CHAPTER IX

Molecular diffraction and the quantum theory of light

79. In the year 1905, Einstein* put forward the hypothesis that the energy of a beam of light is not distributed continuously in space but that it consists of a finite number of localised indivisible energy-bundles or "quanta" capable of being absorbed or emitted only as wholes. The theory had some notable successes to its credit, especially the prediction of the photoelectric equation and the explanation of the phenomena of ionisation of gases by X-rays. Nevertheless it has been felt that very serious difficulties stand in the way of its acceptance. Maxwell's electromagnetic theory conceives the energy of light as distributed in a continuous manner through space and offers a satisfactory explanation of whole groups of phenomena, the mere existence of some of which, especially those classed under the heading of interference and diffraction, seems very difficult to reconcile with the hypothesis of light-quanta. The tendency has therefore been to regard the propagation of light in space as determined by Maxwell's equations, but that these equations for some reason or other fail when we have to deal with the emission or absorption of energy from atoms or molecules. The discontinuity is thus conceived to be limited to the act of emission or the act of absorption or of both. Historically, the quantum hypothesis had its origin in the derivation of Planck's radiation formula, and an assumption that the discontinuity occurs only in emission is apparently sufficient for that limited purpose. Hence, though Planck's hypothesis of quantum emission, reinforced as it has been by the success of Bohr's theory of line-spectra, has passed into general acceptance, Einstein's idea of light-quanta has apparently been regarded as unnecessarily revolutionary in character. This feeling has perhaps been strengthened by the considerable degree of success which has attended the use of the "correspondence-principle" recently introduced by Bohr in which an attempt is made to effect a reconciliation, limited though it be, between Maxwell's theory and the quantum theory of emission of light.

80. If, however, we view the matter from a purely philosophic standpoint, Einstein's original conception of the discontinuous nature of light itself has much to recommend it. It fits in with the assumed discontinuous character of the emission and absorption of energy as part of a consistent and homogeneous
theory, whereas the idea that emission and absorption are discontinuous while
the propagation of light itself is continuous belongs to the class which Poincaré
has described as "hybrid hypotheses." Such a hybrid hypotheses may temporarily
serve as useful planks to bridge gaps in existing knowledge, but there is little
doubt that they must ultimately make way for a more consistent system of
thought. Historically, Maxwell's theory is the embodiment of the belief of
nineteenth-century physicists in the validity of Newtonian dynamics as applied to
physical phenomena in their ultimate analysis, and especially as applied to
phenomena occurring in the medium which was postulated as pervading all
space. The belief in the validity of Newtonian dynamics as applied to the ultimate
particles of matter has however received a rude shock from the success of the
quantum theory as applied to the theory of specific heats, and there seems no
particular reason why we should necessarily cling to Newtonian dynamics in
constructing the mathematical frame-work of field-equations which form the
kernel of Maxwell's theory. Rather, to be consistent, it is necessary that the field-
equations should be modified so as to introduce the concept of the quantum of
action. In other words, the electrical and magnetic circuits should be conceived
not as continuously distributed in the field but as discrete units each representing
a quantum of action, and possessing an independent existence, somewhat in the
manner of vortex rings in a perfect fluid. Interference and diffraction phenomena
may then be conceived of as arising from the approach or separation, i.e. crinkling
of the mean "lines of flow" of energy in the field.

81. Bohr's theory has made the idea familiar that the emission or absorption of
light from the atom or the expulsion of an electron involves something in the
nature of a catastrophic change in the atom itself. If, therefore, we wish to look for
some experimental support for Einstein's conception that light itself consists of
quantum units, we must consider those optical phenomena in which obviously no
such catastrophic change in the atoms or molecules is involved. The molecular
diffraction or scattering of light is obviously such a phenomenon, which stands in
the most intimate relationship with the general theory of the propagation,
reflexion, refraction and dispersion of light. If we found that the phenomena of
molecular scattering of light are completely and satisfactorily explained on the
basis of the classical electromagnetic theory, the case against Einstein's concep-
tion would be enormously strengthened. If, on the other hand, we find that the
classical theory based on the idea of continuous wave-propagation breaks down
and fails to explain the observed facts, we should naturally feel called upon to
revise our ideas regarding the nature of light itself.

