Acta Cryst. (1986). A42, 257-261

Efficient Evaluation of X-ray Scattering Integrals of Cartesian Gaussian-Type Functions

BY MRINMAYEE BARUA AND WOLF WEYRICH

Fakultät für Chemie, Universität Konstanz, D-7750 Konstanz, Federal Republic of Germany

(*Received* 14 *October* 1985; *accepted* 20 *January* 1986)

Abstract

A general recurrence algorithm and explicit analytical results are given for scattering integrals with Cartesian Gaussian-type functions, in a form that is necessary for the evaluation of molecular form factors, Wigner distribution functions and Compton scattering cross sections. Overlap integrals are included as a special case.

In connection with our work on Compton scattering cross sections (Froelich & Weyrich, 1984; Froelich, Flores-Riveros & Weyrich, 1985; Bonham, Pattison & Weyrich, 1986) and on Wigner distribution functions we have encountered the need for compact analytical solutions of two-centre integrals of the type

$$I_{lmn,l'm'n'}(a, b, \mathbf{R}_{AB}) = \int\int\int x_A^l y_A^m z_A^n \exp(-ar_A^2) \exp(i\mathbf{k}.\mathbf{r}) \times x_B^{l'} y_B^{m'} z_B^{n'} \exp(-br_B^2)\, d\tau, \quad (1)$$

which we call scattering integrals for the sake of simplicity. They also occur in the calculation of molecular form factors and electron scattering cross sections. Overlap integrals are included as the special case $\mathbf{k}=0$. In (1), the two Cartesian Gaussian-type functions (CGTF's) with real positive a, b and non-negative integers l, m, n, l', m', n' (Boys, 1950) are centred at the positions **A** and **B**. The absolute position vector **r** related to the centres is $\mathbf{r}_A=\mathbf{r}-\mathbf{A}$ and $\mathbf{r}_B=\mathbf{r}-\mathbf{B}$, respectively, and the distance vector $\mathbf{R}_{AB}$ separating centre **B** from centre **A** is $\mathbf{R}_{AB}=\mathbf{B}-\mathbf{A}$. The Cartesian components of **r**, **A**, **B** are $x, y, z, A_x, A_y, A_z, B_x, B_y, B_z$.

The first solutions to $I_{lmn,\,l'm'n'}$ have been given by McWeeny (1953) for the cases $l=m=n=l'=m'=n'=0$ $(1s, 1s)$, $l=m=n=0$, $l'+m'+n'=1$ $(1s, 2p)$, and $l+m+n=1$, $l'+m'+n'=1$ $(2p, 2p)$. [The $2s$-type solutions of McWeeny are outside the systematics of (1).] Chandler & Spackman (1978) have presented formulae up to l, m, n and $l', m', n'=3$, *i.e.* up to f-type functions, by using the standard approach of replacing the two-centre product of the two CGTF's by a polynomial times a single CGTF centred between **A** and **B** at the position $\mathbf{P}=(a\mathbf{A}+b\mathbf{B})/(a+b)$ (Boys, 1950; Shavitt, 1963; see also Saunders, 1975, 1983). Earlier, Guerillot, Ganachaud & Lissillour (1968) followed the same procedure for scattering integrals formulated in a different way. The work of Groenewegen & Feil (1969) and, in a more general way, the work of Rae (1978) deal with analytical solutions for scattering integrals with *spherical* Gaussian-type functions (SGTF's).

For the complex-coordinate treatment of the Compton scattering cross section (Froelich & Weyrich, 1984; Froelich, Flores-Riveros & Weyrich, 1985), basis sets including functions with unusually high l, m, n are needed. The physical reason is the description of the ejected electron which is hidden in the formalism by closure. Furthermore, the evaluation of the Wigner distribution function of atoms and molecules at a large number of points in phase space requires efficient algorithms in order to make computing times tolerable. Both aspects have led us to search for a general solution for the integrals of (1).

The first step is the Cartesian factorization

$$I_{lmn,l'm'n'}(a, b, \mathbf{R}_{AB}) = I_{ll'}(a, b, B_x-A_x) \times I_{mm'}(a, b, B_y-A_y) \times I_{nn'}(a, b, B_z-A_z) \quad (2)$$

with

$$I_{ll'}(a, b, B_x-A_x) = \int_{-\infty}^{+\infty} (x-A_x)^l \exp[-a(x-A_x)^2] \exp(ik_x x) \times (x-B_x)^{l'} \exp[-b(x-B_x)^2]\, dx \quad (3)$$

and analogous expressions for $I_{mm'}$ and $I_{nn'}$ (see also Chandler & Spackman, 1978). The factorization is based on the relationship

$$r_A^2=(x-A_x)^2+(y-A_y)^2+(z-A_z)^2,$$
$$r_B^2=(x-B_x)^2+(y-B_y)^2+(z-B_z)^2,$$
$$\mathbf{k}.\mathbf{r}=k_x x+k_y y+k_z z. \quad (4)$$

Our approach, which can be considered as the CGTF counterpart to the method of Lofthus (1962) for the recursive evaluation of overlap integrals between Slater-type functions (STF's), then consists of the repeated application of McWeeny's (1953) method of differentiation by A_x or B_x in order to raise l or

0108-7673/86/040257-05$01.50

l', respectively. While McWeeny has done only the special step $l=0$ to $l=1$, it follows from

$$\partial\{(x-A_x)^l \exp[-a(x-A_x)^2]\}/\partial A_x = 2a(x-A_x)^{l+1}\exp[-a(x-A_x)^2] - l(x-A_x)^{l-1}\exp[-a(x-A_x)^2] \quad (5)$$

