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An Atomistic Interpretation of Planck's 1900 Derivation of His Radiation Law

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Abstract

In deriving his radiation law in 1900, Max Planck employed a simple harmonic oscillator to model the exchange of energy between radiation and matter. Traditionally the harmonic oscillator has been viewed as modelling an entity which is itself oscillating, although a suitable oscillating entity has not been forthcoming. (Opinion is divided between a material oscillator, an imaginary oscillator and a need to revise Planck's derivation to apply to cavity modes of oscillation). We offer a novel, atomistic interpretation of Planck's derivation wherein the harmonic oscillator models a transition between the internal quantum states of an atom—not a normal electronic atom characterised by possible energies 0 and $h\nu$, but an atom populated by subatomic bosons (such as pions) and characterised by multiple occupancy of quantum states and possible energies $nh\nu$ ($n = 0, 1, 2, \dots$). We show how Planck's derivation can be varied to accommodate electronic atoms. A corollary to the atomistic interpretation is that Planck's derivation can no longer be construed as support for the postulate that material oscillating entities can have only those energies that are multiples of $h\nu$.

1. Introduction

Planck's 1900 derivation of his radiation law (representing the birth of quantum physics) will be familiar to most readers and needs little introduction (e.g. Jammer 1989). Curiously, a century after its publication, Planck's derivation (described here in Section 2) still presents something of a mystery. In deriving his radiation law, Planck considered the exchange of energy between radiation and a classical or simple harmonic oscillator, but the identity of the entity modelled by the classical oscillator has not been satisfactorily resolved. This does not pose a problem as far as the actual derivation of Planck's law is concerned, but it does pose a problem in that the entity modelled by the classical oscillator is the recipient of Planck's quantisation (energies $nh\nu$, where $n = 0, 1, 2, \dots$) and unless that entity can be invested with a physical identity, then Planck's quantisation is of little more than academic interest. The traditional or *oscillator interpretation* (reviewed in Section 3) is that the entity modelled by the classical oscillator is one which is itself oscillating. Whilst opinion has generally favoured a material oscillator, no suitable entity has been forthcoming. One suggestion has been that Planck's oscillator should be viewed as an imaginary entity. Another suggestion (Debye 1910) has been that the exchange of energy between radiation and

matter is incidental and that Planck's derivation should be revised such that his quantisation is associated with the oscillations of the electromagnetic field itself. Such views, along with other shortcomings of the oscillator interpretation, are discussed in Section 3.

Black-body radiation theory appears to be unique in that the entity modelled by the classical oscillator continues to be sought amongst entities which are themselves oscillating. Elsewhere in atomic spectroscopy the classical oscillator (sometimes called the classical or Lorentz atom) was long ago recognised as modelling an atom exchanging energy with radiation (e.g. Stone 1963; Corney 1977), and it is here proposed that this is how the classical oscillator in Planck's derivation should be interpreted. Specifically we propose (in Section 4) a novel, *atomistic interpretation* of Planck's derivation, wherein the classical oscillator models a transition between the internal quantum states of an atom—not a normal electronic atom characterised by possible energies 0 and $h\nu$, but an atom populated by subatomic bosons (such as pions) and characterised by multiple occupancy of quantum states and possible energies $n h\nu$ ($n = 0, 1, 2, \dots$). The reader whose instinct is to reject such an interpretation as impractical will be interested to see that we also consider the variant of Planck's theory that applies to electronic atoms.

But a derivation (such as Planck's) which mixes classical and quantum ideas is less than convincing anyway, or, to quote Debye (see Hermann 1971, p. 110), is 'illogical'. Not surprisingly it was soon superseded by more quantum-intensive derivations (e.g. Einstein 1917; Bose 1924). In Section 5 we show how to bypass the classical (oscillator) component of Planck's theory and to employ the quantum component in a derivation of Planck's law which involves atoms themselves (rather than the oscillator model of an atom). Thus we offer what may be seen as a revision of Planck's theory, and a revision which competes with Debye's revision of 1910, one difference being that our revision is true to Planck's original intention (the exchange of energy between radiation and matter). In Section 6 we consider a corollary to the atomistic interpretation, namely that Planck's theory can no longer be construed as support for the postulate that material oscillating entities can have only those energies which are multiples of $h\nu$.

Throughout this paper we will refer to the quantisation that emerged from Planck's derivation as 'Planck's quantisation', even though (as discussed by Kuhn 1978, 1983) Planck may not have appreciated its significance in 1900. Throughout the paper we will use a parameter α defined by

$$\alpha = \frac{h\nu}{kT},$$

and we will refer to the limit $\alpha \gg 1$ (i.e. the limit where Planck's radiation law reduces to Wien's law) as the 'Wien limit'.

2. Planck's Derivation

For an account of Planck's derivation, apart from Planck's original papers (Planck 1900*b*, 1900*c*, 1901, 1972), see Whittaker (1953), Kangro (1976), Klein (1977), Kuhn (1978), Mehra and Rechenberg (1982) and Jammer (1989). For an abbreviated account, see Allen and Maxwell (1952), ter Haar (1967), Kangro

(1975) and Pais (1982). The following summary suffices for our present needs.

(2a) *The Classical Oscillator*

Planck's derivation falls into two parts, which we will treat in turn. The first part deals with the classical oscillator, whilst the second part (Section 2b) deals with the procedure that led to the notion of quantisation. A novel variation of the second part is described (Section 2c) for reference later in the paper.

In the late 19th century, as a consequence of the experiments of H. Hertz, the analysis of H. A. Lorentz, and the growing acceptance of Maxwell's electromagnetic theory, the emission and absorption of light was increasingly associated with an accelerating electric charge (or current), including an electric charge executing simple harmonic motion, known as a classical oscillator (for an interesting account of this period of history, see Stehle 1994). When the electromagnetic view of nature gave way to the quantum view in the early 20th century, the classical oscillator remained in use as a model of an atom because it has a number of properties in common with an atom, such as line broadening, absorption and anomalous dispersion (e.g. Jefferies 1968; Siegman 1971; Corney 1977). Planck employed the classical oscillator in studies associated with the second law of thermodynamics in the mid 1890s, as well as in the derivation of the spectral distribution of black-body radiation during the late 1890s.

The equation of motion for a charged particle subject to an elastic restoring force and to the electric field of an incoming wave is well known [equation (29) in Appendix A]. A tractable expression for the power absorbed from a radiation field by such a bound particle is obtained once the phases of the various incoming waves are assumed random, namely (see Appendix A)

$$\xi_a = \frac{\pi e^2}{3m} \rho^{\text{RP}}(\nu). \quad (1)$$

Here we have included the superscript RP as a reminder that this result is dependent on the assumption of random phases, or, in Planck's terminology, is dependent on the assumption of 'natural' or 'disordered' radiation (see Kangro 1976, p. 136). A different assumption about phases would lead to a different result. Random phases would nowadays be associated with conventional or thermal light sources (Haken 1981; Corney 1977, p. 274) or, in the case of cavity radiation, with the regime $\alpha \gg 1$, where (according to Einstein's analysis of fluctuations) wave effects are minimal and corpuscular behaviour dominates (e.g. ter Haar 1969). Cray *et al.* (1982) have discussed how the equation of motion underpinning equation (1) can be expected to describe an atom interacting with the electric field of an incoming wave when the atom is unlikely to be excited (the limit $\alpha \gg 1$).

