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978-1-107-02872-2 - Lectures on Quantum Mechanics
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Historical Introduction

The principles of quantum mechanics are so contrary to ordinary intuition that they can best be motivated by taking a look at their prehistory. In this chapter we will consider the problems confronted by physicists in the first years of the twentieth century that ultimately led to modern quantum mechanics.

1.1 Photons

Physicists in the last decades of the nineteenth century were greatly concerned to understand the nature of black-body radiation — radiation that had come into thermal equilibrium with matter at a given temperature T. The energy $\rho(\nu, T)d\nu$ per volume at frequencies between ν and $\nu + d\nu$ had been measured, chiefly at the Imperial Physical-Technical Institution in Berlin, and it was known on thermodynamic grounds that $\rho(\nu, T)$ is a universal function of frequency and temperature, but how could one calculate this function?

A simple calculation was given in 1900 by John William Strutt (1842–1919), more usually known as Lord Rayleigh.[1] It was familiar that one can think of the radiation field in a box as a Fourier sum over normal modes. For instance, for a cubical box of width L, whatever boundary condition is satisfied on one face of the box must be satisfied on the opposite face, so the phase of the radiation field must change by an integer multiple of 2π in a distance L. That is, the radiation field is the sum of terms proportional to $\exp(i\mathbf{q}\cdot\mathbf{x})$, with

$$\mathbf{q} = 2\pi\mathbf{n}/L\ , \tag{1.1.1}$$

where the vector $\mathbf{n}$ has integer components. (For instance, to maintain translational invariance, it is convenient to impose periodic boundary conditions: each component of the electromagnetic field is assumed to be the same on opposite faces of the box.) Each normal mode is thus characterized by a triplet of integers n_1, n_2, n_3 and a polarization state, which can be taken as either left- or

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[1] J. W. Strutt, Verh. d. deutsch. phys. Ges. **2**, 65 (1900).

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right-circular polarization. The wavelength of a normal mode is $\lambda = 2\pi/|\mathbf{q}|$, so its frequency is given by

$$\nu = \frac{c}{\lambda} = \frac{|\mathbf{q}|c}{2\pi} = \frac{|\mathbf{n}|c}{L} . \tag{1.1.2}$$

Each normal mode occupies a cell of unit volume in the space of the vectors **n**, so the number of normal modes $N(\nu)d\nu$ in the range of frequencies between ν and $\nu + d\nu$ is twice the volume of the corresponding shell in this space:

$$N(\nu)d\nu = 2 \times 4\pi |\mathbf{n}|^2 \, d|\mathbf{n}| = 8\pi (L/c)^3 \nu^2 d\nu , \tag{1.1.3}$$

the extra factor of 2 taking account of the two possible polarizations for each wave number. Rayleigh noted that in classical statistical mechanics, in any system that can be regarded as a collection of harmonic oscillators, the mean energy of each oscillator $\bar{E}(T)$ is simply proportional to the temperature, a relation written as $\bar{E}(T) = k_{\mathcal{B}}T$, where $k_{\mathcal{B}}$ is a fundamental constant, known as Boltzmann's constant. (The derivation is given below.) If this applied to radiation, the energy density in the radiation between frequencies ν and $\nu + d\nu$ would then be given by what has come to be called the Rayleigh–Jeans formula

$$\rho(\nu, T)d\nu = \frac{\bar{E}(T)\, N(\nu)\, d\nu}{L^3} = \frac{8\pi k_{\mathcal{B}} T \nu^2 \, d\nu}{c^3} . \tag{1.1.4}$$

(A numerical error in Rayleigh's derivation was corrected in 1905 by James Jeans (1877–1946).) The prediction that $\rho(\nu, T)$ is proportional to $T\nu^2$ was actually in agreement with observation for small values of ν/T, but failed badly for larger values. Indeed, if it held for all frequencies at a given temperature, then the total energy density $\int \rho(\nu, T)\, d\nu$ would be infinite. This became known as the *ultraviolet catastrophe*.

