The Enigma of Bragg's Law

Sosale Chandrasekhar

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012 (India)

Abstract

It is argued that the fundamental theory of X-ray diffraction is based on a flawed model of wave interference. This is because the macroscopic distances between the crystalline sample on the one hand, and the X-ray source and the detector on the other, cannot be defined to the accuracy of a fractional wave-length. Thus, the inherent 'graininess' of the detector surface does not support the idea of constructive or destructive interference of electromagnetic radiation. This critique then applies equally to the presumed extensions of 'Bragg's Law', particularly the so-called phase problem. The phase problem is thus a theoretical construct that is, practically, an artefact of the Bragg derivation. The Bragg approach, however, has been ingeniously adapted to make contact with the structural theory of chemistry by various guises and protocols. These are, *inter alia*, based on ideas about crystal morphology and internal structure that preceded the Bragg approach. An alternative theory of X-ray scattering, however, needs also to be compatible with the structural theory to be practically meaningful. A model of scattering is proposed herein, that is based on absorption and emission by groups of atoms that are defined by a conventional lattice plane. The Bragg equation is thus re-interpreted as relating the energy of the emitted radiation and the angle of 'reflection'. It is argued that the Bragg approach is essentially empirical, and that its apparent consistency with the structural theory is based on a synergistic evolution of theoretical ideas and experimental observation. In this, therefore, it is not unlike other spectroscopic techniques in common use for structure determination.

Introduction

Roentgen's discovery of X-rays in 1895 was a watershed in the history of science, as it was to have far-reaching practical consequences, particularly in medicine and chemistry. Whilst the applications of X-rays in medicine are now part of popular lore, their applications in chemistry involve an intellectually formidable corpus of theories and protocols. The diffraction of X-rays by crystalline solids was first suggested by Laue in 1912, and was experimentally demonstrated soon after by Friedrich and Knipping. This was rapidly followed up by a quantitative treatment by W. H. Bragg and W. L. Bragg. The Bragg approach has held sway to this day, and with additional insights and improvements over the decades, defines an intriguing experimental technique that seemingly allows mortal man to peer into the inscrutable world of atoms and molecules.

The Bragg treatment is essentially based on two precedents. Firstly, the theory of the internal structure of crystals as was advanced in the nineteenth century, notably by Bravais. Secondly, the theory of wave diffraction by a suitable grating, usually credited to Huygens in the seventeenth century. The diffraction theory is itself based on the idea of constructive and destructive interference of waves, apparently observed on the surface of water. This was seen to produce alternating patterns of horizontally advancing fronts, which apparently served as the analog for the diffraction of electromagnetic radiation.

Analogies, if not odious, can be misleading. In the above case, in fact, the validity of the converse logic needs to be critically examined: does the existence of an alternating pattern imply its creation by a diffraction phenomenon? Intriguingly, Maxwell's contributions – in apparently substantiating the earlier diffraction theory – perhaps completed a circle. This may well explain the uncritical heralding of the Laue-Bragg approaches in the decades following the discovery by Roentgen.

Whilst this paper is not a critique of the wave theory of energy or matter, certain aspects of the theory as applied to the interaction of X-rays with crystalline solids are critically re-examined, as they apparently disregard elementary scientific principles. One of the perceived strengths of the Bragg approach is its apparent consistency with the classical structural theory of chemistry. Indeed, the use of X-ray diffraction to unravel not just the structures of molecules, but also the intricacies of their mutual arrangement and interaction within the crystal lattice, has become almost commonplace. No praise is too high for this signal achievement, the result of intellectual acumen and practical ingenuity in equal measure (not to mention the power of modern high-speed computing). This critique is not aimed at belittling this honourable endeavour.

However, the existence of an intriguing dichotomy – an apparently egregious flouting of normative logic in step with an elegant experimental technique of supreme consistency – needs to be acknowledged, and if possible, the prevailing ambiguity laid to rest. At the heart of the problem lie fundamental questions concerning human abilities to infer a reality beyond direct sensory perception. Whatever the refinement underpinning the theory of the atomic and molecular world, it remains that the practical consequence of any inquisitive approach must be relatively gross and macroscopic, to allow human perception. Then, can we believe in the existence of an interface between two phenomenally different realms of space and time – say, an experimental technique that mediates faithfully between the atomic world and the normal human world? How much of the original refinement is sacrificed in the transduction process? The answer is far from simple, as the discussion below shows.

