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Dispersion Relations and the Phase Problem for the Scattering of Electromagnetic Radiation

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Abstract

The complex amplitude of electromagnetic radiation that is scattered by an object essentially corresponds to the Fourier transform of the charge density if the first Born approximation applies and if the radiation source and the observer are far enough away. It is shown that the phase of a scattered beam principally can be calculated if the dependence of the intensity on the wavelength is known. Special attention is given to the diffraction of X-rays where some experimental difficulties are discovered.

1. Introduction

Structure determinations by means of X-ray diffraction usually rely on the following relation between the complex amplitude F_o of the incoming plane wave and the amplitude F of the diffracted wave observed at a large distance from the scattering object in the direction $\mathbf{k}_1$:

$$F(\mathbf{k}_1-\mathbf{k}_0)=\int f(\mathbf{r})\exp\left[-i(\mathbf{k}_1-\mathbf{k}_0)\mathbf{r}\right]\mathrm{d}^3r\,F_o. \quad (1)$$

The integral extends over the volume of the scattering object, $\mathbf{k}_0$, $\mathbf{k}_1$ are the wave vectors of the incident and outgoing plane waves, respectively, with magnitude $2\pi/\lambda$, $f(\mathbf{r})$ is the scattering strength at the point $\mathbf{r}$ in the medium and it is proportional to the electron density.

Equation (1) may be expected to hold generally for the scattering of electromagnetic waves if absorption and multiple scattering can be neglected (Cowley, 1975). This is known as the first Born approximation or the 'kinematical' or 'single scattering' approximation. Equation (1) tells us that the amplitude of the scattered wave is proportional to the Fourier transform of the charge density. Therefore, in principle, the scattering strength function may be obtained by inverting the Fourier transform:

$$f(\mathbf{r})=\frac{1}{(2\pi)^3}\int F(\boldsymbol{\rho})\exp(i\boldsymbol{\rho}\mathbf{r})\,\mathrm{d}^3\rho, \quad (2)$$

where $\boldsymbol{\rho}=\mathbf{k}_1-\mathbf{k}_0$, F_o is set to unity and the integral is over the complete $\mathbb{R}^3$.

In the case of X-ray diffraction a knowledge of $f(\mathbf{r})$ would give us the electron density at an atomic scale and thus provide all the information necessary to determine the structure of a crystal. Unfortunately, however, in these diffraction experiments only the intensity of the outcoming wave that is proportional to $|F|^2$ can be determined, whereas the phase of the complex amplitude remains unknown. Therefore, it is not possible to apply (2) directly to experimental data without addhe 'kinematical'ion. (For a survey of existing methods see *e.g.* Woolfson, 1970.)

The problem of determining the phase of a complex quantity $A(\omega)$ under the condition that the amplitude can be determined experimentally is also encountered frequently in other fields of physics. Within certain limits it may be treated as a special case of the problem of calculating the imaginary part of a complex function if its real part is known by considering the logarithm of $A(\omega)$. Then it is well known (Toll, 1956) that there exists a relationship between the real and imaginary parts $R(\omega)$ and $X(\omega)$ of a complex function $H(\omega)$ if $H(\omega)$ is the transfer function of a causal linear system, that means it is the Fourier transform of a causal Green function $G(t)$ with the property $G(t)=0$ for $t<0$. Under these conditions $X(\omega)$ and $R(\omega)$ can be shown to be the Hilbert transforms of each other, that is

$$R(\omega)=\frac{1}{\pi}P\int\limits_{-\infty}^{+\infty}\frac{X(\omega')\,\mathrm{d}\omega'}{\omega'-\omega} \quad (3a)$$

$$X(\omega)=-\frac{1}{\pi}P\int\limits_{-\infty}^{+\infty}\frac{R(\omega')\,\mathrm{d}\omega'}{\omega'-\omega}, \quad (3b)$$

where P denotes the Cauchy principal value of the integral, *i.e.* for (3*a*):

$$R(\omega)=\frac{1}{\pi}\lim_{a\to 0}\left[\int\limits_{a}^{\infty}\frac{X(\omega')\,\mathrm{d}\omega'}{\omega'-\omega}+\int\limits_{-\infty}^{-a}\frac{X(\omega')\,\mathrm{d}\omega'}{\omega'-\omega}\right].$$

The equations (3) are used in optics for example to obtain the imaginary part of the refractive index from the frequency dependence of the real part or the phase of the reflectivity from the absolute value

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(Wooten, 1972); in electronics they relate the phase shift of a linear network to the absolute value of the transfer function (see *e.g.* Papoulis, 1962); and in elementary particle physics dispersion relations like (3) provide a connection between the real and imaginary parts of elements of the S matrix (Wigner, 1964).

