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On the use of the Obara–Saika recurrence relations for the calculation of structure factors in quantum crystallography

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Modern methods of quantum crystallography are techniques firmly rooted in quantum chemistry and, as in many quantum chemical strategies, electron densities are expressed as two-centre expansions that involve basis functions centred on atomic nuclei. Therefore, the computation of the necessary structure factors requires the evaluation of Fourier transform integrals of basis function products. Since these functions are usually Cartesian Gaussians, in this communication it is shown that the Fourier integrals can be efficiently calculated by exploiting an extension of the Obara–Saika recurrence formulas, which are successfully used by quantum chemists in the computation of molecular integrals. Implementation and future perspectives of the technique are also discussed.

1. Introduction

Quantum crystallography (QCr) is a branch of crystallography characterized by a strict interplay between quantum mechanical and crystallographic information (Genoni, Bučinský *et al.*, 2018; Novara *et al.*, 2018; Grabowsky *et al.*, 2017; Massa & Matta, 2018; Tsirelson, 2018). This interplay was already clear in the traditional and well known multipole model methods for the determination of experimental charge densities (Hirshfeld, 1971; Stewart, 1976; Kurki-Suonio, 1977; Hansen & Coppens, 1978; Tsirelson & Ozerov, 1996; Coppens, 1997) and in the pioneering techniques for the determination of diagonal and off-diagonal elements of one-particle density matrices (Clinton & Massa, 1972; Clinton *et al.*, 1973; Schmider *et al.*, 1992; Gillet *et al.*, 2001; Gillet, 2007). However, it became even more evident in the modern methods of QCr (Grabowsky *et al.*, 2017), (i) where the results obtained from quantum chemistry calculations are directly exploited in structural refinements to complete the information content of crystallographic measurements [*e.g.* in the Hirshfeld atom refinement (HAR) technique (Jayatilaka & Dittrich, 2008; Capelli *et al.*, 2014; Woińska *et al.*, 2014; Wall, 2016; Woińska *et al.*, 2016; Fugel *et al.*, 2018, 2019; Malaspina *et al.*, 2019)] or (ii) where the experimental crystallographic data are directly used in quantum mechanical computations to enhance the information content of the wavefunction [*e.g.* in the X-ray constrained wavefunction (XCW) fitting approach (Jayatilaka, 1998; Jayatilaka & Grimwood, 2001; Grimwood & Jayatilaka, 2001; Bytheway *et al.*, 2002; Bytheway, Grimwood, Figgis *et al.*, 2002; Grimwood *et al.*, 2003; Hudák *et al.*, 2010; Jayatilaka, 2012)]. Since these new strategies are firmly rooted in quantum chemistry, the electron-density distributions are generally written as two-centre expansions of Cartesian Gaussian-type functions (GTFs) centred on atomic nuclei. This leads to the

$$I_x(a_x + 1|b_x) = \left[P_x - A_x + \frac{ik_x}{2(\alpha_i + \beta_j)} \right] I_x(a_x|b_x) \\ + \frac{a_x}{2(\alpha_i + \beta_j)} I_x(a_x - 1|b_x) \\ + \frac{b_x}{2(\alpha_i + \beta_j)} I_x(a_x|b_x - 1)$$

fact that, for the computation of the needed structure factors, it is necessary to evaluate Fourier integrals of products of Cartesian Gaussians.

Over the years several research groups have faced this problem, from the initial efforts by McWeeny (1953), Chandler & Spackman (1978) and Barua & Weyrich (1986), to the more recent work of the Kirrander group in the context of the *ab initio* X-ray diffraction (AIXRD) method (Northey *et al.*, 2014; Moreno Carrascosa *et al.*, 2019; Northey & Kirrander, 2019). However, so far in this context the most efficient technique remains the one proposed by Jayatilaka (1994), who extended the McMurchie–Davidson (MD) recurrence relations used in quantum chemistry to evaluate molecular integrals (McMurchie & Davidson, 1978). This is actually the strategy used for the computation of structure factors in all the XCW methods implemented in the quantum crystallographic software *Tonto* (Jayatilaka & Grimwood, 2003).

