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1973

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Schlitt, D.W., "The Dirac Relation, Einstein Coefficients, And The Blackbody Spectrum" (1973).
Transactions of the Nebraska Academy of Sciences and Affiliated Societies. 389.
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THE DIRAC RELATION, EINSTEIN COEFFICIENTS, AND THE BLACKBODY SPECTRUM

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This investigation of some interesting interrelationships in physics was brought about by a mistake. In late 1970 a paper appeared in *Physical Review Letters* which purported to calculate the effect of the presence of nearby atoms on the emission and absorption transition probabilities of an atom. (Koutsoyannis 1970). The authors of the paper claimed to show that the usual Dirac relations between these probabilities were altered by collision effects.

It was subsequently pointed out by several physicists that there was a serious mathematical error in the paper which invalidated the results. This was acknowledged in a subsequent erratum. The paper of Koutsoyannis is consequently of no further interest. It is mentioned here only as a historical note on the origins of what follows.

Skepticism about this "result" led me to investigate some of the very fundamental principles behind the Dirac relation and the consequences of its modification. It was found that the black body radiation spectrum would be modified¹. Experimentally measurable consequences of the modification were than investigated.

The results in themselves are probably not terribly important for physics. They do, however, point out some interesting interrelationships. The recognition of this kind of thing is important for the student of physics.

The general principles of time reversal, detailed balance, and thermal equilibrium place strong requirements on the ratio of the emission and absorption probabilities. Stated in a different way, the modification of the Dirac result $W_e/W_a = (\bar{n}_\omega + 1)/\bar{n}_\omega$ requires a modification of the black body radiation formula. Here \bar{n}_ω is the average number of photons, with frequency ω in the radiation field.

To establish this we follow the general outlines of the argument made by Einstein (Bohm, 1951). The probability of absorption can be written

$$W_a = A_{nm} I(\omega) \quad (1)$$

¹ Other modifications of the black body spectrum have recently been investigated (Nesbit, 1971). In this case the relationship between Einstein coefficients is modified in a reasonable way. Thermal equilibrium and the usual black body spectrum are recovered by a reinterpretation of thermal equilibrium.

where $I(\omega)$ is the intensity of radiation at frequency

$$\omega = |E_n - E_m| / \hbar .$$

In terms of the average number of photons \bar{n}_ω with frequency ω , $I(\omega)$ is given by

$$I(\omega) = \hbar \omega^3 \bar{n}_\omega / (2\pi)^2 c . \quad (2)$$

The time reversal invariance of the interaction of the radiation field with matter allows us to write the probability of emission as

$$W_e = A_{nm}I(\omega) + B_{nm} \quad (3)$$

where B_{nm} describes the spontaneous emission.

The Einstein coefficients A_{nm} and B_{nm} depend only on the nature of the atomic system so we can relate them by considering a convenient special case, that of thermal equilibrium at temperature T .

If p_n and p_m are the probabilities of the atom being in state n and state m respectively then in equilibrium

$$p_n / p_m = \exp (- \beta \hbar \omega), \quad \beta = 1/k_B T .$$

Detailed balance requires that

$$W_e p_n = W_a p_m . \quad (5)$$

This is used to relate the spontaneous emission coefficients to the induced. We find that

$$B_{nm} = (\exp (\beta \hbar \omega) - 1) \bar{n}_\omega (\hbar \omega^3 / c) A_{nm} . \quad (6)$$

The temperature dependence must cancel out and therefore

$$\bar{n}_\omega = (\exp (\beta \hbar \omega) - 1)^{-1} \quad (7)$$

which is the black body radiation formula. We then conclude that

$$B_{nm} = (\hbar \omega^3 c^{-1}) (2\pi)^{-2} A_{nm} \quad (8)$$

and

$$W_a / W_e = \bar{n}_\omega / (\bar{n}_\omega + 1) . \quad (9)$$

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The above discussion brings out the close relation between the Dirac result and the black body radiation formula (Heitler, 1944).

We can ask what would happen if the Dirac relation (9) were modified. Suppose we consider a modified formula² of the form

$$W_a/W_e = \bar{n}_\omega (1 + \delta) / (\bar{n}_\omega + 1) . \tag{10}$$

Substituting (10) and (4) into (5) gives a thermal equilibrium black body spectrum

$$\bar{n}_\omega = \left[(1 + \delta) \exp (\beta \hbar \omega) - 1 \right]^{-1} \tag{11}$$

If δ depends on the density of the perturbors as suggested by Koutsoyannis then we would expect that cavity radiation would have a spectrum which depends on the density of atoms in the cavity.

One should note that this modification has unpleasant consequences for the relation between A_{nm} and B_{nm} . Insertion of (11) into (6) leads to a temperature dependant relation between A_{nm} and B_{nm} which is inconsistent with their definition as atomic properties. This again emphasizes the fundamental nature of the Dirac relation.

Measurements of the properties of black body radiation have an accuracy of typically 0.5% . For sufficiently small the deviations predicted by the modified formula might not have been observed.

As an example of the result of the modification, the Stefan-Boltzman constant would become

$$\sigma = \frac{6k_B^4}{4\pi^3} \sum_{n=1}^{\infty} \frac{1}{(1+\delta)^n n^4} \ll \frac{\pi^2 k_B^4}{60 \pi^3 c^2} \frac{1}{(1+\delta)} =$$

$$\frac{5.669 \times 10^{-5}}{(1+\delta)} \text{ erg-sec}^{-1} \text{ cm}^{-2} \text{ deg.}$$

The obvious next question is what value of δ can be accommodated by the best *experimental* determination σ .

- 2 This is just the form which Koutsoyannis claimed to find.
- 3 A concise summary of the situation is given on page 157 of Cohen, Crowe and DuMond's book *Fundamental Constants of Physics* (Cohen, 1957) where they write "The large uncertainties of more than 0.5% in σ and of about 0.2% in $C_2 (= hc/k)$ render these methods of no value for our purposes."

This question provides an interesting sidelight of this investigation. There have been no recent experimental investigations of the black body spectrum. The best value of σ from experiment is discussed by Birge (Birge, 1929) in the first of a series of articles on the best values of fundamental physical constants. He gives

$$\sigma = (5.735 \pm 0.011) \times 10^{-5} \text{ erg-sec}^{-7} \text{ cm}^{-2} \text{ deg.}$$

In the intervening 45 years there apparently has been only one further experimental measurement.

If the entire discrepancy between theory and experiment is attributed to δ then δ might be as large as 0.07.

It is extremely surprising that a subject like black body radiation which receives prominent discussion in texts on modern physics and statistical mechanics is so poorly known experimentally⁴. The total situation can be summarized in the following summary. The constant in the exponent of the distribution, (C_2) is best known experimentally and was last measured in 1948 (Rutgers, 1949).

The remainder of the experimental situation has been reviewed by Birge (Birge, 1929) and two articles by Coblenz (Coblenz, 1921, 1924). After the application of numerous correction factors the experimental spectral distribution agrees with theory within approximately 1%. These experiments were completed basically in 1913 with analysis continuing on into the early 1920's. The most recent measurement of σ was reported in 1933 (Muller, 1933).

The technological advances of the last 20-30 years should permit a substantial increase in the accuracy of measurement of black body radiation. Renewed experimental interest in this subject is in order.

⁴ A similar observation has been made by H. A. Gebbie et al. (Nature, 240, 391 (1972)). They specifically suggest that with the present state of technology black body radiation could serve as a convenient temperature standard.

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