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The Theory of the Spin-Density Patterson Function

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A general treatment is given of the derivation of a spin-density Patterson function from unpolarized neutron-diffraction data, showing that a peak in the function due to atoms m and n with spins $\mathbf{S}^m$, $\mathbf{S}^n$ has a height proportional to $\mathbf{S}^m \,.\, \mathbf{S}^n$ and is elongated in a direction which bisects these spin directions. The elongation is not appreciably affected even when the spin-density distributions of the atoms are highly aspherical.

Introduction

The essential features of the spin-density Patterson function have been described in a previous paper (Wilkinson, 1968). The purpose of the present paper is to provide a more precise treatment of certain parts of theory in which approximations were previously made. The same notation will again be used.

The Patterson function $Q'(u)$ calculated from unpolarized neutron-diffraction intensities from a single crystal is given by

$$Q'(\mathbf{u}) = Q(\mathbf{u}) - R(\mathbf{u})$$

where $Q(\mathbf{u})$ is the scalar-product autocorrelation function of the spin density:

$$Q(\mathbf{u}) = \sum_{1-3}^{i} \sum_{1-3}^{j} \mathscr{S}_i(\mathbf{r}) * \mathscr{S}_j(-\mathbf{r}) \,.$$

$R(\mathbf{u})$ is the sum of the convolutions of the Fourier transform of the appropriate pairs of scattering-vector direction-cosine products with terms in the summation for $Q(\mathbf{u})$ and is

$$R(\mathbf{u}) = \sum_{1-3}^{i} \sum_{1-3}^{j} \overline{(k_i k_j)} * [\mathscr{S}_i(\mathbf{r}) * \mathscr{S}_j(-\mathbf{r})] \,.$$

In the previous theory for the evaluation of $R(\mathbf{u})$ it was assumed that the form factors for all magnetic atoms in the structure could be represented by the function $\exp(-p^2k^2)$. The present treatment shows that this is an unnecessary approximation, but that the main features of the result (*i.e.* Patterson peak height proportional to the scalar product of component spins, elongation of peak in direction bisecting spin directions) remain unchanged. Expressions for $R(\mathbf{u})$ and $Q(\mathbf{u})$ are derived for two and three-dimensional data in Appendices 1 and 2.

$Q'(\mathbf{u})$ for a zone of data measured out to $|\mathbf{k}| = k_0$

In Appendix 1 it is shown that for two-dimensional data the Patterson peak due to atoms m and n which are separated by a distance $\mathbf{u}^{mn}$ is

$$\begin{aligned} Q'(\mathbf{u}^{mn}+\mathbf{x}) = \operatorname*{Lt}_{k_0\to\infty} \{ & \pi k_0^2 (\Lambda_1(2\pi r k_0) \\ & \times [S_\perp^m S_\perp^n + \tfrac{1}{2} S_\parallel^m S_\parallel^n \cos(\omega_m - \omega_n) \\ & - S_\parallel^m S_\parallel^n \cos(2\alpha - (\omega_m + \omega_n))] \\ & + \Omega(2\pi r k_0) S_\parallel^m S_\parallel^n \cos(2\alpha - (\omega_m + \omega_n)) \\ & * (\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r}))\} \,. \end{aligned}$$

The component functions in this expression require some explanation.

(i) The quantity $\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})$ is similar to that which appears in the expression for Patterson peaks calculated from X-ray intensities. In the two-dimensional case it represents the convolution of the projected spin-density distributions associated with atoms m and n and will in future be abbreviated by $\sigma^{mn}(\mathbf{r})$. It is usually almost spherically symmetric and is relatively insensitive to aspherical parts in $\hat{\mathscr{S}}^m(\mathbf{r})$ and $\hat{\mathscr{S}}^n(\mathbf{r})$.

