spread parameter). Of the two distributions, Gaussian and Lorentzian, which can be used for describing the mosaic spread in the Becker–Coppens theory, the Gaussian distribution gives slightly lower R factors and is therefore to be preferred. The isotropic temperature factor of the O atom refines at $0{\cdot}55 \pm 0{\cdot}02$ Å^2 when the temperature factor of the U atom is kept fixed at the value, $0{\cdot}28$ Å^2, derived from powder data. The magnitude of the temperature factor is the same whatever version of the extinction theory is used. The most general form of the Becker–Coppens theory includes both primary and secondary extinction, but this form is not particularly useful because of the very high correlation between the temperature factor $B_{\rm O}$ and the extinction parameter g.

The results of this analysis are consistent with the conclusion of Cooper & Rouse (1976) that the extinction theories do not account adequately for the wavelength dependence of the extinction. However, the extinction in the UO_2 crystal was not sufficiently large for the additional variation with wavelength to be significant in this case.

These results confirm that the values derived for the temperature factors in this type of material are dependent on the correction for extinction, but are insensitive to the exact model which is used for this. In type I crystals, for which the extinction is determined by the mosaic spread of the sample, the Cooper–Rouse and Becker–Coppens theories both provide an adequate model for the extinction properties, even for effects approaching a 60% reduction in intensity. We may therefore conclude that, in general, if extinction effects are significant reliable values of the temperature factors will not be obtained unless an extinction correction is applied, but that the choice of model is not important for type I crystals. However, analysis of data collected at different wavelengths may conceal inadequacies in the wavelength dependence of the models, unless the various sets of data are analysed separately.

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SHORT COMMUNICATIONS

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Fourier transforms of Gaussian orbital products.

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An expression for the Fourier transform of two-centre Gaussian orbital products is obtained which is identical in form with expressions for overlap integrals. The one-centre transform is a special case, and is obtained in a trivial way from the two-centre expression. Explicit expressions of the transform for all combinations up to *ff* products are given.

Introduction

Recently, the calculation of X-ray structure factors from molecular wave-functions has attracted considerable interest (Bentley & Stewart, 1974, 1975; Groenewegen & Feil, 1969; McWeeny, 1953; Stevens, Rys & Coppens, 1977; Stewart, 1969). In the framework of molecular-orbital theory this calculation requires the evaluation of the Fourier transforms of atomic-orbital products;

$$X_{\mu\nu}(\mathbf{S},\mathbf{R}) = \int \chi_\mu^* \chi_\nu \exp(i\mathbf{S}\cdot\mathbf{r})\,\mathbf{d}\mathbf{r}. \qquad (1)$$

Here, χ_μ, χ_ν are atomic-orbital functions, and may be on the same or different centres, **S** is the Bragg vector, **R** is the internuclear vector in the two-centre case. The same integral arises in the application of the Hartree–Fock method to crystals (Harris & Monkhurst, 1969) and in electron-scattering calculations (Ijima, Bonham & Ando, 1963). It is most convenient to have the χ's as Cartesian Gaussian-type functions (GTF's) since most of the current molecular wave-functions are expressed in terms of them and since then, the two-centre and one-centre cases of (1) are equally easy to evaluate, which is not the case if Slater-type functions are employed. In this note we will only be concerned with GTF's.

McWeeny (1953) and Groenewegen & Feil (1969) have obtained an analytical expression for (1) in the case of *ss* orbital products of GTF's. They pointed out that expressions for other products could be obtained by differentiating their result, but the method is cumbersome since the result needs to be obtained explicitly for each symmetry-unique orbital product. Stewart (1969) used McWeeny's (1953) methods to give explicit expressions for *ss*, *sp* and *pp* products. Earlier, Miller & Krauss (1967) had shown that the two-centre case of (1) for GTF products gives a finite sum of Hermite polynomial products and Stevens, Rys & Coppens (1977) have used this expression in their recent work. It is our aim to show that the integral can be expressed in a simpler form, and then the connection with methods used for calculating overlap integrals in widely available LCAO SCF programs can be readily seen. We provide explicit expressions for all combinations up to *ff* orbital products.