The correct result was published a little later by Max Planck (1858–1947), in the same volume of the proceedings of the German Physical Society.[2] Planck noted that the data on black-body radiation could be fit with the formula

$$\rho(\nu, T)\, d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 \, d\nu}{\exp(h\nu/k_{\mathcal{B}}T) - 1} , \tag{1.1.5}$$

where h was a new constant, known ever after as *Planck's constant*. Comparison with observation gave $k_{\mathcal{B}} \approx 1.4 \times 10^{-16}$ erg/K and[3] $h \approx 6.6 \times 10^{-27}$ erg sec. This formula was just guesswork, but a little later Planck gave a derivation of the formula[4], based on the assumption that the radiation was the same as if it were in equilibrium with a large number of charged oscillators with different

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[2] M. Planck, Verh. d. deutsch. phys. Ges. **2**, 202 (1900).

[3] The modern value is $6.62606891(9) \times 10^{-27}$ erg sec; see E. R. Williams, R. L. Steiner, D. B. Newell, P. T. Olson, Phys. Rev. Lett. **81**, 2404 (1998).

[4] M. Planck, Verh. d. deutsch. phys. Ges. **2**, 237 (1900).

frequencies, the energy of any oscillator of frequency ν being an integer multiple of $h\nu$. Planck's derivation is lengthy and not worth repeating here, since its basis is very different from what soon replaced it.

Planck's formula agrees with the Rayleigh–Jeans formula (1.1.4) for $\nu/T \ll k_{\mathcal{B}}/h$, but it gives an energy density that falls off exponentially for $\nu/T \gg k_{\mathcal{B}}/h$, yielding a finite total energy density

$$\int_0^\infty \rho(\nu, T)\, d\nu = a_{\mathcal{B}} T^4 \,., \qquad a_{\mathcal{B}} \equiv \frac{8\pi^5 k_{\mathcal{B}}^4}{15 h^3 c^3}\,. \tag{1.1.6}$$

(Using modern values of constants, this gives $a_{\mathcal{B}} = 7.56577(5) \times 10^{-15}$ erg cm$^{-3}K^{-4}$.) Perhaps the most important immediate consequence of Planck's work was to provide long-sought values for atomic constants. The theory of ideal gases gives the well-known law $pV = nRT$, where p is the pressure of a volume V of n moles of gas at temperature T, with the constant R given by $R = k_{\mathcal{B}} N_{\mathcal{A}}$, where $N_{\mathcal{A}}$ is Avogadro's number, the number of molecules in one mole of gas. Measurements of gas properties had long given values for R, so with $k_{\mathcal{B}}$ known it was possible for Planck to infer a value for $N_{\mathcal{A}}$, the reciprocal of the mass of a hypothetical atom with unit atomic weight (close to the mass of a hydrogen atom). This was in good agreement with estimates of $N_{\mathcal{A}}$ from properties of non-ideal gases that depend on number density and not just mass density, such as viscosity. Knowing the mass of individual atoms, and assuming that atoms in solids are closely packed so that the mass to volume ratio of an atom is similar to the measured density of macroscopic solid samples of that element, one could estimate the sizes of atoms. Similarly, measurements of the amount of various elements produced by electrolysis had given a value for the Faraday, $F = eN_{\mathcal{A}}$, where e is the electric charge transferred in producing one atom of unit valence, so with $N_{\mathcal{A}}$ known, e could be calculated. It could be assumed that e is the charge of the electron, which had been discovered in 1897 by Joseph John Thomson (1856–1940), so this amounted to a measurement of the charge of the electron, a measurement much more precise than any direct measurement that could be carried out at the time. Thomson had measured the ratio of e to the mass of the electron, by observing the bending of cathode rays in electric and magnetic fields, so this also gave a value for the electron mass. It is ironic that all this could have been done by Rayleigh before the advent of the Planck black-body formula, by comparing measured values of $\rho(\nu, T)$ with the Rayleigh–Jeans formula (1.1.4) at small values of ν/T, where the formula works, and using the result to find $k_{\mathcal{B}}$ — for this, h is not needed.