However, it seems that dispersion relations have not yet attracted attention as a possible means for solving the phase problem in the diffraction of electromagnetic radiation by atomic systems. It is the purpose of this paper to investigate whether a knowledge of the intensities of the scattered waves in a continuous range of wavelengths may lead to the determination of the phases with the help of dispersion relations like (3).

2. The phase problem

If the diffracted wave is observed in a fixed direction at different wavelengths, (1) may be rewritten to stress the dependence of F on the absolute value k of the difference $\mathbf{k}_1-\mathbf{k}_0=\mathbf{n}k$, where $\mathbf{n}$ is the unit vector in the direction of the difference vector. As $|\mathbf{k}_1|=|\mathbf{k}_0|$, $\mathbf{n}$ depends only on the direction of the incoming beam and on the direction of observation. Then, with $F_\mathbf{n}(k)=F(\mathbf{k})$ (1) becomes

$$F_\mathbf{n}(k)=\int f(\mathbf{r})\exp(-i\mathbf{r}\mathbf{n}k)\,\mathrm{d}^3r. \qquad (4)$$

Now the question arises if the phase of $F_\mathbf{n}(k)$ can be computed if $|F_\mathbf{n}(k)|$ is known for all k. The previous considerations suggest to take the complex logarithm $\ln F_\mathbf{n}=\ln|F_\mathbf{n}|+i\varphi$, where φ is the unknown phase, and then calculate φ using (3*b*) and the relation $F_\mathbf{n}(k)=F_\mathbf{n}^*(-k)$, which holds because $f(\mathbf{r})$ is real ($F_\mathbf{n}^*$ denotes the complex conjugate of $F_\mathbf{n}$). This yields the following expression:

$$\tilde{\varphi}(k)=-\frac{2k}{\pi}\int\limits_0^\infty\frac{\ln|F_\mathbf{n}(k')|\,\mathrm{d}k'}{(k')^2-k^2}. \qquad (5)$$

We have used the notation $\tilde{\varphi}$ instead of φ to stress that (5) cannot give the correct value for φ in every case as $|F_\mathbf{n}|$, and consequently the integral in (5), does not change if $F_\mathbf{n}$ is multiplied by a function whose absolute value equals unity, while the phase is usually changed by such an operation.

Toll (1956) discusses the relationship between $\varphi(k)$ and $\tilde{\varphi}(k)$. He arrives at the conclusion that under certain conditions, which will be given below, the relationship between φ and $\tilde{\varphi}$ can be expressed in the following way:

$$\varphi(k)=\tilde{\varphi}(k)+\xi(k)+\frac{2k}{\pi}\int\limits_0^\infty\frac{\mathrm{d}\alpha(k')}{(k')^2-k^2}+d_0k, \qquad (6)$$

where d_0 is a number and $\alpha(k)$ is a nondecreasing bounded function of k with a derivative that exists and vanishes for almost all k. The integral term containing $\alpha(k)$ relates in our context to infinitely narrow diffraction peaks at a finite number of k values and we shall exclude such cases from this discussion. The meaning of d_0 becomes clear if one recalls the effect on $F_\mathbf{n}$ of a shift of the origin of the coordinate system by a vector $\mathbf{R}$. An inspection of (4) shows that $F_\mathbf{n}(k)$ has to be multiplied by a factor $\exp(i\mathbf{R}\mathbf{n}k)$ in order to take account of this change. This means that the absolute value of $F_\mathbf{n}$ remains unchanged, but the new phase differs from the old one by $\mathbf{R}\mathbf{n}k$. It follows that d_0 can be identified with the product $\mathbf{R}\mathbf{n}$ and the postulate $d_0=0$ fixes the origin of the coordinate system in a certain way with respect to the scattering object. $\xi(k)$ is defined in the following way:

$$\xi(k)=-i\sum_n\ln\frac{k-\mu_n^*}{k-\mu_n}, \qquad (7)$$

where the sum is to contain all the zeros of the analytic continuation of $F_\mathbf{n}(k)$ in the upper half plane [that means all those μ_n with imaginary part greater than zero for which $F_\mathbf{n}(\mu_n)=0$]. It should be noted that $\xi(k)$ is always real if k is real.

