Einstein’s Quanta, Entropy, and the Photoelectric Effect

ELEGANT CONNECTIONS IN PHYSICS

by Dwight E. Neuenschwander

“On a Heuristic Point of View Concerning the Production and Transformation of Light”[1] was the first of the five papers published by Albert Einstein in his 1905 “miraculous year.”[2] In that paper, Einstein introduced the concept of “light quanta,” or “photons” as we call them today.

The quantum of action was introduced into physics by Max Planck in 1900.[3] Planck derived the thermal equilibrium energy distribution for electromagnetic radiation (also called the “blackbody problem” because of the experimental apparatus). The quantity of interest was $d\rho/df$ where ρ denotes the energy density and f the frequency (Fig. 1). No one had been able to derive $d\rho/df$ from the first principles of statistical mechanics. One serious problem was in the high frequencies, which contributed infinite energy when one integrated over all frequencies to obtain the total energy!

Planck thought about the charged particles whose simple harmonic motion generated harmonic electromagnetic waves of the same frequency. He discovered that if he assumed a particle oscillating with frequency f could carry only the discrete energies 0, hf, $2hf$, $3hf$..., where h was a constant, he could derive the distribution function:

$$d\rho/df = (8\pi h/c^3)\, f^3\, (e^{hf/kT} - 1)^{-1}\,,$$

where c denotes the speed of light in vacuum, k Boltzmann’s constant, and T the absolute temperature. This function fit the data provided h was assigned the value 6.6×19^{-34} J · s, now called Planck’s constant.[4] The smallness of h accounted for the lack of energy graininess in macroscopic oscillators such as pendulums.

To Planck in 1900, the quantum was a property of the *mechanical oscillators* that happen to generate light. Radiation itself, in principle, would still be described by continuous functions, as Maxwell’s equations assume. In 1905 Einstein greatly enlarged Planck’s concept. To Einstein, *light itself* was quantized into little pellets of energy. *This was revolutionary.* Where Planck saw the quantum as a calculation device to solve a particular problem, Einstein saw the quantum as a fundamental reality.

As in so many of his papers, Einstein began by critiquing a lack of consistency in the accepted network of concepts. Physicists had started to realize that treating *matter* as continuous was only an approximation, valid when the size scale was an average over huge numbers of atoms. At the microscopic level, matter was starting to be recognized as quantized; for example, the charge-to-mass ratio of the electron was measured in 1897. Yet physicists continued to treat electromagnetic *fields* as continuous functions. Why should matter be discrete but radiation continuous? Einstein questioned this assumption by introducing his 1905 paper with these words:[4]

> *A profound formal difference exists between the theoretical concepts that physicists have formed about gases and other ponderable bodies, and Maxwell’s theory of electromagnetic processes in so-called empty space. While we consider the state of a body to be completely determined by the positions and velocities of an indeed very large yet finite number of atoms and electrons, we make use of continuous spatial functions to determine the electromagnetic state of a volume of space, so that a finite number of quantities cannot be considered as sufficient for the complete determination of the electromagnetic state of space. According to Maxwell’s theory, energy is considered to be a continuous spatial function for all purely electromagnetic phenomena, hence also for light, whereas according to the present view of physicists, the energy of a ponderable body should be represented as a sum over the atoms and electrons. The energy of a ponderable body cannot be broken up into arbitrarily many, arbitrarily small parts, but according to Maxwell’s theory (or, more generally, according to any wave theory) the energy of a light ray emitted by a point source continuously spreads out over an ever-increasing volume.*

This was a brazen challenge to a debate that had been thought settled for a century. In the days of Newton, Hooke, and Huygens, the question of *what light is* stirred controversy. The battle was carried under the flags of “particles” and “waves.” They form orthogonal mental pictures, extrapolated from our experience with

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projectiles and surf, for the propagation of energy and information. Hooke and Huygens argued for light as waves, citing thin-film interference and light's enormous speed. Newton argued for light as particles, pleading the lack of convincing diffraction.[5]

With the optical interference experiments of Thomas Young in 1800 and diffraction theory and experiments of Augustin Fresnel over the two following decades, light was clearly shown to be a wave. The smallness of its wavelength explained why we do not casually observe optical diffraction in everyday life. The measurement of the speed of light in water by Foucalt in 1850 also ruled out the particle interpretation.

