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Equation (7) is a relativistically invariant general expression for the wavelength shift.

Free Electron

For a free stationary electron $p=0$, $\epsilon=m$, $p^2-\epsilon^2=p'^2-\epsilon'^2=-m^2$, and Eq. (7) reduces to the Compton equation given by Eq. (1). For a free moving electron $p=\gamma m\beta$, $\epsilon=\gamma m$, $p^2-\epsilon^2=p'^2-\epsilon'^2=-m^2$, and Eq. (7) reduces to Eq. (2) as given by DuMond.

Bound Electron

If the electron is not free, but bound to a nucleus $p^2-\epsilon^2\neq -m^2$. The boundedness of the electron may be described as added inertia of the electron. To the incident photon, the electron appears heavier by an amount δm than would a free electron.[10] Invoking the relativistic mass–energy equivalence principle, we write

$$\epsilon^2-p^2=(m+\delta m)^2=(m+\epsilon_b)^2, \tag{8}$$

where ϵ_b is the binding energy (positive) of the electron–nucleus system. From Eq. (8) we have that $\epsilon^2-p^2=m^2+2m\epsilon_b$, and $\epsilon=m+2\epsilon_b$ to first power in ϵ_b. Inserting these values in Eq. (7) yields

$$\lambda'-\lambda=\frac{(2\pi/m)(1-\cos\theta)+(\lambda p/m)(\cos\alpha-\cos\alpha')-\lambda^2\epsilon_b/2\pi}{1+(2\epsilon_b/m)-(p/m)\cos\alpha+\lambda\epsilon_b/2\pi}. \tag{9}$$

Equation (9) clearly shows the Compton, broadening, and defect terms, and for $\lambda\epsilon_b/2\pi\ll 1$, $m\lambda\gg 1$, and $p=0$, it reduces to the form given by Ross and Kirkpatrick.

When only the condition of Ross and Kirkpatrick that $p=0$ is inserted in Eq. (9), the equation differs from Eq. (3) by the terms in the denominator of Eq. (9). Expansion of the denominator and rearrangement of terms shows that our defect term contains explicit dependence on the scattering angle θ as previously suggested by the authors.[1]

[10] This idea was alluded to by H. A. Kirkpatrick and J. W. M. DuMond, Phys. Rev. 54, 802 (1938).

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It is shown that those molecular collisions which tend toward equalization of molecular energies also tend to maximize the phase space available to a closed system. This helps to motivate the hypothesis that a functional relationship exists between the thermodynamic entropy and the available phase space for a closed system. The calculation, simple enough for an introductory course, is also illuminating in itself as an insight into the statistical nature of the second law of thermodynamics.

Classical statistical mechanics can be considered to begin with the postulate[1,2] that the thermodynamic entropy of a closed system is a function of the phase space available to the system. As with all postulates, the justification of this hypothesis rests ultimately upon experimental verification of the predictions deduced from it. Pedagogically, however, at the outset one would like to present as cogent as possible motivation for entertaining this statement as a plausible hypothesis. This article endeavors to strengthen this motivation by showing that in a closed system of particles, those particle collisions which bring the system closer to equilibrium also increase the phase space available

[1] C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1958).

[2] D. K. C. MacDonald, *Introductory Statistical Mechanics for Physicists* (John Wiley & Sons, Inc., New York, 1963).

to the system, while those particle collisions which drive the system farther from equilibrium will decrease the available phase space. This parallels the behavior of the entropy function of thermodynamics and greatly adds to the plausibility of the basic postulate of classical statistical mechanics. Furthermore, the demonstration of this entropy-like behavior of available phase space is simple and easily presented on the undergraduate level. The calculation is also illuminating in itself, apart from its pragmatic use as a motivational argument.

Consider a closed system of two point-particles confined to a volume V and sharing a fixed total kinetic energy. The phase space available to the system is the product of the phase spaces available to each of the particles. Each single-particle phase space is the product of the volume of real space, V, and the amount of momentum space available to the particle. The single-particle momentum space depends upon the energy of the particle and is simply the surface area of a sphere defined by

$$p_x^2+p_y^2+p_z^2=2mE,$$

where m and E are the mass and energy of the particle, and p_x, p_y, and p_z are the Cartesian components of its momentum vector. The momentum space available to this particle is then $4\pi(2mE)$, and the phase space available to it is $V8\pi mE$. Then the phase space available to the system of two particles is

$$V^2 64\pi^2 m_1 m_2 E_1 E_2.$$

If these particles now collide with each other and come away with changed energies, the phase space available to the system changes by

$$d\Gamma = V^2 64\pi^2 m_1 m_2 (E_1 dE_2 + E_2 dE_1).$$

If the system is closed, $dE_1 = -dE_2$, so that

$$d\Gamma = V^2 64\pi^2 m_1 m_2 dE_1 (E_2 - E_1).$$

Now consider what we mean by the phrase "those collisions which bring the system closer to equilibrium." By this phrase we can only mean those collisions which tend to equalize the sharing of the total energy between the two particles, i.e., those collisions in which the more energetic particle loses energy to the less energetic particle. It is certainly possible for the more energetic particle to gain even more energy in a collision, but such collisions drive the system even farther from equilibrium.

The above expression for $d\Gamma$ makes evident that if $E_1 > E_2$ then (although the laws of mechanics allow dE_1 to be either negative or positive) if dE_1 is negative (a change toward equilibrium), then $d\Gamma$ is positive (an increase in the phase space available to the system), while if dE_1 is positive (a change farther from equilibrium) then $d\Gamma$ is negative (a decrease in the phase space available to the system). It is also evident that Γ is maximized when $E_1 = E_2$.

Thus, in the interactions between "hot" and "cold" molecules, there is a direct correlation between progress toward equilibrium and expansion of available phase space. A functional relationship between available phase space and thermodynamic entropy is thus strongly suggested as a plausible hypothesis.

The above very simple analysis also helps to bring home to the student the statistical nature of the second law of thermodynamics. He sees directly that even though collisions in which the "hotter" molecules acquire still more energy are dynamically possible, each such collision constricts the system into a smaller portion of phase space, while equilibrium-producing collisions expand the system into the maximum phase space consistent with the system energy.

Note that the above analysis is not restricted to a two-particle system. The collision considered here could be between any two particles of a many-particle system. Since the phase space of a many-particle system is the product of the single-particle phase spaces, the expression for the change in the system phase space will be the above expression for $d\Gamma$ multiplied by a constant factor. Thus, also for a many particle system the conclusion follows that the system phase space is maximized by equilibrium-producing collisions.

It is of at least academic interest to point out to the student that it is possible for the system phase space to change even though the system energy is conserved, because the system phase space is a function of the product of the particle energies, while the system energy is the sum of the particle energies. As is evident in the calculation, the physical fact that the phase space, and therefore the entropy, of a closed system can change with time rests upon the arithmetic fact that if two quantities change so that their sum is conserved, their product need not be conserved.