Equation (6) holds if the analytic continuation of $F_\mathbf{n}(k)$ in the upper half plane satisfies these conditions:

(i) $F_\mathbf{n}(k)$ is bounded, that is there exists a real number M so that $|F_\mathbf{n}(k)|<M$ for all $k=k_1+ik_2$ with k_1, k_2 real and $k_2\geq 0$.

(ii) $$\int\limits_0^\infty\frac{\ln|F_\mathbf{n}(k')|\,\mathrm{d}k'}{(k')^2+1}<\infty.$$

(iii) $$\sum_n\frac{\operatorname{Im}\mu_n}{|\mu_n|^2}<\infty,$$

where $\operatorname{Im}\mu_n$ denotes the imaginary part of μ_n.

So it only remains to show that $F_\mathbf{n}(k)$ actually satisfies these conditions. For this purpose we write the analytic continuation of $F_\mathbf{n}(k)$ with the notation $k=k_1+ik_2$:

$$F_\mathbf{n}(k_1+ik_2)=\int f(\mathbf{r})\exp(\mathbf{r}\mathbf{n}k_2)\exp(-i\mathbf{r}\mathbf{n}k_1)\,\mathrm{d}^3r. \qquad (8)$$

If $F_\mathbf{n}(k)$ is bounded for real k and if $f(\mathbf{r})$ is nonzero only in a finite region of space, the analytic continuation as given by (8) does not have poles at finite k values, but $F_\mathbf{n}(k)$ may be unbounded for $k_2\to\infty$. Now it can be seen that the asymptotic behavior for $k_2\to\infty$ of the integral in (8) is like

$$C\frac{\exp[(\mathbf{n}\mathbf{r})_{\max}k_2]}{n_xn_yn_zk_2^3}, \qquad (9)$$

where C is a complex number, $(\mathbf{n}\mathbf{r})_{\max}$ is the maximum of all products $(\mathbf{n}\mathbf{r})$ and n_x, n_y, n_z are the x, y, and z components of the unit vector $\mathbf{n}$. It is evident that (9) is only bounded for $k_2 \to \infty$ if $(\mathbf{nr})_{\max} \leq 0$. The logarithm of (9) is

$$\ln C - \ln(n_x n_y n_z) - 3\ln k_2 + (\mathbf{nr})_{\max} k_2. \quad (10)$$

It can be seen that $(\mathbf{nr})_{\max} < 0$ leads to an essentially linear increase of $|\ln F_\mathbf{n}(k)|$ for $k_2 \to \infty$ exactly in the same way as for $(\mathbf{nr})_{\max} > 0$, therefore it only remains to postulate $(\mathbf{nr})_{\max} = 0$. In this case $F_\mathbf{n}(k)$ is still bounded and $|\ln F_\mathbf{n}(k)|$ rises toward infinity only logarithmically as $k_2 \to \infty$. It can be shown (Wooten, 1972) that in such a situation (5) can still be applied.

Geometrically $(\mathbf{nr})_{\max} = 0$ means that the origin of the coordinate system must lie in the plane perpendicular to $\mathbf{n}$, which passes through the point(s) of the scattering object, which is (are) next to an observer looking at the object in the direction $-\mathbf{n}$. This is illustrated in Fig. 1 for two dimensions and a triangular object. In this example the origin must be situated somewhere at the straight line g perpendicular to $\mathbf{n}$. It should be noted, however, that in this example there are actually only three different locations for the origin necessary: point C for all $\mathbf{n}$ in section III, point A for section I and B for section II.

Resuming, one may say that condition (i) is fulfilled by choosing the origin of the coordinate system so that $(\mathbf{nr})_{\max} = 0$. It should be recalled that this can be obtained only if the scattering object is finite. In this case (6) holds with $d_0 = 0$. If the scattering object is a polyhedron there exists for every $\mathbf{n}$ a vertex so that $(\mathbf{nr})_{\max} = 0$ if the origin is placed at this vertex. If the object is 'smooth', for each $\mathbf{n}$ there will be usually a different origin so that $\varphi(k) = \tilde{\varphi}(k) + \xi(k)$, but the plane in which it must be contained is still uniquely determined by the shape of the object.

Condition (ii) restricts the class of allowed diffraction amplitudes $F_\mathbf{n}(k)$. As knowledge of $F_\mathbf{n}(k)$ is needed only for real k, which is experimentally accessible, (ii) can and should be checked directly in each individual case.