But what was waving? Maxwell's theory of electromagnetism, published in a series of papers in 1861-64, showed that waves in the electromagnetic field move at the speed of light. Maxwell's equations also predict optical phenomena such as Snell's law, the law of reflection, dispersion, and polarization. The question of what light IS seemed settled in favor of a *wave in the electromagnetic field.*

So in 1905 along comes this 26-year-old physicist, fresh out of graduate school and working in the Swiss patent office, one Albert Einstein, daring to resurrect the light-as-particle concept again. He acknowledged the obvious success of wave optics:

> *The wave theory of light, which operates with continuous spatial functions, has proved itself superbly in describing purely optical phenomena and will probably never be replaced by another theory.*

But Einstein pointed out in the same paragraph a loophole in the "light as wave" doctrine:

> *One should keep in mind, however, that optical observations refer to time averages rather than instantaneous values; and it is quite conceivable, despite the complete confirmation of the theory of diffraction, reflection, refraction, dispersion, etc., by experiment, that the theory of light, operating with continuous spatial functions, leads to contradictions when applied to the phenomena of emission and transformation of light.*

A wave model of light works fine for understanding pure electromagnetic radiation. In classical antenna theory a macroscopic alternating current produces radiation fields that are, for all practical purposes, described by continuous functions. But when the "antenna" consists of a single molecule or lone electron, Planck's quantum might have the dominant influence. Einstein's argument was supported by the fact that situations already existed where the *interaction of light with matter* could *not* be completely understood in terms of light as a continuum. In a sweet irony of history, in 1887 Heinrich Hertz was testing Maxwell's theory by attempting to produce radio waves artificially in the laboratory. In this he affirmed Maxwell (and the development of radio technology by others soon followed). But in the course of his experiments that confirmed light to be wave-like, he also stumbled across an occurrence that would come to be called the "photoelectric effect," interpreted by Einstein in 1905, as a collision between electrons and particles of light! Hertz noticed that when certain metals were illuminated with ultraviolet light, some spurious electric currents appeared in his apparatus. He had the presence of mind to recognize this glitch as worth investigating. Several investigators besides Hertz studied the phenomena. Wilhelm Hallwachs, Julius Elster and Hans Geitel, Phillip Lenard, and J. J. Thompson assembled data on the photoelectric effect and its properties.

As students we were introduced to the quantum through Einstein's explanation of this photoelectric effect. But it was merely one *application* whereby he tested his broader concept of light quanta. He wrote,

> *Indeed, it seems to me that the observations of "blackbody radiation," photoluminescence, production of cathode rays by ultraviolet light, and other related phenomena associated with the emission or transformation of light appear more readily understood if one assumes that the energy of light is discontinuously distributed in space. According to the assumption considered here, 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 only as complete units.*
>
> *In this paper I wish to present the train of thought and cite the facts that led me onto this path, in the hope that the approach to be presented will prove of use to some researchers in their investigations.*

Einstein always began with fundamentals. Among the fundamental principles of physics are the First and Second Laws of Thermodynamics. When we first learned about photons we probably did not realize that Einstein's "train of thought" was pulled by entropy!

ENTROPY AND EINSTEIN'S QUANTA

Einstein's derivation contains two parts. In Section 3 of his paper he began,

> *The following treatment is contained in a well-known study by Mr. Wein and is presented here only for the sake of completeness.*

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In essence Einstein recalled the Planck distribution. In thermal equilibrium, the energy density of electromagnetic radiation in the frequency interval f to $f+\Delta f$ is given by[6]

$$U/V = (8\pi h\Delta f/c^3)\, f^3\, (e^{hf/kT} - 1)^{-1} . \tag{1}$$

For brevity here let $A \equiv 8\pi h\Delta f/c^3$. If $hf >> kT$ then

$$U \approx VAf^3\, e^{-hf/kT} \tag{2}$$

so that

$$1/T = -\,(k/hf)\ \ln(U/VA\,f^3) . \tag{3}$$

Set this temporarily aside and recall the combined first and second laws of thermodynamics. A system's internal energy can be changed either by putting heat into the system or by the system doing work, so that for any reversible process

$$dU = TdS - PdV \tag{4}$$

where S denotes the entropy of the system and P its pressure. For a constant volume process Eq. (4) says

$$1/T = dS/dU . \tag{5}$$

Equating the two expressions for $1/T$ from Eqs. (3) and (5) shows that

$$-(k/hf)\ \ln(U/VA\,f^3) = dS/dU , \tag{6}$$

which we integrate:

$$S = -(k/hf) \int \ln(U/VA\,f^3)\, dU . \tag{7}$$

Using the integral $\int \ln x\, dx = x\,(\ln x - 1)$, we find

$$S = -(kU/hf)[\ln(U/VA\,f^3) - 1] + \text{const.} \tag{8}$$

This was known before 1905. But at this point Einstein did something with it that was new:[7]

