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Effect of a Choleresteric Texture on X-ray Diffraction Patterns from Liquid Crystalline Polypeptides

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Calculation is made of the effect on the X-ray diffraction pattern obtainable when a cholesteric twist is superimposed on the otherwise ordered packing of rod-like molecules. Reflections corresponding to repeats along the twist axis are unaffected, but the intensity of all other reflections is reduced by a factor that depends, among other parameters, upon the size of the coherent domain. The results are illustrated with numerical values that apply to the solutions of poly-γ-benzylglutamate previously studied by Robinson and others.

INTRODUCTION

The technique of X-ray diffraction is often employed for the study of structure of liquid crystalline substances, and the subject has been recently discussed by McMillan.[1] Because of the much reduced degree of order present in these as compared to crystalline solids, the information that can be gained by the X-ray technique is more limited, and interpretation of the results is often difficult. The

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technique, however, has been found useful when the molecules comprising the liquid crystalline phase are polymeric as, for example, with a polypeptide. Then the order arising from the polymeric structure itself augments the small degree of order normally present in liquid crystalline phases of small molecules, and the X-ray diffraction pattern accordingly contains more information of value. For this reason there are a number of papers published which deal with aspects of X-ray diffraction from polymeric liquid crystals.[2,3]

The X-ray diffraction patterns that are obtained from such materials embody the interference between the diffraction effects due both to the liquid crystalline structure and to the inherent molecular order. It appears that little is known about the result of such interactions. One may ask what kind of change is expected in the diffraction pattern when the material undergoes a phase change from isotropic liquid to liquid crystalline phase or from the latter to a crystalline (or paracrystalline) phase.

In 1958 Robinson[3] studied solutions of poly-γ-benzyl-L-glutamate (PBLG) by X-ray and other techniques and proposed that a local hexagonal order perpendicular to the molecular axis is present even when the solution, on an optical scale, maintains the Grandjean texture of a cholesteric liquid crystal. He showed X-ray diagrams with a definite ring, the spacing of which varies with concentration. The spacing, when extrapolated to 100 percent PBLG, corresponds to the $d_{1\bar{1}0}$ spacing found with solid PBLG films. The finding was later confirmed by Samulski and Tobolsky[4] with solid PBLG films containing varying concentrations of a plasticizer.

In this work we seek to find the effect on the diffraction pattern of superimposing a Grandjean texture upon the local molecular order. For this purpose we calculate the Fourier transform of a structure consisting of long rod-like molecules of uniform electron density in which the long axes of molecules in successive layers are offset from parallel by some small angle. A square of the Fourier transform, which represents the intensity of the diffracted X-rays obtainable from such a collection of molecules, is then compared with the corresponding quantity obtained in the absence of the cholesteric twist.

CALCULATION OF THE INTENSITY RATIO

Model

We consider a collection of rigid, rod-like molecules of unit electron density and length S which are arranged in such a way that the cross section perpendicular to the molecular axis will result in a rectangular net, as shown in Figure 1, if the torsion due to the Grandjean texture is temporarily removed. The spacing along z is c, and along x is a. When the Grandjean twist is present, with the z-axis

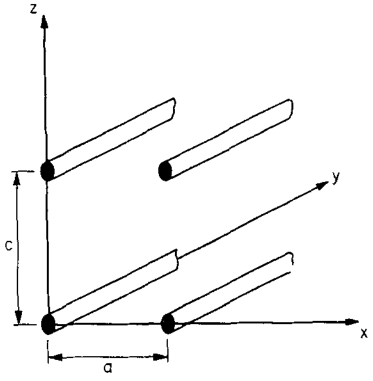

FIGURE 1 Schematic representation of the rectangular packing of rod-like molecules in the absence of the Grandjean twist.