Planck's quantization assumption applied to the matter that emits and absorbs radiation, not to radiation itself. As George Gamow later remarked, Planck thought that radiation was like butter; butter itself comes in any quantity, but it can be bought and sold only in multiples of one quarter pound. It was Albert Einstein (1879–1955) who in 1905 proposed that the energy of radiation of frequency ν was itself an integer multiple of $h\nu$.[5] He used this to predict that in the photoelectric effect no electrons are emitted when light shines on a metal surface unless the frequency of the light exceeds a minimum value $\nu_{\rm min}$, where $h\nu_{\rm min}$ is the energy required to remove a single electron from the metal (the "work function"). The electrons then have energy $h(\nu - \nu_{\rm min})$. Experiments[6] by Robert Millikan (1868–1953) in 1914–1916 verified this formula, and gave a value for h in agreement with that derived from black-body radiation.

The connection between Einstein's hypothesis and the Planck black-body formula is best explained in a derivation of the black-body formula by Hendrik Lorentz (1853–1928) in 1910.[7] Lorentz made use of the fundamental result of statistical mechanics due to J. Willard Gibbs (1839–1903),[8] that in a system containing a large number of identical systems in thermal equilibrium at a given temperature (like light quanta of the same frequency in a black-body cavity), the probability that one of these systems has an energy E is proportional to $\exp(-E/k_{\mathcal{B}}T)$. If the energies of light quanta were continuously distributed, this would give a mean energy

$$\bar{E} = \frac{\int_0^\infty \exp(-E/k_{\mathcal{B}}T)\, E\, dE}{\int_0^\infty \exp(-E/k_{\mathcal{B}}T)\, dE} = k_{\mathcal{B}}T \ ,$$

the assumption used in deriving the Rayleigh–Jeans formula (1.1.4). But if the energies are instead integer multiples of $h\nu$, then the mean energy is

$$\bar{E} = \frac{\sum_{n=0}^\infty \exp(-nh\nu/k_{\mathcal{B}}T)\, nh\nu}{\sum_{n=0}^\infty \exp(-nh\nu/k_{\mathcal{B}}T)} = \frac{h\nu}{\exp(h\nu/k_{\mathcal{B}}T) - 1} \ . \tag{1.1.7}$$

The energy density in radiation between frequencies ν and $\nu + d\nu$ is again given by $\rho\, d\nu = \bar{E} N d\nu / L^3$, which now with Eqs. (1.1.3) and (1.1.7) yields the Planck formula (1.1.5).

Even after Millikan's experiments had verified Einstein's prediction for the energies of photoelectrons, there remained considerable skepticism about the reality of light quanta. This was largely dispelled by experiments on the scattering of X-rays by Arthur Compton (1892–1962) in 1922–23.[9] The energy of X-rays is sufficiently high so that it is possible to ignore the much smaller binding energy of the electron in a light atom, treating the electron as a free particle. Special relativity says that if a quantum of light has energy $E = h\nu$, then it has momentum $p = h\nu/c$, in order to have $m_\gamma^2 c^4 = E^2 - p^2c^2 = 0$. If, for instance, a light quantum is scattered backwards, then the scattered quantum has

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[5] A. Einstein, Ann. d. Physik **17**, 132 (1905).

[6] R. A. Millikan, Phys. Rev. **7**, 355 (1916).

[7] H. A. Lorentz, Phys. Z. **11m** 1234 (1910).

[8] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (New York, 1902).

[9] A. H. Compton, Phys. Rev. **21**, 207 (1923).

