inertial and gravitational masses recognized by Newton [38] in 1681 led AE in 1915 to the General Theory of Relativity [1, 2]. Einstein reached this result missed by Newton, as well as his brilliant contemporaries

Lorenz and Poincaré [36] because he alone (although kudos to Lorentz and Poincaré) was able to find his way through the haze and boldly discard misconceptions inherent in Newtonian physics.

(2) Einstein took seriously the long-standing, wave-particle contradiction (TheStarGarden.CO. UK/Newton's-theory-of-light.html) in the behavior, discussion and understanding of light.

The particle (corpuscular) theory of light was arguably first introduced by Rene Descartes in the 1660s based on Epicurean [39-42] atomic theory. Isaac Newton began in 1666 the experimental study of light (mainly using prisms) that led to his 1672 masterpiece, *Opticks* [43], in which he reached the conclusion that the reflection and refraction of light only can be understood by light-particles because he thought waves do not travel in a straight line. The light particle idea had significant support.

However, in 1660 (published in 1665) Francesco Grimaldi discovered the contradictory diffraction of light, which could and can only be understood by assuming light is a wave. Other advocates of a wave-theory of light included Robert Hooke (1672) and Christiaan Huygens (1678). The situation remained in flux until Maxwell's [44, 45] (1881) description of light as electromagnetic waves [45] seemingly had firmly established by 1905 that light is an electromagnetic wave, not a particle.

Einstein was able in 1905 to accept the wave-particle duality and suggest light, despite its sometime wave-like behavior, is composed of tiny particles that travel in straight lines with a finite velocity and possess impetus (momentum).

(3) The PE was recognized by AE as an observation (Hertz [46] 1877 and Lenard [47, 48] 1902) that is not explainable in terms of the wave properties of light. Something more was required.

(4) It had been observed the heat capacity of crystalline solids [20] goes to zero before ambient temperature goes to zero. Einstein realized this only can be rationalized by the existence of discreet energy levels in crystals.

2.4.2. Personal aspects

Other not so widely understood facets of AE's genius are personal: his rebellious and independent nature, his profound confidence in the conclusions he reached, and his boldness in presenting revolutionary ideas (especially in the cases of the light quantum and relativity) with little support beyond his own clear thinking [36]. The idea of light particles (quanta/photons) was in 1905 heretical and anathema to classical, Maxwellian physicists, and it remained so for a number of years, largely because understanding $E = h\nu$ was and is a very difficult intellectual problem.

Another aspect of AE's personal genius came into play after 1905, his crusading perseverance. Stone [49] notes AE called himself in correspondence with his eventual wife Mileva, "The Valiant Swabian" after "the swashbuckling crusader-knight invented by the Swabian romantic poet Ludwig Uhland." We highly recommend Stone's book *Einstein and the Quantum. The Quest of the Valiant Swabian* [49] to readers desiring a more detailed story than ours of AE's long quantum crusade. Crusaders often attract serious personal resistance, especially in areas as intense as physics research. However, AE's comfortable, collegial personality in maturity allowed him to disagree with his peers without being disagreeable [36], a powerful force in his favor he used well.

The youthful Einstein did have difficulty getting a Ph.D. thesis accepted and initially he failed to obtain an academic position, both largely because of his forceful intellectual and personal independence. He eventually obtained via a personal friend, Michele Besso [36], a position (1902-1905) as "Clerk, Patent Examiner" in the Swiss Patent office. He was promoted to "Technical Expert, Second Class" in 1906 after reluctant acceptance of his Ph.D. thesis by University of Zurich. His dissertation [18] was entitled, *A New Determination of Molecular Dimensions* and concerned the existence of molecules (still in doubt in the minds of some physicists in 1905) as determined from his measurement of the viscosity of aqueous sugar solutions. It was prepared under the pro-forma direction of the experimentalist Alfred Kleiner.

His boldness in 1905 under this circumstance, especially in confident publication of his theory of relativity and the light-quantum idea, truly is shocking. His career in academic physics might have ended right there. However, he was correct, and things started going his way! His first full- time academic position was as Associate Professor at University of Zurich, 1909-1910; his first Professorship was in Prague, 1911-1913. His final European position was as Director, Kaiser Wilhelm Physical Institute, Berlin 1914-1933, the most prestigious physics position in the world. He joined the Institute of Advanced Study at Princeton University in 1933 at age 54, retired in 1945 and died in Princeton in 1955 at age 76 of an aortal embolism.

3. Part 2. The Boltzmann/Planck energy discontinuity in Black-Body Radiation Theory and AE'S analysis of the PE

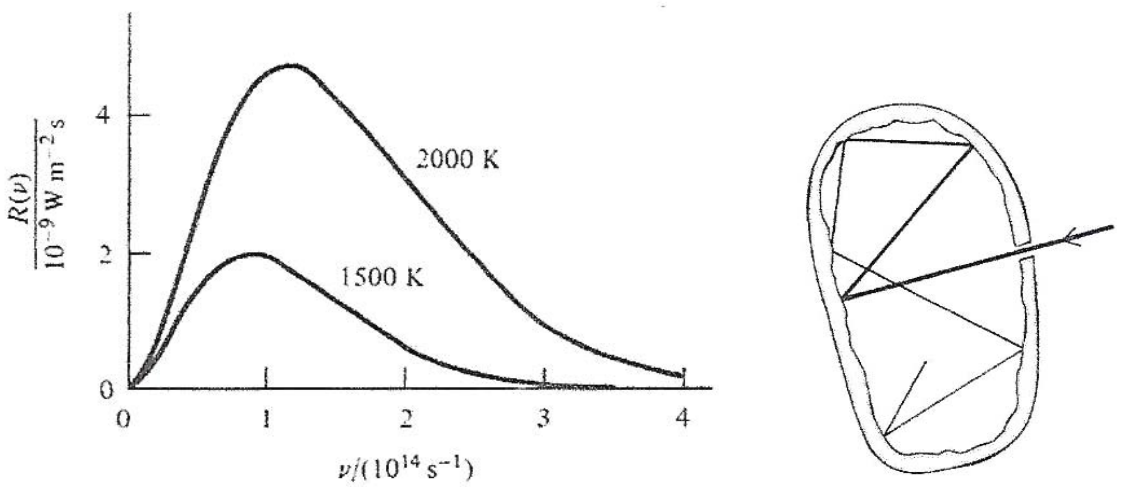
3.1. Black-Body-Radiation

3.1.1. Experimental characterization

Artificial lighting based on electrically heated, incandescent filaments became available late in the second-half of the 19^{th} century [50]. Practical considerations of interest to the electrical industry accelerated investigation of the temperature (T) and frequency (v)-dependent light-energy flux emitted by heated objects, the quantity $R(v,T)$, given as erg/m^{2}s or W/m^2. This light was referred to by Kirchhoff [51, 52] as Black-Body Radiation. $R(v,T)$ is observed to increase from near zero at very low values of v, pass through a maximum as v continues to increase, and finally diminish to zero asymptotically and exponentially at very high values of v (See Fig. 1a). The position (wavelength) and height of the maximum increase with increasing temperature.

An incandescent lamp should emit as much higher-v (visible) radiation as possible in order to appear white to the eye; lower-v radiation appears in the red or infra-red spectral region. Experimental work in this area was largely centered, by 1900 in Berlin, at the Kaiser Wilhelm Institute Reichsanstalt [53, 54].