For the power emitted by a classical oscillator of energy $U(C)$, we have the well known result (see e.g. Born 1962, p. 253)

$$\xi_e = \left(\frac{8\pi\nu^2}{c^3} \frac{\pi e^2}{3m} \right) U(C).$$

In thermal equilibrium $\xi_e = \xi_a$, and

$$U(C)_1 = \frac{\rho^{\text{RP}}(\nu)}{8\pi\nu^2/c^3}. \quad (2)$$

Here $U(C)_1$ denotes the particular value of $U(C)$ for a classical oscillator whose motion is governed by equation (29) and which is in thermal equilibrium with a radiation field subject to the assumption of random phases. Equation (2) (or similar) was originally derived by Planck (1899; 1900*a*), although in a manner somewhat different to the foregoing.

(2b) Thermodynamics, Statistics and Analogy

Planck saw equation (2) not as a relationship restricted by the assumptions underpinning its derivation, but as a general relationship between oscillator energy and the energy density of black-body radiation, $\rho(\nu)$. He envisaged that he could derive a formula for the oscillator energy as a function of T , which, when substituted for $U(C)_1$ in (2), would lead to a formula for $\rho(\nu)$ valid over the whole spectrum. Guided by his earlier interest in the second law of thermodynamics, Planck believed that he should first endeavour to express the oscillator energy U as a function of entropy, S . He experimented with expressions for d^2S/dU^2 and he required on thermodynamic grounds that

$$\frac{d^2S}{dU^2} < 0. \quad (3)$$

By arguing *a posteriori* from the known form of Wien's radiation law, and guided by considerations of simplicity (plus a little guesswork), he arrived (in October 1900) at the expression (in the present notation)

$$\frac{d^2S}{dU^2} = -\frac{k}{U(\epsilon + U)}, \quad (4)$$

where k and ϵ are constants independent of temperature (Planck 1900*b*). Integration leads to $dS/dU = (k/\epsilon)\ln(\epsilon/U+1)$ and, by putting $dS/dU = T^{-1}$ and rearranging, we obtain

$$U = \frac{\epsilon}{\exp(\epsilon/kT) - 1}.$$

When substituted for $U(C)_1$ in equation (2), this leads to Planck's law.

Dissatisfied with the rather superficial reasoning which led to the above result, Planck sought to put the assumed relationship between entropy and energy on a more secure physical basis. He looked to the association of entropy with statistics and (in December 1900) introduced (Planck 1900*c*) a statistical argument based on a counting procedure which 'prefigures the Bose–Einstein counting of a quarter century later' (Pais 1982, p. 371) and which will be referred to here simply as Bose–Einstein counting. Briefly (and I use the notation of Pais 1982), Planck considered a system composed of a large number, N , of entities, and he

subdivided the total energy of the system, U_N , into a large number, P , of equal energy elements or quanta ϵ , so that $U_N = P\epsilon$. He counted the number of ways, W_N , of distributing the P indistinguishable energy elements amongst the N distinguishable entities of the system, assuming no restriction on the number of energy elements assigned to any one entity, viz.

$$W_N = \frac{(N + P - 1)!}{(N - 1)!P!}. \quad (5)$$

Planck then advanced a procedure (see Appendix B) grounded in thermodynamics which leads to a formula for the mean energy which we label $U(B)$, this being the mean energy of an entity subject to Bose–Einstein counting, viz.

$$U(B) = \frac{\epsilon}{\exp(\epsilon/kT) - 1}, \quad (6)$$

which is the same as U above. We emphasise that the foregoing derivation of $U(B)$ draws only on statistics and thermodynamics and not at all on electromagnetic or oscillator theory. There is nothing in the derivation of $U(B)$ to associate it with an entity that is oscillating.

Substitution of $U(B)$ for $U(C)_1$ in equation (1) leads (with $\epsilon = h\nu$) to Planck’s law, which (in December 1900) Planck wrote in the form (1900c)

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3(\exp(h\nu/kT) - 1)} \quad (7)$$

and which proved to be in very good agreement with experiment. However, given the obvious (in hindsight) disparity between the quantum physics underlying equation (6) and the classical physics underlying equation (2), we are not entitled to simply substitute (6) into (2). In fact, to proceed by substituting (6) into (2) is to invoke the assumption that the equation linking $\rho(\nu)$ to $U(B)$ is analogous, or similar in form, to (2), viz. the assumption that

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}U(B). \quad (8)$$

This assumption served to bridge the gap between classical and quantum theory. It is the second quantum assumption in Planck’s derivation and (like the other quantum assumption $\epsilon = h\nu$) was justified in a practical sense by the fact that the final result (Planck’s law) gave very good agreement with experiment. Einstein (1906) appears to be the first to have discussed the second assumption. Debye, in 1910, refers to a ‘weak point’ in Planck’s theory, namely that ‘the two parts on which the proof of the radiation law is based differ in their fundamental assumptions (quoted from Hermann 1971, p. 110). And H. Poincaré is quoted (McCormach 1967) as referring to a ‘very shaky argument’ in Planck’s theory. In due course Planck’s analogy-based derivation of Planck’s law was supplanted by more quantum-intensive derivations (e.g. Einstein 1917; Bose 1924) and has passed into history, leaving us to ponder the nature of the quantum entity which

is characterised by equations (6) and (8). It should be emphasised that the above derivation of (8) (if ‘derivation’ is the correct word for a procedure based on analogy) does not imply that (8) is underpinned by electromagnetic or oscillator theory. In particular it provides no grounds for supposing that the quantum entity in question is one that is physically oscillating.

(2c) *A Variant of Planck’s Derivation*

Experimentation (with formulae) led Planck to equation (4). Experimentation might equally lead to

$$\frac{d^2 S}{dU^2} = -\frac{k}{U(\epsilon - U)}. \quad (9)$$

This differs from (4) in only one sign, and satisfies equation (3), provided that $\epsilon > U$. When integrated it gives equation (33) (in Appendix B) and thence (proceeding as beneath equation 4)

$$U = \frac{\epsilon}{\exp(\epsilon/kT) + 1}.$$

Planck (1900*b*) referred to equation (4) as ‘by far the simplest of all expressions which give S as a logarithmic function of U (see equation 31)—which is suggested from probability considerations—and which moreover for small values of U reduces to Wien’s expression.’ Yet equation (9) also gives S as a logarithmic function of U (see equation 32) and is no less simple than equation (4). It, too, is suggested from probability considerations (see below) and, for small values of U , it also reduces to Wien’s expression.*

We could, if we wished, emulate Planck and put the foregoing on a more secure physical basis by invoking an alternative form of what might be called quantum counting. Instead of assuming no restriction on the number of energy elements assigned to any one entity, let us now assume that only zero or one energy element is assigned to any one entity. Such a procedure is similar to that encountered with Fermi–Dirac statistics, and will be referred to here as Fermi–Dirac counting. Now define W_N to be the number of ways in which P indistinguishable energy elements can be distributed over the N distinguishable entities, subject to the restriction that each entity receives only zero or one energy element, viz.

$$W_N = \frac{N!}{(N - P)!P!}. \quad (10)$$

Proceeding as in Section 2*b* (see Appendix B for details) we obtain a formula for the mean energy which we now label as $U(F)$, this being the mean energy of an entity subject to Fermi–Dirac counting, viz.