The MD approach is only one of the many efficient strategies proposed and used by quantum chemists to compute molecular integrals efficiently. Many excellent reviews are currently available on the subject (Clementi & Corongiu, 1989; Gill, 1994; Helgaker *et al.*, 2000; Reine *et al.*, 2012). Among these techniques, one of the most popular and efficient is the strategy based on the recurrence relations introduced by Obara & Saika (1986), which were also discussed in the context of the Fourier transform operation in a follow-up paper (Obara & Saika, 1988). The Obara–Saika (OS) approach has actually been used very recently to compute structure factors corresponding to quantum chemistry-like electron densities: in XCW methods (Genoni, 2013*a,b*; Dos Santos *et al.*, 2014; Genoni & Meyer, 2016; Genoni, 2017; Casati *et al.*, 2017) based on the concept of extremely localized molecular orbitals (Stoll *et al.*, 1980; Meyer, Guillot, Ruiz-Lopez & Genoni, 2016*a*; Meyer, Guillot, Ruiz-Lopez, Jelsch & Genoni, 2016*b*; Meyer & Genoni, 2018), in the novel X-ray constrained spin-coupled technique (Genoni, Franchini *et al.*, 2018; Genoni *et al.*, 2019), in charge-density investigations of molecular magnets (Thomsen *et al.*, 2019; Gao *et al.*, 2019) and in the study of the capability of the XCW strategy in capturing electron correlation effects on electron density (Genoni *et al.*, 2017).

However, in all the cases mentioned above, the use of OS recurrence relations for the calculation of structure factors has barely been mentioned, and never discussed in detail. Therefore, the goal of this article is to fill this gap, by showing the theoretical details and the derivation of the extended OS formulas for theoretical structure factors, their implementation and, where possible, their comparison with other existing approaches.

2. Theory

2.1. Structure factors and electron-density expressions

As is well known (Tsirelson & Ozerov, 1996; Coppens, 1997; Schwarzenbach, 1996; Giacovazzo, 2002), structure factors are

Fourier transforms of the space- and time-averaged unit-cell electron density $\bar{\rho}_{\text{cell}}(\mathbf{r})$,

$$F_{\mathbf{H}} = \int d\mathbf{r} \bar{\rho}_{\text{cell}}(\mathbf{r}) \exp(i2\pi\mathbf{H} \cdot \mathbf{r}), \quad (1)$$

with \mathbf{H} the product of the reciprocal-lattice matrix and the vector representing the triad of Miller indices associated with the reflection under consideration. If one exploits the unit-cell symmetry operations $\{\mathbf{R}_j, \mathbf{t}_j\}_{j=1}^{N_m}$ (with \mathbf{R}_j and \mathbf{t}_j as a rotation matrix and a translation vector, respectively), $\bar{\rho}_{\text{cell}}(\mathbf{r})$ can actually be written in terms of the space- and time-averaged electron density $\bar{\rho}_0(\mathbf{r})$ of the symmetry-independent fragment in the unit cell. Equation (1) thus becomes

$$F_{\mathbf{H}} = \sum_{j=1}^{N_m} \exp(i2\pi\mathbf{t}_j \cdot \mathbf{H}) \int d\mathbf{r} \bar{\rho}_0(\mathbf{r}) \exp[i2\pi(\mathbf{R}_j^T \mathbf{H}) \cdot \mathbf{r}]. \quad (2)$$

The averaged density $\bar{\rho}_0(\mathbf{r})$ can be expressed as the convolution of the static electron density $\rho_0(\mathbf{r})$ with the probability distribution function $P(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_N)$ for the nuclear positions, namely

$$\bar{\rho}_0(\mathbf{r}) = \rho_0(\mathbf{r}) \star P(\mathbf{u}_1, \mathbf{u}_2, \dots, \mathbf{u}_N). \quad (3)$$