Experimental and theoretical investigation of the form of $R(v,T)$ involves use of an ideal Black-Body model conceived by Gustav Kirchhoff [48, 52] as a substance that when in thermal equilibrium with its surroundings absorbs and emits light of all frequencies according to $R(v,T)$. Lummer and Kurlbaum [54] later (1898) suggested that $R(v,T)$ can be experimentally approximated by use of a heated metal container (cavity) with a small aperture as in Fig. 1b. The cavity wall is assumed to contain oscillators (vibrating atoms) of all possible frequencies and in thermal equilibrium with electromagnetic radiation of the allowed (*vide infra*) frequencies. Experiment and theory both show $R(v,T)$ to be independent of the cavity shape and material and in fact depends only on T. Fig. 1a shows typical observed emission flux (erg/m^{2}s) vs. frequency distributions at 1500 K (redder) and 2000 K (whiter).



a **b**

Fig. 1. a (left)-Black-Body Radiation Frequency Distribution. **b** (right)-Black-Body Cavity.

3.1.2. Early theoretical ideas

It was important in order to clarify fundamental understanding of Black-Body radiation to derive the observed $R(v,T)$ function from first-principles. John William Strutt, Lord Rayleigh [55], (1900) assumed vibrational frequencies are continuous within the cavity but are discretized by the requirement that only standing waves with amplitude zero at the cavity walls (boundaries) are stable. The classical Equipartition-of-Energy (EOE) principle [48] is assumed, although this turns out to be true only at very low values of v. The EOE principle states that molecules in thermal equilibrium have the same energy (k_BT) associated with each independent motion (degree of freedom). Sir James Jeans [56] provided the final detailed form of an entirely classical energy density within the cavity, Eq. 1, which is often referred to as the Rayleigh-Jeans Equation.

$$\rho_v(v,T) = (8\pi v^2 k_B T)/c_0^3\, dv \quad (\text{erg/cm}^3) \qquad (1)$$

The quantity $\rho_v(v,T)$ is the energy density within the cavity in erg/cm^3. The speed of light is given as c_0, and k_BT is the EOE average energy associated with a particular v at thermal equilibrium. Many waves may have the same frequency, v. The Boltzmann constant, k_B, is given by R/N_{Avo}, where R is the universal gas constant and N_{Avo} is Avogadro's number. The quantity $R(v,T)$ results from multiplication of $\rho_v(v,T)$ by $1/4c_0$, the conversion factor between energy density in the cavity (erg/cm^3) and energy flux through the aperture (erg/m^{2}s).

$$R(v,T) = (2\pi v^2 k_B T/c_0^2)\, dv \quad (\text{erg/cm}^2\text{s}) \qquad (2)$$

Equation 2 matches observation (Fig. 1a) reasonably well when v is very small but quickly diverges toward infinity as v^2 increases rather than passing through the observed maximum. Furthermore, integration of Eq. 2 over all frequencies leads to infinite values of total energy emitted. This failure of electromagnetic wave theory was referred to by Ehrenfest [57] as the *Ultraviolet Catastrophe*. Indeed, classical wave theory offers no possibility of matching the experimentally observed maximum in $R(v,T)$.

However, Wien [58] earlier (1896) had derived on the basis of some thermodynamic assumptions the mostly empirical Eq. 3 for $\rho_v(v,T)$.

$$\rho_v(v,T) = \alpha\, v^3 \exp(-\beta v/T)\, dv. \quad (\text{erg/cm}^3) \qquad (3)$$

In modern terms, $\alpha = 2\pi h/c_0^3 = 1.550 \times 10^{-57}$ erg s^4/cm^3 and $\beta = h/k_B = 4.801 \times 10^{-34}$Ks. The $\exp(-\beta v/T)$ term causes the maximum as seen in Fig. 1a, which crudely results because according to Boltzmann statistics [59] higher energy states are less likely to be occupied than lower states, thus the equipartition of energy theorem $E_{average} = k_BT$ is not fulfilled at higher values of v. Eq. 3 initially was thought to agree well with observation, but as more-precise measurements were made over wider ranges of v, it became apparent Eq. 3 gives values of $R(v,T)$ systematically smaller than observed [60], especially at lower values of v.

3.1.3. Max Planck

Max Planck [61, 62] was in 1900 the very highly respected [63], 42-year-old Professor of Theoretical Physics at Friedrich-Wilhelms-Universität in Berlin. His previous work had been in basic thermodynamic theory, especially clarification of entropy and the Second Law. He had begun about 1894 to apply fundamental thermodynamic methods to the practical problem of exactly rationalizing the form of $R(v,T)$ by relating entropy to Maxwellian electromagnetic waves. Planck used in this work the intuition that fellow physicist Max von Laue is said to have referred to as his, "incomparably delicate thermodynamic sensitivity."

Planck presented his most important results [64-66] at meetings of the *German Society for Physics* in Berlin over about two months in late 1900. He disclosed Eq. 4 on Sunday, October 14.

$$\rho_v(v,T) = (\alpha v^3)/(\exp(\beta v/T) - 1)\, dv \,(\text{erg/cm}^3) \qquad (4)$$

Eq. 4 is completely classical in origin and did not have a compelling thermodynamic basis. It did, however, precisely match within experimental error very accurate measurements [60] over all frequencies, including those where the maximum occurs. Planck further calculated from experiment [60] the values of $\alpha = 6.10 \times 10^{-57}$ erg s^4/cm^3 and $\beta = 4.886 \times 10^{-11}$ *Ks*.

However, not all was lost for the classical approach because Eqs.1 and 4 both fit experiment [21] as $v \rightarrow 0$. Further, expansion of $\exp(\beta v/T)$ in Eq. 4 as $1 + (\beta v/T) + (\beta v/T)^2 + (\beta v/T)^3 + \ldots$ and substitution of the first two expansion terms into Eq. 4 yields Eq. 5, which is valid only as $v \rightarrow 0$.

$$\rho_v(v,T) = \alpha v^2 T/\beta\, dv \,(\text{erg/cm}^3) \qquad (5)$$

Equating Eqs. 1 and 5 yields the remarkable Eq. 6.

$$N_{\mathrm{Avo}} = (\beta/\alpha)\,(8\pi R/c_0^3) = 6.19 \times 10^{23}\text{molecules/mole} \quad (6)$$

The modern value of N_{Avo} is 6.022×10^{23} molecule/mole, a difference of 2.6%. The classical theory works nearly quantitatively at very low frequencies!

Planck presented his masterstroke, Eqs. 7*a,b*, at the same venue a little more than two months later on Wednesday, December 19, 1900 [66].

$$\rho_v(v,T) = (8\pi h v_0^3)/c_0^3)/(\exp(hv/k_{\mathrm{B}}T) - 1)\,dv\ (\text{erg/cm}^3) \quad (7a)$$

$$R(v,T) = (2\pi h v_0^3/c_0^2)/(\exp(hv/k_{\mathrm{B}}T) - 1)\,dv\ (\text{erg/cm}^2\text{s}) \quad (7b)$$

Equation 7*b* also fitted very precise experimental data over the entire range of experimentally accessible frequencies.

Where did Eqs. 7*a,b* come from? Planck had tried hard but failed to find convincing, purely thermodynamic support connecting Eq. 4 to fundamental physical principles. Indeed, doubt of the EOE Principle itself had begun to appear. He finally turned to Boltzmann's fundamental statistical entropy methods (based on $S = k \ln W$) to help motivate an atomic model of the cavity-wall oscillators. Each atom was suggested to vibrate in place and to be in thermal equilibrium with standing-wave electromagnetic radiation. The cavity thus fills with standing-wave radiation that leaks out through the aperture. He further followed Boltzmann's earlier work by assuming the atomic oscillators to be harmonic with the energy difference between vibrational energy levels given by hv_0, where h is a new fundamental constant of nature (Planck's constant) and v_0 is the fundamental frequency of the harmonic oscillators. Boltzmann's work had supplied support for the form hv_0. This changed approach had to be very difficult to accept for Planck, who at this time wasn't at all sure atoms existed and was completely convinced that the Second-Law was always exactly true, not just statistically true on average. These non-classical, discrete energy levels were far from where he started. It apparently did not occur to Planck, or anybody else in 1900, that light itself might exist as discrete particles of energy.