82. In view of the foregoing remarks, the fact already mentioned in a previous
chapter that the scattering power of compressed carbon dioxide gas as deter-

matter and of Maxwell's electromagnetic theory of light. It expresses the scattering power of a gas at ordinary pressures correctly, and also the scattering power of liquids with tolerable accuracy. But it fails altogether to express the scattering power of compressed carbon dioxide gas under the conditions of Lord Rayleigh's experiments, that is, when it is in the form of a saturated vapour below the critical temperature. There are three possible alternatives in explanation of this failure: firstly that the derivation of the formula is not valid for some reason or another in the particular conditions of Lord Rayleigh's experiment; secondly that the conceptions of the kinetic theory are invalid under those conditions; thirdly that the continuous wave theory of light does not represent facts.

83. In respect of the alternative explanations referred to in the preceding paragraph, it may be pointed out that the experimentally observed result is precisely what might be expected according to the conception that light consists of discrete quanta moving through space. If we imagine a stream of such quanta passing through a highly compressed gas, scattering of light would result when a quantum encounters a molecule and suffers a large-angle deviation in its path. Such encounters would occur according to the laws of chance; in other words, the molecules should be regarded not as scattering light continuously but only occasionally, and at any instant, only a small proportion of the molecules distributed at random through the gas are in action. Hence the total number of quanta scattered in any appreciable interval of time would be simply proportional to the number of molecules per unit volume, and would be practically independent of the actual manner in which they are distributed in the space, so long as a quantum is regarded as impinging on only one molecule at a time and not on two or more simultaneously. In other words, the principle of additivity of the energies scattered by the individual molecules would be applicable even in the case of a highly compressed gas for which Boyle's law does not apply. This is the result actually obtained, whereas on the continuous wave theory in which all the molecules are conceived of as scattering light all the time, the resultant effect would depend on their distribution in space, and in the case of a highly compressible gas would not be determined by the additive principle. In fact, the observations of Lord Rayleigh were regarded by him as supporting the principle of additivity of the energy-effects of individual molecules, and this principle, as we have seen, cannot be reconciled with the results of the classical wave theory under the conditions of the experiments.

84. Though, *prima facie*, the phenomena of molecular scattering in highly compressed gases seem thus to support Einstein's conception of light-quanta, the cautious reader would naturally wish to make sure that the two alternative explanations of the result suggested above must be excluded. So far as can be judged on the available evidence, neither of the two alternatives seems very probable. In order, however, to exclude them definitely, two series of experiments have been undertaken in the author's laboratory at Calcutta. In the first series of
being made to confirm Rayleigh's result for the scattering by compressed carbon
dioxide and extend it to the case of unsaturated vapours and also to gases at
temperatures considerably above the critical temperature. It is hoped to find the
scattering power of various gases and vapours besides carbon dioxide over a wide
range of pressures and temperatures. If the experiments support Rayleigh's result,
the experimental basis for inferring the failure of the Einstein–Smoluchowski
formula would be greatly strengthened. In the second series of experiments which
has been undertaken by Mr J C Kameswararao, an attempt is being made to
study the Brownian movement quantitatively in gases and vapours under high
pressures, in order to find whether the energy of molecular movement indicated
by the kinetic theory agrees substantially with that found in experiment. The
results of the two sets of experiments may well enable a final judgement to be
arrived at regarding the validity of Einstein's conception of the propagation of
light in quanta.

85. The belief in the correctness of the principles of the wave theory is to a large
extent based on the quantitative agreement between the coefficients of reflexion
and refraction indicated by Fresnel's formulae and those found in experiment.
Already certain failures of Fresnel's formulae are known, as for instance the
existence of reflection at the boundary between two media having equal refractive
index,* and it seems important to make a careful reinvestigation of the
coefficients of reflexion and refraction in various cases, e.g. at the boundary
between a liquid and its vapour slightly below the critical temperature, in order to
find whether the quantitative agreement between the results of the classical wave
theory and the facts is really so brilliant as is generally believed.

86. The phenomena presented by the scattering of the X-rays and especially
the well-known failure to obtain any refraction of X-rays will no doubt have to be
rediscussed in the light of foregoing remarks and the results of the optical
experiments.