* When $U \ll \epsilon$, equations (4) and (9) both reduce to $d^2 S/dU^2 = -k/U\epsilon$, which leads to [proceeding as beneath (4)] $U = \epsilon \exp(-\epsilon/kT)$, and thence [substituting for $U(C)_1$ in equation (2) and putting $\epsilon = h\nu$] to Wien’s law, $\rho(\nu) = (8\pi h\nu^3/c^3)\exp(-h\nu/kT)$.

$$U(F) = \frac{\epsilon}{\exp(\epsilon/kT) + 1}, \quad (11)$$

which is the same as U above. We recognise this as the mean energy of a two-state electronic atom (to be discussed in Section 4a). Further discussion of quantum counting is reserved for Appendix C, where we consider the limit $N \gg P$ (the same as $\alpha \gg 1$) common to both Bose–Einstein and Fermi–Dirac counting.

To further emulate Planck and derive Planck’s law, we would need a classical equation from which the equation linking $\rho(\nu)$ to $U(F)$ (equation 17) could be inferred by analogy. No such classical equation appears to exist [other than in the Wien limit where equation (17) reduces to (18), which is similar in form to equation (2)], and we are thus frustrated in our attempt to have a second analogy-based derivation of Planck’s law (other than in the Wien limit). This should come as no surprise. Rather, we should be surprised to find even one analogy-based derivation of Planck’s law. As noted by Einstein (1911), it is a ‘pure stroke of luck’ that Planck’s arguments yield an equation (equation 2) on which a quantum theory can be based. (Einstein was specifically referring to the quantum theory of specific heat but he might equally have been referring to Planck’s theory of black-body radiation.)

3. Oscillator Interpretation of Planck’s Derivation

(3a) *Introducing the Oscillator Interpretation*

We have seen that Planck’s derivation is in two parts. The first part deals with the classical oscillator model, culminating in equation (2). The second part deals with the procedure that led to the notion of quantisation, although it provides no clue as to the recipient of that quantisation. The statistical procedure utilised by Planck to distribute energy elements amongst entities does not require the entities to be identified. Equation (8) was ‘derived’ by analogy, and both equations (6) and (8) are independent of charge and mass. Perhaps not surprisingly, the entity which was modelled by the classical oscillator and which was the recipient of Planck’s quantisation was perceived as one which was itself oscillating. Whilst this may have been the obvious interpretation, ‘obviousness is always the enemy to correctness’ (Russell 1954) and the present case proved to be no exception.

Planck offered little guidance in this regard,* for several reasons. First, there was no requirement to be specific. Not only were equations (6) and (8) independent of charge and mass, but Kirchhoff’s theorem (which underpins Planck’s derivation) makes no demand on the nature of the entity being modelled. (According to Kirchhoff’s theorem, the spectral distribution of radiation within an isothermal enclosure is independent of the composition of the enclosure.) Second, even had Planck wished to be specific, he would have been constrained by the limited information available. Only in 1897 was the electron confirmed as a particle, and in 1900 there still remained some doubt about the very existence

* By contrast, the harmonic oscillator which Lorentz utilised in his 1896 theory of the Zeeman effect was deemed to model an electron oscillating back and forth inside an atom. We now recognise this as an early example of the harmonic oscillator modelling a transition between the internal quantum states of an atom.

of atoms (e.g. Bernal 1954; Pais 1995). And thirdly, according to Klein (1977, p. 4), Planck treated harmonic oscillators not because they were thought to be a realistic model for matter, but because oscillators were simplest to treat. Simplicity is a recurring theme in Planck's theory.* R. Harré (1983, p. 144) thinks that adherence to the principle of simplicity is 'a case of the fallacy of confusing one's model for the understanding of the world with the world itself', and that it is a fallacy to which eminent scientists are peculiarly liable.

(3b) *Quantum Harmonic Oscillator*

Whilst the above remarks give little cause for optimism as regards an oscillator interpretation of Planck's theory, it nevertheless behoves us to treat such an interpretation on its merits and to consider an oscillating entity as a possible recipient for Planck's quantisation. A quantum harmonic oscillator (QHO) has a large number of quantum states, each characterised by a separate quantum number n and energy $(n + \frac{1}{2})h\nu$, where $n = 0, 1, 2, \dots$ and ν is the frequency of oscillation (Pauling and Wilson 1935). The probability of a quantum harmonic oscillator being excited to the n th quantum state is proportional to $\exp[-(n + \frac{1}{2})\alpha]$, implying a mean energy

$$\begin{aligned} U(\text{QHO}) &= \sum_{n=0}^{\infty} (n + \tfrac{1}{2})h\nu \exp[-(n + \tfrac{1}{2})\alpha] \bigg/ \sum_{n=0}^{\infty} \exp[-(n + \tfrac{1}{2})\alpha] \\ &= \frac{h\nu}{\exp(\alpha) - 1} + \frac{h\nu}{2}. \end{aligned} \quad (12)$$

The only allowed dipole transitions (assuming the oscillator to have a dipole moment) are those for which $\Delta n = \pm 1$. All such transitions are of frequency ν and all such transitions contribute to the emission and absorption of radiation of frequency ν . Starting with the appropriate equations (e.g. Pauli 1929), one can show that a quantum harmonic oscillator in thermal equilibrium with black-body radiation is characterised by the equation

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3} [U(\text{QHO}) - h\nu/2]. \quad (13)$$

This result is similar to that derived by Pauli (1929), the difference being that Pauli did not include the zero-point energy $h\nu/2$. Substitution of (12) into (13) leads to Planck's law, as it must (any entity emitting and absorbing radiation in thermal equilibrium must, via the principle of detailed balance, lead to Planck's law).