> *If we restrict ourselves to investigating the dependence of the entropy on the volume occupied by the radiation, and denote the entropy of radiation by* S_o *at volume* V_o *, we obtain*

$$\Delta S = S - S_o = (kU/hf)\ \ln(V/V_o) . \tag{9}$$

> *This equation shows that the entropy of monochromatic radiation of sufficiently low density varies with the volume according to the same law as the entropy of an ideal gas...*

To see what Einstein means, consider an ideal gas. With Einstein we consider the definition of entropy and the combined First and Second Laws of Thermodynamics,

$$\begin{aligned}\Delta S &= \int dQ/T \\ &= \int (dU + PdV)/T .\end{aligned} \tag{10}$$

An ideal gas has the equations of state

$$PV = NkT \tag{11}$$

and

$$U = Nk\, c_V\, T \tag{12}$$

where N denotes the number of gas particles and c_V the heat capacity per molecule evaluated at constant volume. At constant temperature $dU = 0$ and $P = NkT/V$, so that

$$\begin{aligned}\Delta S &= \int NkT\, dV/T \\ &= Nk\ \ln(V_2/V_1) .\end{aligned} \tag{13}$$

Now compare Eqs. (9) and (13): if we treat monochromatic electromagnetic radiation of frequency f as an *ideal gas of particles*, then upon equating these two expressions for entropy change we discover, for the total energy of this gas of N *particles of light* the expression,

$$U = Nhf . \tag{14}$$

Because energy is additive, the energy E of a *single* particle of electromagnetic energy, corresponding to *waves* of frequency f is

$$E = hf . \tag{15}$$

Einstein observed,[8]

> *From this we further conclude that monochromatic radiation of low density...behaves thermodynamically as if it consisted of mutually independent energy quanta of magnitude hf.*

Where one may say there exists a harmonic electromagnetic wave of frequency f and wavelength λ, one may also say that there exists a swarm of free particles, the photons, each with energy $E = hf$.[9] One is tempted to ask, "Well, what is light *really*, particle or wave?" That is not the question. Einstein has shown us something important in the philosophy of science. Science is the art of *creating and testing concepts* in terms of which the physical world becomes comprehensible. "Particles" and "waves" are *models*, conceptual representations of light. Light is *like* waves in some situations, and *like* particles for different situations. David Bohm remarked,

> *We find a strong analogy here to the fable of the seven*

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blind men who ran into an elephant. One man felt the trunk and said that "an elephant is like a rope," another felt the leg and said that "an elephant is obviously a tree," and so on. The question that we have to answer is: Can we find a single concept that will unify our different experiences with light, just as our concept of the elephant unifies the experiences of the seven blind men? [10]

Having created the concept of radiation quanta, Einstein turned to experimental tests. He discussed phenomena in photoluminescence, the ionization of gases by UV light, and "the generation of cathode rays by illumination of solid bodies" that we call the photoelectric effect.

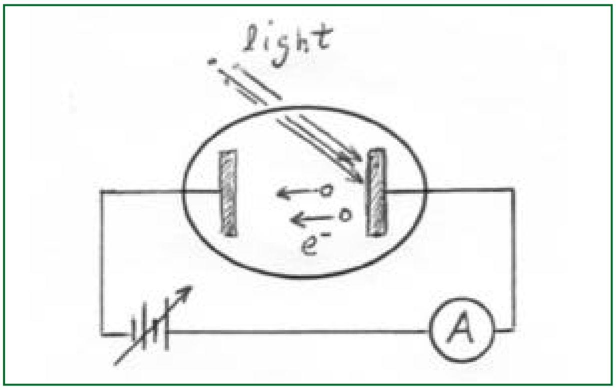

Fig. 1. Apparatus of the photoelectric effect.

QUANTA AND THE PHOTOELECTRIC EFFECT

This photoelectric effect occurs when you hook up a circuit but use light instead of a battery as the energy source. The heart of the apparatus is a "photocell," consisting of a good conductor such as potassium or cesium mounted inside a transparent evacuated tube. Conducting wires, one embedded in the sample, form a cathode and an anode. Light shines on the metallic solid and liberates electrons, or "cathode rays," completing the circuit (see Fig. 1).