Condition (iii) points to a serious difficulty that is encountered in our approach to the phase problem: it is not possible to determine the zeros μ_m of $F_\mathbf{n}(k)$ in the upper half of the complex plane from our knowledge of $|F_\mathbf{n}(k)|$ only for real k and therefore also the correction term $\xi(k)$ principally remains unknown. Fortunately, however, it is possible to see in what way $\xi(k)$ influences $f(\mathbf{r})$. More exactly, we shall derive the way $\xi(k)$ disturbs the projection $p_\mathbf{n}(w)$ of the function $f(\mathbf{r})$ onto an axis parallel to $\mathbf{n}$. $p_\mathbf{n}(w)$ is defined by

$$p_\mathbf{n}(w) = \int_{(\mathbf{nr})=w} f(\mathbf{r})\,\mathrm{d}^2 r \quad (11)$$

and this may be used to calculate $F_\mathbf{n}(k)$ by

$$F_\mathbf{n}(k) = \int_{(\mathbf{nr})_{\min}}^{0} p_\mathbf{n}(w)\exp(-iwk)\,\mathrm{d}w, \quad (12)$$

so $F_\mathbf{n}(k)$ is the one-dimensional Fourier transform of $p_\mathbf{n}(w)$. We define $\tilde{F}_\mathbf{n}$ by

$$\tilde{F}_\mathbf{n}(k) = |F_\mathbf{n}(k)|\exp[i\tilde{\varphi}(k)]$$

and therefore get

$$F_\mathbf{n}(k) = \tilde{F}_\mathbf{n}(k)\exp[i\xi(k)]. \quad (13)$$

Taking into account that $f(\mathbf{r})$ is real and therefore with $\mu_m = x_m + iy_m$ $F_\mathbf{n}(x_m + iy_m) = F_\mathbf{n}(-x_m + iy_m) = 0$, we obtain

$$\exp[i\xi(k)] = \prod_m \frac{(k - x_m + iy_m)(k + x_m + iy_m)}{(k - x_m - iy_m)(k + x_m - iy_m)}. \quad (14)$$

By performing some calculations we realized that each term in the product on the right-hand side of (14) is the Fourier transform of this function:

$$g_m(w) = \begin{cases} \delta(w) + 4y_m\exp(-y_m w) & \\ \quad\times[-\cos x_m w + (y_m/x_m)\sin x_m w] & \text{for } w \geq 0 \\ 0 & \text{for } w < 0. \end{cases} \quad (15)$$

Now we apply the convolution theorem, which states that the Fourier transform of the convolution integral of two functions equals the product of their Fourier transforms to obtain

$$p_\mathbf{n}(w) = \tilde{p}_\mathbf{n}(w) \underset{m}{*} g_m(w), \quad (16)$$

where $\tilde{p}_\mathbf{n}(w)$ is a function such that $\tilde{F}_\mathbf{n}(k)$ is its Fourier transform, $*$ designates the convolution, which is defined as

$$\tilde{p}_\mathbf{n}(w) * g_m(w) = \int_{-\infty}^{+\infty} \tilde{p}_\mathbf{n}(w')g_m(w - w')\,\mathrm{d}w', \quad (17)$$

and it should be recalled that the associative law holds. Thus, $p_\mathbf{n}(w)$ is related to $\tilde{p}_\mathbf{n}(w)$ by the convolution integral

$$p_\mathbf{n}(w) = G(w) * \tilde{p}_\mathbf{n}(w), \quad (18)$$

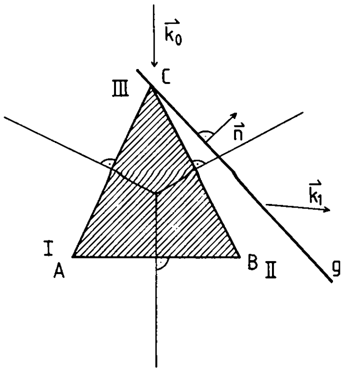

Fig. 1. An incoming plane wave with wave vector $\mathbf{k}_0$ is scattered by a triangular object in the direction $\mathbf{k}_1$. In a Fourier synthesis of the charge density inside the triangle from the scattered amplitudes $F(\mathbf{nk})$ the origin of the coordinate system will be located at g if the phase is computed from the intensity data by the dispersion formula given in the text.