The quantisation characteristic of a quantum harmonic oscillator $(n + \frac{1}{2})h\nu$, whilst (coincidentally) similar to Planck's quantisation $n h\nu$, nevertheless differs from Planck's quantisation by the zero-point energy $h\nu/2$. And equations (12)

* H. Kangro has drawn attention to the principle of simplicity at work in Planck's theory and elsewhere—see Planck (1972, notes 11 and 21); Kangro (1976, footnote 200b on p. 205); and Kangro (1975, p. 12).

and (13) likewise differ from the corresponding equations of Planck's theory [equations (6) and (8)] by $h\nu/2$. In other words, the oscillator interpretation of Planck's theory requires us to believe that Planck's quantisation is in error (Eisberg 1961) or at least in need of correction (Haken and Wolf 1994) by an amount $h\nu/2$. As the proponents of this interpretation rightly point out, such an error would not show up in Planck's derivation of $\rho(\nu)$, since the zero-point energy is not a consideration where the emission and absorption of radiation are concerned. (Only the energy separation between states is important in this case.)

Inevitably there must be doubt about an interpretation which requires us to believe that the facts being interpreted are in error, particularly when there is an alternative interpretation (in Section 4) which makes no such demand. However, the principal objection to the oscillator interpretation is that, as we shall now see, the nature of the oscillating entity has not (after a century) been resolved. The reader who feels that the twofold appearance of the harmonic oscillator (first as a model for the emission and absorption of radiation, and second as the recipient of Planck's quantisation) gives the oscillator interpretation of Planck's derivation the stamp of self-consistency would do well to remember the words of Lycinus in the work of Lucian (1965), namely, '... then consistency drags you onward, and it never enters your head that a thing can be self-consistent but still false.'

(3c) Quest for a Suitable Oscillating Entity

A stumbling block as regards the oscillator interpretation of Planck's derivation has been the difficulty experienced in investing the harmonic oscillator with a physical identity. Early opinion favoured a material oscillating entity which was atomistic in character. From letters of Planck to Wien in 1900 and 1907, Kangro (1976, p. 222) infers that 'Planck considered resonators as real physical entities as he did in 1899, when he associated resonators with ponderable atoms.' Einstein (1905) refers to electronic resonators, and later (1906) suggests that we envision the resonators as ions. As noted by Hermann (1971, pp. 89, 90), Wien (in 1909) viewed the electromagnetic resonators as real atoms. Einstein and Hopf (1910) imagined the oscillator to be attached to a molecule. However, the view of the classical oscillator as modelling a material oscillating entity was not without its critics. E. Whittaker (1953, footnote on p. 79), writing about Planck's use of vibrators, warned 'This, of course, does not mean (as it has sometimes been wrongly interpreted to mean) that actual matter necessarily has this character.' And R. Resnick and D. Halliday (1985) remind us that the walls of cavities are composed, not of oscillators, but of atoms which are 'much more complex than the simple harmonic oscillators that Planck assumed.'

However, a theory which gave excellent agreement with experiment wasn't about to undergo major alterations, particularly at a time when quantisation was recognised as the key to understanding a wide range of phenomena apart from black-body radiation. One alternative was to view the oscillator in Planck's theory as a hypothetical or imaginary entity.* Kuhn (1978, p. 117, 118) writes that

* R. Harré (1983, p. 145) advises that 'When a theory breaks down we may choose to invent a hypothetical entity which at the time of its introduction we have no way of observing, rather than make large-scale alterations to the theory, and this choice is often determined by considerations of simplicity.'

‘His [Planck’s] resonators were imaginary entities, not susceptible to experimental investigation. Their introduction was simply a device for bringing radiation to equilibrium,...’. However, we can hardly be satisfied with an imaginary entity as the recipient of Planck’s quantisation.

Ehrenfest (1906) outlined and Debye (1910) detailed a method for deriving Planck’s law based on a model which we associate with Rayleigh and Jeans, whereby the radiant energy within a cavity is carried by standing electromagnetic waves. This yields the relation

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}U(M),$$

which is similar to Planck’s equation (2), except that $8\pi\nu^2/c^3$ here denotes the number density of cavity modes of frequency ν , and $U(M)$ denotes the mean energy per mode. [We will not concern ourselves as to whether this equation is correct or whether it should have the form in equation (13).] Substitution of Planck’s $U(B)$ for $U(M)$ then leads to Planck’s law. Curiously the foregoing has come to be viewed as a revision of Planck’s derivation. According to this view, the exchange of energy between radiation and matter (as considered by Planck) is incidental or (Born 1962, p. 267) is a ‘circuitous route’ to the above equation, and Planck’s quantisation should be associated with the cavity modes of oscillation.* In due course Planck’s original intentions were also ‘revised’ to accord with the revised view of his theory. We read, for example, that (Kittel 1969) ‘Planck introduced the concept of a harmonic oscillator of frequency ω to represent a mode of frequency ω of the electromagnetic field in a cavity. The oscillator is associated with the electromagnetic field and not with the walls of the cavity.’

Needless to say, such a revised view of Planck’s theory was far from unanimous. A. Pais (1995, p. 70) writes with emphasis that ‘Planck’s oscillators were *material* objects, present within the black-body radiation to ensure radiation mixing.’ H. Young and R. Freeman (1996) seek to reconcile the situation by associating a cavity mode of frequency ν with a material oscillator (an electron) of the same frequency in the walls of the cavity. That the oscillator interpretation of Planck’s theory still remains unresolved after a century might signal that the wrong path is being followed and that a new interpretation is called for. The new interpretation presented below was inspired by the fact that, elsewhere in atomic spectroscopy, the classical oscillator was long ago recognised as modelling a transition between the internal quantum states of an atom [sometimes known as an atomic or quantum oscillator, as in Ditchburn (1958)].

4. Atomistic Interpretation of Planck’s Derivation

The radiation within an isothermal enclosure originates in a complex manner from quantum transitions within the solid wall material (Rutgers 1958; Blau

* Cavity modes of oscillation are characterised by energies $(n+\frac{1}{2})h\nu$ appropriate to a quantum harmonic oscillator. That these energies are similar to (although not the same as) the energies $nh\nu$ to emerge from Planck’s theory is interesting, but unhelpful as regards the nature of the material entity emitting and absorbing radiation in Planck’s theory.

and Fischer 1962; Garbuny 1965). This subject is not covered by Planck's theory. Planck treated the case of entities permeated by a homogeneous, isotropic radiation field, and this is the problem addressed in this section and throughout the paper.

(4a) *Electronic Atoms*

Next in our search for the entity characterised by equations (6) and (8), we consider a transition between the internal quantum states of an electronic atom (or muonic atom or other atom populated by subatomic fermions). We proceed as in Einstein's quantum theory of radiation (Einstein 1917) and consider a collection of (two-state) atoms in thermal equilibrium with black-body radiation of energy density $\rho(\nu)$. Let N_0 denote the number density of unexcited atoms (i.e. the number density of atoms which, in thermal equilibrium, are assigned zero energy elements) and let N_1 denote the number density of excited atoms (i.e. the number density of atoms which, in thermal equilibrium, are assigned one energy element ϵ). Let A_{10} , B_{10} and B_{01} denote the usual Einstein coefficients for spontaneous emission, induced emission and absorption respectively. The power absorbed by an atom in thermal equilibrium with black-body radiation may thus be written

$$\xi_a(F) = h\nu(B_{01}N_0 - B_{10}N_1)\rho(\nu)/(N_0 + N_1) \quad (14)$$

$$= h\nu B_{01}\rho(\nu)CY(F), \quad (15)$$

where

$$C = 1 - \frac{N_1}{N_0} = 1 - \exp(-\alpha), \quad Y(F) = \frac{N_0}{N_0 + N_1} = \frac{1}{1 + \exp(-\alpha)},$$

$$CY(F) = \frac{N_0 - N_1}{N_0 + N_1} = \frac{1 - \exp(-\alpha)}{1 + \exp(-\alpha)}.$$

Here we have put $N_1/N_0 = \exp(-\alpha)$ (Boltzmann's law) and $B_{01} = B_{10}$, assuming the states to be non-degenerate. The physical significance of the parameters C and $Y(F)$ is discussed in Appendix C.