In the most recent methods of quantum crystallography (*i.e.* HAR and XCW techniques), the static electron density is written as a quantum chemistry-like electron distribution and, in the most general way (which is valid for both single-determinant and multi-determinant wavefunction-based approaches), it can be expressed in terms of natural orbitals,

$$\rho_0(\mathbf{r}) = \sum_{i=1}^M n_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}), \quad (4)$$

with ϕ_i the generic *i*th natural orbital associated with the obtained wavefunction, ϕ_i^* the complex conjugate of ϕ_i , n_i the occupation number for the *i*th natural orbital ($0 \leq n_i \leq 2$) and M the total number of basis functions used in the calculation. It is worth pointing out that, in the case of a single-determinant wavefunction, the natural orbitals correspond to the more usual molecular orbitals (MOs) and the occupation numbers are equal to 2 for the occupied MOs and 0 for the virtual ones.

In quantum chemistry, molecular orbitals are generally expanded in terms of basis functions centred on nuclei:

$$\phi_i(\mathbf{r}) = \sum_{\alpha=1}^M C_{\alpha i} \chi_{\alpha}(\mathbf{r} - \mathbf{A}), \quad (5)$$

where $\mathbf{A} = (A_x, A_y, A_z)$ is the position vector of the nucleus *A* on which the basis function χ_{α} is centred and the quantities $C_{\alpha i}$ are the molecular orbital expansion coefficients. Therefore, equation (4) can be rewritten as

$$\rho_0(\mathbf{r}) = \sum_{\alpha=1}^M \sum_{\beta=1}^M \chi_{\alpha}(\mathbf{r} - \mathbf{A}) D_{\alpha\beta}^0 \chi_{\beta}(\mathbf{r} - \mathbf{B}), \quad (6)$$

with the one-electron density matrix \mathbf{D}^0 defined as

$$D_{\alpha\beta}^0 = \sum_{i=1}^M n_i C_{\alpha i}^* C_{\beta i}. \quad (7)$$

It is clear that the expression of $\rho_0(\mathbf{r})$ given by equation (6) is an expansion involving basis functions χ_α and χ_β , which can possibly be centred on two different nuclei. If we use this expression for the static electron density in equation (3) and, consequently, in equation (2), and if we exploit the convolution theorem, the structure-factor expression becomes

$$F_{\mathbf{H}} = \sum_{\alpha=1}^M \sum_{\beta=1}^M D_{\alpha\beta}^0 I_{\beta\alpha}^{\mathbf{H}} = \text{Tr}[\mathbf{D}^0 \mathbf{I}^{\mathbf{H}}], \quad (8)$$

where $\mathbf{I}^{\mathbf{H}}$ is the matrix of the averaged Fourier integrals of the basis function products, namely the matrix having elements

$$I_{\alpha\beta}^{\mathbf{H}} = \sum_{j=1}^{N_m} \exp(i2\pi \mathbf{t}_j \cdot \mathbf{H}) F[P(\mathbf{A}, \mathbf{B})] \\ \times \int d\mathbf{r} \chi_\alpha(\mathbf{r} - \mathbf{A}) \chi_\beta(\mathbf{r} - \mathbf{B}) \exp[i2\pi(\mathbf{R}_j^T \mathbf{H}) \cdot \mathbf{r}], \quad (9)$$

with $F[P(\mathbf{A}, \mathbf{B})]$ as the Fourier transform of the probability distribution function for the nuclei A and B on which the basis functions χ_α and χ_β are centred, respectively. Since $P(\mathbf{A}, \mathbf{B})$ is not available, the factor $F[P(\mathbf{A}, \mathbf{B})]$ is usually approximated through methods that use parameters related to one-atom probability distribution functions, namely, the usual anisotropic displacement parameters (Stewart, 1969; Coppens *et al.*, 1971; Tanaka, 1988; Michael & Koritsanszky, 2015).

The other important factor in equation (9) is the Fourier integral of the product of basis functions. By setting $\mathbf{k} = 2\pi(\mathbf{R}_j^T \mathbf{H})$, that factor can be rewritten as

$$I = \int d\mathbf{r} \chi_\alpha(\mathbf{r} - \mathbf{A}; L_\alpha) \chi_\beta(\mathbf{r} - \mathbf{B}; L_\beta) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (10)$$

where, for the two basis functions, we have also explicitly indicated their total angular momenta L_α and L_β .