Integral evaluation

We begin with a GTF centred at **A**

$$\chi(\mathbf{A},\alpha_A,l,m,n) = N_A x_A^l y_A^m z_A^n \exp(-\alpha_A r_A^2), \tag{2}$$

where N_A is the normalizer and $\mathbf{r}_A = \mathbf{r} - \mathbf{A}$.

Substituting (2) in (1) gives

$$X_{\mu\nu}(\mathbf{S},\mathbf{R}) = N_A N_B \int_0^\infty x_A^{l_1} x_B^{l_2} y_A^{m_1} y_B^{m_2} z_A^{n_1} z_B^{n_2} \times \exp(-\alpha_A r_A^2 - \alpha_B r_B^2 + i\mathbf{S}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{3}$$

But,

$$x_A^{l_1} x_B^{l_2} = (x - A_x)^{l_1}(x - B_x)^{l_2} = \sum_{j=0}^{l_1+l_2} f_j(l_1,l_2,-A_x,-B_x)\,x^j, \tag{4}$$

where f_j is

$$f_j(l,m,a,b) = \sum_{i=\max(0,j-m)}^{i=\min(j,l)} \binom{l}{i}\binom{m}{j-i} a^{l-l}\, b^{m+i-j}$$

and is tabulated by Clementi & Mehl (1971).

After (4) is substituted into (3) the integral can be separated into Cartesian components involving integrations over each component of the following form,

$$\int_{-\infty}^{\infty} x^n \exp(-px^2 + 2q_x x)\,\mathrm{d}x = \exp\left(\frac{q_x^2}{p}\right)\left(\frac{\pi}{p}\right)^{1/2} g_n(p,q_x) \tag{5}$$

Table 1. *Expressions for $g_n(p,q)$ for ss to ff products, $n = 0$ to 6*

n	$g_n(p,q)$
0	1
1	q/p
2	$1/2p + (q/p)^2$
3	$3q/2p^2 + (q/p)^3$
4	$3/4p^2 + 3q^2/p^3 + (q/p)^4$
5	$15q/4p^3 + 5q^3/p^4 + (q/p)^5$
6	$15/8p^3 + 45q^2/4p^4 + 15q^4/2p^5 + (q/p)^6$

where

$$p = \alpha_A + \alpha_B,$$

$$\mathbf{q} = \alpha_A\mathbf{A} + \alpha_B\mathbf{B} + (i/2)\mathbf{S}$$

and

$$g_n(p,q_x) = n!\left(\frac{q_x}{p}\right)^n \sum_{k=0}^{[n/2]} \frac{1}{(n-2k)!k!}\left(\frac{p}{4q_x^2}\right)^k$$

where $[n/2]$ is the largest integer less than or equal to $n/2$. $g_n(p,q_x)$ is tabulated in Table 1 for $n = 0$ to 6. It is related to the Hermite polynomial of order n by the expression

$$g_n(p,q_x) = \frac{1}{(-2i\sqrt{p})^n} H_n\left(\frac{-iq_x}{\sqrt{p}}\right). \tag{6}$$

The final form for the integral is then

$$x_{\mu\nu}(\mathbf{S},\mathbf{R}) = N_A N_B \left(\frac{\pi}{p}\right)^{3/2} \exp\left(\frac{q^2}{p} - \alpha_A A^2 - \alpha_B B^2\right) \times \sum_{i=0}^{l_1+l_2} f_i(l_1,l_2,-A_x,-B_x)\,g_i(p,q_x) \times \sum_{j=0}^{m_1+m_2} f_j(m_1,m_2,-A_y,-B_y)\,g_j(p,q_y) \times \sum_{k=0}^{n_1+n_2} f_k(n_1,n_2,-A_z,-B_z)\,g_k(p,q_z) \tag{7}$$

where

$$\exp\left(\frac{q^2}{p} - \alpha_A A^2 - \alpha_B B^2\right) = \exp\left\{\left[-\alpha_1\alpha_2 R^2 + i\mathbf{S}(\alpha_A\mathbf{A} + \alpha_B\mathbf{B}) - \frac{S^2}{4}\right]\Big/p\right\}.$$

For $|\mathbf{R}| = 0$ (7) reduces to a simplified form of the one-centre formula given by Stewart (1969). The form of (7) is identical with that for overlap integrals given by Taketa, Huzinaga & O-ohata (1966) and used by Davis & Clementi (1968) in the *IBMOL* programs.