All these vibrating atoms must interfere with each other, but it turns out the details of the oscillations are not important. All that matters is the absorption and emission of electromagnetic radiation by the cavity-wall, harmonic oscillators.

Planck then was able to derive the complete form of $R(v,T)$, Eqs. 7*a,b*. He began by assuming the Boltzmann distribution governs the number of oscillators (N_n) of energy $E_n = nhv_0$ via the equation $N_n = N_0 \exp(- E_n/k_{\mathrm{B}}T)$, where N_0 is the number of oscillators in the lowest energy state. The total number of oscillators, N, is then given by the sum Eq. 8.

$$N = N_0\,(1 + \exp(-hv_0/k_BT) + \exp(-2hv_0/k_{\mathrm{B}}T) + \exp(-3hv_0/k_{\mathrm{B}}T) + \ldots) \quad (8)$$

The total energy for oscillators in their various quantum states is given by the sum Eq. 9.

$$E_{\mathrm{tot}} = N_0\,(0) + N_0(hv_0)\exp(-hv_0/k_{\mathrm{B}}T) + N_0\,(2hv_0)\exp(-2hv_0/k_{\mathrm{B}}T) + N_0\,(3hv_0)\exp(-3hv_0/k_{\mathrm{B}}T) \ldots + \ldots \quad (9)$$

The infinite series in Eqs. 8 and 9 are of standard forms yielding Eq. 10 for the average oscillator energy.

$$E_{\mathrm{average}} = E_{\mathrm{tot}}/N = hv_0\,/(\exp(-hv_0/k_{\mathrm{B}}T - 1) \quad (10)$$

Note that when $k_{\mathrm{B}}T >> hv_0$, Eq. 10 approaches the classical Equipartition of Energy result $E_{\mathrm{average}} = k_{\mathrm{B}}T$. Substitution of Eq. 10 for $k_{\mathrm{B}}T$ into Eq. 1 or 2 yields Planck's Black-Body frequency-distribution formulas, Eqs. 7*a,b*.

The importance in 1900 of the accurate values of N_{Avo}, k_{B}, h, and e (the electron charge) Planck was able to extract from the Berlin Black-Body data [60] fitted to Eq. 7 does not seem to be remembered today. No value of h existed before 1900 and existing values of the remaining constants had been indirectly inferred. Planck's values could be used with confidence and turn out to be very close to modern values [36, 49, 53, 61]. His values are: $N_{Avo} = 6.19 \times 10^{23}$ molecules/mole, within 2.6 % of the modern value; $h = 6.55 \times 10^{-34}$ Js, within 1.1 % of the modern value; $e = 1.56 \times 10^{-19}$C/electron, within 2.6 % of the modern value; and $k_{\mathrm{B}} = 1.35 \times 10^{-23}$ J/molecule deg, within 2.5 % of the modern value. Planck's value of e apparently was obtained from his value of N_{Avo} and the mole yield (n) of Ag^0 resulting from passage through $Ag^+(aq)$ of a measured electrical charge, q, with

$e = q/nN_{Avo}$. Arrhenius [49] suggested such an accurate value of e merited in and of itself a Nobel Prize for Planck!

The classical and quantum roles of h have been contrasted [67, 68]. Boltzmann at the end would have allowed h go to zero to yield a continuous system. However, this option was not available to Planck; Eqs. 7*a,b* go to infinity as $h \rightarrow 0$. The form $E_n = nh\nu_0$ thus was irrevocably introduced into physics, but not as the quantum of electromagnetic radiation. It seemed to be the curious, harmonic Black-Body oscillators that allowed only certain vibrational energies, given by $nh\nu_0$, that led to Eqs. 7*a,b*. Planck himself [69, 70] thought at this time his assumed separation between oscillator energy levels of $h\nu_0$ was a "purely formal assumption… actually I didn't think much about it." Planck's unsuccessful efforts to understand the quantum of action, h erg s, over several years were a frustration to him, but he was certain h had a precise, non-zero value.

Max Born [63] described Planck: "He was, by nature, a conservative mind: he had nothing of the revolutionary and was thoroughly skeptical about speculations. Yet his belief in the compelling force of logical reasoning from facts was so strong he did not flinch from announcing the most revolutionary idea that ever has entered microscopic physics." However, he was never comfortable with h. He admitted later concerning Eq. 4, that it was "an interpolation formula, guessed by good luck." And presumably thermodynamic intuition! Plank's conservatism concerning his revolutionary work was shared by Maxwell and Hubble concerning their revolutionary ideas [71].

Why do quantum effects become dominant only at high frequencies in Black-Body radiation, while very low frequencies seem nearly classical?

The classical Equipartition EOE principle [48] assumes electromagnetic waves of all frequencies are equally probable. However, in Planck's Black-Body Radiation theory, electromagnetic waves are in equilibrium with harmonic atomic oscillators. Furthermore, combination of the constraint $E_n = nh\nu_0$ for allowed oscillator energy levels with the strong Boltzmann discrimination against higher-energy oscillator states causes higher-n radiation to be less probable than lower-n radiation in the Black-Body cavity; a violation of the EOE principle. The probability of a particular energy electromagnetic wave being present in the cavity is given by the Boltzmann equation for the atomic oscillators as $N_n/N_0 = \exp(-nh\nu_0/k_BT)$. $R(\nu,T)$ thus rises initially as ν^2 increases, Eqs. 7, but not so fast as N_n/N_0 exponentially falls at higher values of ν. The maximum in $R(\nu,T)$ thus appears, after which $R(\nu,T) \rightarrow 0$ exponentially as $\nu \rightarrow \infty$. It is in fact the quantization of oscillator energy, $E_n = nh\nu_0$, in the Planck treatment that causes the maximum in $R(\nu,T)$ to appear. It does turn out the quantum-mechanical (Eq. 27) solution for the allowed energy levels of a Hooke's Law oscillator, $V = -kx$, is harmonic with $E_n = (n + 1/2)h\nu_0$.

3.1.4. Low-temperature heat capacity of crystals: Einstein and Debye

Einstein [20] supported the existence in solids of vibrational energy levels given by $E_n = nh\nu_0$ by using this assumption to rationalize the thermal behavior of crystals at very low temperatures. Atomic or molecular materials exchange heat with their surroundings until they reach ambient temperature. The relation between heat flow (dq) as temperature changes (dT) is given by $dq = C_v\,dT$, where the proportionality constant C_v is the temperature-dependent heat capacity of a material at constant volume, often given in J/mol K.

Ideal monoatomic gases absorb heat only as translational energy of atoms. Ideal polyatomic gases absorb heat as translational, rotational and vibrational energies that are often separable. Liquids at intermediate temperatures absorb heat as tangled translational-rotational-vibrational energies. However, a crystalline solid may be assumed to absorb heat at very low temperatures only as vibrational energy, with translational and rotational motions having been "frozen out" in the crystal lattice. It is found experimentally that the C_v of a material falls as temperature falls (See Fig. 2) because of loss of thermally accessible translational, rotational and vibrational energy levels. Furthermore, C_v surprisingly reaches 0 in crystals slightly before T reaches 0 K (See Fig. 2). There is no classical explanation for this phenomenon. It results because k_BT becomes so small at very low temperatures that all excited vibrational levels become inaccessible, thus no heat is absorbed. Only the ground state is significantly populated. This observation provides