2.2. Recurrence relations for integrals

In quantum chemical calculations, the adopted basis functions are generally contracted Cartesian Gaussian-type functions (GTFs). In other words, they are linear combinations of primitive Cartesian GTFs (Boys, 1950):

$$\chi_\alpha(\mathbf{r} - \mathbf{A}) = \sum_{i=1}^{K_\alpha} N_{i\alpha} C_{i\alpha} g_{i\alpha}(\mathbf{r} - \mathbf{A}; L_\alpha) \quad (11)$$

and

$$\chi_\beta(\mathbf{r} - \mathbf{B}) = \sum_{j=1}^{K_\beta} N_{j\beta} C_{j\beta} g_{j\beta}(\mathbf{r} - \mathbf{B}; L_\beta), \quad (12)$$

where K_α and K_β are the degrees of contraction, $N_{i\alpha}$ and $N_{j\beta}$ are normalization constants, $C_{i\alpha}$ and $C_{j\beta}$ are the contraction coefficients for the primitive functions, and $g_{i\alpha}(\mathbf{r} - \mathbf{A}; L_\alpha)$ and $g_{j\beta}(\mathbf{r} - \mathbf{B}; L_\beta)$ are un-normalized primitive Cartesian Gaus-

sian-type functions centred on the nuclear positions \mathbf{A} and \mathbf{B} and of total angular momenta L_α and L_β , respectively.

Substituting (11) and (12) into (10), the integral I becomes

$$I = \sum_{i=1}^{K_\alpha} \sum_{j=1}^{K_\beta} N_{i\alpha} N_{j\beta} C_{i\alpha} C_{j\beta} \\ \times \int d\mathbf{r} g_{i\alpha}(\mathbf{r} - \mathbf{A}; L_\alpha) g_{j\beta}(\mathbf{r} - \mathbf{B}; L_\beta) \exp(i\mathbf{k} \cdot \mathbf{r}) \\ = \sum_{i=1}^{K_\alpha} \sum_{j=1}^{K_\beta} N_{i\alpha} N_{j\beta} C_{i\alpha} C_{j\beta} I_{i\alpha}^{j\beta}. \quad (13)$$

The un-normalized primitive Cartesian GTFs are usually written as

$$g_{i\alpha}(\mathbf{r} - \mathbf{A}; L_\alpha) \\ = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} \\ \times \exp \left\{ -\alpha_i \left[(x - A_x)^2 + (y - A_y)^2 + (z - A_z)^2 \right] \right\} \quad (14)$$

and

$$g_{j\beta}(\mathbf{r} - \mathbf{B}; L_\beta) \\ = (x - B_x)^{b_x} (y - B_y)^{b_y} (z - B_z)^{b_z} \\ \times \exp \left\{ -\beta_j \left[(x - B_x)^2 + (y - B_y)^2 + (z - B_z)^2 \right] \right\}. \quad (15)$$

$g_{i\alpha}$ is an un-normalized Cartesian GTF centred on $\mathbf{A} = (A_x, A_y, A_z)$, with angular momentum indices $\mathbf{a} = (a_x, a_y, a_z)$ and total angular momentum $L_\alpha = a_x + a_y + a_z$, while $g_{j\beta}$ is an un-normalized Cartesian GTF centred on $\mathbf{B} = (B_x, B_y, B_z)$, with angular momentum indices $\mathbf{b} = (b_x, b_y, b_z)$ and total angular momentum $L_\beta = b_x + b_y + b_z$.