(with an analogous expression in B_x) and the interchange of the order of differentiation and integration that

$$\partial I_{ll'}/\partial A_x = 2aI_{l+1,l'} - lI_{l-1,l'} \quad (6a)$$

and

$$\partial I_{ll'}/\partial B_x = 2bI_{l,l'+1} - l'I_{l,l'-1}. \quad (6b)$$

Given the integrals

$$I_{000,000} = \iiint \exp(-ar_A^2)\exp(i\mathbf{k}\cdot\mathbf{r})\exp(-br_B^2)\,d\tau = [\pi/(a+b)]^{3/2}\exp\{[-abR_{AB}^2 + i\mathbf{k}(a\mathbf{A}+b\mathbf{B}) - k^2/4]/(a+b)\} \quad (7a)$$

(McWeeny, 1953) or

$$I_{00} = \int \exp[-a(x-A_x)^2]\exp(ik_x x) \times \exp[-b(x-B_x)^2]\,dx = [\pi/(a+b)]^{1/2}\exp\{[-ab(B_x-A_x)^2 + ik_x(aA_x+bB_x) - k_x^2/4]/(a+b)\}, \quad (7b)$$

it is possible to evaluate *all* integrals $I_{ll'}$ *analytically* by upward recurrence

$$I_{l+1,l'} = (1/2a)[\partial I_{ll'}/\partial A_x + lI_{l-1,l'}] \quad (8a)$$

and

$$I_{l,l'+1} = (1/2b)[\partial I_{ll'}/\partial B_x + l'I_{l,l'-1}]. \quad (8b)$$

However, doing the recurrence by a paper-and-pencil approach quickly becomes very tedious, all the more so since possibilities of simplifying the expressions are frequently overlooked. It is therefore desirable to cast the recurrence into such a form that it can be computed using standard science-oriented programming languages.

Differentiation of I_{00} by A_x and B_x yields

$$\partial I_{00}/\partial A_x = \{[2ab(B_x-A_x)+iak_x]/(a+b)\}I_{00} \quad (9a)$$

and

$$\partial I_{00}/\partial B_x = \{[2ab(A_x-B_x)+ibk_x]/(a+b)\}I_{00}. \quad (9b)$$

Since I_{00} is an exponential function, it persists as a common factor in all integrals $I_{ll'}$ under the recurrence. If we abbreviate the factor of I_{00} in (9a) by F_x and the factor in (9b) by G_x, we can write

$$\partial F_x/\partial A_x = \partial G_x/\partial B_x = -2ab/(a+b) \quad (19a)$$

and

$$\partial F_x/\partial B_x = \partial G_x/\partial A_x = +2ab/(a+b) \quad (10b)$$

for their differentiation. Since the right-hand sides of (10a) and (10b) no longer contain A_x and B_x, all integrals $I_{ll'}$ are eventually sums of terms of the form

$$\mu F_x^\alpha G_x^\beta (1/2a)^\gamma (1/2b)^\delta [2ab/(a+b)]^\varepsilon I_{00}, \quad (11)$$

where α, β, γ, δ, ε and μ are integer numbers. Differentiation and division by $2a$ or $2b$ of such a term $\mu\{\alpha,\beta;\gamma,\delta,\varepsilon\}$ leads to

$$(1/2a)\partial\mu\{\alpha,\beta;\gamma,\delta,\varepsilon\}/\partial A_x = -\mu\alpha\{\alpha-1,\beta;\gamma+1,\delta,\varepsilon+1\} + \mu\beta\{\alpha,\beta-1;\gamma+1,\delta,\varepsilon+1\} + \mu\{\alpha+1,\beta;\gamma+1,\delta,\varepsilon\} \quad (12a)$$

and

$$(1/2b)\partial\mu\{\alpha,\beta;\gamma,\delta,\varepsilon\}/\partial B_x = +\mu\alpha\{\alpha-1,\beta;\gamma,\delta+1,\varepsilon+1\} - \mu\beta\{\alpha,\beta-1;\gamma,\delta+1,\varepsilon+1\} + \mu\{\alpha,\beta+1;\gamma,\delta+1,\varepsilon\}, \quad (12b)$$

respectively. Addition of terms

$$l(1/2a)\nu\{\zeta,\eta;\theta,\iota,\kappa\} = l\nu\{\zeta,\eta;\theta+1,\iota,\kappa\} \quad (13a)$$

or

$$l'(1/2b)\nu\{\zeta,\eta;\theta,\iota,\kappa\} = l'\nu\{\zeta,\eta;\theta,\iota+1,\kappa\} \quad (13b)$$

completes the recurrence. At every recursive step the number of terms of an integral is almost quadrupled at first glance. However, terms with the same set of five exponents can be collected as

$$\mu\{\alpha,\beta;\gamma,\delta,\varepsilon\} + \nu\{\alpha,\beta;\gamma,\delta,\varepsilon\} = (\mu+\nu)\{\alpha,\beta;\gamma,\delta,\varepsilon\} \quad (14)$$

and, if $\mu+\nu=0$, be deleted from the list.

By this reformulation of the recurrence, complete analogy to the approach of Lofthus (1962) for overlap integrals between STF's is achieved, with the only difference that here five indices are to be handled rather than two. If the integrals $I_{ll'}$ are specialized to $k_x=0$, *i.e.* to overlap integrals, the number of indices reduces to four according to

$$\{\alpha,\beta;\gamma,\delta,\varepsilon\}_{k_x=0} = (-1)^\beta[2ab(B_x-A_x)/(a+b)]^{\alpha+\beta} \times (1/2a)^\gamma(1/2b)^\delta[2ab/(a+b)]^\varepsilon = (-1)^\beta(B_x-A_x)^{\alpha+\beta}(1/2a)^\gamma \times (1/2b)^\delta[2ab/(a+b)]^{\alpha+\beta+\varepsilon} = (-1)^\beta[\![\alpha+\beta;\gamma,\delta,\alpha+\beta+\varepsilon]\!] \quad (15)$$

because $G_x(k_x=0) = -F_x(k_x=0)$. How (12a) to (14) simplify in this case is obvious.