(ii) The function $\Lambda_1(2\pi rk)$ is illustrated in Fig. 1. It may be shown that $\int_{\text{all space}} \pi k_0^2\ \Lambda_1(2\pi rk_0)\ \mathrm{d}\tau_r \equiv 1$ for any k_0. Thus when k_0 is very large (data from all reciprocal space are included) and $\Lambda_1(2\pi rk_0)$ is consequently sharply peaked at the origin of real space, the convolution involving Λ_1 gives

$$\underset{k_0\to\infty}{\mathrm{Lt}}\ \{\pi k_0^2 \Lambda_1(2\pi rk_0)\ [S_\perp^m S_\perp^n + \tfrac{1}{2} S_\parallel^m S_\parallel^n \cos(\omega_m-\omega_n)$$
$$- S_\parallel^m S_\parallel^n \cos(2\alpha-(\omega_m+\omega_n))] * \sigma^{mn}(\mathbf{r})\}$$
$$=[S_\perp^m S_\perp^n + \tfrac{1}{2} S_\parallel^m S_\parallel^n \cos(\omega_m-\omega_n)]\sigma^{mn}(\mathbf{x})\,.$$

This contribution to $Q'(\mathbf{u}^{mn}+\mathbf{x})$ is therefore an approximately spherically symmetric function of $\mathbf{x}$.

(iii) Similar simplification of the term involving $\Omega(2\pi rk)$ [$\Omega(2\pi rk)$ is shown in Fig. 1] is not possible as the integral $\int_{\text{all space}} \pi k_0^2 \Omega(2\pi rk_0)\mathrm{d}\tau_r$ is not bounded. However, certain features of this term may be noted. It depends upon the product of the planar components of $\mathbf{S}^m$ and $\mathbf{S}^n$. It is highly asymmetric with a cos 2α-type dependence, the positive lobes of the function making an angle $\alpha=(\omega_m+\omega_n)/2$ with axis 1. The radial distribution of the function depends upon the precise nature of $\sigma(\mathbf{r})$ but has value zero at $\mathbf{x}=0$ and falls at large $|\mathbf{x}|$ as $\sigma(\mathbf{r})$ falls off with $|\mathbf{r}|$. The type of spatial variation to be expected from this term is shown in Fig. 2. The $\sigma^{mn}(\mathbf{r})$ used in this case was the autocorrelation function for a Gaussian distribution $\hat{\mathscr{S}}(\mathbf{r})$.

The overall expression for $Q'(\mathbf{u}^{mn}+\mathbf{x})$ is therefore

$$Q'(\mathbf{u}^{mn}+\mathbf{x})=[S_\perp^m S_\perp^n+\tfrac{1}{2}S_\parallel^m S_\parallel^n \cos(\omega_m-\omega_n)]\sigma^{mn}(\mathbf{x})$$
$$+\underset{k_0\to\infty}{\mathrm{Lt}}\ \{S_\parallel^m S_\parallel^n \pi k_0^2 \Omega(2\pi rk_0)$$
$$\times\cos[2\alpha-(\omega_m+\omega_n)]\} * \sigma^{mn}(\mathbf{r})$$

and its main features are

(*a*) A peak height $S_\perp^m S_\perp^n+\tfrac{1}{2}S_\parallel^m S_\parallel^n \cos(\omega_m-\omega_n)\sigma^{mn}(0)$.

(*b*) A peak elongation in the direction of the bisector of the angle between $\mathbf{S}^m$ and $\mathbf{S}^n$.

[$\sigma^{mn}(0)$ varies with the electron distributions of the atoms m, n but is usually $\sim 0{\cdot}75$ for $3d$ electrons.]

$Q'(\mathbf{u})$ for three-dimensional data

In Appendix 2 it is shown that for three-dimensional data

$$Q'(\mathbf{u}^{mn}+\mathbf{x})=\underset{k_0\to\infty}{\mathrm{Lt}}\left\{\frac{4\pi k_0^3}{3}[(\Phi(2\pi k_0 r)-\Theta(2\pi k_0 r))\mathbf{S}^m\,.\,\mathbf{S}^n\right.$$
$$+\{3\Theta(2\pi k_0 r)-\Phi(2\pi k_0 r)\}S^m S^n(\hat{\mathbf{S}}^m\,.\,\hat{\mathbf{x}})$$
$$\left.\times(\hat{\mathbf{S}}^n\,.\,\hat{\mathbf{x}})]\right\} * \sigma^{mn}(\mathbf{r})\,.$$