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978-1-107-02872-2 - Lectures on Quantum Mechanics
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frequency ν' and the electron scattered forward has momentum $h\nu/c + h\nu'/c$, where ν' is given by the energy conservation condition:

$$h\nu + m_e c^2 = h\nu' + \sqrt{m_e^2 c^4 + (h\nu/c + h\nu'/c)^2 c^2},$$

(where m_e is the electron mass), so

$$\nu' = \frac{\nu\, m_e c^2}{(2h\nu + m_e c^2)} \; .$$

This is conventionally written as a formula relating the wavelengths $\lambda = c/\nu$ and $\lambda' = c/\nu'$:

$$\lambda' = \lambda + 2h/m_e c \; . \tag{1.1.8}$$

The length $h/m_e c = 2.425 \times 10^{-10}$ cm is known as the Compton wavelength of the electron. (For scattering at an angle θ, the factor 2 in Eq. (1.1.8) is replaced with $1 - \cos\theta$.) Verification of such relations convinced physicists of the existence of these quanta. A little later the chemist G. N. Lewis[10] gave the quantum of light the name by which it has been known ever since, the *photon*.

1.2 Atomic Spectra

Another problem confronted physicists throughout the nineteenth and early twentieth centuries. It had been discovered early in the nineteenth century that hot atomic gases emit and absorb light only at certain definite frequencies, the pattern of frequencies, or spectrum, depending on the element in question. This became a useful tool for chemical analysis, and for the discovery of new elements, such as helium, discovered in the spectrum of the Sun. But like writing in a forgotten language, these atomic spectra provided no intelligible message.

No progress could be made in understanding atomic spectra without knowing something about the structure of atoms. After Thomson's discovery of the electron in 1897, it was widely believed that atoms were like puddings, with negatively charged electrons stuck in like raisins in a smooth background of positive charge. This picture was radically changed by experiments carried out in the laboratory of Ernest Rutherford (1871–1937) at the University of Manchester in 1909–1911. In these experiments a post-doc, Hans Geiger (1882-1945) and an undergraduate Ernest Marsden (1889–1970) let a collimated beam of alpha particles (He^4 nuclei) from a radium source strike a thin gold foil. The alpha particles passing through the foil were detected by flashes of light when they struck a sheet of zinc sulphide. As expected, the beam was found to be slightly spread out by scattering of alpha particles by the gold atoms. Then for some

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[10] G. N. Lewis, Nature, December 18, 1926.

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reason Rutherford had the idea of asking Geiger and Marsden to check whether any alpha particles were scattered at large angles. This would not be expected if the alpha particle hit a much lighter particle like the electron. If a particle of mass M with velocity v hits a particle of mass m that is at rest, and continues along the same line with velocity v', giving the target particle a velocity u, the equations of momentum and energy conservation give

$$Mv = mu + Mv', \quad \frac{1}{2}Mv^2 = \frac{1}{2}Mv'^2 + \frac{1}{2}mu^2 \,. \tag{1.2.1}$$

(In the notation used here, a positive velocity is in the same direction as the original velocity of the alpha particle, while a negative velocity is in the opposite direction.) Eliminating u, we obtain a quadratic equation for v'/v:

$$0 = (1 + M/m)(v'/v)^2 - 2(M/m)(v'/v) - 1 + M/m \,.$$

This has two solutions. One solution is $v' = v$. This solution is one for which nothing happens — the incident particle just continues with the velocity it had at the beginning. The interesting solution is the other one:

$$v' = -v\left(\frac{m - M}{m + M}\right). \tag{1.2.2}$$

But this has a negative value (that is, a recoil backwards) only if $m > M$. (Somewhat weaker limits on m can be inferred from scattering at any large angle.)

Nevertheless, alpha particles were observed to be scattered at large angles. As Rutherford later explained, “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper, and it came back and hit you.”[1]

So the alpha particle must have been hitting something in the gold atom much heavier than an electron, whose mass is only about 1/7300 the mass of an alpha particle. Furthermore, the target particle must be quite small to stop the alpha particle by the Coulomb repulsion of positive charges. If the charge of the target particle is $+Ze$, then in order to stop the alpha particle with charge $+2e$ at a distance r from the target particle, the kinetic energy $Mv^2/2$ must be converted into a potential energy $(2e)(Ze)/r$, so $r = 4Ze^2/Mv^2$. The velocity of the alpha particles emitted from radium is 2.09×10^9 cm/sec, so the distance at which they would be stopped by a heavy target particle was $3Z \times 10^{-14}$ cm, which for any reasonable Z (even $Z \approx 100$) is much smaller than the size of the gold atom, a few times 10^{-8} cm.