where

$$G(w) = \underset{m}{*}\, g_m(w) = g_1(w) * g_2(w) * \ldots . \quad (19)$$

It should also be noted that $g_m(w)$ approaches the δ function as $y_m \ll 1$ or $y_m \gg 1/w_0$, where w_0 is a distance over which $p_\mathbf{n}(w)$ does not change significantly. If this holds for all the zeros of $F_\mathbf{n}(k)$ and for all $\mathbf{n}$, $G(w)$ would be approximately the δ function, $p_\mathbf{n}(w)$ would be equal to $\tilde{p}_\mathbf{n}(w)$ and $f(\mathbf{r})$ would be correctly given by the inverse three-dimensional Fourier transform of $\tilde{F}(\mathbf{k})$ as $f(\mathbf{r})$ is uniquely determined if $p_\mathbf{n}(w)$ is known for all $\mathbf{n}$. But even if $G(w)$ differs remarkably from the δ function its effect is essentially a 'blurring' of $\tilde{p}_\mathbf{n}(w)$ and therefore it may be expected that $\tilde{p}_\mathbf{n}(w)$ still contains essential features of $p_\mathbf{n}(w)$. In particular, if $p_\mathbf{n}(w)$ consists of a series of sharp peaks that are separated by comparatively small values of $p_\mathbf{n}(w)$ it is expected that the position of the peaks is still recognizable in $\tilde{p}_\mathbf{n}(w)$. Unfortunately, for each $\mathbf{n}$ there will be in general a different 'blurring' function $G(w)$ acting on $\tilde{p}_\mathbf{n}(w)$, but if in all these cases the positions of the peaks is preserved so will they be in the reconstruction of $f(\mathbf{r})$. This is of special importance if the problem consists in the determination of atomic structures by X-ray diffraction.

3. X-ray diffraction at single crystals

We have seen that in principle it is possible to calculate the phase of a diffracted beam from the frequency dependence of its intensity. Now the question arises of whether it is possible to use our results for the calculation of the phase in the case of X-ray diffraction at single crystals. The important difference from the situation that we have discussed before is that a single crystal gives rise to diffraction peaks only for discrete $\mathbf{k}$ vectors $\mathbf{n}k_m = \mathbf{k}_m$. Therefore, (5) certainly cannot be applied directly as the integral obviously is divergent. Now it might be supposed that these peaks at discrete $\mathbf{k}$ vectors are exactly what is meant by the third term at the right-hand side of (6). Unfortunately, however, (6) is valid only if conditions (i) to (iii) are satisfied. The reason why diffraction occurs only at discrete $\mathbf{k}$ vectors is that to a very good approximation a crystal is a periodical object with infinite extension. In the preceding paragraph we have seen that the scattering object must have a finite volume if the analytic continuation (8) is to exist and condition (i) is to be satisfied. Therefore, condition (i) is violated by diffraction at a monocrystal and consequently (6) must not be used. It seems that the third term in (6) does not have a physical meaning in the context of elastic scattering.

We could try to solve the problem by insisting on the fact that the crystal, in reality, of course is finite. In this case we acknowledge that the intensity is not really zero between the difraction peaks, but it is very small and changes rapidly as a function of $\mathbf{k}$. In principle, (5) could then be used, but as the integral in (5) depends on the logarithm of the intensity, we realize that the integral is determined mainly by the small intensity values, which yield a large absolute value of the logarithm. As there is little hope that it will be possible to detect these small intensities with sufficient accuracy, this idea also fails.

A different situation arises if the part of the crystal that is contained in the X-ray beam consists only of a few unit cells. Then the periodicity would be practically hidden and the results of the preceding paragraph could be applied directly. This could be achieved principally by using a thin monocrystalline film of the material under investigation and by focusing the incident X-rays at a spot on the film with a diameter of about 100 times the X-ray wavelength. This is possible from the point of view of a physicist, but the main technical obstacle is that no efficient focusing devices for X-rays seem to exist.

To resume, it should be recalled that no connection between phase and amplitude exists with an infinite scattering object as a consequence of condition (i). As long as an experimental technique is used whose results can be explained adequately by the assumption of an infinite object, it cannot be expected to extract information about the phase. The essential difficulty in applying the ideas that are described in this paper to diffraction by single crystals is because these experiments usually correspond in good approximation to scattering by an infinite object. Some proposals to deal with this problem were discussed but at present do not seem realistic.

It is, however, obvious that the experimental constraints are not founded on any law of physics and the procedures are not far from feasibility. As it was not possible to describe a safe procedure for solving the phase problem for diffraction at single crystals, this work is intended only to draw attention to dispersion relations as a possible and promising tool for this task.

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