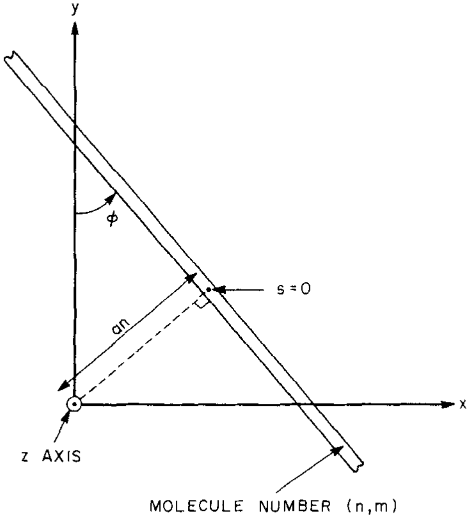

FIGURE 2 Orientation of a molecule in the presence of the Grandjean twist. The position of the molecule is uniquely characterized by a pair of integers, n and m; the z coordinate is then given by cm and φ by $2\pi z/p$.

chosen as the axis of torsion, the orientation of the molecular axis is a function of z:

$$\varphi = 2\pi z/p \tag{1}$$

where p is the period of the Grandjean twist. A molecule in this collection can be uniquely indexed by a pair of integers (n,m) where $z = cm$ and the distance to the molecule from the z axis is given by an (see Figure 2). The cartesian coordinates of a point on a molecule are then expressed as

$$x = an \cos\varphi - s \sin\varphi \tag{2}$$

$$y = an \sin\varphi + s \cos\varphi \tag{3}$$

where s is the distance measured along the molecule (with $s = 0$ taken as the point nearest the z-axis).

The Fourier transform of such a structure, evaluated at a point $\mathbf{R} = (X, Y, Z)$ in reciprocal space, is given by

$$T(\mathbf{R}) = \sum_{n=1}^{N} \sum_{m=1}^{M} \int_{-S/2}^{S/2} (\exp 2\pi i \mathbf{r}\,\mathbf{R})\, ds \tag{4}$$

where $\mathbf{r} = (x, y, z)$ is a point on the molecular axis, and the summation is over all the molecules in the collection. N is the number of molecules in the xy- plane, M is the number of molecular layers along the z- axis in a block, and S is the molecular length. Substitution of (2) and (3) into (4) leads to

$$T(\mathbf{R}) = \sum_{m} (\exp 2\pi i \cdot cm \cdot Z)\; A(m) \cdot B(m) \tag{5}$$

where

$$A(m) = \sum_{n} \exp\left[2\pi i \cdot an\,(X \cos m\psi + Y \sin m\psi)\right] \tag{6}$$

$$B(m) = \int \exp\left[2\pi i \cdot s\,(Y \cos m\psi - X \sin m\psi)\right] ds \tag{7}$$

and

$$\psi = 2\pi c/p \tag{8}$$

The intensity of the X-rays diffracted from the collection of molecules is given by $|T(\mathbf{R})|^2$. The X-ray intensity observed in experiments, on the other hand, is usually a function of two variables, Z and Θ, only (Θ being the polar angle of $\mathbf{R}$), because of the rotational symmetry about the Z-axis. Such rotational symmetry arises from the presence, within the volume of liquid crystal irradiated by the X-rays, of a large number of "blocks" of molecules, each differing in the rotation around z, and also by temporal averaging during the time of X-ray measurements. Thus the observed intensity of the diffracted X-rays is proportional to

$$I(Z, \Theta) = \frac{1}{2\pi} \int_{0}^{2\pi} |T(\mathbf{R})|^2 \, d\Phi \tag{9}$$

where Φ is the azimuthal angle of $\mathbf{R}$.

Equation (9) can be evaluated by inspection for the special case of $\Theta = 0$ and is given by

$$I(Z, 0) = S^2 N^2 M^2 \tag{10}$$

when Z is equal to an integral multiple of $1/c$. Equation (10) states that the diffraction corresponding to repeats along the twist direction is unaltered by the presence of the twist, and its intensity is proportional to the square of the sum of the electron density.