For the mean energy per atom we have

$$U(F) = \frac{h\nu N_1}{N_0 + N_1} = \frac{h\nu}{\exp(\alpha) + 1}. \quad (16)$$

Upon equating the emitted power per atom, $A_{10}U(F)$, to the absorbed power (equation 15), we obtain (putting $A_{10}/B_{01} = 8\pi h\nu^3/c^3$)

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3} \frac{U(F)}{CY(F)} = \frac{8\pi\nu^2}{c^3} \frac{U(F)}{1 - 2U(F)/h\nu}. \quad (17)$$

Substitution of (16) into (17) gives Planck's law (as it must). Equations (16) and (17) are dissimilar to equations (6) and (8) (except in the Wien limit),

thereby excluding electronic atoms as the quantum entity of concern in Planck's derivation (except in the Wien limit). In the Wien limit (allowing that $U(F) \ll h\nu$ when $\alpha \gg 1$)

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3} U(F); \quad \alpha \gg 1, \quad (18)$$

which is similar to equation (8). It is of interest that an equation of this form was employed by Ladenburg (1921) in a study of atomic dispersion.

We have introduced equation (17) only for comparison with Planck's theory. If our intention were to derive Planck's law, we would have no need for the intermediary equation (17) but would proceed in the manner of Einstein (1917) and utilise a rate equation (as described in Section 5a).

(4b) Atoms populated by Bosons

Finally in our search for the entity characterised by equations (6) and (8), we will consider an atom whose quantum states are populated by subatomic bosons (such as pions). That such atoms (produced in particle interactions)* are unstable and short-lived would suggest that the variant of Planck's theory which deals with electronic atoms (see Sections 2c and 5a) is of more practical interest. Whereas an electronic atom may be assigned either zero or one energy element (i.e. may be either unexcited or singly excited), an atom populated by bosons (and continue to think of a two-state atom) may be assigned any number of energy elements (i.e. may be multi-excited). A quantum state may be occupied by more than one particle (a boson).

As before (see Section 4a) we consider a collection of (two-state) atoms in thermal equilibrium with black-body radiation, except that any number of energy elements may now be assigned to an atom. Let N_n denote the number density of n times excited atoms (i.e. the number density of atoms which, in thermal equilibrium, are assigned n energy elements). The appropriate expressions for emitted and absorbed power must now include transitions between n and $(n-1)$ times excited atoms, where n varies from 1 to ∞ . The probability of the transition whereby an n times excited atom becomes $n-1$ times excited is nA_{10} (spontaneous emission) and nB_{10} (induced emission). [Refer, for example, to the method used by Pauli (1926, 1929) to calculate the spontaneous transition probability for the case of a quantum harmonic oscillator.] It follows (given the well known relationship between the Einstein coefficients) that the probability for the transition whereby an $n-1$ times excited atom becomes n times excited is nB_{01} . The power absorbed by an atom when in thermal equilibrium with black-body radiation may now be written

$$\xi_a(B) = h\nu \left[\sum_{n=0}^{\infty} (n+1)B_{01}N_n - \sum_{n=0}^{\infty} (n+1)B_{10}N_{n+1} \right] \rho(\nu) / \sum_{n=0}^{\infty} N_n.$$

* For pionic atoms, see Hüfner (1975). For muonic atoms, see Haken and Wolf (1994, sect. 8.7). For exotic atoms in general, see Barrett *et al.* (1990) and Horváth (1994). For additional references, see Horváth and Lambrecht (1984).

The first and second terms in square brackets represent absorption and induced emission respectively. The ratio of the second term to the first is $\exp(-\alpha)$, bearing in mind that $N_{n+1}/N_n = \exp(-\alpha)$ independently of n (Boltzmann's law generalised). The above equation may be written

$$\xi_a(B) = h\nu B_{01}\rho(\nu)CY(B), \quad (19)$$

where

$$C = 1 - \exp(-\alpha),$$

$$\begin{aligned} Y(B) &= \sum_{n=0}^{\infty} (n+1)N_n \bigg/ \sum_{n=0}^{\infty} N_n \\ &= \sum_{n=0}^{\infty} (n+1)(\exp(-\alpha))^n \bigg/ \sum_{n=0}^{\infty} (\exp(-\alpha))^n \\ &= \frac{1}{1 - \exp(-\alpha)}, \end{aligned}$$

from which we see that $CY(B) = 1$. The physical significance of the parameters C and $Y(B)$ is discussed in Appendix C.

For the mean energy per atom we have

$$\begin{aligned} U(B) &= h\nu \sum_{n=1}^{\infty} nN_n \bigg/ \sum_{n=0}^{\infty} N_n \\ &= h\nu \sum_{n=1}^{\infty} n(\exp(-\alpha))^n \bigg/ \sum_{n=0}^{\infty} (\exp(-\alpha))^n \\ &= \frac{h\nu}{\exp(\alpha) - 1}. \end{aligned} \quad (20)$$

Upon equating the emitted power per atom, $A_{10}U(B)$, to the absorbed power (equation 19) we obtain

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3} \frac{U(B)}{CY(B)},$$

or [since $CY(B) = 1$]

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3} U(B). \quad (21)$$

Thus, whilst the factors C and $Y(B)$ are separately dependent on Planck's constant h , the product $CY(B)$ ($= 1$) is independent of h , leaving the factor of $U(B)$ in equation (21) (namely $8\pi\nu^2/c^3$) independent of h . Observe that (21), like equation (17), is (a) independent of charge and mass and (b) independent of the values chosen for the Einstein coefficients A_{10} and B_{01} , but dependent on the universal ratio of these coefficients. Substitution of (20) into (21) gives Planck's law (as it must). *Significantly, equations (20) and (21) are the same as equations (6) and (8) of Planck's derivation (with $\epsilon = h\nu$), thereby identifying an atom populated by bosons as the quantum entity of concern in Planck's derivation.*

We have introduced equation (21) only for comparison with Planck's theory. If our intention were to derive Planck's law, we would have no need for the intermediary equation (21) but would utilise rate equations (as described in Section 5b).