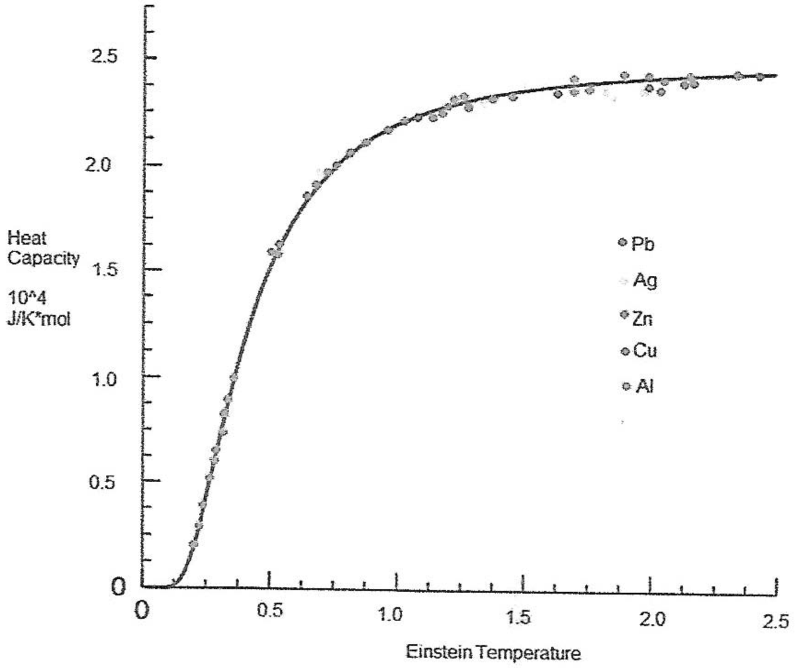


Fig. 2. The heat capacities of several crystalline metals at low temperatures vs. the Einstein temperature scaled by θ_D given in Eq. 13.

unequivocal evidence of the existence of non-classical energy levels in crystals.

Einstein [20] applied $E_n = nh\nu_0$ in 1906 to crystal vibrations in order to derive the low-temperature dependence of C_v on T from first principles. He assumed each atom in a crystal acts as an independent harmonic oscillator and that all oscillators have the same fundamental frequency, ν_0. He then extended Planck's equation for the average energy of a collection of N harmonic oscillators (Eq. 10) to arrive at his low-temperature C_v, Eq. 11.

$$C_v = 3Nk_B(h\nu_0/k_BT)^2\exp(h\nu_0/k_BT)/(\exp(h\nu_0/k_BT) - 1)^2 \quad (11)$$

Eq. 11 fits experimental data quite well except at the very lowest temperatures where Eq. 11 approaches Eq. 12 as $T \rightarrow 0$.

$$C_v \approx 3Nk_B(h\nu/k_BT)^2\exp(-h\nu_0/k_BT) \quad (12)$$

Because the exponential factor dominates the T^2 factor, $C_v \rightarrow 0$ exponentially as $T \rightarrow 0$. However, C_v is observed to approach zero according to T^3, in contradiction to Eq. 12.

Peter Debye [72] later pictured a crystal as a three-dimensional isotropic medium in which waves of all wavelengths propagate much like what occurs in shaken Jello®. He then derived Eq. 13 where the decrease in C_v is indeed proportional to T^3 as $T \rightarrow 0$, as is observed.

$$C_v = 12/5\,\pi^4 N_0\,k_B\,(T/\theta_D)^3\ \theta_D(\text{Debye } T) = h\nu_D/k_B \quad (13)$$

A comparison of the Einstein and Debye models is given in Fig. 3. Both models qualitatively fit the experimental data. However, the exponential decay of C_v in the Einstein model vs. the decay with T^3 in the Debye model is apparent.

One of us (Troy [73]) reworked the Einstein-Debye low-T C_v derivation for Fermi-Dirac, Boltzmann, and Bose-Einstein statistics. Part of this work involves approximating $\ln(N_n!)$ where N_n is the number of oscillators in the n th quantum state, $n > 1$. However, $N_1 \rightarrow N$ as $T \rightarrow 0^+$, where N = total number of oscillators. Even the first excited state thus is not strongly populated. Einstein used Stirling's approximation $\ln(N_i!) \approx N_i \ln(N_i) - N_i$, (not a good approximation when N is small)) to evaluate ln $N_i!$), which introduces a technical error as $T \rightarrow 0^+$. Troy used the gamma function for $\ln(N_i!) = \ln(\Gamma(N + 1))$ to obtain a better agreement with experiment than earlier work had provided.

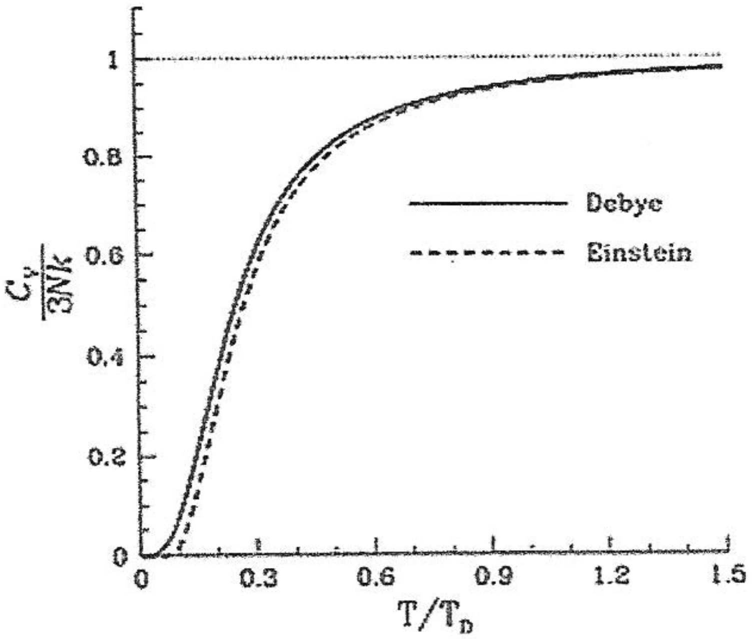


Fig. 3. Comparison of Einstein and Debye low- temperature heat capacity theories.

The Einstein-Debye heat-capacity work says little about the existence of light photons with $E = hv$. It does support Planck's assumption that atomic vibrations are characterized by harmonic energy levels given by $E_n = nhv_0$ where $n = 1,2, \ldots$, and v_0 is again an atomic vibrational-frequency rather than the frequency associated with a photon.

3.2. Einstein's treatment of the PE

It cannot be known what was in AE's mind concerning energy discontinuities at a particular time in 1902-5. We know only of his 1905 suggestion that electromagnetic radiation exists as independent particles of energy given by $E = h\text{v}$, which first appeared publicly within the context of his rationalization of Lenard's [47] experimental work on the PE.

3.2.1. Experimental characterization of the PE

The PE is the ejection of electrons when light is shone on a reasonably electropositive material, typically a metal, e.g., Na, K, Ca, or Al [28-32, 47]. The effect is attributed to the transfer of energy from light to an electron in the metal, which then may or may not be ejected (perhaps with considerable kinetic energy) from the metal surface. Classical electromagnetic theory suggested that the number of electrons ejected should depend only on the intensity of the light; even dim light would eject electrons after a time delay while the necessary energy is deposited.

Work on the interaction of light with metals to produce photovoltaic cells [74] had been proceeding since Becquerel's radioactivity work. However, Hertz's direct observation [46] of the PE in 1887 was serendipitous during his work to demonstrate the existence and transmission of Maxwell's [44] electromagnetic waves. Hertz's apparatus comprised a transmitter and a similarly constructed receiver located a few feet away. The transmitter consisted of a spark-gap (connected to an antenna) supporting an intense, high-voltage, AC discharge (arc). The receiver was a similar spark-gap/antenna with no applied potential. A smaller and dimmer spark appeared across the receiver gap when the larger transmitter spark was on. The appearance of the receiver spark indicated the apparent transmission of energy from the transmitter to receiver *via* electromagnetic waves; all other known means of wireless transmission of energy were thought to have been excluded. It is ironic that while confirming a major feature of Maxwell's Electromagnetic Theory, Hertz observed a phenomenon that turned out to be impossible to understand by Maxwell's theory alone.