Making use of the Gaussian product rule (Gill, 1994; Helgaker *et al.*, 2000), we can set

$$E_{i\alpha}^{j\beta} = \exp \left[-\frac{\alpha_i \beta_j}{\alpha_i + \beta_j} (\mathbf{A} - \mathbf{B})^2 \right] \quad (16)$$

and

$$\mathbf{P} = \frac{\alpha_i \mathbf{A} + \beta_j \mathbf{B}}{\alpha_i + \beta_j}. \quad (17)$$

Therefore, if we introduce equations (14) and (15) into (13), the integral $I_{i\alpha}^{j\beta}$ becomes

$$I_{i\alpha}^{j\beta} = E_{i\alpha}^{j\beta} \int dx \exp(ik_x x) (x - A_x)^{a_x} (x - B_x)^{b_x} \\ \times \exp \left[-(\alpha_i + \beta_j) (x - P_x)^2 \right] \\ \times \int dy \exp(ik_y y) (y - A_y)^{a_y} (y - B_y)^{b_y} \\ \times \exp \left[-(\alpha_i + \beta_j) (y - P_y)^2 \right] \\ \times \int dz \exp(ik_z z) (z - A_z)^{a_z} (z - B_z)^{b_z} \\ \times \exp \left[-(\alpha_i + \beta_j) (z - P_z)^2 \right], \quad (18)$$

which, in short notation, is equivalent to

$$I_{i\alpha}^{j\beta}(\mathbf{a}|\mathbf{b}) = I_{i\alpha}^{j\beta}(a_x, a_y, a_z|b_x, b_y, b_z) \\ = E_{i\alpha}^{j\beta} I_x(a_x|b_x) I_y(a_y|b_y) I_z(a_z|b_z). \quad (19)$$

Now, let us focus only on the factor $I_x(a_x|b_x)$:

$$I_x(a_x|b_x) = \int dx \exp(ik_x x) (x - A_x)^{a_x} (x - B_x)^{b_x} \\ \times \exp[-(\alpha_i + \beta_j)(x - P_x)^2]. \quad (20)$$

Taking into account the binomial theorem, we can actually write

$$(x - A_x)^{a_x} (x - B_x)^{b_x} = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (x - P_x)^{i_x+j_x} \\ \times (P_x - A_x)^{a_x-i_x} (P_x - B_x)^{b_x-j_x}. \quad (21)$$

Therefore, $I_x(a_x|b_x)$ can also be expressed as

$$I_x(a_x|b_x) = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x-i_x} (P_x - B_x)^{b_x-j_x} \\ \times \int dx \exp(ik_x x) \exp[-(\alpha_i + \beta_j)(x - P_x)^2] \\ \times (x - P_x)^{i_x+j_x}. \quad (22)$$

We also know that the Fourier transform switches from Cartesian to Hermite Gaussians (Čársky *et al.*, 1996):

$$\int dx \exp(ik_x x) \exp[-\alpha(x - A_x)^2] (x - A_x)^l \\ = \left(\frac{\pi}{\alpha}\right)^{1/2} \left[\frac{i}{2(\alpha^{1/2})}\right]^l H_l\left[\frac{k_x}{2(\alpha^{1/2})}\right] \exp\left(-\frac{k_x^2}{4\alpha}\right) \exp(ik_x A_x), \quad (23)$$

where H_l is a Hermite polynomial, namely

$$H_l(x) = (-1)^l \exp(x^2) \frac{d^l}{dx^l} \exp(-x^2). \quad (24)$$

Therefore, using relations (23) and (24), equation (22) can be rewritten as

$$I_x(a_x|b_x) = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} \\ (P_x - A_x)^{a_x-i_x} (P_x - B_x)^{b_x-j_x} \exp(ik_x P_x), \quad (25)$$

where $\Upsilon_{i_x+j_x}$ is defined as follows:

$$\Upsilon_{i_x+j_x} = \left(\frac{\pi}{\alpha_i + \beta_j}\right)^{1/2} \left[\frac{i}{2(\alpha_i + \beta_j)^{1/2}}\right]^{i_x+j_x} \\ \times H_{i_x+j_x}\left[\frac{k_x}{2(\alpha_i + \beta_j)^{1/2}}\right] \exp\left[-\frac{k_x^2}{4(\alpha_i + \beta_j)}\right]. \quad (26)$$