5. Deriving Planck's Law using Quantum Counting in conjunction with Atoms

(5a) Electronic Atoms

Inevitably a theory which mixes quantum and classical concepts is less than convincing or (to quote Debye) is 'illogical'.* Suppose we now retain the quantum component but discard the classical component of Planck's theory. That is, suppose we retain quantum counting in a derivation of Planck's law which utilises atoms themselves rather than the oscillator model of an atom. We will first treat electronic atoms (and Fermi–Dirac counting), these being more familiar to us than atoms populated by bosons. Moreover, in the case of electronic atoms there has been no classical model and no analogy-based derivation to muddy the waters.

We start by equating the rate of de-excitation to the rate of excitation for the two-state atom described at the beginning of Section 4a, to give

$$[A_{10} + B_{10}\rho(\nu)]N_1 = B_{01}\rho(\nu)N_0. \quad (22)$$

This is the same starting point as that adopted by Einstein in his well known derivation of Planck's law (Einstein 1917). Einstein invoked Boltzmann's law to provide a relationship between N_1 and N_0 , viz. $N_1/N_0 = \exp(-\epsilon/kT)$. (We assume the states to be non-degenerate.) Substitution into equation (22) then leads to Planck's law in a manner which is too well known to reproduce here, but which involves determining the ratios $A_{10}/B_{10} = 8\pi h\nu^3/c^3$ and $B_{10}/B_{01} = 1$ (for non-degenerate states) and putting $\epsilon = h\nu$.

Our approach is somewhat different. We define

$$n_1 = \frac{N_1}{N_0 + N_1} \quad \text{and} \quad n_0 = \frac{N_0}{N_0 + N_1} = 1 - n_1,$$

* In an interview for the Sources for History of Quantum Physics, Debye offered the following recollection (quoted by Hermann 1971, p. 110): 'My whole business was, Planck is illogical. On the other hand, it looks as if the whole thing is very good. Can we get rid of the illogical part?'

and rewrite equation (22) as

$$[A_{10} + B_{10}\rho(\nu)]n_1 = B_{01}\rho(\nu)n_0. \quad (23)$$

Statistical and thermodynamical considerations based on Fermi–Dirac counting (see the second paragraph of Section 2c) provide us with a formula for $U(F)$ (equation 11) and thence for

$$n_1 = U(F)/\epsilon = [\exp(\epsilon/kT) + 1]^{-1},$$

$$n_1/n_0 = \exp(-\epsilon/kT).$$

When substituted into equation (23), this again leads to Planck’s law (if we proceed in the manner of Einstein). Whereas Einstein invoked Boltzmann’s law, we have invoked an argument based on Fermi–Dirac counting to provide information on the distribution of fermions amongst available atomic states.

The foregoing should not be confused with a derivation of Planck’s law that draws on the Fermi–Dirac distribution function (Zitter and Hilborn 1987; Crawford 1988). According to this function, the mean thermal occupation number n_2 (n_1) is related to the energy E_2 (E_1) of a quantum state by

$$n_2 = [\exp(E_2 - \mu)/kT + 1]^{-1} \quad \text{and} \quad n_1 = [\exp(E_1 - \mu)/kT + 1]^{-1}.$$

It has been argued (Zitter and Hilborn 1987; Crawford 1988) that the appropriate rate equation in this case is

$$[A_{21} + B_{21}\rho(\nu)]n_2(1 - n_1) = B_{12}\rho(\nu)n_1(1 - n_2),$$

where A_{21} , B_{21} and B_{12} are the appropriate rate coefficients. Since

$$n_2(1 - n_1)/n_1(1 - n_2) = \exp[-(E_2 - E_1)/kT]$$

it is apparent that Planck’s law will follow from the above equation if we proceed in the manner of Einstein (1917).

(5b) Atoms populated by Bosons

By equating the rate of de-excitation to the rate of excitation for the two-state atom described at the beginning of Section 4b, we obtain

$$[A_{10} + B_{10}\rho(\nu)] \sum_{n=1}^{\infty} nN_n = B_{01}\rho(\nu) \sum_{n=0}^{\infty} (n+1)N_n. \quad (24)$$

Here the left-hand side is the sum total rate of de-excitation and the right-hand side is the sum total rate of excitation. We put

$$n_1 = \sum_{n=1}^{\infty} nN_n / \sum_{n=0}^{\infty} N_n, \quad n_0 = \sum_{n=0}^{\infty} (n+1)N_n / \sum_{n=0}^{\infty} N_n = 1 + n_1,$$

in which case equation (24) may be written

$$[A_{10} + B_{10}\rho(\nu)]n_1 = B_{01}\rho(\nu)n_0. \quad (25)$$

If we were to proceed in a manner analogous to Einstein's for an electronic atom (see beneath equation 22), we would put $N_{n+1}/N_n = \exp(-\epsilon/kT)$ (Boltzmann's law generalised) and obtain

$$n_1 = [\exp(\epsilon/kT) - 1]^{-1}, \quad (26)$$

$$n_1/n_0 = \exp(-\epsilon/kT). \quad (27)$$

When substituted into equation (25) this leads to Planck's law (if we proceed in the manner of Einstein). This may be seen as Einstein's derivation of Planck's law adapted to an atom populated by bosons.

But with an eye to the quantum component of Planck's theory, we proceed rather differently. Statistical and thermodynamical considerations based on Bose-Einstein counting (see the second paragraph of Section 2*b*) provide us with a formula for $U(B)$ (equation 6) and thence for

$$n_1 = U(B)/\epsilon = [\exp(\epsilon/kT) - 1]^{-1}.$$

This expression and the corresponding one for n_1/n_0 are the same as equations (26) and (27), and, when substituted into equation (25), lead (as above) to Planck's law if we proceed in the manner of Einstein. Whereas the initial derivation (in the previous paragraph) invoked the generalised form of Boltzmann's law, we have now invoked an argument based on Bose-Einstein counting to describe the distribution of bosons amongst the available atomic states.

The foregoing should not be confused with a derivation of Planck's law which draws on the Bose-Einstein distribution function (Zitter and Hilborn 1987). According to this function, the mean thermal occupation number n_2 (n_1) is related to the energy E_2 (E_1) of an appropriate quantum state by

$$n_2 = [\exp(E_2 - \mu)/kT - 1]^{-1} \quad \text{and} \quad n_1 = [\exp(E_1 - \mu)/kT - 1]^{-1}.$$

It has been argued (Zitter and Hilborn 1987) that the appropriate rate equation in this case is

$$[A_{21} + B_{21}\rho(\nu)]n_2(1 + n_1) = B_{12}\rho(\nu)n_1(1 + n_2),$$

where A_{21} , B_{21} and B_{12} are the appropriate rate coefficients. Since

$$n_2(1 + n_1)/n_1(1 + n_2) = \exp[-(E_2 - E_1)/kT],$$

it is apparent that Planck's law will again follow if we proceed in the manner of Einstein (1917).