Discussion

Statement of the problem

The Bragg derivation is based on the idea of reflection of X-rays by planes of atoms within the crystal lattice (Fig. 1). It begins by calculating the difference in path lengths for the case of two successive parallel planes, and posits that this must be equal to an integral number of wave lengths (λ) for a strong reflection to be observed at the indicated glancing angle (θ). This is because only then would there be constructive interference involving the two wave fronts, with a summation of intensity. This leads, *via* elementary trigonometry, to the famous Bragg's law (Eq. 1, d being the inter-planar spacing).

$$n\lambda = 2d\sin\theta \tag{1}$$

Although this is unassailable as a theoretical construct, it is practically improbable as an explanation for the observed lines. This is simply because it is impossible to define the path-length difference to the level of accuracy of a wave length. This is a consequence of the fact that the surface of the detecting screen cannot be defined to the level of accuracy of a wave length. Thus, the surface has an inherent 'graininess' that would be orders of magnitude greater than the wave length of X-rays (λ) as also the inter-planar spacing (d).

This implies that the macroscopic distance between the crystal planes and the detector screen would have an error far exceeding a wave length. This error would then be carried over to the difference between the distances. It needs to be appreciated that the above surface 'graininess' implies that the idea of constructive interference is meaningless, and consequently Eq. 1 does not possess its assumed significance. These arguments are made clear in Fig. 2, which includes the 'graininess' in the conventional derivation of Bragg's law.

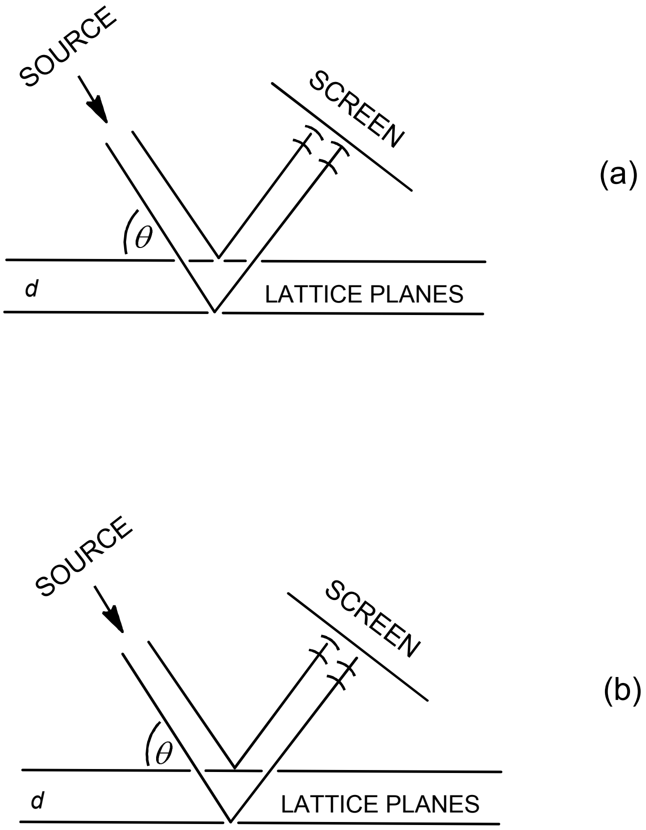

Fig. 1. The conventional Bragg treatment of X-ray scattering, leading to Eq. 1; (a) represents the in-phase approach of the scattered rays towards the detecting screen (leading to constructive interference); (b) represents the corresponding out-of-phase approach

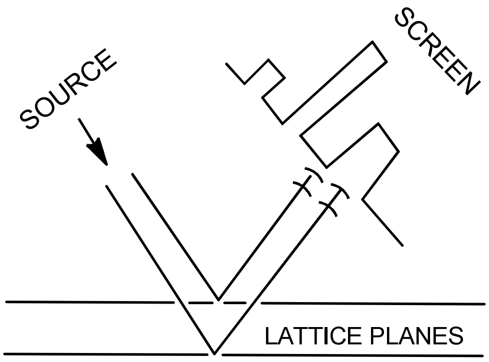

Fig. 2. Representation of the flaw in the conventional derivation of Bragg's law (*cf.* Fig. 1), depicting the 'graininess' of the detector surface (screen), which far exceeds the wave-length of the X-rays and the inter-planar spacing (*d*)