In a world with continuous electromagnetic energy the emission of electrons would seem inevitable sooner or later. A bound electron would only have to soak up the light's energy until it saved enough to be set free. Alternatively, the electron might be a little resonator bound to its atom with restoring forces, like a mass held by a spring. A continuous light wave of frequency f would exert a harmonic driving force on the electron. A resonance could occur, and the electron's oscillation could grow so large that the "spring" breaks, liberating the electron. If that mechanism operates then one should see the electron currents occur only for a spectrum of overtones based on a fundamental frequency.

There's only one problem with these soaking and resonance mechanisms. The resonances do not occur, and the soaking model contradicts the facts. To illustrate the issues, let there be two knobs on our light source. With one we tune the light frequency f, with the other we control the light intensity I (average power per unit area). Since some electrons come from the surface while others come from deeper within the metal, we expect a range of electron kinetic energies. For a way to measure the maximum electron kinetic energy $K_{\max}$ we place in the circuit a battery whose polarity *opposes* the electron flow. One increases its opposing voltage from zero (requiring a third knob) until the most energetic electrons are stopped, making the current zero. By conservation of energy, $K_{\max}$ and the stopping voltage V_{stop} are related by

$$K_{\max} = eV_{\text{stop}} \qquad (16)$$

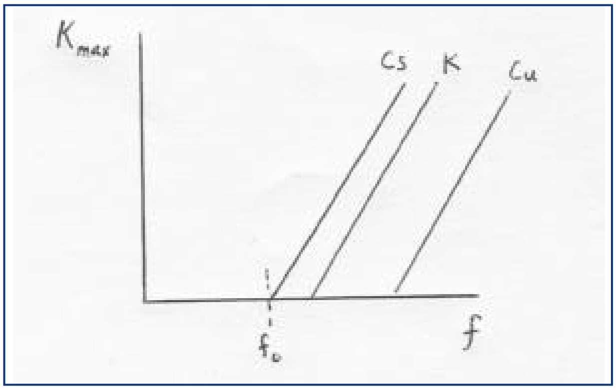

Fig. 2. Photoelectric phenomenology: maximum kinetic energy vs. frequency of the incident radiation.

where e denotes the quantized unit of charge, $e = 1.6\times10^{-19}$ C.

Suppose we crank up the light source intensity very high. It shouldn't take long to liberate those electrons and produce a current! That indeed occurs, but *only* if the frequency lies above a threshold value! If we keep the intensity bright but decrease the frequency, we find a "threshold" frequency f_0 characteristic of each metal. Once the incident radiation frequency drops *below* threshold, the electron current *abruptly* stops, no matter how bright the intensity! For a given metal sample, we can measure $K_{\max}$ as a function of frequency. We find a linear relationship, with the *same slope* for all metals:

When the frequency lies *above* threshold, photoelectrons are emitted astonishingly fast, even if the intensity is so low that it would take two weeks for the electrons to acquire enough energy via the "soaking" model! Furthermore, increasing the incident intensity at fixed frequency does not give *individual* electrons more energy; rather, it merely gives the same energy distribution to *more electrons*. This we know because the stopping

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voltage at fixed frequency is independent of intensity.

In terms of continuous waves, most features of the photoelectric effect make no sense. But the *sudden* emission of electrons under feeble light sounds like a *collision*! That's how Einstein interpreted the photoelectric effect: an electron was knocked from the metal in a collision between one particle of light and the electron. In Section 8, "On the Generation of Cathode Rays by Illumination of Solid Bodies" Einstein explains:

The usual view that the energy of light is continuously distributed over the space through which it travels faces especially great difficulties when one attempts to explain photoelectric phenomena, which are expounded in a pioneering work by Mr. Lenard.[11]

According to the view that the incident light consists of energy quanta of energy hf, the production of cathode rays can be conceived in the following way. The body's surface layer is penetrated by energy quanta whose energy is converted at least partially into kinetic energy of the electrons. The simplest conception is that a light quantum transfers its entire energy to a single electron...