(5c) A Revision of Planck's Derivation

The above derivation of Planck's law based on Bose–Einstein counting (and that in Section 5a based on Fermi–Dirac counting) has proceeded without any reference to harmonic oscillators. We have divorced Bose–Einstein counting (and Planck's quantisation) from Planck's theory and have presented it within the broader framework of quantum counting. Quantum counting has, in turn, been associated with atoms—Fermi–Dirac counting with electronic atoms (and other atoms populated by subatomic fermions) and Bose–Einstein counting with atoms populated by subatomic bosons. Since matter is composed of atoms (as distinct from oscillators), one could hardly wish for a more general interpretation.

It might be felt that to replace the oscillator interpretation of Planck's theory with the atomistic interpretation is to replace one elusive entity (a material oscillator) with another (an atom populated by bosons). However, this is a narrow point of view, and ignores the fact that there is a second half to Planck's theory which is potentially able to provide a derivation of Planck's law involving electronic atoms. I say 'potentially' because, to bring the second half into play, we need a classical equation whose quantum analogue is equation (17) for an electronic atom. But a theory which mixes quantum and classical concepts is 'illogical' and in need of revision anyway. More logical is the above revision, which combines the quantum component of Planck's theory (Bose–Einstein counting) with atoms (atoms populated by bosons). And there is a second half to this revision, which combines Fermi–Dirac counting with electronic atoms. Our revision of Planck's theory thus embraces not only atoms populated by bosons but also common electronic atoms. And unlike Debye's revision mentioned in Section 3c (which dispensed altogether with a material entity), our revision remains true to Planck's original intention (the exchange of energy between radiation and matter).

6. Implications of the Atomistic Interpretation

The implications of the atomistic interpretation are far-reaching. No longer can Planck's derivation be cited as support for the postulate that oscillators can have only those energies which are multiples of $h\nu$. Examples where Planck's derivation has been thus cited need to be revised. This includes Debye's derivation of Planck's law, which cited Planck's theory when assigning the mean energy $U(B)$ to cavity modes of oscillation. It also includes Einstein's derivation of his well known formula for the specific heat of solids. In 1906 Einstein introduced a statistical procedure (Einstein 1906), which he later expanded upon (Einstein 1907), whereby the integrals in the usual formula for the mean energy, namely

$$\bar{E} = \int_0^\infty E\omega(E)\exp(-E/kT)dE \Big/ \int_0^\infty \omega(E)\exp(-E/kT)dE,$$

were replaced by summations, leading to a formula of the form

$$\bar{E} = \sum_{n=0}^{\infty} E_n\omega(E_n)\exp(-E_n/kT) \Big/ \sum_{n=0}^{\infty} \omega(E_n)\exp(-E_n/kT).$$

By putting $\omega(E_n) = \text{constant}$ and $E_n = n\epsilon$, Einstein obtained a result

$$\bar{E} = \frac{\epsilon}{\exp(\epsilon/kT) - 1}, \quad (28)$$

which was the same as Planck's $U(B)$. Observe that there is nothing in the above formulation to align equation (28) with an oscillating entity (it might equally be aligned with an atom populated by bosons).^{*} Einstein elected to align equation (28) with an oscillating entity because he believed that Planck's $U(B)$ was apposite to an oscillating entity (the oscillator interpretation of Planck's theory, but a case of confusing a model with the entity being modelled).

In his paper of 1907, Einstein was concerned with the calculation of the specific heat of solids. He, like others before him, believed the heat capacity of solids to be associated with oscillatory motion, which he modelled according to the harmonic oscillator. Using Planck's $U(B)$, which he believed to be apposite to a harmonically oscillating entity, Einstein obtained a very useful formula for specific heat—due in part to the fact that the difference between $U(B)$ and $U(\text{QHO})$, namely the zero-point energy, does not manifest in a calculation of specific heat (which is dependent on the derivative $dU(\text{QHO})/dT$). Given the present atomistic interpretation of Planck's theory, wherein Planck's quantisation is to be associated with the internal quantum states of an atom, the success achieved by Einstein when associating Planck's quantisation with oscillatory motion must be seen as serendipitous.

Historically, the identification of Planck's quantisation with the harmonic oscillator may have impeded our understanding of Planck's derivation, but (as we have just seen) it initiated our understanding of the quantum harmonic oscillator (and of specific heat). It is of interest that Planck himself contributed to this process, not in his derivation of 1900, but later in his lectures of 1906 (see Klein 1963; Mehra and Rechenberg 1982, pp. 57, 58) and at the Solvay Congress of 1911 (see Reiche 1924; Jammer 1989, pp. 42, 43), when he described the now familiar partition of the coordinate–momentum phase space for a system of harmonic oscillators into ellipses.

7. Concluding Remarks

A comparison has been made between the traditional oscillator and a novel atomistic interpretation of Planck's 1900 derivation of Planck's radiation law. The oscillator interpretation is seen to be outside mainstream atomic spectroscopy (wherein the harmonic oscillator models transitions between internal quantum states of atoms), it does not accommodate Fermi–Dirac counting, and it requires Planck's theory to be corrected (for the zero-point energy). Moreover, after nearly a century, the identity of the oscillating entity has not been resolved. By contrast, the atomistic interpretation is free of the above shortcomings and can therefore claim to be the preferred interpretation. It is within mainstream atomic spectroscopy, it accommodates Fermi–Dirac counting (and electronic atoms), it makes no demand for correction and it readily identifies the entity being modelled, as an atom populated by subatomic bosons (such as pions). A corollary to the

^{*} Do not be confused by the fact that, in the course of deriving equation (28), Einstein evaluated $\bar{E} = (R/N)T (= kT)$ for a classical oscillator (Einstein 1907).

atomistic interpretation is that Planck's 1900 derivation of Planck's law can no longer be construed as support for the postulate that material oscillating entities can have only those energies which are multiples of $h\nu$.

In due course Planck's derivation of his law was supplanted by more quantum-intensive derivations and has passed into history. Planck's oscillator model should be applauded for its role in the origin of quantum theory, but the time has come to let it go and maybe even (as with the Bohr–Sommerfeld orbital model of the atom in 1933)* to write an obituary. Planck disliked analogies and models, and believed that 'earlier hypotheses, however successful, became a present danger, 'the most dangerous enemy of progress', once their work was done' (quoted from Heilbron 1986). It is ironic that Planck's oscillator hypothesis should continue to dominate the interpretation of the quantum component of his theory long after its work was done.

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* As noted by J. Heilbron (1968), the Bohr–Sommerfeld theory of the atom was so clearly superseded by quantum mechanics that, in the early 1930s, the editors of the second edition of the *Handbuch der Physik* decided to commission an obituary notice to it. The obituary was composed by A. Rubinowicz (1933).