We are interested in finding the dependence of $I(Z,\Theta)$ on ψ, the angle of twist per unit translation along z axis. Instead of $I(Z,\Theta)$ itself, we will therefore evaluate the normalized intensity

$$Q(Z,\Theta) = I(Z,\Theta)/I_0(Z,\Theta) \tag{11}$$

where I_0 (Z, Θ) is the value of I (Z, Θ) at $\psi = 0$. $Q(k/c, 0)$ is then equal to 1, k being an integer.

Evaluation of $Q(Z,\Theta)$

Inspection of Eq. (5) with $\psi = 0$ shows readily that the value of $I_0(Z,\Theta)$ is very small except when $Z = k/c$ and $Z \cos\Theta = h/a$, k and h being integers. This of course represents the condition of diffraction from an ordered structure. $Q(Z'\Theta)$ is therefore meaningful and will be evaluated only for these discrete values of Z and Θ.

By substituting Eq. (5), (6) and (7) into (9) and making the transformation from (X,Y,Z) to (Z,Θ,Φ), we obtain

$$I(Z,\Theta) = \frac{S^2N^2}{2\pi}\int_0^{2\pi} \sum_{m_1}\sum_{m_2} f_c(\Phi-\psi m_1) f_c(\phi-m_2) f_s(\Phi-\psi m_1) f_s(\Phi-\psi m_2)\,d\Phi \tag{12}$$

where the functions f_c (χ) and f_s (χ) are defined by

$$\begin{aligned} f_c(\chi) &= \frac{1}{N}\sum_n \exp(2\pi i\cdot hn\cdot\cos\chi) \\ &= \frac{\sin(N\pi h\cos\chi)}{N\sin(\pi h\cos\chi)} \end{aligned} \tag{13}$$

and

$$\begin{aligned} f_s(\chi) &= \frac{1}{S}\int_{-S/2}^{S/2} \exp[2\pi i\,(h/a)\cdot\cos\chi\cdot s]\,ds \\ &= \frac{\sin[S\pi(h/a)\sin\chi]}{S\pi(h/a)\sin\chi} \end{aligned} \tag{14}$$

Employing the following shorthand notations

$$\chi_1 \equiv \Phi - \psi m_1 \tag{15}$$

$$\Delta m = m_2 - m_1 \tag{16}$$

$$f(\chi) = f_s(\chi) f_c(\chi) \tag{17}$$

Equation (12) can be rearranged to

$$\begin{aligned} I(Z,\Theta) &= \frac{S^2N^2}{2\pi} \sum_{m_1} \sum_{m_2} \int_0^{2\pi} f(\chi_1) f(\chi_1 - \psi\Delta m)\, d\chi_1 \\ &= S^2N^2M \int_0^{2\pi} [f(\chi_1)]^2\, d\chi_1 \\ &\quad + S^2N^2 \cdot 2 \sum_{j=1}^{M-1} (M-j) \int_0^{2\pi} f(\chi_1) f(\chi_1 - j\psi)\, d\chi_1 \end{aligned} \tag{18}$$

By letting $\psi = 0$ in (18) we obtain $I_0\ (Z, \Theta)$, and therefore $Q\ (Z, \Theta)$ is given by

$$Q(Z,\Theta) = \frac{1}{M}\left[1 + 2\sum_{j=1}^{M-1}\left(1 - \frac{j}{M}\right) g(j\psi)\right] \tag{19}$$

where

$$g(\alpha) = \frac{\int_0^{2\pi} f(\chi) f(\chi-\alpha)\, d\chi}{\int_0^{2\pi} [f(\chi)]_2\, d\chi} \tag{20}$$

Approximate values of $g(\alpha)$ can be evaluated readily when the values of various constants such as S/a, N, etc. are confined to the ranges of values which are physically relevant, as is discussed in the Appendix. Referring to the approximate formula for g (α) given there, it is then readily seen that as $j\psi$ becomes larger than $2a/Sh$, the term $g\ (j\psi)$ vanishes until $j\psi$ reaches the vicinity of π. This means physically that the diffraction by molecules in an xy-plane interferes destructively with the diffraction by molecules in other xy-planes unless the angles between them are less than $2a/Sh$. As a result, only a few out of N terms given in Eq. (19) contribute to the summation.