The receiver spark was dim and hard to see in the bright light emitted by the transmitter spark. Hertz thus put a box around the receiver to shade it and noticed the spark seemed smaller when the receiver gap was shaded. To quote Isaac Asimov" The most exciting phrase in science, the one that heralds new discoveries, is often not "Eureka!" but "that's funny…". It was soon demonstrated it was UV light from the transmitter that enhanced the receiver spark, presumably by helping to kick electrons out of the spark-gap electrodes. This result seems to us to be a truly remarkable piece of scientific deduction!

This discovery was pursued by a number of people over the next few years including Stoletow [75] and Lenard [47], who had been Hertz's assistant in the original 1887 work. Lenard carried out a systematic investigation of the photoelectric effect. His apparatus (Fig. 4) comprised an evacuated glass chamber into which UV radiation could be shone (through a quartz window) onto a target being the clean surface of a suitable electropositive metal, e,g., Al, K, Li, or Na. Electrons were found to be ejected from the target surface with varying amounts of kinetic energy, depending upon the frequency of the impinging radiation, v. An amount of energy called the Work Function (P) is required to eject an electron from the metal, and its value depends only on the metal used, Al in Lenard's work. A positively biased metal electrode located above and parallel to the target plate collects the ejected electrons, and the resulting current flow between the target and collector is a measure of the rate of electron ejection at a particular value of v.

Lennard surprisingly found there exists a threshold value of v below which no electrons are emitted, regardless of the intensity of the applied light. Furthermore, a negative potential could be applied to a wire grid between the target and collector that repels electrons with insufficient kinetic energy (KE) to overcome the grid potential and pass on to the collector. As the strength of the negative bias on the grid is increased, the flow of electrons decreases until it reaches zero at what is referred to as the Stopping Potential (Π) for a particular frequency of impinging radiation. The value of Π is assumed to measure the KE of electrons ejected exactly in the direction of the collector at the particular frequency used, i.e.,

$$\mathrm{KE} = e\Pi. \tag{14}$$

The KE of electrons ejected at the threshold v is zero but increases as v increases beyond the threshold. Unfortunately, Lenard's experiments did not have the resolution to determine the functional form of the increase in KE with v. However, he could see the measured current at a particular value of v seems to increase with radiation intensity.

Lenard received the 1905 Nobel Prize in Physics [36] for his experimental work on cathode rays

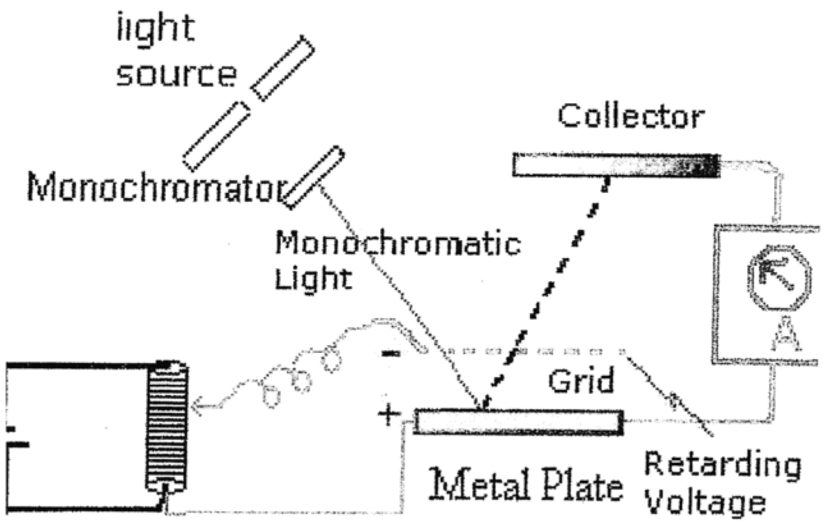


Fig. 4. Schematic of Lenard's Apparatus.

with only a short closing comment on his PE work in the citation. He was a German Nationalist with anti-Semitic leanings quite resistant to "Jewish Physics," especially after AE's public criticism [36, 53] of his rejection of Relativity Theory. Lenard also seems to have resented that AE's theoretical work attracted so much more attention than did his experimental work. He and Johannes Stark [49], the 1919 Nobelist in Physics (Stark Effect of electric fields on cathode rays), were co-leaders of the ultimately unsuccessful "Deutsche Physik" movement associated with the Nazi Party.

3.2.2. Einstein and the PE, *E = hv*

i. Initial thoughts: Klein [76] summarizes AE's early thoughts on the quantum of electromagnetic radiation. The "PE" paper [9] starts by defining "ponderable bodies," e.g. atoms and molecules, whose energy is a sum carried over the nuclei and electrons constituting an independent particle. Such highly localized objects are then contrasted to Maxwell's propagating electromagnetic radiation waves, whose energy is continuously spreading through an expanding volume. Einstein's recognition of this localized/delocalized misfit is near to the beginning of his long route to the wave-particle duality [22]. He seems to imply in this section that there are not energy levels in atoms and molecules but later changed his mind on that.

Einstein goes on to point out that while the spatially dispersed Maxwell electromagnetic wave model works well in optics, it does not fit well with phenomena associated with the local emission and absorption of light by atoms and molecules. He cites as examples observations associated with Black-Body radiation, fluorescence, and the production of cathode rays (moving electrons) by UV light. He thus suggests that radiation itself has a particle nature and is composed of localized energy quanta, and he provides several examples of the success of this proposal, the most easily grasped being his treatment of the PE.

The first parts of the PE paper treat the Black-Body problem and the nature of radiation thermodynamically and statistically in a constant volume V in a manner very different from that of Planck discussed above [66, 77]. Einstein's arguments are elegant, especially for so early in the development of statistical mechanics [78, 79].

ii. Einstein's statistical mechanics: Ludwig Boltzmann's profound contribution to physics was his interpretation [59, 79] of the Second Law of Thermodynamics [48, 80] recognizing the essentially atomic, statistical nature of the microscopic world. Einstein's early independent work extended and clarified with great originality Boltzmann's as well as Gibbs' [81] statistical ideas. Three early publications [12-14] describe the heat-transfer and thermodynamic properties of molecular systems, including fluctuations, always present in statistically driven systems. His approach was more physical than Gibbs' abstract work. Einstein's thinking in 1905 was based firmly in the statistical mechanics he had thus perfected [21]. Indeed, it seems possible that his conception of the discontinuous nature of electromagnetic radiation had its start in these early papers. Thus AE perhaps had been prepared by 1905 to understand the PE on the basis of the quantum of radiation.

Einstein based his thermodynamic treatment of electromagnetic radiation on relating its entropy to the equilibrium spectral distribution, $\rho_v(v,T)$, of energy among the various wavelengths of radiation present from $v = 0$ to $v = \infty$. He thus considered Black-Body radiation confined within a container of volume V and in equilibrium with oscillators of all frequencies at a given T. The kinetic-energy distribution of molecules in this container also is in equilibrium with the oscillators. He chose Wien's [58] form of the Black-Body spectral distribution function, $\rho_v(v) = \alpha v^3 \exp(-\beta v/T)$, Eq. 3, to describe the kinetic-energy distribution within V. This approximate form had been confirmed experimentally at higher values of v/T, used earlier by Planck [64-66], and is the simplest $\rho_v(v,T)$ function that shows the Black-Body maximum. It seems reasonable to suggest it was the form of Eq. 3 that led to the hint of quantum discontinuity as AE's work progressed.

Einstein's resulting derivation of the entropy of monochromatic radiation of wavelength v yields the logarithmic Eq. 15 for the change in entropy resulting from a change in container volume from V_0 to V at constant total energy E.

$$S–S_0 = (E/\beta v) \ln V/V_0 \qquad (15)$$

Use of the Wien spectral distribution function gives Eq. 15 a strong physical connection to

Black-Body radiation. It seems Eq. 15 makes little physical sense unless the energy E is distributed among N discrete packets, all associated with its frequency v.