The functions $\Theta\ (2\pi k_0 r)$ and $\Phi(2\pi k_0 r)$ are shown in Fig. 3. $\sigma^{mn}(\mathbf{r})$ is again very nearly spherically symmetric, despite asphericities in $\hat{\mathscr{S}}^m(\mathbf{r})$ and $\hat{\mathscr{S}}^n(\mathbf{r})$. This is illustrated in Fig. 4 by the {100} section of $\sigma(\mathbf{r})$ for the self convolution of an Fe^{2+} $3d\ e_g$ electron-density

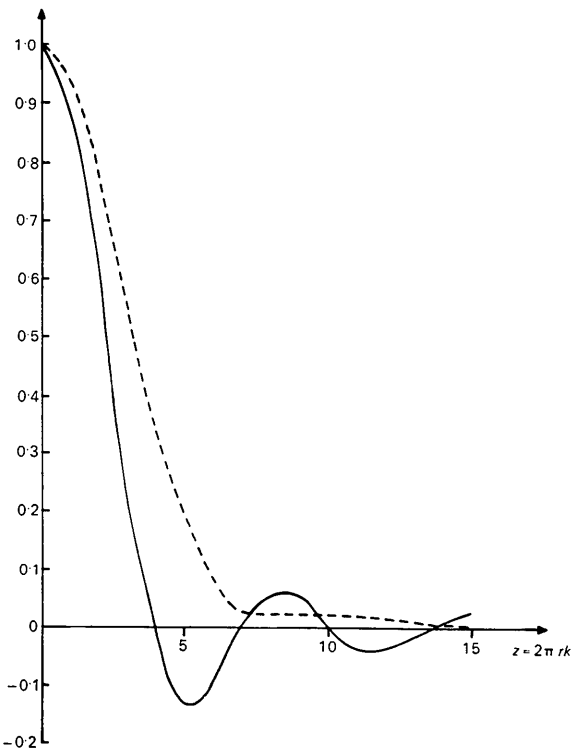


Fig. 1. The functions $\Lambda_1(z)$ and $\Omega(z)$ (dashed curve).

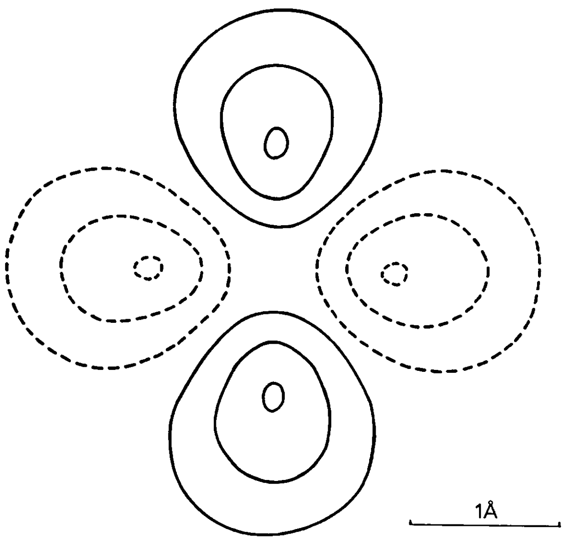


Fig. 2. Contribution to a 2D Patterson peak of the term $\underset{k_0\to\infty}{\mathrm{Lt}}\ \Omega(2\pi k_0 r)\ \{\cos[2\alpha-(\omega_m+\omega_n)]\} * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^m(-\mathbf{r})\}$ for a Gaussian distribution $\hat{\mathscr{S}}^m(\mathbf{r})$. Contours are drawn at intervals of 0·05. The zero contour is omitted.

distribution. Also shown is the same section of the e_g density function. It can be seen that the asphericity is considerably reduced by the convolution. The convolution was performed by transforming the square of the e_g form factor, to which an analytic approximation was made by use of the j_0 and j_4 functions fitted by Lisher & Forsyth (1971) to the calculations of Watson & Freeman (1961).