The implementation of the expansion of the formulae by (12a) to (13b) and of the compression by (14) has been programmed here in analogy to the technique introduced by Zupan (1974) for the Lofthus

Table 1. *Sextuplets of parameters μ_i, α_i, β_i, γ_i, δ_i, ε_i for pairs of quantum numbers ll' (or mm', nn'); the first two columns contain l and l' while the remaining part of the table gives the sextuplets in the form $\mu_i * \{\alpha_i, \beta_i; \gamma_i, \delta_i, \varepsilon_i\}$ for equations* (17), (19), (20) *and* (21)

0 0	+1*(0,0;0,0,0)				
0 1	+1*(0,1;0,1,0)				
0 2	+1*(0,2;0,2,0)	-1*(0,0;0,2,1)	+1*(0,0;0,1,0)		
0 3	+1*(0,3;0,3,0)	-3*(0,1;0,3,1)	+3*(0,1;0,2,0)		
0 4	+1*(0,4;0,4,0)	-6*(0,2;0,4,1)	+6*(0,2;0,3,0)	+3*(0,0;0,4,2)	
	-6*(0,0;0,3,1)	+3*(0,0;0,2,0)			
0 5	+1*(0,5;0,5,0)	-10*(0,3;0,5,1)	+10*(0,3;0,4,0)	+15*(0,1;0,5,2)	
	-30*(0,1;0,4,1)	+15*(0,1;0,3,0)			
1 0	+1*(1,0;1,0,0)				
1 1	+1*(1,1;1,1,0)	+1*(0,0;1,1,1)			
1 2	+1*(1,2;1,2,0)	-1*(1,0;1,2,1)	+1*(1,0;1,1,0)	+2*(0,1;1,2,1)	
1 3	+1*(1,3;1,3,0)	-3*(1,1;1,3,1)	+3*(1,1;1,2,0)	+3*(0,2;1,3,1)	
	-3*(0,0;1,3,2)	+3*(0,0;1,2,1)			
1 4	+1*(1,4;1,4,0)	-6*(1,2;1,4,1)	+6*(1,2;1,3,0)	+3*(1,0;1,4,2)	
	-6*(1,0;1,3,1)	+3*(1,0;1,2,0)	+4*(0,3;1,4,1)	-12*(0,1;1,4,2)	
	+12*(0,1;1,3,1)				
1 5	+1*(1,5;1,5,0)	-10*(1,3;1,5,1)	+10*(1,3;1,4,0)	+15*(1,1;1,5,2)	
	-30*(1,1;1,4,1)	+15*(1,1;1,3,0)	+5*(0,4;1,5,1)	-30*(0,2;1,5,2)	
	+30*(0,2;1,4,1)	-30*(0,0;1,4,2)	+15*(0,0;1,5,3)	+15*(0,0;1,3,1)	
2 0	+1*(2,0;2,0,0)	-1*(0,0;2,0,1)	+1*(0,0;1,0,0)		
2 1	+1*(2,1;2,1,0)	+2*(1,0;2,1,1)	-1*(0,1;2,1,1)	+1*(0,1;1,1,0)	
2 2	+1*(2,2;2,2,0)	-1*(2,0;2,2,1)	+1*(2,0;2,1,0)	+4*(1,1;2,2,1)	
	-1*(2,0;2,2,1)	+1*(0,2;1,2,0)	-1*(0,0;2,1,1)	+3*(0,0;2,2,2)	
	-1*(0,0;1,2,1)	+1*(0,0;1,1,0)			
2 3	+1*(2,3;2,3,0)	-3*(2,1;2,3,1)	+3*(2,1;2,2,0)	+6*(1,2;2,3,1)	
	-6*(1,0;2,3,2)	+6*(1,0;2,2,1)	-1*(0,3;2,3,1)	+1*(0,3;1,3,0)	
	+9*(0,1;2,3,2)	-3*(0,1;2,2,1)	-3*(0,1;1,3,1)	+3*(0,1;1,2,0)	
2 4	+1*(2,4;2,4,0)	-6*(2,2;2,4,1)	+6*(2,2;2,3,0)	+3*(2,0;2,4,2)	
	-6*(2,0;2,3,1)	+3*(2,0;2,2,0)	+8*(1,3;2,4,1)	-24*(1,1;2,4,2)	
	+24*(1,1;2,3,1)	-1*(0,4;2,4,1)	+1*(0,4;1,4,0)	+18*(0,2;2,4,2)	
	-6*(0,2;2,3,1)	-6*(0,2;1,4,1)	+6*(0,2;1,3,0)	-15*(0,0;2,4,3)	
	+18*(0,0;2,3,2)	+3*(0,0;1,4,2)	-3*(0,0;2,2,1)	-6*(0,0;1,3,1)	
	+3*(0,0;1,2,0)				
2 5	+1*(2,5;2,5,0)	-10*(2,3;2,5,1)	+10*(2,3;2,4,0)	+15*(2,1;2,5,2)	
	-30*(2,1;2,4,1)	+15*(2,1;2,3,0)	+10*(1,4;2,5,1)	-60*(1,2;2,5,2)	
	+60*(1,2;2,4,1)	-60*(1,0;2,4,2)	+30*(1,0;2,5,3)	+30*(1,0;2,3,1)	
	-1*(0,5;2,5,1)	+1*(0,5;1,5,0)	+30*(0,3;2,5,2)	-10*(0,3;2,4,1)	
	-10*(0,3;1,5,1)	+10*(0,3;1,4,0)	-75*(0,1;2,5,3)	-15*(0,1;2,3,1)	