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[1] Quoted by E. N. da Costa Andrade, *Rutherford and the Nature of the Atom* (Doubleday, Garden City, NY, 1964).

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Rutherford concluded[2] then that the positive charge of the atom is concentrated in a small heavy nucleus, around which the much lighter negatively charged electrons circulate in orbits, like planets around the Sun. But this only heightened the mystery surrounding atomic spectra. A charged particle like the electron circulating in orbit would be expected to radiate light, with the same frequency as the orbital motion. The frequencies of these orbital motions could be anything. Worse, as the electron lost energy to radiation it would spiral down into the atomic nucleus. How could atoms remain stable?

In 1913 an answer was offered by a young visitor to Rutherford's Manchester laboratory, Niels Bohr (1885–1962). Bohr proposed in the first place that the energies of atoms are quantized, in the sense that the atom exists in only a discrete set of states, with energies (in increasing order) $E_1,\ E_2,\ \dots$. The frequency of a photon emitted in a transition $m \to n$ or absorbed in a transition $n \to m$ is given by Einstein's formula $E = h\nu$ and energy conservation by

$$\nu = (E_m - E_n)/h\ . \tag{1.2.3}$$

A bright or dark spectral line is formed by atoms emitting or absorbing photons in a transition from a higher to a lower energy state, or vice versa. This explained a rule, known as the Ritz combination principle, that had been noticed experimentally by Walther Ritz (1878–1909) in 1908,[3] (but without explaining it), that the spectrum of any atom could be described more compactly by a set of so-called "terms," the frequencies of the spectrum being all given by differences of the terms. These terms, according to Bohr, were just the energies E_n, divided by h.

Bohr also offered a method for calculating the energies E_n, at least for electrons in a Coulomb field, as in hydrogen, singly ionized helium, etc. Bohr noted that Planck's constant h has the same dimensions as angular momentum, and he guessed that the angular momentum $m_e v r$ of an electron of velocity v in a circular atomic orbit of radius r is an integer multiple of some constant $\hbar$,[4] presumably of the same order of magnitude as h:

$$m_e v r = n\hbar\ , \quad n = 1,\ 2,\ \dots\ . \tag{1.2.4}$$

(Bohr did not use the symbol $\hbar$. Readers who know how $\hbar$ is related to h should temporarily forget that information; for the present $\hbar$ is just another constant.) Bohr combined this with the equation for the equilibrium of the orbit

$$\frac{m_e v^2}{r} = \frac{Ze^2}{r^2} \tag{1.2.5}$$

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[2] E. Rutherford, Phil. Mag. **21**, 669 (1911).

[3] W. Ritz, Phys. Z. **9**, 521 (1908).

[4] N. Bohr, Phil. Mag. **26**, 1, 476, 857 (1913); Nature **92**, 231 (1913).

and the formula for the electron's energy

$$E = \frac{m_e v^2}{2} - \frac{Ze^2}{r} . \tag{1.2.6}$$

This gives

$$v = \frac{Ze^2}{n\hbar} , \quad r = \frac{n^2\hbar^2}{Zm_e e^2} , \quad E = -\frac{Z^2 e^4 m_e}{2n^2\hbar^2} . \tag{1.2.7}$$

Using the Einstein relation between energy and frequency, the frequency of a photon emitted in a transition between an orbit with quantum number n to one with quantum number $n' < n$ is

$$\nu = \frac{\Delta E}{h} = \frac{Z^2 e^4 m_e}{2h\hbar^2}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \tag{1.2.8}$$