If we consider the derivative of equation (20) with respect to the nuclear coordinate A_x , we obtain

$$\frac{\partial I_x(a_x|b_x)}{\partial A_x} = -a_x \int dx \exp(ik_x x) (x - A_x)^{a_x-1} (x - B_x)^{b_x} \\ \times \exp[-(\alpha_i + \beta_j)(x - P_x)^2] \\ + 2\alpha_i \int dx \exp(ik_x x) (x - A_x)^{a_x+1} (x - B_x)^{b_x} \\ \times \exp[-(\alpha_i + \beta_j)(x - P_x)^2] \\ + 2\alpha_i(A_x - P_x) \int dx \exp(ik_x x) (x - A_x)^{a_x} (x - B_x)^{b_x} \\ \times \exp[-(\alpha_i + \beta_j)(x - P_x)^2] \quad (27)$$

which, in short notation, can be rewritten as

$$\frac{\partial I_x(a_x|b_x)}{\partial A_x} = -a_x I_x(a_x - 1|b_x) + 2\alpha_i I_x(a_x + 1|b_x) \\ + 2\alpha_i(A_x - P_x) I_x(a_x|b_x). \quad (28)$$

In an analogous way, the derivative of equation (20) with respect to the nuclear coordinate B_x is

$$\frac{\partial I_x(a_x|b_x)}{\partial B_x} = -b_x I_x(a_x|b_x - 1) + 2\beta_j I_x(a_x|b_x + 1) \\ + 2\beta_j(B_x - P_x) I_x(a_x|b_x). \quad (29)$$

Considering equation (25), the derivative with respect to A_x (see supporting information for more details) is

$$\frac{\partial I_x(a_x|b_x)}{\partial A_x} = \left(\frac{\alpha_i}{\alpha_i + \beta_j} - 1\right) a_x I_x(a_x - 1|b_x) \\ + \frac{\alpha_i}{\alpha_i + \beta_j} b_x I_x(a_x|b_x - 1) + ik_x \frac{\alpha_i}{\alpha_i + \beta_j} I_x(a_x|b_x). \quad (30)$$

In an analogous way, for the derivative of equation (25) with respect to B_x , we have

$$\frac{\partial I_x(a_x|b_x)}{\partial B_x} = \left(\frac{\beta_j}{\alpha_i + \beta_j} - 1\right) b_x I_x(a_x|b_x - 1) \\ + \frac{\beta_j}{\alpha_i + \beta_j} a_x I_x(a_x - 1|b_x) + ik_x \frac{\beta_j}{\alpha_i + \beta_j} I_x(a_x|b_x). \quad (31)$$

Since the derivatives $\partial I_x(a_x|b_x)/\partial A_x$ given by equations (28) and (30) must be identical, we can equate the right-hand sides of the two relations and obtain

$$I_x(a_x + 1|b_x) = \left[P_x - A_x + \frac{ik_x}{2(\alpha_i + \beta_j)}\right] I_x(a_x|b_x) \\ + \frac{a_x}{2(\alpha_i + \beta_j)} I_x(a_x - 1|b_x) \\ + \frac{b_x}{2(\alpha_i + \beta_j)} I_x(a_x|b_x - 1). \quad (32)$$

This is the vertical recurrence relation (VRR) for the ‘bra’ part of the Fourier integral. In the same way, equating the right-hand sides of equations (29) and (31) we get

$$I_x(a_x|b_x+1) = \left[P_x - B_x + \frac{ik_x}{2(\alpha_i + \beta_j)} \right] I_x(a_x|b_x) + \frac{a_x}{2(\alpha_i + \beta_j)} I_x(a_x-1|b_x) + \frac{b_x}{2(\alpha_i + \beta_j)} I_x(a_x|b_x-1) \quad (33)$$

which is the VRR for the 'ket' part of the Fourier integral.

Finally, comparing equations (32) and (33), one can also obtain

$$I_x(a_x|b_x+1) = I_x(a_x+1|b_x) + (A_x - B_x) I_x(a_x|b_x), \quad (34)$$

which is the horizontal recurrence relation (HRR).