	+15*(0,1;1,5,2)	+90*(0,1;2,4,2)	-30*(0,1;1,4,1)	+15*(0,1;1,3,0)	
3 0	+1*(3,0;3,0,0)	-3*(1,0;3,0,1)	+3*(1,0;2,0,0)		
3 1	+1*(3,1;3,1,0)	+3*(2,0;3,1,1)	-3*(1,1;3,1,1)	+3*(1,1;2,1,0)	
	-3*(0,0;3,1,2)	+3*(0,0;2,1,1)			
3 2	+1*(3,2;3,2,0)	-1*(3,0;3,2,1)	+1*(3,0;3,1,0)	+6*(2,1;3,2,1)	
	-3*(1,2;3,2,1)	+3*(1,2;2,2,0)	-3*(1,0;3,1,1)	+9*(1,0;3,2,2)	
	-3*(1,0;2,2,1)	+3*(1,0;2,1,0)	-6*(0,1;3,2,2)	+6*(0,1;2,2,1)	
3 3	+1*(3,3;3,3,0)	-3*(3,1;3,3,1)	+3*(3,1;3,2,0)	+9*(2,2;3,3,1)	
	-9*(2,0;3,3,2)	+9*(2,0;3,2,1)	-3*(1,3;3,3,1)	+3*(1,3;2,3,0)	
	+27*(1,1;3,3,2)	-9*(1,1;3,2,1)	-9*(1,1;2,3,1)	+9*(1,1;2,2,0)	
	-9*(0,2;3,3,2)	+9*(0,2;2,3,1)	+15*(0,0;3,3,3)	-9*(0,0;2,3,2)	
	-9*(0,0;3,2,2)	+9*(0,0;2,2,1)			
3 4	+1*(3,4;3,4,0)	-6*(3,2;3,4,1)	+6*(3,2;3,3,0)	+3*(3,0;3,4,2)	
	-6*(3,0;3,3,1)	+3*(3,0;3,2,0)	+12*(2,3;3,4,1)	-36*(2,1;3,4,2)	
	+36*(2,1;3,3,1)	-3*(1,4;3,4,1)	+3*(1,4;2,4,0)	+54*(1,2;3,4,2)	
	-18*(1,2;3,3,1)	-18*(1,2;2,4,1)	+18*(1,2;2,3,0)	-45*(1,0;3,4,3)	
	+54*(1,0;3,3,2)	+9*(1,0;2,4,2)	-9*(1,0;3,2,1)	-18*(1,0;2,3,1)	
	+9*(1,0;2,2,0)	+12*(0,3;2,4,1)	-12*(0,3;3,4,2)	+60*(0,1;3,4,3)	
	+36*(0,1;2,3,1)	-36*(0,1;2,4,2)	-36*(0,1;3,3,2)		
3 5	+1*(3,5;3,5,0)	-10*(3,3;3,5,1)	+10*(3,3;3,4,0)	+15*(3,1;3,5,2)	
	-30*(3,1;3,4,1)	+15*(3,1;3,3,0)	+15*(2,4;3,5,1)	-90*(2,2;3,5,2)	
	+90*(2,2;3,4,1)	-90*(2,0;3,4,2)	+45*(2,0;3,5,3)	+45*(2,0;3,3,1)	
	-3*(1,5;3,5,1)	+3*(1,5;2,5,0)	+90*(1,3;3,5,2)	-30*(1,3;3,4,1)	
	-30*(1,3;2,5,1)	+30*(1,3;2,4,0)	-225*(1,1;3,5,3)	-45*(1,1;3,3,1)	
	+45*(1,1;2,5,2)	+270*(1,1;3,4,2)	-90*(1,1;2,4,1)	+45*(1,1;2,3,0)	
	+15*(0,4;2,5,1)	-15*(0,4;3,5,2)	+150*(0,2;3,5,3)	+90*(0,2;2,4,1)	
	-90*(0,2;2,5,2)	-90*(0,2;3,4,2)	-45*(0,0;3,3,2)	+150*(0,0;3,4,3)	
	-105*(0,0;3,5,4)	-90*(0,0;2,4,2)	+45*(0,0;2,5,3)	+45*(0,0;2,3,1)	
4 0	+1*(4,0;4,0,0)	-6*(2,0;4,0,1)	+6*(2,0;3,0,0)	+3*(0,0;4,0,2)	
	-6*(0,0;3,0,1)	+3*(0,0;2,0,0)			
4 1	+1*(4,1;4,1,0)	+4*(3,0;4,1,1)	-6*(2,1;4,1,1)	+6*(2,1;3,1,0)	
	-12*(1,0;4,1,2)	+12*(1,0;3,1,1)	-6*(0,1;3,1,1)	+3*(0,1;4,1,2)	
	+3*(0,1;2,1,0)				
4 2	+1*(4,2;4,2,0)	-1*(4,0;4,2,1)	+1*(4,0;4,1,0)	+8*(3,1;4,2,1)	
	-6*(2,2;4,2,1)	+6*(2,2;3,2,0)	-6*(2,0;4,1,1)	+18*(2,0;4,2,2)	
	-6*(2,0;3,2,1)	+6*(2,0;3,1,0)	-24*(1,1;4,2,2)	+24*(1,1;3,2,1)	
	-6*(0,2;3,2,1)	+3*(0,2;4,2,2)	+3*(0,2;2,2,0)	+3*(0,0;4,1,2)	
	-15*(0,0;4,2,3)	-6*(0,0;3,1,1)	+18*(0,0;3,2,2)	-3*(0,0;2,2,1)	
	+3*(0,0;2,1,0)				
4 3	+1*(4,3;4,3,0)	-3*(4,1;4,3,1)	+3*(4,1;4,2,0)	+12*(3,2;4,3,1)	
	-12*(3,0;4,3,2)	+12*(3,0;4,2,1)	-6*(2,3;4,3,1)	+6*(2,3;3,3,0)	
	+54*(2,1;4,3,2)	-18*(2,1;4,2,1)	-18*(2,1;3,3,1)	+18*(2,1;3,2,0)	
	-36*(1,2;4,3,2)	+36*(1,2;3,3,1)	+60*(1,0;4,3,3)	-36*(1,0;3,3,2)	
	-36*(1,0;4,2,2)	+36*(1,0;3,2,1)	-6*(0,3;3,3,1)	+3*(0,3;4,3,2)	