The corresponding classical thermodynamic logarithmic equation for an ideal gas of n particles in an isothermal process is Eq. 16.

$$S–S_0 = nR \ln V/V_0 \quad (16)$$

Comparison of Eqs. 15 and 16 suggests by analogy (Set $E/\beta v = nR = NR/N_{\text{Avo}}$) that the radiation may be considered to be composed of N quanta of energy given by eq. 17.

$$E = NR\beta v/N_{\text{Avo}}. \quad (17)$$

Remember [65, 66] $\beta = h/k_{\text{B}}$, yielding $E = Nhv$ from Eq. 17. The quantities h and k_{B} are both fundamental physical constants, i.e., they are independent of the details of the system under consideration, with h scaling radiative energy with v and k_{B} scaling kinetic energy with T.

Equations 15-17 are such a remarkable result that AE considered them very carefully. In particular, he showed that the logarithmic form of Eq. 15 results directly and entirely from Boltzmann's statistical-mechanical statement of the Second Law of Thermodynamics for a transition between two states Eq. 18.

$$S–S_0 = R/N_{\text{Avo}} \ln W/W_0 \quad (18)$$

The quantity W is an *a priori* probability defined by Boltzmann as, for example, the number of ways (complexions) a certain amount of energy can be distributed among N distinguishable particles. No special assumptions need be made concerning the mechanics of gases or dilute solutions. This result suggests consideration of whether the laws regarding transformation of light, for example, its interaction with atoms and molecules, also might show experimental evidence of electromagnetic discontinuity. This is part of the "heuristic" point of view mentioned in the title of the Photoelectric paper.

The power of Einstein's development of statistical mechanics [21] is further illustrated by his analysis of the *a priori* "probability" W used by Boltzmann in Eq. 18. Boltzmann's quantity W was not defined as a real, physical, statistical probability. Einstein found it necessary instead to allow the natural motion of the system itself to determine the probabilities of its various states (e.g., energy distributions, $i, j,\ldots,n$). A given system will over a very long period of time, say T_{O}, run through all accessible energy states many times. The corresponding probabilities, W_i of each state, i, are then given by t_i/T_{O}, where t_i is the time the system spent in state i during T_{O}. It also is true that t_i/T_{O} is the same as the fraction of members in state i in a very large ensemble of identical systems [82]. This process demands the existence of fluctuations in statistical molecular systems and offers methods for their investigation.

The above insights are the basis of Einstein's statistical mechanics. They distinguish between static thermodynamic equilibrium and fluctuating statistical equilibrium, and allowed Einstein to make progress in many areas, e.g., Brownian motion [15]. Einstein suggests that V in Eq. 15 may be a fluctuation from V_0, an idea criticized by Irons [83]. In general, Einstein's approach in this work has been criticized as not properly taking into account changes in translational energy levels as volume changes [53].

iii . Rationalization of Lenard's observations using E = *hv*: Lenard's work [47] is about the most Einstein could have known empirically of the PE in 1905. It was enough! He seems to have connected, to the support of both, the PE threshold with his thermodynamic insight that electromagnetic radiation might consist of energy packets (quanta) of magnitude hv, i.e., $E = hv$. Electrons can be kicked out of a metal only by higher-energy photons whose energy exceeds the metal's work function, P.

The value of P for Al now is known [84] to be 6.536×10^{-19} J/electron and to correspond ($E = hv$) to a frequency of 9.864×10^{14} s^{-1}. It seems reasonable to assume Einstein would have had an idea of the value of P from the approximate threshold frequency observed by Lenard, yet he does not seem to have had a sense of this quantity.

The quantity Πe is the KE of the ejected electron, Eq. 14. The energy of the radiation packet at frequency v is given by AE in Planck's form as $R\beta v/N_{Avo}$. Noting that $R/N_{Avo} = k_{\text{B}}$ and $\beta = h/k_{\text{B}}$ we see $R\beta v/N_{\text{Avo}} = hv$. Einstein then wrote the profound relation: KE of ejected electron = energy of radiation quantum – Work Function (P), or as an algebraic equation,

$$KE = \Pi e = (R/N_{Avo})\,\beta\nu - P. \quad (19)$$

Multiplying Eq. 19 through by N_{Avo} yields Eq. 20,

$$\Pi E_{Faraday} = R\beta\nu - P', \quad (20)$$

where $P' = PN_{Avo} = 3.936 \times 10^5$ J/mole and $E_{Faraday}$ is the Faraday constant = eN_{Avo}. Einstein apparently used Planck's 1900 values of e and N_{Avo} to yield essentially the modern value $E_{Faraday}$ = 96,500 C/mole. Einstein carried out calculations designed to support Eq. 20 using $\nu = 1.03 \times 10^{15}$ s^{-1}, the "ultraviolet limit of the solar spectrum." No rationale is given for the use of this particular value of ν. The modern value of β is 4.7979×10^{-11} Ks. $R\beta\nu$ then becomes 4.108×10^5 J/mole, within computational error of the modern value of P for Al, 3.936×10^5 J/mole. The value of Π for AE's frequency very near to the threshold frequency is then expected to be close to zero. All of these calculations were done using modern values of physical constants, which are quite close to those used by AE except for the value of P for Al. There is a typo in the original AE paper where the Faraday constant is incorrectly listed as 9.6×10^3 C/mole rather than 9.6×10^4 C/mole. It appears AE used the correct value.

Einstein wished to support Eq. 20 by carrying out a calculation showing the value of Π obtained is reasonable. He thus assumed $P' << R\beta\nu$, i.e., P' is essentially zero compared to $R\beta\nu$ in Eq. 20. A value of Π then can be calculated readily from Eq. 21

$$\Pi = R\beta\nu/F = 4.108 \times 10^5 \text{ J/mole}/9.647 \times 10^4 \text{ C/mole} = 4.3 \text{ V} \quad (21)$$

He then offers this as evidence for Eq. 20 and thus radiation quanta because this stopping potential (Π) is in the "few volts" range measured by Lenard [47]. In fact, the correct result is $\Pi \approx 0$ for the assumed value of ν because the value of P' is $\approx R\beta\nu$. A choice by AE of $P' \approx 4 \times 10^{-19}$ J/electron or 2.408×10^5 J/mole would have yielded $\Pi \approx 1.8$ V which actually is in the range observed by Milikan [29-32].

Ohanian [53] suggests it was not unknown for Einstein to let his physical intuition overrule mathematics. However, Einstein's calculations here are internally consistent. Following his assumption that $(h/e)\nu >> P/e$ yields from Eq. 20 the relation $e = h\nu/\Pi$, which using Planck's value of h and AE's values of ν and Π recovers Planck's value $e = 1.56 \times 10^{-19}$C. Planck's values of e and N_{Avo} entered the calculation *via* $E_{Faraday}$.

Albert Einstein's intellectual genius is in deducing Eqs. 19 and 20 and rearranging the result to Eq. 22, which states a plot of Π vs. ν is expected to be linear with slope equal to h/e for an electropositive material of Work Function P/e.

$$\Pi = (h/e)\,\nu - P/e \quad (22)$$

Unfortunately, Lenard's data lacked the precision to support Eq. 22 strongly; its experimental confirmation waited until the 1912/1913 work of Richardson and Compton [85], Compton and Richardson [86] and finally Millikan [29-32], who demonstrated Eq. 22 fits his exceptionally precise data within experimental uncertainty.

The personal genius in the PE paper is AE's boldness to accept the result of his intellectual genius.

4. Part 3. The path from $E = h\nu$ and $\lambda = h/p$ to $H\Psi = E\Psi$

4.1. Initial resistance to $E = h\nu$

Einstein challenged, it seems largely based on his intuition, the well-established, Maxwellian, continuous, electromagnetic wave theory by the suggestion electromagnetic radiation consists of localized independent packets (quanta) with energy given by $E = h\nu$. His support for the quantum of radiation in the PE paper was not strong. Millikan [32] wrote the suggestion was "without basis in established theory." Einstein saw the wave-particle duality problem early [22] and worried greatly about it. However, to the modern mind it is difficult to visualize a highly dispersed electromagnetic wave easily interacting with a localized atom. Modern treatments of the quantum are given by Atkins [87] and Klein [76].