The starting point for the recurrence formulas (32), (33) and (34) is the Fourier integral of the product that involves only *s*-type Cartesian Gaussian-type functions (*i.e.* Cartesian GTFs with a total angular momentum equal to zero). This integral is easy to compute:

$$I_x(0|0) = \int dx \exp(ik_x x) \exp[-(\alpha_i + \beta_j)(x - P_x)^2] = \left(\frac{\pi}{\alpha_i + \beta_j} \right)^{1/2} \exp \left[-\frac{k_x^2}{4(\alpha_i + \beta_j)} \right] \exp(ik_x P_x). \quad (35)$$

The recurrence relations obtained above can obviously be extended to the factors $I_y(a_y|b_y)$ and $I_z(a_z|b_z)$ in (19), and therefore equations (32), (33) and (34) can, respectively, be generalized to the three-dimensional case as follows:

$$I_{ia}^{jb}(\mathbf{a} + \mathbf{1}_n|\mathbf{b}) = \left[P_n - A_n + \frac{ik_n}{2(\alpha_i + \beta_j)} \right] I_{ia}^{jb}(\mathbf{a}|\mathbf{b}) + \frac{a_n}{2(\alpha_i + \beta_j)} I_{ia}^{jb}(\mathbf{a} - \mathbf{1}_n|\mathbf{b}) + \frac{b_n}{2(\alpha_i + \beta_j)} I_{ia}^{jb}(\mathbf{a}|\mathbf{b} - \mathbf{1}_n), \quad (36)$$

$$I_{ia}^{jb}(\mathbf{a}|\mathbf{b} + \mathbf{1}_n) = \left[P_n - B_n + \frac{ik_n}{2(\alpha_i + \beta_j)} \right] I_{ia}^{jb}(\mathbf{a}|\mathbf{b}) + \frac{a_n}{2(\alpha_i + \beta_j)} I_{ia}^{jb}(\mathbf{a} - \mathbf{1}_n|\mathbf{b}) + \frac{b_n}{2(\alpha_i + \beta_j)} I_{ia}^{jb}(\mathbf{a}|\mathbf{b} - \mathbf{1}_n), \quad (37)$$

$$I_{ia}^{jb}(\mathbf{a}|\mathbf{b} + \mathbf{1}_n) = I_{ia}^{jb}(\mathbf{a} + \mathbf{1}_n|\mathbf{b}) + (A_n - B_n) I_{ia}^{jb}(\mathbf{a}|\mathbf{b}), \quad (38)$$

where $n = x, y$ or z and $\mathbf{1}_n = (\delta_{nx}, \delta_{ny}, \delta_{nz})$ with δ as the Kronecker delta, and where the starting point is the integral

$$I_{ia}^{jb}(\mathbf{0}|\mathbf{0}) = E_{ia}^{jb} I_x(0|0) I_y(0|0) I_z(0|0) = E_{ia}^{jb} \left(\frac{\pi}{\alpha_i + \beta_j} \right)^{3/2} \exp \left[-\frac{k^2}{4(\alpha_i + \beta_j)} \right] \exp(i\mathbf{k} \cdot \mathbf{P}). \quad (39)$$

Equation (38) depends only on the nuclear centres of the primitives. Therefore, it can be directly used to evaluate integrals I between contracted basis functions [see equation (10)],

$$I[\mathbf{a}|\mathbf{b} + \mathbf{1}_n] = I[\mathbf{a} + \mathbf{1}_n|\mathbf{b}] + (A_n - B_n) I[\mathbf{a}|\mathbf{b}], \quad (40)$$

where the square brackets indicate integrals involving contracted basis functions. This relation provides a significant reduction in the computational cost associated with the evaluation of Fourier integrals involving highly contracted Cartesian GTFs.

Finally, since spherical Gaussian-type functions can be written as linear combinations of Cartesian Gaussian-type functions (Schlegel & Frisch, 1995), it is worth noting that the Obara–Saika recurrence relations can also be trivially used to evaluate Fourier integrals of spherical Gaussian products. In fact, it is enough to use the derived recurrence relations to compute the necessary Fourier integrals of Cartesian Gaussian products, which are afterwards properly combined to obtain the desired integrals involving spherical Gaussians.