	+3*(0,3;2,3,0)	+54*(0,1;3,3,2)	-18*(0,1;3,2,1)	-45*(0,1;4,3,3)	
	+9*(0,1;4,2,2)	-9*(0,1;2,3,1)	+9*(0,1;2,2,0)		
4 4	+1*(4,4;4,4,0)	-6*(4,2;4,4,1)	+6*(4,2;4,3,0)	+3*(4,0;4,4,2)	
	-6*(4,0;4,3,1)	+3*(4,0;4,2,0)	+16*(3,3;4,4,1)	-48*(3,1;4,4,2)	
	+48*(3,1;4,3,1)	-6*(2,4;4,4,1)	+6*(2,4;3,4,0)	+108*(2,2;4,4,2)	
	-36*(2,2;4,3,1)	-36*(2,2;3,4,1)	+36*(2,2;3,3,0)	-90*(2,0;4,4,3)	
	+108*(2,0;4,3,2)	+18*(2,0;3,4,2)	-18*(2,0;4,2,1)	-36*(2,0;3,3,1)	
	+18*(2,0;3,2,0)	+48*(1,3;3,4,1)	-48*(1,3;4,4,2)	+240*(1,1;4,4,3)	
	+144*(1,1;3,3,1)	-144*(1,1;3,4,2)	-144*(1,1;4,3,2)	+3*(0,4;4,4,2)	
	-6*(0,4;3,4,1)	+3*(0,4;2,4,0)	+18*(0,2;4,3,2)	+108*(0,2;3,4,2)	
	-90*(0,2;4,4,3)	-36*(0,2;3,3,1)	-18*(0,2;2,4,1)	+18*(0,2;2,3,0)	
	-90*(0,0;4,3,3)	+105*(0,0;4,4,4)	-18*(0,0;3,2,1)	+9*(0,0;4,2,2)	
	-90*(0,0;3,4,3)	+9*(0,0;2,4,2)	+108*(0,0;3,3,2)	-18*(0,0;2,3,1)	
	+9*(0,0;2,2,0)				
4 5	+1*(4,5;4,5,0)	-10*(4,3;4,5,1)	+10*(4,3;4,4,0)	+15*(4,1;4,5,2)	
	-30*(4,1;4,4,1)	+15*(4,1;4,3,0)	+20*(3,4;4,5,1)	-120*(3,2;4,5,2)	
	+120*(3,2;4,4,1)	-120*(3,0;4,4,2)	+60*(3,0;4,5,3)	+60*(3,0;4,3,1)	
	-6*(2,5;4,5,1)	+6*(2,5;3,5,0)	+180*(2,3;4,5,2)	-60*(2,3;4,4,1)	
	-60*(2,3;3,5,1)	+60*(2,3;3,4,0)	-450*(2,1;4,5,3)	-90*(2,1;4,3,1)	
	+90*(2,1;3,5,2)	+540*(2,1;4,4,2)	-180*(2,1;3,4,1)	+90*(2,1;3,3,0)	
	+60*(1,4;3,5,1)	-60*(1,4;4,5,2)	+600*(1,2;4,5,3)	+360*(1,2;3,4,1)	
	-360*(1,2;3,5,2)	-360*(1,2;4,4,2)	-180*(1,0;4,3,2)	+600*(1,0;4,4,3)	
	-420*(1,0;4,5,4)	-360*(1,0;3,4,2)	+180*(1,0;3,5,3)	+180*(1,0;3,3,1)	
	-6*(0,5;3,5,1)	+3*(0,5;4,5,2)	+3*(0,5;2,5,0)	+30*(0,3;4,4,2)	
	-60*(0,3;3,4,1)	+180*(0,3;3,5,2)	-150*(0,3;4,5,3)	-30*(0,3;2,5,1)	
	+30*(0,3;2,4,0)	-450*(0,1;3,5,3)	-90*(0,1;3,3,1)	-450*(0,1;4,4,3)	
	+540*(0,1;3,4,2)	+45*(0,1;4,3,2)	+45*(0,1;2,5,2)	+525*(0,1;4,5,4)	
	-90*(0,1;2,4,1)	+45*(0,1;2,3,0)			
5 0	+1*(5,0;5,0,0)	-10*(3,0;5,0,1)	+10*(3,0;4,0,0)	+15*(1,0;5,0,2)	
	-30*(1,0;4,0,1)	+15*(1,0;3,0,0)			
5 1	+1*(5,1;5,1,0)	+5*(4,0;5,1,1)	-10*(3,1;5,1,1)	+10*(3,1;4,1,0)	
	-30*(2,0;5,1,2)	+30*(2,0;4,1,1)	-30*(1,1;4,1,1)	+15*(1,1;5,1,2)	
	+15*(1,1;3,1,0)	-30*(0,0;4,1,2)	+15*(0,0;5,1,3)	+15*(0,0;3,1,1)	
5 2	+1*(5,2;5,2,0)	-1*(5,0;5,2,1)	+1*(5,0;5,1,0)	+10*(4,1;5,2,1)	
	-10*(3,2;5,2,1)	+10*(3,2;4,2,0)	-10*(3,0;5,1,1)	+30*(3,0;5,2,2)	
	-10*(3,0;4,2,1)	+10*(3,0;4,1,0)	-60*(2,1;5,2,2)	+60*(2,1;4,2,1)	
	-30*(1,2;4,2,1)	+15*(1,2;5,2,2)	+15*(1,2;3,2,0)	+15*(1,0;5,1,2)	
	-75*(1,0;5,2,3)	-30*(1,0;4,1,1)	+90*(1,0;4,2,2)	-15*(1,0;3,2,1)	
	+15*(1,0;3,1,0)	+30*(0,1;3,2,1)	-60*(0,1;4,2,2)	+30*(0,1;5,2,3)	
5 3	+1*(5,3;5,3,0)	-3*(5,1;5,3,1)	+3*(5,1;5,2,0)	+15*(4,2;5,3,1)	
	-15*(4,0;5,3,2)	+15*(4,0;5,2,1)	-10*(3,3;5,3,1)	+10*(3,3;4,3,0)	