DISCUSSION

First we present some numerical results to illustrate the magnitude of Q obtainable from Eq. (19). For this we take the values of the physical constants which are relevant to the solution of PBLG described by Robinson.[3] The ordered arrangement of rod-like PBLG molecules in the solution is such that, when the cholesteric twist is absent, the cross section by a plane perpendicular to the molecular axis will show an approximately hexagonal array of molecular axes. Although the results in the previous section were derived for a rectangular arrangement of rod-like molecules, the results can be applied to a hexagonal net with only minor modifications, since a hexagonal net can be represented as a staggered superposition of two rectangular nets. There are two possible directions of

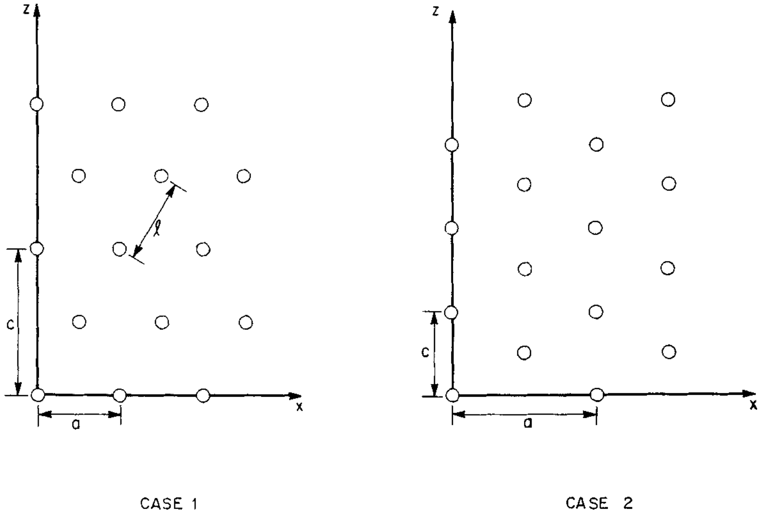

FIGURE 3 Diagrams illustrate the two possible orientations[3] of the twist axis in relation to the hexagonal net present in liquid crystalline solutions of PBLG.

the torsion axis with respect to the hexagonal net, referred to as Cases 1,and 2 by Robinson[3], and illustrated in Figure 3. If l is the distance between the nearest neighbors, then in Case 1, $a = l$ and $c = \sqrt{3}l$, while in Case 2, $a = \sqrt{3}l'$ and $c = l$. The lowest order reflection in the direction perpendicular to the torsion axis then corresponds to the spacing of $l/2$ in Case 1 and $(\sqrt{3}/2)l$ in Case 2. Taking the values of $l = 22$ Å and $p = 4\ \mu$, the calculated values of the Q for these "equatorial" reflections are shown in Figure 4 as a function of S and M for these two cases. (N is always taken to be equal to S/a). The block of molecules under consideration, of volume approximately equal to $S{\cdot}aN{\cdot}cM$, constitutes a domain from which difracted X-ray beams interfere coherently, and Figure 4 shows that as the size of the domain is increased the value of Q is reduced.