Planck, as well as many other physicists, was very uneasy in 1905 with AE's quantization of light. Planck himself [71] was uneasy even with his earlier blackbody results invoking $E_n = nh\nu_0$, for harmonic oscillators suggesting "it results from the peculiar structure of phase space." In his 1913 introduction of Einstein to the Prussian Academy of Sciences for membership, Planck *et al*. [26] praised Einstein's remarkable (bold) contributions to modern physics, but demurred on $E = h\nu$,

"In sum, it can be said that among the important problems, which are so abundant in modern physics, there is hardly one in which Einstein did not take a position in a remarkable fashion. That he might sometimes have overshot the target in his speculations, *as for example in his light-quantum hypothesis*, should not be counted against him too much. Because without taking risk from time to time it is impossible, even in the most exact natural science, to introduce real innovations."

Jeans [56] suggested "the correct value of h is zero," a position held by others [68] but strongly criticized by Planck, who knew from his work it had to be non-zero. Resistance to the attack on classical physics by the quantum was fierce and lasted nearly 25 years in some quarters. However, Planck's (1918) acceptance [27] speech on the occasion of his receiving the Nobel Prize in Physics for "my theory" was focused on the quantum, although he also suggested "there still is no real quantum theory." Arnold Sommerfeld is quoted [88] as saying, "This kills the wave theory of light!" However, the wave theory of radiation remained indispensable to understanding of interference, diffraction, and similar phenomena; a conundrum finally solved in 1924 by Louis de Broglie [89, 90].

4.2. Einstein's frustration

Planck's derivation of Eqs. 7 was carried out *via* an entropy calculation based on the Boltzmann [59] equation, $S = k_B \ln W$, where W is thought of as the number of complexions or states in a system. Evaluation of W requires use of a statistical counting procedure. The Planck discontinuity allowed him the counting of distinguishable states. Einstein recognized [91] in 1909 that in a classical system assuming: (1) Boltzmann statistics, (2) the distinguishability [92] of atom/molecules/ photons by their trajectories, and (3) the EOE principle [48, 93], it always will be necessary to introduce quantum states artificially in order to get Eqs. 7.

Furthermore, Einstein put a great deal of fruitless effort 1905-1909 into merging the particle and wave aspects of electromagnetic radiation by somehow inserting h into Maxwell's wave equations [22, 91]. He had concluded by 1909 that some kind of wave-particle fusion must occur [22, 91] for further theoretical progress to be made. Not knowing how to do this at that time, he boldly made the decision to spend the next several years (1910-1916) mostly working intensely on his other passion, general relativity [1, 2] and returned in force to quantum theory only in 1916 when he developed in support of $E = h\nu$ a quantum treatment of the absorption and emission of light by atoms and molecules [3-5]. Einstein developed his idea of stimulated emission of photons from excited states in this work.

4.3. Compton and Richardson

After some delay, solid experimental support for $E = h\nu$ began to appear. Richardson and K.T. Compton [85], as well as K.T. Compton and Richardson [86] experimentally demonstrated the linear dependence of Π on ν for a number of electropositive metals.

4.4. The Bohr atom

Niels Bohr in 1913 built [94] upon Ernest Rutherford's nuclear model of the atom [94-96]. He created a planetary model for the hydrogen atom in which the negatively charged electron is electrostatically attracted to and revolves around the positively charged proton in a closed circular orbit of radius r. Such an orbit is unstable according to classical physics because the accelerations associated with the nonlinear (curved) motion of the electron charge would cause it to emit energy as electromagnetic radiation and eventually fall onto the proton.

Bohr avoided this orbital instability simply by assuming that only orbits in which the electron has certain mean kinetic energies, W, are stable. He further calculated the relationship between W and the electron rotational frequency, ω, given by Eq. 23,

$$\omega = 2^{1/2} W^{1/2} / (\pi e E m^{1/2}), \tag{23}$$

where e is the electron charge, E is the nuclear charge, and m is the electron mass. Bohr further declared by intuition the allowed energy levels are given by Eq. (24), where n is an integer able to take on the values 1,2,3….∞

$W_n = ½nh\omega$ (24)

Elimination of ω between Eqs. 23 and 24 yields the allowed hydrogen-atom energy levels, Eq. 25.

$W_n = 2\pi^2e^2E^2m/ (n^2h^2)$ (25)

The quantization of Eq. 25 also can be reached by recognizing that the allowed electron orbits contain an integer number of de Broglie [89, 90] wavelengths [96]. See below.

Bohr completed his model by recognizing the electron can move back-and-forth among allowed energy levels *via* the absorption or emission of photons. The spectrum of radiation emitted or absorbed by such transitions comprises frequencies given by $v = \Delta W/h = (W_2 - W_1)/h$, where ΔW is the energy difference between the orbits (energy levels) involved in the transition. The resulting equation is able to predict nearly quantitatively the spectroscopic Balmer series of hydrogen when W_2 corresponds to $n = 2$ and W_1 corresponds to any $n > 2$. Indeed, the Bohr model predicts quantitatively within experimental uncertainty the principle energy levels leading to the entire hydrogen-atom spectrum! It does not predict [97] either the intensity of the transitions or their splitting; it is a two-dimensional model in a three-dimensional world. However, it provided very strong support for $E = hv$ and the photon. Schrödinger's 1926 three-dimensional formulation [98, 99] of quantum mechanics, also based on the de Broglie relation, predicted many more properties of the hydrogen atom [97].

4.5. Robert A. Millikan

Millikan remained forever a fierce opponent of light corpuscles starting from AE's 1905 initial suggestion of Eq. 22. Experimental work [28-32] from 1913 to 1917 in his own laboratory unequivocally demonstrated the qualitative validity of its form. However, he still was unable to accept $E = hv$. In 1916 he stated [29],

"We are confronted, however, by the astonishing situation that these facts were correctly and accurately predicted nine years ago by a form of quantum theory which has now been pretty generally abandoned."

"It was in 1905 that Einstein made the first coupling of photo effects with any form of quantum theory by bringing forward the bold, not to say reckless, hypothesis of an electromagnetic light corpuscle of energy hv, which energy was transferred upon absorption to an electron. This hypothesis may well be called reckless first because an electromagnetic disturbance which remains localized in space seems a violation of the very conception of an electromagnetic disturbance, and second because it flies in the face of the thoroughly established facts of interference."

Millikan argued his initial PE results were not convincing because various metals had been investigated, and there were numerical discrepancies among the results for different metals. He still hoped to discredit Eq. 22 by demonstrating the value of the ratio (h/e) determined from it significantly differs from the ratio of independently determined values of h and e. He thus determined using an elegant oil-drop experiment [28] a very precise, independent value of e of $1.5924 \pm 0.017 \times 10^{-19}$C. The difference between this value and the currently accepted, $e = 1.602\ 176\ 565 \pm 0.000\ 000\ 040 \times 10^{-19}$C is 0.6 %. The modern value of e differs from Planck's 1900 value by only 2 %! A very sophisticated PE apparatus [29, 30, 32] was then built and used to obtain data that fits Eq. 22 exceedingly well. Multiplying the value of (h/e) he obtained from this fit by his value of e yields $h = 6.569 \times 10^{-34}$ Js. Planck's value of h is 6.55×10^{-34} Js! The modern value is 6.6260700408181 8181818181 $\times 10^{-34}$ Js. A very good fit! However, Millikan still hoped that Eq. 22 would be eventually reached by a route not requiring use of corpuscular light quanta, $E = hv$.

Holton [100] noted in Millikan's notebooks some experimental points had been discarded as being unreliable because they were not near a multiple of the average. This did not significantly affect the oil-drop value of e but did improve its apparent precision. Millikan was assisted anonymously in the oil-drop experiment by University of Chicago graduate student Harvey Fletcher [101], who went on to be elected to the U.S. National Academy of Sciences for his work in acoustics.