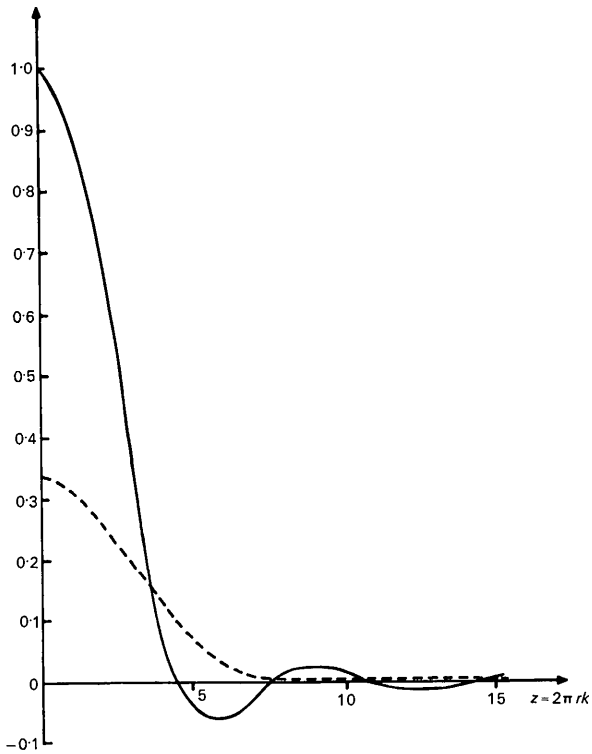


Fig. 3. The functions $\Phi(z)$ and $\Theta(z)$ (dashed curve).

The first term in the expression for $Q'(\mathbf{u}^{mn}+\mathbf{x})$ is therefore nearly spherically symmetric, while the second term is highly aspherical and produces a peak elongation along the bisector of spin direction $\mathbf{S}^m$ and $\mathbf{S}^n$. It can be shown that at $\mathbf{x}=0$ the expression reduces to $Q'(\mathbf{u}^{mn})=\frac{2}{3}\mathbf{S}^m . \mathbf{S}^n\sigma^{mn}(0)$ [$\sigma^{mn}(0)\sim 0{\cdot}71$ for $3d$ electrons].

Discussion and conclusions

The present more rigorous derivation of expressions for the forms of peaks in a spin-density Patterson distribution function has shown the conclusions of the original paper to be correct. The heights of the Patterson peaks are $\frac{2}{3}\mathbf{S}^m . \mathbf{S}^n\sigma^{mn}(0)$ [3D] or $(\mathbf{S}^m . \mathbf{S}^n+\frac{1}{2}\mathbf{S}^m_\parallel . \mathbf{S}^n_\parallel)\sigma^{mn}(0)$ [2D], with $\sigma^{mn}(0)$ usually $\sim 0{\cdot}7$. The elongation of peaks is in the direction of the bisector of the spin directions $\mathbf{S}^m . \mathbf{S}^n$ (or $\mathbf{S}^m_\parallel . \mathbf{S}^n_\parallel$), as $\sigma^{mn}(\mathbf{r})$ is normally an almost spherically symmetric function of $\mathbf{r}$. Convolution of highly aspherical electron-density distributions has shown that the resultant $\sigma^{mn}(\mathbf{r})$ is almost spherically symmetric and therefore the direction of the peak elongation will not be affected by such asphericities.

APPENDIX 1

Q' (u) for a zone of data

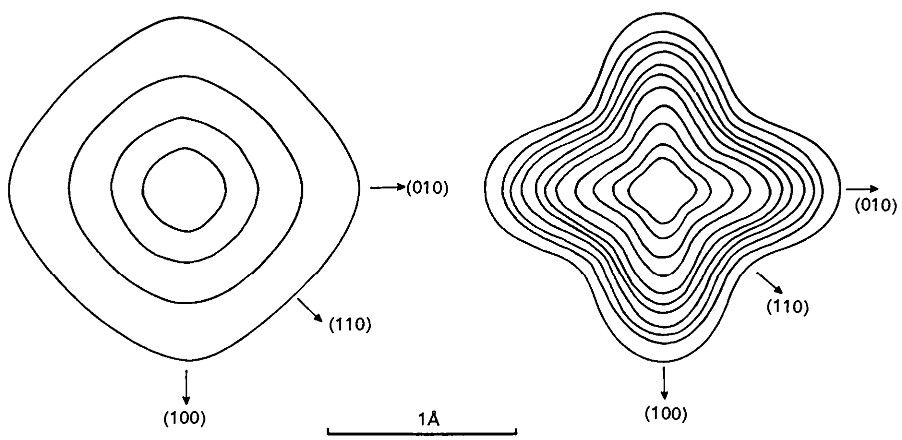
The Patterson function $Q'(\mathbf{u})$ is given by