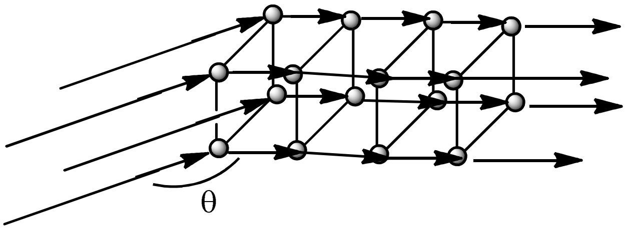

Fig. 3. Depiction of X ray scattering *via* a reinforcement mechanism by groups of atoms in a crystal lattice, which possibly absorb and re-emit in unison

An alternative interpretation

The above collapse of the conventional Bragg treatment raises the question of an explanation for the 'diffraction pattern' observed when X-rays impinge upon a crystalline substance. In fact, another objection to the Bragg treatment is particularly noteworthy at this juncture. This concerns the assumption of 'reflection'. Although the original derivation was based on the classical model of mirror reflection – replete with the equating of the angles of incidence and reflection – modern extensions apparently invoke scattering by electrons. However, these retain the quintessential character of the original derivation.

In fact, not only is there no evidence to support the mirror-reflection model, it also apparently conflicts with much that is now known about the interaction of radiation with matter. In general, the emission of radiation is isotropic relative to the preceding absorption event. Also, the mirror-reflection model is perhaps compatible with the corpuscular theory of radiation, but is difficult to justify in any treatment involving a wave model.

An interesting alternative possibility is based on an absorption-emission model. In this, the incident X-rays are absorbed and re-emitted by groups of atoms (Fig. 3). These groups correspond to the (parallel) lattice planes in the conventional Bragg treatment. This possibly implies a resonant condition, with a three-dimensional block of atoms emitting in unison, at a defined angle relative to the incident rays.

$$(nch)/2d = E\sin\theta \tag{2}$$

Interestingly, Eq. 1 may be recast in terms of energy (E) to arrive at Eq. 2, both sides of which possess units of energy. (Note: $E = h\nu = hc/\lambda$, c being the velocity of light). As $0 \leq \sin\theta \leq 1$ and (nch) is constant, Eq. 2 relates the spacing factor d inversely to a depletion of the original energy (E) (except for $\theta = 90^o$). This possibly indicates that emission from a closely packed layer of atoms (small d) relates to a higher energy of emission. Also, lines farthest from the source involve the least energy as they are produced from low glancing angles. These features seem to support the above idea of a resonant emission in unison.

It is worth stating that what is being questioned herein is not the theory of interference itself. It is perhaps possible – in principle – for closely spaced parallel rays of electromagnetic radiation to interfere, whether constructively or not, in the manner proposed in the Bragg approach. However, the substance of this critique is that the effect cannot be captured as proposed, for the aforementioned reasons. (Note that the mirror-reflection model is itself dubious, so the proposed interference model is also unlikely as the origin of the effect.)

The 'Phase Problem'

Bragg's law (Eq. 1) itself sets the stage for the unfolding of an involved and sophisticated series of protocols designed to unravel the details of the internal structure of the crystal being studied. These protocols are based on the idea that each reflection represents a lattice plane from which it originates, the entire crystalline lattice being obtained by the 3-dimensional translation of a standard repeat unit (the unit cell). The unit cell is accurately described in terms of the Miller indices *(h, k, l)* assigned to the various atomic planes contained within it. Each of the Miller indices is the reciprocal of the fraction of a side of the parallelepiped unit cell that is formed by the intersection of the side and the plane in question. Relationships between the various possible crystalline unit cells (Triclinic, Cubic, etc.), and the expected reflections may be derived by geometric reasoning. This leads to the identification of the planes in terms of their *(h, k. l)* values, the corresponding glancing angles θ and the inter-planar spacing values (d) by Eq. 1.