Let the *least*-tightly bound electron be held to the metal with a binding energy of magnitude w (the "work function"); this electron emerges with *maximum* kinetic energy. Apply conservation of energy to the inelastic photon-electron collision. The energy of incoming photon equals the energy received by the electron. The electron spends the amount w of this energy in breaking free of the metal; anything left over sends it forth with kinetic energy K_{max}. Conservation of energy thus gives,

$$hf = w + K_{\mathrm{max}} \,. \tag{17}$$

In terms of the directly observable stopping voltage, the value of kinetic energy can be written

$$eV_{\mathrm{stop}} = hf - w \geqslant 0 \,, \tag{18}$$

which means there can be no emitted electrons when f equals or drops below the threshold frequency $f_{\mathrm{o}} = w/h$. The collision model thereby explains the threshold. In our notation for the stopping potential, Einstein said

If this formula derived is correct, then V_{stop} when plotted in Cartesian coordinates as a function of the frequency of the incident light, must give a straight line whose slope is independent of the nature of the substance under study.

As far as I can tell, this conception of the photoelectric effect does not contradict its properties as observed by Mr. Lenard. If each energy quantum of the incident light transmits its energy to the electrons, independently of all others, then the velocity distribution of the electrons, i.e.., the nature of cathode rays produced, will be independent of the intensity of the incident light; on the other hand, under otherwise identical circumstances, the number of electrons leaving the body will be proportional to the intensity of the incident light.[12]

The photoelectric effect data (available in Einstein's time, and repeated by every generation of physics students since), shows that a plot of eV_{stop} vs. f has a slope, within experimental error, equal to Planck's constant! That the same number h would emerge as just that needed to explain the Planck distribution *and* the photoelectric effect (and Einstein's other applications) could hardly be a fluke; h, the quantum of action was fundamental. From the moment of the publication of Einstein's paper, everyone had to take the quantum seriously. For this paper Einstein was recognized in 1921 with the Nobel Prize.

REFERENCES

[1] Albert Einstein, "On a Heuristic Point of View Concerning the Production and Transformation of Light," *Annalen der Physik* 17 (1905), 132–148.

[2] For annotated translations of Einstein's 1905 papers see John Stachel, *Einstein's Miraculous Year: Five Papers That Changed the Face of Physics* (Princeton Univ. Press, 1998).

[3] Max Planck, "Ueber das Gesetz der Energieverteilung im Normalspectrum," *Annalen der Physik* 4 (1901), 553.

[4] Paragraphs in italics are Einstein's quotations from Stachel's translation in Ref. 2.

[5] For a tongue-in-cheek review of the history of "what is light," see "The Book of Lumen," *Radiations*, Fall 2001, pp. 7–10.

[6] In Einstein's paper he used β to denote what today we denote h/k, the ratio of Planck's and Boltzmann's constant.

[7] Einstein considers two different but fixed volumes that contain the same energy U of radiation having frequency f. How can the radiation have the same energy and frequency in different volumes? In terms of *waves* the radiation may have different amplitudes; in terms of *photons* the two volumes contain different numbers of particles.

[8] Einstein used ν for frequency, and said "independent energy quanta of magnitude $R\beta\nu/N$" (see note [6]). The ideal gas constant R is one mole of Boltzmann's constants, $R = N_A k$. I have modified Einstein's quotation by substituting modern notation for these constants.

[9] It's instructive to see where the photon concept leads when combined with Einstein's special theory of relativity. Because these particles *are* light, they move at the speed c. The energy and momentum of a free particle of mass m moving with velocity v are $E = mc^2\gamma$ and $\mathrm{p} = m\mathrm{v}\gamma$, respectively, where $\gamma \equiv (1-v^2/c^2)^{-½}$. Transpose the relation between mass and energy into $m = (E/c^2)(1-v^2/c^2)^{½}$. If $v = c$ then $m = 0$ regardless of E. Because $E^2 - (pc)^2 = (mc^2)^2$, for massless particles $E = pc$. For our single photon this becomes $hf = pc$, which by virtue of $c = f\lambda$ (where λ denotes the wavelength) gives $p = h/\lambda$. So much for massless particles. But this inspired Louis de Broglie in 1926 to postulate that, for *any* free particle, even massive particles, one could invoke wave-particle duality through $E = hf$ and $p = h/\lambda$, founding quantum mechanics as it's usually introduced.

[10] David Bohm, *Quantum Theory* (Prentice-Hall, 1951), p. 26.

[11] P. Lenard, *Annalen der Physik* 8 (1902), 169–170 (Einstein's reference to Lenard).

[12] P. Lenard, *Annalen der Physik* 8 (1902), 166–168 (Einstein's reference).