$$Q'(\mathbf{u})=Q(\mathbf{u})-R(\mathbf{u})$$

where

$$R(\mathbf{u})=\sum_{1-2}^{i}\sum_{1-2}^{j}\overline{(\hat{k}_i\hat{k}_j)} * [\mathscr{S}_i(\mathbf{r}) * \mathscr{S}_j(\mathbf{r})]$$

and $\mathscr{S}_i(\mathbf{r})$, $\mathscr{S}_j(\mathbf{r})$ are the components on the ith and jth axis of the projected spin-density distribution.



(a) (b)

Fig. 4. (a) {100} section of the self convolution of an Fe^{2+} ion with a completely e_g $3d$ electron-density distribution. Contours are drawn at intervals of 0·156 e^2 Å^{-3}. The zero contour is omitted. (b) {100} section of the e_g density function. Contours are drawn at intervals of 0·156 e Å^{-3}. The zero contour is omitted.

Now

$$\overline{\hat{k}_1\hat{k}_1} = \underset{k_0\to\infty}{\mathrm{Lt}} \int_0^{k_0}\int_0^{2\pi} \cos^2(\alpha+\theta)\exp(2\pi irk\cos\theta)k\mathrm{d}k\mathrm{d}\theta$$

$$= \underset{k_0\to\infty}{\mathrm{Lt}} \frac{\pi k_0^2}{2}[\Lambda_1(2\pi k_0 r)(1+\cos 2\alpha) + \Omega(2\pi k_0 r)\cos 2\alpha]$$

where

$$\Lambda_1(z) = \frac{J_1(z)}{(z/2)}, \quad \Omega(z) = \frac{1-J_0(z)}{(z/2)^2}$$

while α is the angle between $\mathbf{r}$ and axis 1 and θ is the angle between $\mathbf{r}$ and $\mathbf{k}$. Similarly

$$\overline{\hat{k}_2\hat{k}_2} = \underset{k_0\to\infty}{\mathrm{Lt}} \frac{\pi k_0^2}{2}[\Lambda_1(2\pi k_0 r)(1-\cos 2\alpha) + \Omega(2\pi k_0 r)\cos 2\alpha]$$

and

$$\overline{\hat{k}_1\hat{k}_2} = \overline{\hat{k}_2\hat{k}_1} = \underset{k_0\to\infty}{\mathrm{Lt}} \frac{\pi k_0^2}{2}[\Lambda_1(2\pi k_0 r)\sin 2\alpha - \Omega(2\pi k_0 r)\cos 2\alpha]\,.$$

Combining these terms gives

$$R(\mathbf{u}^{mn}+\mathbf{x}) = \underset{k_0\to\infty}{\mathrm{Lt}} \frac{\pi k_0^2}{2} S_\parallel^m S_\parallel^n \{\Lambda_1(2\pi k_0 r) \times[\cos(2\alpha-(\omega_m+\omega_n))+\cos(\omega_m-\omega_n)] - \Omega(2\pi k_0 r)[\cos(2\alpha-(\omega_m+\omega_n))]\} * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})\}$$

where $\hat{\mathscr{S}}^m(\mathbf{r})$ is the 'unitary' spin-density distribution function defined by $\hat{\mathscr{S}}^m(\mathbf{r}) = \mathscr{S}_\parallel^m(\mathbf{r})/S_\parallel^m$, $S_\parallel^m$ is the component in the plane of the total projected spin density associated with atom m, ω_m is the angle between $S_\parallel^m$ and axis 1 and $\mathbf{x}$ is the vector distance measured from the vector position $\mathbf{u}^{mn}$.