The results given above were obtained with a model in which molecules having no structural detail are separated from each other in a strictly ordered manner. Real liquid crystalline materials, even of helical rod-like polypeptides, deviate from this ideal model because of the structural regularity along the direction of the molecular axis and also because the ordering of neighboring molecules is not as regular as is depicted here. But as long as we are concerned with the effect of the cholesteric twist and the basis of comparison is taken as the structure which is identical except for the twist, conclusions that can be drawn from Eq. (19) should be still valid. When the molecules constituting the liquid crystalline phase are of small size and cannot be regarded as long rod-like

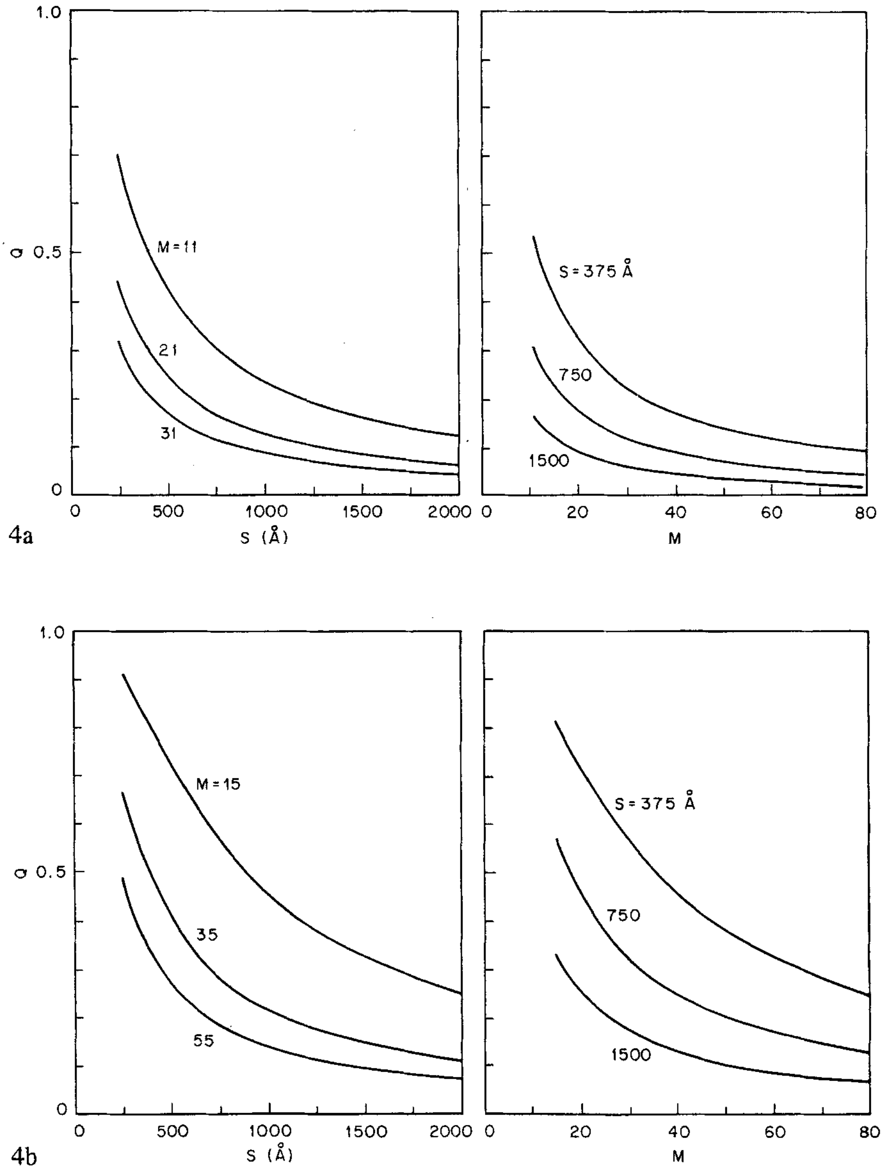

FIGURE 4 Values of Q calculated by Eq. (19) are plotted against S and M. The values of constants were chosen to apply to the solutions of PBLG, with (a) representing Case 1 and (b) Case 2. The Q values given refer to those for the first order equatorial reflections of Bragg spacing 11 Å in Case 1 and 19 Å in Case 2.

molecules, the concept of the coherent domain becomes somewhat ambiguous. In order to carry out a calculation similar to that shown here, one then has to make a more specific assumption concerning the arrangement of these small molecules in the plane perpendicular to the twist axis. Even in such cases the overall qualitative results are expected to be similar to the one in this work. The mathematical technique employed here could probably be employed with some modifications.