To find $\hbar$, Bohr relied on a *correspondence principle*, that the results of classical physics should apply for large orbits — that is, for large n. If $n \gg 1$ and $n' = n - 1$, Eq. (1.2.8) gives $\nu = Z^2 e^4 m_e / h\hbar^2 n^3$. This may be compared with the frequency of the electron in its orbit, $v/2\pi r = Z^2 e^4 m_e / 2\pi n^3 \hbar^3$. According to classical electrodynamics these two frequencies should be equal, so Bohr could conclude that $\hbar = h/2\pi$. Using the value of h obtained by matching observations of black-body radiation with Planck's formula, Bohr was able to derive numerical values for velocity, radial coordinate, and energy of the electron:

$$v = \frac{Ze^2}{n\hbar} \simeq \frac{Zc}{137n} , \tag{1.2.9}$$

$$r = \frac{n^2\hbar^2}{Zm_e e^2} \simeq n^2 \times 0.529\, Z^{-1} \times 10^{-8}\ \text{cm} , \tag{1.2.10}$$

$$E = -\frac{Z^2 e^4 m_e}{2n^2\hbar^2} \simeq -\frac{13.6\, Z^2\ \text{eV}}{n^2} . \tag{1.2.11}$$

The striking agreement of Eq. (1.2.11) with the atomic energy levels of hydrogen inferred from the frequencies of spectral lines was a strong indication that Bohr was on the right track.

In this derivation Bohr had relied on the old idea of classical radiation theory, that the frequencies of spectral lines should agree with the frequency of the electron's orbital motion, but he had assumed this only for the largest orbits, with large n. The light frequencies he calculated for transitions between lower states, such as $n = 2 \to n = 1$, did not at all agree with the orbital frequency of the initial or final state. So Bohr's work represented another large step away from classical physics.

Bohr's formulas could be used not only for hydrogen ($Z = 1$), but also roughly for the innermost orbits in heavier atoms, where the charge of the

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nucleus is not screened by electrons, and we can take Ze as the actual charge of the nucleus. For $Z \geq 10$, the energy of a photon emitted in a transition from $n = 2$ to $n = 1$ orbits is greater than 1 keV, and hence is in the X-ray spectrum. By measuring these X-ray energies, H. G. J. Moseley (1887–1915) was able to find Z for a range of atoms from calcium to zinc. He discovered that, within experimental uncertainty, Z is an integer, suggesting that the positive charge of atomic nuclei is carried by particles of charge $+e$, much heavier than the electron, to which Rutherford gave the name *protons*. Also, with just a few exceptions, Z increased by one unit in going from any element to the element with the next largest atomic weight A (roughly, the mass of the atom in units of the hydrogen atom mass). But Z turned out to be not equal to A. For instance, zinc has $A = 60.37$, and it turned out to have $Z = 20.00$. For some years it was thought that the atomic weight was equal to the number of protons, with the extra charge canceled by $A - Z$ electrons. The discovery of the neutron by James Chadwick (1891–1974) in 1932,[5] found to have a mass close to that of the hydrogen atom, showed that instead nuclei contain Z protons and approximately $A - Z$ neutrons.

Incidentally, Eqs. (1.2.9)–(1.2.11) also hold roughly for electrons in the outermost orbits in heavy atoms, where most of the charge of the nucleus is screened by inner electrons, and Z can therefore be taken to be of order unity. This is why the sizes of heavy atoms are not very much larger than those of light atoms, and the frequency of light emitted in transitions of electrons in the outer orbits of heavy atoms is comparable to the corresponding energies in hydrogen, and hence in the visible range of the spectrum.