	+90*(3,1;5,3,2)	-30*(3,1;5,2,1)	-30*(3,1;4,3,1)	+30*(3,1;4,2,0)	
	-90*(2,2;5,3,2)	+90*(2,2;4,3,1)	+150*(2,0;5,3,3)	-90*(2,0;4,3,2)	
	-90*(2,0;5,2,2)	+90*(2,0;4,2,1)	-30*(1,3;4,3,1)	+15*(1,3;5,3,2)	
	+15*(1,3;3,3,0)	+270*(1,1;4,3,2)	-90*(1,1;4,2,1)	-225*(1,1;5,3,3)	
	+45*(1,1;5,2,2)	-45*(1,1;3,3,1)	+45*(1,1;3,2,0)	+45*(0,2;3,3,1)	
	-90*(0,2;4,3,2)	+45*(0,2;5,3,3)	+150*(0,0;4,3,3)	+45*(0,0;5,2,3)	
	-105*(0,0;5,3,4)	-45*(0,0;3,3,2)	-90*(0,0;4,2,2)	+45*(0,0;3,2,1)	
5 4	+1*(5,4;5,4,0)	-6*(5,2;5,4,1)	+6*(5,2;5,3,0)	+3*(5,0;5,4,2)	
	-6*(5,0;5,3,1)	+3*(5,0;5,2,0)	+20*(4,3;5,4,1)	-60*(4,1;5,4,2)	
	+60*(4,1;5,3,1)	-10*(3,4;5,4,1)	+10*(3,4;4,4,0)	+180*(3,2;5,4,2)	
	-60*(3,2;5,3,1)	-60*(3,2;4,4,1)	+60*(3,2;4,3,0)	-150*(3,0;5,4,3)	
	+180*(3,0;5,3,2)	+30*(3,0;4,4,2)	-30*(3,0;5,2,1)	-60*(3,0;4,3,1)	
	+30*(3,0;4,2,0)	+120*(2,3;4,4,1)	-120*(2,3;5,4,2)	+600*(2,1;5,4,3)	
	+360*(2,1;4,3,1)	-360*(2,1;4,4,2)	-360*(2,1;5,3,2)	+15*(1,4;5,4,2)	
	-30*(1,4;4,4,1)	+15*(1,4;3,4,0)	+90*(1,2;5,3,2)	+540*(1,2;4,4,2)	
	-450*(1,2;5,4,3)	-180*(1,2;4,3,1)	-90*(1,2;3,4,1)	+90*(1,2;3,3,0)	
	-450*(1,0;5,3,3)	+525*(1,0;5,4,4)	-90*(1,0;4,2,1)	+45*(1,0;5,2,2)	
	-450*(1,0;4,4,3)	+45*(1,0;3,4,2)	+540*(1,0;4,3,2)	-90*(1,0;3,3,1)	
	+45*(1,0;3,2,0)	+60*(0,3;3,4,1)	-120*(0,3;4,4,2)	+60*(0,3;5,4,3)	
	-180*(0,1;3,4,2)	-360*(0,1;4,3,2)	+180*(0,1;5,3,3)	+180*(0,1;3,3,1)	
	+600*(0,1;4,4,3)	-420*(0,1;5,4,4)			
5 5	+1*(5,5;5,5,0)	-10*(5,3;5,5,1)	+10*(5,3;5,4,0)	+15*(5,1;5,5,2)	
	-30*(5,1;5,4,1)	+15*(5,1;5,3,0)	+25*(4,4;5,5,1)	-150*(4,2;5,5,2)	
	+150*(4,2;5,4,1)	-150*(4,0;5,4,2)	+75*(4,0;5,5,3)	+75*(4,0;5,3,1)	
	-10*(3,5;5,5,1)	+10*(3,5;4,5,0)	+300*(3,3;5,5,2)	-100*(3,3;5,4,1)	
	-100*(3,3;4,5,1)	+100*(3,3;4,4,0)	-750*(3,1;5,5,3)	-150*(3,1;5,3,1)	
	+150*(3,1;4,5,2)	+900*(3,1;5,4,2)	-300*(3,1;4,4,1)	+150*(3,1;4,3,0)	
	+150*(2,4;5,5,1)	-150*(2,4;5,5,2)	+1500*(2,2;5,5,3)	+900*(2,2;4,4,1)	
	-900*(2,2;4,5,2)	-900*(2,2;5,4,2)	-450*(2,0;5,3,2)	+1500*(2,0;5,4,3)	
	-1050*(2,0;5,5,4)	-900*(2,0;4,4,2)	+450*(2,0;4,5,3)	+450*(2,0;4,3,1)	
	-30*(1,5;4,5,1)	+15*(1,5;5,5,2)	+15*(1,5;3,5,0)	+150*(1,3;5,4,2)	
	-300*(1,3;4,4,1)	+900*(1,3;4,5,2)	-750*(1,3;5,5,3)	-150*(1,3;3,5,1)	
	+150*(1,3;3,4,0)	-2250*(1,1;4,5,3)	-450*(1,1;4,3,1)	-2250*(1,1;5,4,3)	
	+2700*(1,1;4,4,2)	+225*(1,1;5,3,2)	+225*(1,1;3,5,2)	+2625*(1,1;5,5,4)	
	-450*(1,1;3,4,1)	+225*(1,1;3,3,0)	+75*(0,4;3,5,1)	+75*(0,4;5,5,3)	
	-150*(0,4;4,5,2)	-450*(0,2;3,5,2)	-1050*(0,2;5,5,4)	+450*(0,2;5,4,3)	
	+450*(0,2;3,4,1)	-900*(0,2;4,4,2)	+1500*(0,2;4,5,3)	+225*(0,0;5,3,3)	
	+1500*(0,0;4,4,3)	+225*(0,0;3,5,3)	-450*(0,0;4,3,2)	-1050*(0,0;4,5,4)	
	-1050*(0,0;5,4,4)	-450*(0,0;3,4,2)	+945*(0,0;5,5,5)	+225*(0,0;3,3,1)	