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Appendix A: Absorption by a Classical Oscillator

Consider that a wave field is decomposed into Fourier components $E_\omega \cos(\omega t + \delta_\omega)$, where E_ω and δ_ω denote the electric field amplitude and phase respectively, and consider that the motion of a charged particle subject to such a component is given by

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{eE_\omega}{m} \cos(\omega t + \delta_\omega). \quad (29)$$

The solution, $x(t)$, of this equation, and thence the velocity, $\dot{x}(t)$, and the power absorbed by the oscillator, $\dot{x}(t)eE_\omega \cos(\omega t + \delta_\omega)$, must allow for the initial phase of the oscillator relative to the electric field of the incoming wave (e.g. Griem 1964; Jefferies 1968). By assuming the phases δ_ω to be random, we obtain a tractable solution for the absorbed power, namely [equation (1–21) of Griem 1964]

$$\bar{P}_a = \frac{\pi e^2}{4m} E_\omega^2, \quad (30)$$

where we have averaged over a period of oscillation and have integrated over the line profile (an integration which is simplified by the damping constant γ being

very small). With the electric field assumed to consist of an incoherent isotropic superposition of frequencies in thermal equilibrium at temperature T , we have $\rho(\omega) = 3E_w^2/8\pi$, where $\rho(\omega)$ denotes the energy density of the electromagnetic or radiation field (Pauli 1929, Sect. 6). In this way the absorbed power, now denoted ξ_a , becomes [on substitution into equation (30) and conversion from units of angular frequency to cycles per second]

$$\xi_a = \frac{\pi e^2}{4m} \frac{8\pi \rho^{\text{RP}}(\nu)}{3 \times 2\pi} = \frac{\pi e^2}{3m} \rho^{\text{RP}}(\nu). \quad (1)$$

Appendix B: Quantum Counting and the Derivation of Mean Energy

(a) *Bose-Einstein Counting*

Starting with equation (5) and proceeding in the usual way (e.g. Pais 1982, p. 370; Allen and Maxwell 1952, p. 761), that is by equating the total entropy of the system S_N to $k \ln W_N$ and applying Stirling's approximation, we obtain a formula for S_N . With $S_N = NS$ this then becomes

$$S = k \left[\left(1 + \frac{U}{\epsilon}\right) \ln \left(1 + \frac{U}{\epsilon}\right) - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} \right], \quad (31)$$

where U is defined by $U_N = NU$ and where, since $U_N = P\epsilon$ (see Section 2b), we have put $P/N = U/\epsilon$. Differentiation then gives

$$\frac{dS}{dU} = \frac{k}{\epsilon} \ln \left(\frac{\epsilon}{U} + 1 \right),$$

and, by putting $dS/dU = T^{-1}$ and rearranging, we are led to a formula for mean energy which we label as $U(B)$, viz.

$$U(B) = \frac{\epsilon}{\exp(\epsilon/kT) - 1}. \quad (6)$$

The statistical basis for equations (5) and (31) has been discussed by a number of authors (e.g. Klein 1977; Mehra and Rechenberg 1982, Sect. I.2; Kuhn 1978, chs 4 and 5).

(b) *Fermi-Dirac Counting*

Starting with equation (10) and proceeding as outlined above, we obtain

$$S = k \left[- \left(1 - \frac{U}{\epsilon}\right) \ln \left(1 - \frac{U}{\epsilon}\right) - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} \right], \quad (32)$$

which, upon differentiation, becomes

$$\frac{dS}{dU} = \frac{k}{\epsilon} \ln \left(\frac{\epsilon}{U} - 1 \right). \quad (33)$$

By putting $dS/dU = T^{-1}$ and rearranging, we are led to a formula for mean energy which we label as $U(F)$, viz.

$$U(F) = \frac{\epsilon}{\exp(\epsilon/kT) + 1}. \quad (11)$$

Appendix C: Classical Regime of Quantum Counting

In the limit $N \gg P$, equations (5) and (10) both reduce to

$$W_N = \frac{N^P}{P!}. \quad (34)$$

Since $P/N = U/\epsilon$, the limit $N \gg P$ corresponds to $\epsilon \gg U$ and thence (see equations 6 or 11) to $\epsilon \gg kT$ or $\alpha \gg 1$ (the Wien limit). With equation (34) as starting point and proceeding as in Appendix B, we obtain $S = k(U/\epsilon)[1 - \ln(U/\epsilon)]$ and thence $U = \epsilon \exp(-\epsilon/kT)$. When substituted into equation (8) (with $\epsilon = h\nu$), this leads to Wien's law.

Counting theory provides us with an independent means of deriving equation (34). Consider that the number of ways of distributing P energy elements over N distinguishable entities is N^P . This assumes that energy elements assigned to different entities are distinguishable. It also assumes that energy elements assigned to the same entity are indistinguishable, though this ceases to be of concern when $N \gg P$, since the likelihood of an entity then being assigned more than one element of energy is negligible. Thus, when $N \gg P$, the number of ways of distributing P distinguishable energy elements over N distinguishable entities is N^P , and equation (34) now follows when the energy elements are assumed indistinguishable. This result (corrected classical counting) is similar to that encountered in corrected classical or corrected Boltzmann statistics (e.g. Davidson 1962). It represents the limit of Bose–Einstein and Fermi–Dirac counting and, by analogy with the classical regime of quantum statistics (Kittel 1969, p. 160), might be referred to as the classical regime of quantum counting. It should not be confused with the classical limit of black-body radiation (the limit $\alpha \ll 1$).

In the Wien limit (or classical regime of quantum counting) we have (see the appropriate equations of Sections 4a and 4b with $\alpha \gg 1$) $C = 1$, $Y(F) = 1$ and $Y(B) = 1$, in which case $\xi_a(F) = \xi_a(B) = \xi_a(W)$, where

$$\xi_a(W) = h\nu B_{01} \rho(\nu) = \frac{\pi e^2}{3m} \rho(\nu),$$

where we have put $h\nu B_{01} = \pi e^2/3m$, as befits a two-state atom.* This is similar

* We have $h\nu B_{01} = (\pi e^2/mc)f$ when the radiation field is expressed in the usual way (Jefferies 1968, p. 56) as an energy flux, or $h\nu B_{01} = (\pi e^2/3m)f$ when the radiation field is isotropic and expressed as an energy density. The absorption oscillator strength f is equal to unity in a two-state system.

to the classical result in equation (1). It follows that the absorbed power per atom (equations 15 and 19) may be written

$$\xi_a(F) = \xi_a(W)CY(F) \quad \text{and} \quad \xi_a(B) = \xi_a(W)CY(B).$$

In the Wien limit there are relatively few excited atoms compared to the number of unexcited atoms. Away from the Wien limit the presence of a significant number of excited atoms causes the absorbed power to differ from the Wien value, $\xi_a(W)$, by a factor C because of induced emission and by a factor Y because the ability of an atom to capture a photon is influenced by the excitation of the atom. For an atom populated by bosons these two factors cancel [i.e. $CY(B) = 1$], demonstrating (surprising as it may seem) that a transition from the classical equation (2) to the quantum equation (8) is possible without our necessarily having a knowledge of quantum states and induced emission.

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