Returning to the solution of PBLG, we employ the result of the previous section to determine whether the direction of torsion is in fact as represented by Case 1 or Case 2. The clue here is to find out which of the two reflections corresponding to the spacings of 11 and 19 Å is equatorial – with consequent reduction in its intensity – in the presence of the twist. The extent of the intensity reduction depends on the size of the coherent domain. The molecular weight of the PBLG sample emplyed by Robinson corresponds to $S \approx 400$ Å. A crude estimate of the lower bound to the dimension cM can be obtained from the line broadening of the reflections by $\lambda/\beta \cos\theta$, where λ is the wavelength, θ half the scattering angle, and β the angular width of the diffraction line radians.[5] From the line width of the 19 Å reflection in the photograph given by Robinson[3], we estimate cM to be no smaller than 750 Å (or $M \geqslant 20$) if the torsion axis is as in Case 1. for these S and M, the Q value for the 11 Å reflection is calculated to be 0.3. Robinson's photograph shows a single ring of spacing 19 Å and is therefore consistent with Case 1. If the torsion axis were as in Case 2, however, we would expect to find a reflection at 11 Å. For a more positive conclusion one would need an X-ray photograph taken from an isotropic of PBLG for comparison.

There has recently been much interest[6] in textures of possible liquid crystalline origin in solid films of PBLG containing 0 to 30 percent plasticizer (3,3′-demethylbiphenyl). It is expected that reexamination of these films in light of the present results will lead to resolving some of the ambiguities left unanswered before.

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Appendix

APPROXIMATE EVALUATION OF THE FUNCTION g (a)

The function $f(\chi)$ occurring in the definition of g (a) in Eq. (20) consists of a product of two functions, f_s and f_c, both of which are peaked at $\chi = 0$, with f_s $(0) = f_c$ $(0) = 1$. The behavior of these two functions is illustrated in Figure 5 for $S/a = 25, N = 25$, and $h = 2$. The width of the peak, defined as the smallest positive zero of $f_s(\chi)$ or $f_c(\chi)$, is given by

$$\delta_s = \sin^{-1}(a/Sh) \approx a/Sh \qquad \text{(A1)}$$

and

$$\delta_c = \cos^{-1}(1-1/Nh) \approx (2/Nh)^{\frac{1}{2}}. \qquad \text{(A2)}$$

When S/a is comparable to N, so that the block of molecules we are considering is approximately cylindrical, and when both S/a and N are much larger than 1, δ_s is much smaller than δ_c. As is evident from Figure 5, in fact, $f_c(\chi)$ scarcely deviates from unity over the region $(-\delta_s, \delta_s)$. Thus in evaluating $f(\chi)$ for the present purpose, $f_c(\chi)$ can be neglected and $f(\chi)$ equated to $f_s(\chi)$ to a good approximation.