formulae. The practically important difference arises from the Cartesian factorization of (2).

In the case of STF's the factorization is not possible, and the number of overlap integrals $\langle nlma\mathbf{A}|n'l'm'b\mathbf{B}\rangle$ increases with n^6, which increases the computer code for higher n excessively. The recurrence of only two indices, on the other hand, makes it feasible to *derive* the required formula every time an overlap integral is needed, although we find this situation by no means ideal with the need to calculate many such integrals for reciprocal form factors

$$B(\mathbf{r}) = \sum_i \sum_k \sum_j n_j c_{ij}^* c_{kj} \times \int\int\int \varphi_i^*(\mathbf{s}-\mathbf{R}_i+\mathbf{r})\varphi_k(\mathbf{s}-\mathbf{R}_k)\,\mathrm{d}\tau_s \quad (16)$$

as the Fourier transform of electron momentum densities (Benesch, Singh & Smith, 1971; Thulstrup, 1976; Pattison & Williams, 1976; Pattison, Weyrich & Williams, 1977; Schülke, 1977; Weyrich, 1978; Weyrich, Pattison & Williams, 1979).

Because of the factorization according to (2) the number of integrals over CGTF's increases only with the square of the angular quantum number l, whence it is advisable to implement ready analytical solutions in the computer code for all $I_{ll'}$ needed. Probably the most efficient way is to work with the six-parameter terms of (11). The parameters $\mu, \alpha, \beta, \gamma, \delta, \varepsilon$ for all $I_{ll'}$ with l, l' up to 5 (*i.e.* h orbitals and higher) are given in Table 1. All formulae are verified by quadrature; they exhibit no numerical instabilities.

In summary the integrals $I_{ll'}$ are thus written as

$$\begin{aligned} I_{ll'}(a, b, B_x - A_x) &= I_{00}(a, b, B_x - A_x) \times \sum_i \mu_i\{\alpha_i, \beta_i; \gamma_i, \delta_i, \varepsilon_i\} \\ &= I_{00}(a, b, B_x - A_x) \times \sum_i \mu_i F_x^{\alpha_i} G_x^{\beta_i} \times (1/2a)^{\gamma_i}(1/2b)^{\delta_i} \times [2ab/(a+b)]^{\varepsilon_i} \end{aligned} \quad (17)$$

with

$$F_x \equiv [2ab(B_x - A_x) + iak_x]/(a+b), \quad (18a)$$

$$G_x \equiv [2ab(A_x - B_x) + ibk_x]/(a+b) \quad (18b)$$

and a set of $\mu_i, \alpha_i, \beta_i, \gamma_i, \delta_i, \varepsilon_i$ that depends on l, l' as given in Table 1. The formulae for $I_{mm'}(a, b, B_y - A_y)$ and $I_{nn'}(a, b, B_z - A_z)$ are based on the same set of parameters $\mu_i, \alpha_i, \beta_i, \gamma_i, \delta_i, \varepsilon_i$ in

$$I_{mm'}(a, b, B_y - A_y) = I_{00}(a, b, B_y - A_y) \times \sum_i \mu_i F_y^{\alpha_i} G_y^{\beta_i} \times (1/2a)^{\gamma_i}(1/2b)^{\delta_i} \times [2ab/(a+b)]^{\varepsilon_i} \quad (19)$$

and

$$I_{nn'}(a, b, B_z - A_z) = I_{00}(a, b, B_z - A_z) \times \sum_i \mu_i F_z^{\alpha_i} G_z^{\beta_i} \times (1/2a)^{\gamma_i}(1/2b)^{\delta_i} \times [2ab/(a+b)]^{\varepsilon_i}, \quad (20)$$

where F_y, G_y and F_z, G_z are given by (18a) and (18b) with x replaced by y and z, respectively.

The total scattering integral for a given vector $\mathbf{k}$ is then

$$\begin{aligned} &I_{lmn,l'm'n'}(a, b, \mathbf{R}_{AB}) \\ &= [\pi/(a+b)]^{3/2} \exp\{[-abR_{AB}^2 + i\mathbf{k}\,.\,(a\mathbf{A}+b\mathbf{B}) - k^2/4]/(a+b)\} \\ &\times \sum_{i(ll')} \mu_i F_x^{\alpha_i} G_x^{\beta_i} (1/2a)^{\gamma_i}(1/2b)^{\delta_i} [2ab/(a+b)]^{\varepsilon_i} \\ &\times \sum_{j(mm')} \mu_j F_y^{\alpha_j} G_y^{\beta_j} (1/2a)^{\gamma_j}(1/2b)^{\delta_j} [2ab/(a+b)]^{\varepsilon_j} \\ &\times \sum_{k(nn')} \mu_k F_z^{\alpha_k} G_z^{\beta_k} (1/2a)^{\gamma_k}(1/2b)^{\delta_k} [2ab/(a+b)]^{\varepsilon_k}. \end{aligned} \quad (21)$$

The summation indices i, j, k are here discriminated for the sake of greater clarity. The notation $i(ll')$, $j(mm')$, $k(nn')$ means that they are the current numbers of terms in the sets given in Table 1 for ll', mm' and nn', respectively.

The similarity of (21) with the result of Chandler & Spackman (1978) raises the question of in what respect they differ. The difference lies in the sums, as becomes immediately apparent when counting the number of terms. In the case of $l = l' = 3$, Table 1 shows 18 terms, while the corresponding (triple) sum in the result of Chandler & Spackman contains 36 terms in total.