The Bohr theory applied only to circular orbits, but just as in the solar system, the generic orbit of a particle in a Coulomb field is not a circle, but an ellipse. A generalization of the Bohr quantization condition (1.2.4) was proposed by Arnold Sommerfeld (1868–1951) in 1916,[6] and used by him to calculate the energies of electrons in elliptical orbits. Sommerfeld's condition was that in a system described by a Hamiltonian $H(q, p)$, with several coordinates q_a and canonical conjugates p_a satisfying the equations $\dot{q}_a = \partial H/\partial p_a$ and $\dot{p}_a = -\partial H/\partial q_a$, if all qs and ps have a periodic time-dependence (as for closed orbits), then for each a

$$\oint p_a \, dq_a = n_a h \; , \tag{1.2.12}$$

(with n_a an integer), the integral taken over one period of the motion. For instance, for an electron in a circular orbit we can take q as the angle traced out by the line connecting the nucleus and the electron, and p as the angular momentum $m_e v r$, in which case $\oint p \, dq = 2\pi m_e v r$, and (1.2.12) is the same as

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[5] J. Chadwick, Nature, February 27, 1932).

[6] A. Sommerfeld, Ann. d. Physik **51**, 1(1916)

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Bohr's condition (1.2.4). We will not pursue this approach here, because it was soon made obsolete by the advent of wave mechanics.

In 1916 (in his spare time while discovering the general theory of relativity), Einstein returned to the theory of black-body radiation,[7] this time combining it with the Bohr idea of quantized atomic energy states. Einstein defined a quantity A_m^n as the rate at which an atom will spontaneously make a transition from a state m to a state n of lower energy, emitting a photon of energy $E_m - E_n$. He also considered the absorption of photons from radiation (not necessarily black-body radiation) with an energy density $\rho(\nu)d\nu$ at frequencies between ν and $\nu + d\nu$. The rate at which an individual atom in such a field makes a transition from a state n to a state m of higher energy is written as $B_n^m \rho(\nu_{nm})$, where $\nu_{nm} \equiv (E_m - E_n)/h$ is the frequency of the absorbed photon. Einstein also took into account the possibility that the radiation would stimulate the emission of photons by the atom in transitions from a state m to a state n of lower energy, at a rate written as $B_m^n \rho(\nu_{nm})$. The coefficients B_n^m and B_m^n like A_m^n are assumed to depend only on the properties of the atoms, not the radiation.

Now, suppose the radiation is black-body radiation at a temperature T, with which the atoms are in equilibrium. The energy density of the radiation will be the function $\rho(\nu, T)$, given by Eq. (1.1.5). In equilibrium the rate at which atoms make a transition $m \to n$ from higher to lower energy must equal the rate at which atoms make the reverse transition $n \to m$:

$$N_m \left[A_m^n + B_m^n \rho(\nu_{nm}, T)\right] = N_n \, B_n^m \rho(\nu_{nm}, T) \ , \tag{1.2.13}$$

where N_n and N_m are the numbers of atoms in states n and m. According to the Boltzmann rule of classical statistical mechanics, the number of atoms in a state of energy E is proportional to $\exp(-E/k_{\mathcal{B}}T)$, so

$$N_m/N_n = \exp\left(-(E_m - E_n)/k_{\mathcal{B}}T\right) = \exp\left(-h\nu_{nm}/k_{\mathcal{B}}T\right) . \tag{1.2.14}$$

(It is important here to take the N_n as the numbers of atoms in individual states n, some of which may have precisely the same energy, rather than the numbers of atoms with energies E_n.) Putting this together, we have

$$A_m^n = \frac{8\pi h}{c^3} \frac{\nu_{nm}^3}{\exp(h\nu_{nm}/k_{\mathcal{B}}T) - 1} \Big(\exp(h\nu_{nm}/k_{\mathcal{B}}T) \, B_n^m - B_m^n \Big). \tag{1.2.15}$$

For this to be possible at all temperatures for temperature-independent A and B coefficients, these coefficients must be related by

$$B_m^n = B_n^m \ , \qquad A_m^n = \left(\frac{8\pi h \nu_{nm}^3}{c^3}\right) B_m^n \ . \tag{1.2.16}$$

Hence, knowing the rate at which a classical light wave of a given energy density is absorbed or stimulates emission by an atom, we can calculate the rate

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[7] A. Einstein, Phys. Z. **18**, 121 (1917).