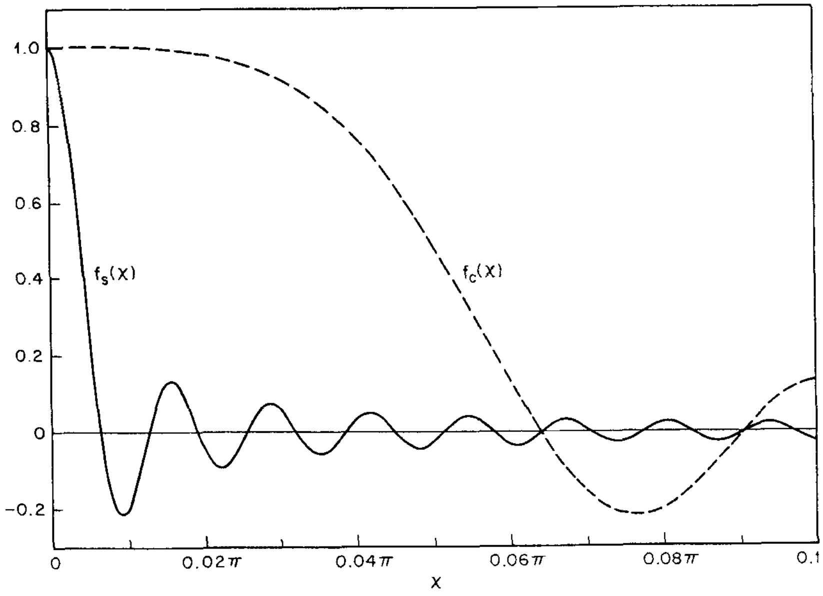

FIGURE 5 Plot of $f_s(\chi)$ and $f_c(\chi)$ for $S/a = 25$, $N = 25$ and $h = 2$.

The function $f_s(\chi)$ is periodic with a period π. Within the interval $(-\frac{1}{2}\pi, \frac{1}{2}\pi)$ there is a major peak of height unity at $\chi = 0$, and a large number of minor peaks of alternately positive and negative heights (see Figure 5). When the absolute values of the areas bounded by the minor peaks and the χ-axis are summed, the total is only about one fourth of the area under the major peak. Moreover, the width of the minor peaks is δ_s while that of the major peak is $2\delta_s$. The integrand appearing in the numerator of $g(\alpha)$ in Eq. (20) is a product of two $f(\chi)$ functions displaced from each other by α. Because of the small size of the minor peaks, their mutual product contributes very little to the integral. A product of the major peak with minor peaks also contributes negligibly to the integral because within the width of the major peak of $f(\chi)$ there are two minor peaks of $f(\chi\text{-}\alpha)$ of opposite signs. Thus the minor speaks in $f(\chi)$ can be entirely neglected without significant error. In the denominator of $g(\alpha)$ the integrand is a square of $f(\chi)$, and the contribution to the integral by the minor peaks after squaring is only about 10 percent of the total. Thus in the denominator, too, the minor peaks in $f(\chi)$ can be neglected. The validity of the various approximations indications above can be demonstrated in a more rigorous manner, as is shown elsewhere.[7]

In order to simplify the computation we further approximate the major peak in $f(\chi)$ by a triangle of height unity and basal width, $2\delta_s$. In other words, $f(\chi)$ is now approximated by a function consisting of a series of triangles with peaks at $\chi = l\pi$ $(l = 0, \pm 1, \pm 2,)$ and equal to zero at all values of χ except within the narrow intervals $(l\pi - \delta_s, l\pi + \delta_s)$. The error accruing to $g(\alpha)$ from the above approximation is still fairly small when physically realistic values are substituted to the various physical parameters, such as M, S/a, ψ, etc. A more detailed analysis of the error is given in Ref. 7.

With the above approximations introduced, the integrals in Eq. (20) can be evaluated analytically, and $g(\alpha)$ is then obtained as

$$g(\alpha) = 1 - (3/2)\,(Sh\,[\alpha]\,/a)^2 + 3/4\,(Sh\,[\alpha]\,/a)^3 \quad \text{for } |\,[\alpha]\,| \leqslant \delta_s \qquad \text{(A3)}$$

$$g(\alpha) = 2 - 3(Sh\,[\alpha]\,/a) + (3/2)\,(Sh\,[\alpha]\,/a)^2 - (1/4)\,(Sh\,[\alpha]\,/a)^3 \quad \text{for } \delta_s < |\,[\alpha]\,| \leqslant 2\delta_s \qquad \text{(A4)}$$

and

$$g(\alpha) = 0 \quad \text{for } |[\alpha]| > 2\delta_s \qquad \text{(A5)}$$

Where $[\alpha]$ is the "principal" value of α, which is equal to α , $l\pi$ with the integer l so chosen that α - $l\pi$ is within the interval $(-\frac{1}{2}\pi, \frac{1}{2}\pi)$.

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