We are very grateful for the efficient support by the Fonds der Chemischen Industrie.

References

BENESCH, R., SINGH, S. R. & SMITH, V. H. JR (1971). *Chem. Phys. Lett.* **10**, 151-153.

BONHAM, R. A., PATTISON, P. & WEYRICH, W. (1986). In preparation.

BOYS, F. S. (1950). *Proc. R. Soc. London Ser. A*, **200**, 542-554.

CHANDLER, G. S. & SPACKMAN, M. A. (1978). *Acta Cryst.* A**34**, 341-343.

FROELICH, P., FLORES-RIVEROS, A. & WEYRICH, W. (1985). *J. Chem. Phys.* **82**, 2305-2312.

FROELICH, P. & WEYRICH, W. (1984). *J. Chem. Phys.* **80**, 5669-5676.

GROENEWEGEN, P. P. M. & FEIL, D. (1969). *Acta Cryst.* A**25**, 444-450.

GUERILLOT, C. R., GANACHAUD, J. P. & LISSILLOUR, R. (1968). *Theor. Chim. Acta*, **9**, 230-241.

LOFTHUS, A. (1962). *Mol. Phys.* **5**, 105-114.

MCWEENY, R. (1953). *Acta Cryst.* **6**, 631-637.

PATTISON, P., WEYRICH, W. & WILLIAMS, B. (1977). *Solid State Commun.* **21**, 967–970.
PATTISON, P. & WILLIAMS, B. (1976). *Solid State Commun.* **20**, 585–588.
RAE, A. D. (1978). *Acta Cryst.* A**34**, 719–724.
SAUNDERS, V. R. (1975). In *Computational Techniques in Quantum Chemistry and Molecular Physics*, edited by G. H. F. DIERCKSEN, B. T. SUTCLIFFE & A. VEILLARD. *NATO Advanced Study Institute Series, Series C: Mathematical and Physical Sciences*, Vol. 15, pp. 347–424. Dordrecht, Boston: Reidel.
SAUNDERS, V. R. (1983). In *Methods in Computational Molecular Physics*, edited by G. H. F. DIERCKSEN & S. WILSON. *NATO Advanced Study Institute Series, Series C: Mathematical and Physical Sciences*, Vol. 113, pp. 1–36. Dordrecht, Boston, Lancaster: Reidel.
SCHÜLKE, W. (1977). *Phys. Status Solidi B*, **82**, 229–235.
SHAVITT, I. (1963). In *Methods in Computational Physics*, edited by B. ALDER, S. FERNBACH & M. ROTENBERG, Vol. 2, pp. 1–45. New York, London: Academic Press.
THULSTRUP, P. W. (1976). *J. Chem. Phys.* **65**, 3386–3387.
WEYRICH, W. (1978). *Einige Beiträge zur Compton-Spektroskopie.* Habilitationsschrift, Darmstadt.
WEYRICH, W., PATTISON, P. & WILLIAMS, B. G. (1979). *Chem. Phys.* **41**, 271–284.
ZUPAN, J. (1974). *Croat. Chim. Acta*, **46**, 199–207.

Acta Cryst. (1986). A**42**, 261–271

Crystallography of Quasi-Crystals

BY T. JANSSEN

Institute for Theoretical Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(*Received* 15 *October* 1985; *accepted* 3 *February* 1986)

Abstract

The symmetry of quasi-crystals, a class of materials that has recently aroused interest, is discussed. It is shown that a quasi-crystal is a special case of an incommensurate crystal phase and that it can be described by a space group in more than three dimensions. A number of relevant three-dimensional quasi-crystals is discussed, in particular dihedral and icosahedral structures. The symmetry considerations are also applied to the two-dimensional Penrose patterns.

1. Introduction

Recently an Al–Mn alloy was found (Shechtman, Blech, Gratias & Cahn, 1984) that shows a number of uncommon properties. It has sharp peaks in its diffraction pattern, indicating long-range ordering. Its point-group symmetry, however, is not one of the crystallographic ones but contains fivefold axes, a fact that is incompatible with a periodic lattice. The phenomenon was considered so remarkable that its discovery reached the newspapers and it was stated that a new state of matter had been discovered. Fivefold axes had already been found in computer simulations of alloys (Steinhardt, Nelson & Ronchetti, 1983). Perhaps that is not so surprising, because fivefold symmetry was reported much earlier for packings in space. Coxeter refers in his beautiful book *Introduction to Geometry* (Coxeter, 1961, 1980) to an experiment carried out in 1727 by Stephen Hales who studied the form of peas pressed together in a box and observed the appearance of regular dodecahedra. A similar experiment with lead spheres was performed by Marvin in 1939 (see also Matzke, 1950).

The diffraction pattern is certainly new, but can be considered as a special case of a larger and already intensively studied class of materials: incommensurate crystal phases. Such a phase is characterized by the fact that its diffraction spots are sharp but need for their labelling more than the usual three integer indices. The five points of a regular pentagon are rationally dependent (their sum is zero), but four of them are rationally independent. Therefore, one needs at least four integers for the indices of a pattern with fivefold symmetry. The difference with the crystal phases observed until now is that there is no lattice of main reflections, such as present in, for example, incommensurately modulated crystals. For incommensurate crystal (IC) phases it has been shown (de Wolff, 1977; Janner & Janssen, 1977; de Wolff, Janssen & Janner, 1981) that the symmetry group is a group of transformations in a space with more than three dimensions. Here we shall address the questions how to describe the symmetry in the more general case and to study the possible structures.

In their study of the liquid–solid phase transition, Alexander & McTague (1978) showed in the framework of Landau theory that under certain conditions b.c.c. crystal structures are favoured. In the same paper they pointed out the possibility of a transition to a structure for which the wave vectors are points of a regular icosahedron and which has, consequently, no space-group symmetry. After the

0108-7673/86/040261-11$01.50