It can be similarly shown that

$$Q(\mathbf{u}^{mn}+\mathbf{x}) = \underset{k_0\to\infty}{\mathrm{Lt}} \pi k_0^2\{\Lambda_1(2\pi k_0 r) \times[S_\perp^m S_\perp^n + S_\parallel^m S_\parallel^n\cos(\omega_m-\omega_n)]\} * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})\}$$

and thus

$$Q'(\mathbf{u}^{mn}+\mathbf{x}) = \underset{k_0\to\infty}{\mathrm{Lt}} \pi k_0^2\{\Lambda_1(2\pi k_0 r) \times[S_\perp^m S_\perp^n + \tfrac{1}{2}S_\parallel^m S_\parallel^n\cos(\omega_m-\omega_n) - S_\parallel^m S_\parallel^n\cos(2\alpha-(\omega_m+\omega_n))] + \Omega(2\pi k_0 r)S_\parallel^m S_\parallel^n[\cos(2\alpha-(\omega_m+\omega_n))]\} * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})\}\,.$$

APPENDIX 2

Three-dimensional data

In this case

$$R(\mathbf{u}) = \sum_{1-3}^{i}\sum_{1-3}^{j}\overline{\hat{k}_i\hat{k}_j} * \{\mathscr{S}_i(\mathbf{r}) * \mathscr{S}_j(\mathbf{r})\}\,.$$

The quantities involved in the summation are of the type

(*a*)

$$\overline{\hat{k}_i\hat{k}_i} = \int_{0\,\varphi}^{2\pi}\int_{0\,\theta}^{\pi}\int_{0\,k}^{\infty} \hat{k}_i\hat{k}_i\exp(2\pi irk\cos\theta)\,k^2\sin\theta\mathrm{d}\theta\mathrm{d}k\mathrm{d}\varphi$$

$$= \underset{k_0\to\infty}{\mathrm{Lt}} \frac{4\pi k_0^3}{3}\{\cos^2\alpha_i[\Theta(2\pi k_0 r)-2\Phi(2\pi k_0 r)] + \sin^2\alpha_i\Phi(2\pi k_0 r)\}$$

where

$$\begin{cases}\Phi(z) = \dfrac{3(\sin z - z\cos z)}{z^3}\\ \Theta(z) = \dfrac{3[\mathscr{S}i(z)-\sin z]}{z^3}\end{cases}$$

and

$$\mathscr{S}i(z) = \int_0^z \frac{\sin y}{y}\,\mathrm{d}y\,.$$

(*b*)

$$\overline{\hat{k}_i\hat{k}_j} = \underset{k_0\to\infty}{\mathrm{Lt}} \frac{4\pi k_0^3}{3}\cos\alpha_i\cos\alpha_j\{3\Theta(2\pi k_0 r)-\Phi(2\pi k_0 r)\}$$

and summing over all nine terms gives

$$R(\mathbf{u}) = \underset{k_0\to\infty}{\mathrm{Lt}} -\tfrac{4}{3}\pi k_0^3\{(S_1^m\cos\alpha_1+S_2^m\cos\alpha_2+S_3^m\cos\alpha_3) \times(S_1^n\cos\alpha_1+S_2^n\cos\alpha_2+S_3^n\cos\alpha_3) \times[3\Theta(2\pi k_0 r)-\Phi(2\pi k_0 r)] - \mathbf{S}^m\,.\,\mathbf{S}^n\Theta(2\pi k_0 r)\} * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})\}\,.$$

It may similarly be shown that

$$Q(\mathbf{u}) = \underset{k_0\to\infty}{\mathrm{Lt}} \tfrac{4}{3}\pi k_0^3\Phi(2\pi k_0 r)\mathbf{S}^m\,.\,\mathbf{S}^n * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})\}$$

and therefore

$$Q'(\mathbf{u}^{mn}+\mathbf{x}) = \underset{k_0\to\infty}{\mathrm{Lt}} \tfrac{4}{3}\pi k_0^3\{[\Phi(2\pi k_0 r)-\Theta(2\pi k_0 r)]\mathbf{S}^m\,.\,\mathbf{S}^n + S^m S^n[3\Theta(2\pi k_0 r)-\Phi(2\pi k_0 r)](\hat{\mathbf{S}}^m\,.\,\hat{\mathbf{x}}) \times(\hat{\mathbf{S}}^n\,.\,\hat{\mathbf{x}})\} * \{\hat{\mathscr{S}}^m(\mathbf{r}) * \hat{\mathscr{S}}^n(-\mathbf{r})\}\,.$$

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