Hence, modification of the appropriate sub-routines to incorporate the complex **S** dependence of the integral is a convenient route to the evaluation of (1).

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Concerning an unnecessary approximation made by Zachariasen in treating the perfect-crystal Bragg case.

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An approximation in Zachariasen's [*Theory of X-Ray Diffraction in Crystals* (1945). New York: John Wiley] treatment of X-ray diffraction from a perfect plane-parallel crystal in the Bragg case is pointed out and eliminated. The corresponding unapproximated expression for the transmitted beam is also given. It transpires that Zachariasen's approximation leads to significant errors for 'thin' crystals (*i.e.* those for which the path length is less than or of the order of the extinction length). Some illustrations of the nature of the error are given.

In the course of some calculations it has come to our notice that there is an unnecessary approximation in Zachariasen's (1945) equation (3.139), which, from the text, might be thought to give the general solution for the diffraction of X-rays from a perfect plane-parallel crystal in the Bragg case, treated within the framework of Zachariasen's explicit assumptions. The nature of the approximation is such that it only leads to significant errors for 'thin' crystals (*i.e.* those for which the path length is less than or of the order of the extinction length) and then, apparently only when ψ''_H (or F''_H) is non-zero (for a review concerning another unnecessary approximation introduced by Zachariasen, see Fingerland, 1971).

As Zachariasen's book is widely used as a source for results of X-ray dynamical theory and also because, to our knowledge, the general solution for the Bragg case has not been given in the same convenient form elsewhere, it seems worthwhile to present the unapproximated expression for the diffracted-beam intensity. In addition, we also give the corresponding unapproximated result for the transmitted beam, which is not given by Zachariasen.

Following Zachariasen's notation, we find on substituting for x_1, x_2, c_1 and c_2 in his equation (3.137) that the diffracted intensity is given without approximation by

$$\frac{I_H}{I_o^e} = \frac{b^2|\psi_H|^2[\sin^2 av + \sinh^2 aw]}{D}, \tag{1}$$

where the denominator

$$\begin{aligned} D = {} & |q + z^2| + \{|q + z^2| + |z|^2\} \sinh^2 aw \\ & - \{|q + z^2| - |z|^2\} \sin^2 av + \mathrm{Re}(-z^* u) \sinh(2aw) \\ & + \mathrm{Im}(z^* u) \sin(2av), \end{aligned} \tag{2}$$

while

$$u \equiv v + iw \equiv (q + z^2)^{1/2} \tag{3}$$

and an asterisk denotes the complex conjugate.

Expression (1) may be shown to agree with that given by Zachariasen but for the question of the signs in the fourth and fifth terms in the denominator D. More specifically, Zachariasen effectively takes the moduli of these terms. Following some careful analysis, we find that, at least for the centrosymmetric case, Zachariasen's choice of sign for the fourth term is correct, but that his corresponding treatment of the fifth term in (2) is not valid if

$$\kappa \equiv \frac{\psi''_H}{\psi'_H} \equiv \frac{F''_H}{F'_H} \neq 0, \tag{4}$$

when the fifth term may become negative. The fifth term in (2) only makes a significant contribution for path lengths which are less than or of the order of the extinction length (*i.e.* $A \lesssim \pi$).

The transmitted beam intensity is similarly found from Zachariasen's equation (3.138) to be

$$\frac{I_e^o}{I_o^e} = \frac{|q + z^2| \exp\{-2a\beta\,\mathrm{Im}(z)\}}{D}, \tag{5}$$

where the asymmetry parameter β is given by

$$\beta = \frac{b+1}{b-1} \quad \text{with} -1 \leq \beta \leq 1. \tag{7}$$

and D is again given by (2).

In order to illustrate the nature of the error introduced by Zachariasen's approximation, we have taken the centrosymmetric case and plotted out diffracted- and transmitted-beam rocking curves for various values of the parameters A, g, β and κ. Two illustrative examples are presented in Figs. 1 and 2.

In calculating the reflectivity $R = P_H/P_O$, we have used the standard approximation that $P_H/P_O = I_H/|b|I_O$, which is valid for beam widths which are large compared to the depth of penetration in the crystal. For the transmissivity T we have correspondingly taken $T = I_e^o/I_o^e$. The 'Zachariasen