Millikan was awarded the 1923 Nobel Prize in Physics. The citation [102] focusses mainly on the oil-drop experiment itself and the derived values of e and h and concluded with, "if these researches of Millikan had given a different result, the law of

Einstein would have been without value and the theory of Bohr without support." Still Millikan resisted $E = hv$. Indeed, the last pages of his 1923 Nobel lecture are devoted to an unconvincing search for an alternative to it. In 1923 Millikan [31] made the statement below concerning AE's 1905 assumption of the existence of quanta of electromagnetic radiation of energy, $E = hv$.

"I shall not attempt to present the basis for such an assumption, for, as a matter of fact, it had almost none at the time."

Millikan's statement above was essentially correct, but AE's genius, leadership and boldness had carried the day by 1923. Millikan ironically received his Nobel Prize essentially for experimental verification of a theory he apparently didn't believe.

From 1921 to 1945 Millikan was President of California Institute of Technology during its period of growth into an international center of scientific teaching and research. In the early 1930s it became apparent to AE that the Nazi menace would eventually drive him from Europe. Millikan was most anxious to attract him to CalTech and greatly disappointed when he chose the Institute of Advanced Study, Princeton, NJ as his American home [36].

4.6. Compton scattering

Nearly universal acceptance of $E = hv$ by the physics community came with events of 1923-1926. In 1923 A.H. Compton [23, 25], younger brother of K.T. Compton [85, 86] investigated the scattering of X-rays by electrons and rationalized his results as the result of a collision of two particles, an X-ray of initial momentum hv_0/c_0 and scattered momentum hv_Θ/c_0 and the initially stationary electron. The photon scattering angle is θ. Application of the conservation of vector momentum [32] yields the relationship $v_\Theta = v_0/(1 + 2\alpha \sin^{-1} ½ \theta)$ with $\alpha = hv_\Theta/m_e c_0^2$, which matches experiment. Arthur Compton [23-25] received the 1927 Nobel Prize in Physics for this work.

4.7. Quantum statistics, De Broglie wavelength, and the Schrödinger equation

4.7.1. Quantum statistics

S.N. Bose [103-105] found in 1924 the solution to Einstein's 1909 conundrum that $E = hv$ could not appear naturally in Planck's entropic derivation of the Black-Body Radiation formula. He suggested some microscopic particles, called Bosons, e.g., photons, have spin-1 and are not distinguishable by trajectory. He was in this way able to enumerate $S = k_B \ln W$ in such a way as to derive the Planck equation naturally assuming only the existence of energy levels but knowing nothing of their nature, i.e., not assuming $E_n = nhv_0$.

After failing to get this work published from his Indian base, Bose appealed to Einstein, who recognized its great significance and supported its publication. What has come to be known as Bose-Einstein quantum statistics developed [6, 7, 104] from this work and allowed AE's prediction of the Bose-Einstein condensate [106], a confirmation of quantum statistics.

4.7.2. λ = *h*/*mv*

Louis de Broglie reports [107] saying on September 10, 1923, "After long reflection in solitude and meditation, I suddenly had the idea, during the year 1923, that the discovery made by Einstein in 1905 should be generalized [108] by extending it to all material particles and notably to electrons." That is, if light has both wave and particle properties, should not subatomic particles have wave properties? De Broglie's resulting suggestion [89, 90] moving particles may be described as matter waves of wavelength $\lambda = h/p = h/mv$ was soon verified by Thomson and Reid [109] and Davisson and Germer [110]. Microscopic particles (including photons) indeed do show interference. Einstein's 1909 argument [111] that wave and particle must be fused to make theoretical physics work at the atomic/molecular level resulted from his failure to find a way to insert *h* into Maxwell Equations. De Broglie achieved this fusion instead by inserting *h* into classical mechanics ($E = hv = hc_0 /\lambda = mc_0^2 = pc_0 \rightarrow \lambda = h/p = h/mv$) for very light particles.

4.7.3. The quantum wave equation

Erwin Schrödinger was in late 1925 a 39-year-old Viennese Polymath and Professor of Physics at the University of Zurich [112] who had become in close correspondence with AE on the quantum ideal gas and Bose-Einstein-Statistics. They had worked together on a statistical state-counting problem involving a proposal by Planck, and this work was based on the indistinguishability of atoms [6, 7, 106]. Einstein had strongly supported in the course of this work the importance of de Broglie's particle-wave idea [113]. The combination of AE's support and Schrödinger's obtaining the de Broglie Ph.D. thesis [107] started him thinking of particles in his statistical work as being associated with waves.

Schrödinger started thinking of electrons as de Broglie waves and especially about fitting integer numbers of various wavelengths into Bohr orbits. In this sense, wave mechanics was born in statistics. He (a superb lecturer) presented his ideas at a Zurich physics colloquium, probably on November 23, 1925. Moore [112] reports that after the colloquium Peter Debye (then at Zurich ETH) suggested that Arnold Sommerfeld had taught him that one must deal with waves using a wave equation. Whether or not Schrödinger heard and understood Debye's words, he did in fact soon write down a wave equation for electrons [49, 114].

Equation 26 describes the standing motion in 3D space of a string vibrating with wavelength λ.

$$\partial^2\Psi/\partial x^2 + \partial^2\Psi/\partial y^2 + \partial^2\Psi/\partial z^2 + k^2\Psi = 0, \text{ with } k = 2\pi/\lambda \quad (26)$$

The function $\Psi(x,y,z)$ is the displacement of the wave. Substitution of $\lambda = h/mv$, $E = T + V$, and $T = ½\ mv^2$ into Eq. 26 yields Eq. 27, solution of which using the appropriate potential-energy function, V, and boundary conditions provides the discrete stationary states and energies of a de Broglie particle in a 3D box or the electron in a hydrogen atom.

$$-[h^2/(8\pi^2 m)]\,(\partial^2\Psi/\partial x^2 + \partial^2\Psi/\partial y^2 + \partial^2\Psi/\partial z^2) + V\Psi = E\Psi \quad (27)$$

Equation 27 is the simplest example of what is now called time-independent Quantum Theory. It contains both *h* and *m*! It does not provide the trajectory of a de Broglie particle. Instead, $|\Psi|^2$ is believed to provide a probability density associated with the spatial distribution of electron charge density. The proof is in the pudding. Schrödinger [98, 99] quickly showed that a suitably modified Eq. 27 reproduces a great deal more of the observed detailed spectrum of the hydrogen atom [97] than does the Bohr atom [94, 97].

5. Epilogue

Equation 27 is the triumph of the crusade of the valiant Swabian [49]. Albert Einstein was the major contributor to as well as the maestro of the orchestra of brilliant minds that over 20 years created a quantum theory. Schrödinger's wave mechanics provided the fundamental quantum theory of microscopic physics yearned for by Planck, Einstein, Millikan and presumably many others.

Einstein's rebellious nature moderated with age as his early work, including both relativity and quantum theories, led to places intellectually and personally very uncomfortable for him [115-118]. He had great difficulty accepting the predictions made on the basis of the generalized mathematics of relativity [115] as well as the statistical nature [119] and the prediction of entangled states [120] inherent in quantum mechanics, which he referred to as "spooky action at a distance." He spent his greatest scientific effort in 1923-1931 attempting to create a unified-field theory able to encompass electricity and magnetism, gravity and quantum mechanics. The last part of his scientific career was largely spent attempting to understand the apparent "incompleteness" of quantum mechanics [36, 116-118]. He required that an adequate theory provide objective, real states of individual systems.

However, his work had revolutionized physics and ushered in the technological age we now live in.

CONFLICT OF INTEREST STATEMENT

Richard J. Field and William C. Troy know of no conflicts of interest associated with this work.

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