The above 'indexing of the reflections', however, does not lead to the atomic positions *per se*. In order to obtain these, the electron-density distribution within the unit cell needs to be calculated. The amplitude of a wave reflected off a plane is a complex function of the scattering factors of the involved atoms and the phase difference (φ) in their reflections, φ being a function of the *(h, k. l)* values of the plane and the atomic coordinates. This is a general treatment for the case of a partially constructive interference, only a fully in-phase case leading to the maximal reflected intensity.

$$F_{hkl} = \sum_{i} f_i e^{\mathrm{i}(\varphi_i)} \qquad (3)$$

$$[\varphi_i = 2\pi(hx_i + ky_i + lz_i)]$$

The total amplitude, summed over all the i atoms in a plane, is termed the structure factor F_{hkl} (Eq. 3), φ_i being the phase difference in terms of the Miller indices and the atomic coordinates (x, y, z). F_{hkl} can be related to the electron density distribution (ρ) in the unit cell, and expressed as the product $|(F_{hkl})|e^{\mathrm{i}\alpha}$, $|(F_{hkl})|$ being the magnitude and α the phase of the reflected wave. The observed intensities (I), however, may be related only to $|(F_{hkl})|^2$ and do not furnish the phase (α), so ρ cannot be obtained. This then is a statement of the well-known 'phase problem'.

It is noteworthy, however, that the phase problem is never solved in practice, but only circumvented. This is achieved by either the heavy atom method involving the Patterson synthesis, or the more recent 'direct methods'. In the former, a heavy atom derivative rather than the original crystal is employed, and the latter is essentially a trial-and-error approach involving an enormous number of calculations (facilitated by high-speed computers). These exercises, however, are tantamount to deducing the ‘mythical’ phases from the structures deduced otherwise!

Therefore, not only is the phase problem a theoretical construct that is an extended artefact of the Bragg law, but it is also of little practical import as it is circumvented as noted above. Thus, the phase problem is at best an indication of the complex relationship between the electron density distribution and the observed intensities, based on the constructive interference model, now seen to be unviable.

These arguments extend to the calculation of the electron density distribution $\rho(r)$ from the structure factor F_{hkl}, *via* the Fourier synthesis procedure. This, of course, is predicated on the structure factors being known along with their phases, so the procedure is essentially a theoretical construct. (Also, a purely mathematical model, which relates the $\rho(r)$ and F_{hkl} *via* the Fourier transform operation, cannot capture the physical essence of the scattering process!)

Alternative approaches

An alternative theory of X-ray scattering, based on an in-unison absorption-emission model, was discussed above. This, along with the reinterpretation of Eq. 1 in terms of Eq. 2, can merge with the subsequent protocols of the Bragg approach (delineated above). This ‘hybrid’ approach would retain the practical essence of the Bragg method, but imbued with an element of rigor. As mentioned above, any new theory of scattering would have to make contact with the structural theory to be meaningful. The above absorption-emission model achieves this by retaining the classical Bravais models of the crystalline lattice and then merging with the Bragg approach *via* Eq. 2.

Of course, to the extent that the new model is unproven, it too remains empirical. However, it is not logically objectionable (at least not palpably so). These arguments raise the question as to whether the X-ray technique of structure determination should be considered a spectroscopic (or perhaps a spectrometric) technique. Thus, the exercise of indexing the reflections and defining the unit cell is performed in relation to *a priori* ideas involving the Bravais lattices. The calculation of the electron density distribution, designed to extend these ideas, depends on further assumptions involving the structure factors (*vide supra*). Thus, the structural theory is interwoven into the protocols, which evolve iteratively based on analogy – both prior and evolving – between theory and experimental observation.

Bragg's law and the structural theory: an enduring enigma?

The above critique pits itself against the inescapable fact that the Bragg treatment ultimately 'delivers' in terms of the structural theory of chemistry. However, it is noteworthy that this occurs against the backdrop of key enabling assumptions, perhaps most importantly the Bravais model of the internal structure of crystals. Also, the idea of the structure factor, the fulcrum of the Bragg approach, is predicated on employing 'reasonable' values for the atomic coordinates (*cf.* Eq. 3), in consonance with the canons of the structural theory. These approximations apparently streak the method with the brush of empiricism. Although it is not easy to see how else the observed patterns could be rendered meaningful, a re-evaluation of the fundamental theory is equally to be demanded, in the interests of rigor and the scientific truth.

Thus, it is undeniably true that the reflections – whatever their origins – secrete the essence of a chemical structure in a codified form, from which the structure can be recovered by following defined protocols. These, however, were developed with the original Bragg approach, the collapse of which now raises intriguing questions about the validity of the protocols themselves. The ingenious evolution of the technique and its undoubted practical success apparently derive from a modest and possibly flawed theoretical underpinning: A stunning commentary on the scientific method itself that historians and philosophers of science would do well to examine!