3. Implementation of the Obara–Saika relations for the calculation of structure factors

3.1. Structure of the algorithm

In this section we will briefly illustrate how the OS recurrence relations have been implemented for the computation of structure factors, for example in the program associated with the X-ray constrained ELMO method (Genoni, 2013*a,b*). The formal structure of the algorithm is presented in Fig. 1, from which it is immediately evident that the implementation requires four nested loops. The outermost loop is over the reflections for which we want to compute the structure factors. The second loop is over the shell pairs, where the term 'shell' is that used in quantum chemistry to indicate a group of contracted Cartesian Gaussian-type functions having the same total angular momentum. It must not be confused with the term normally used in atomic physics to indicate electron shells (*i.e.* a group of electrons with the same principal quantum number). For this reason we can immediately compute the total angular momentum $m = L_\alpha + L_\beta$ of the shell pair and, consequently, of the integral. Furthermore, since all the basis functions of a shell are centred on the same nucleus, we can also calculate and store the distance between the nuclei associated with the shell pair under consideration. The third loop is over the equivalent positions in the unit cell to compute the different contributions to the matrix element $I_{\alpha\beta}^H$ [see equation (9)]. In this case, before starting the innermost loop, it is advantageous to compute the exponential and thermal pre-factors [*i.e.* $\exp(i2\pi\mathbf{t}_j \cdot \mathbf{H})$ and $F[P(\mathbf{A}, \mathbf{B})]$ in equation (9), respectively] and the vector \mathbf{k} [see equation (10)]. Finally, the innermost loop runs over all possible pairs of primitives for the considered pair of shells, and the OS recurrence relations really come into play to compute the required integrals.

For a given pair of primitives, the first step is the computation of the vector \mathbf{P} [see equation (17)] and the starting integral $I_{ia}^{jb}(\mathbf{0}|\mathbf{0})$ through equation (39). Note that, for the sake of simplicity and clarity, in Fig. 1 integrals $I_{ia}^{jb}(\mathbf{a}|\mathbf{b})$ are indicated as integrals $I(\mathbf{a}|\mathbf{b})$. If the total angular momentum m of the shell pair is different from 0, the vertical recurrence relation expressed by equation (36) is applied to obtain integrals $I_{ia}^{jb}(\mathbf{w}|\mathbf{0})$, where $\mathbf{w} = (w_x, w_y, w_z)$ and $0 \leq w_x + w_y + w_z \leq m$. Afterwards, some of these integrals (*i.e.* those with $L_\alpha \leq w_x + w_y + w_z \leq m$) are contracted incrementally. Obviously, if the total angular momentum m is equal to zero, the integral is immediately contracted.

After completing the innermost loop, all the necessary contracted integrals $I_{ia}^{jb}[\mathbf{w}|\mathbf{0}]$ are available and used to complete the loop over the equivalent positions in the unit cell, where the horizontal recurrence relation (40) is applied to compute the target integrals [if the angular momentum of the 'ket' part (L_β) is different from zero]. The target integrals are then multiplied by the normalization constants and by the exponential and thermal pre-factors. Finally, the computed integrals are used for the calculation of the desired structure factor [through equation (8)] in the last step of the loop over the reflections. Analysing the structure of the algorithm, it is also worth noting that the procedure is easily parallelizable, which would further increase the computational advantages of the OS approach in quantum crystallography.

Table 1

Mean absolute deviations between structure factors computed in double precision through the OS and MD approaches.

	cc-pVDZ	cc-pVTZ
α -Glycine	1.5×10^{-7}	1.5×10^{-7}
L-Alanine	2.6×10^{-8}	2.3×10^{-8}
Salicylic acid	2.2×10^{-7}	2.3×10^{-7}

3.2. Benchmark calculations

In order to demonstrate the accuracy and robustness of the OS method in the calculation of structure factors, in this subsection we show the results obtained using our in-house Fortran90 program that implements the algorithm described above. To accomplish this task we computed structure factors associated with static electron densities (namely, by setting the anisotropic displacement parameters to 0) calculated at the Hartree–Fock level on the crystal geometries of α -glycine (Destro *et al.*, 2000), L-alanine (Destro *et al.*, 1988) and salicylic acid (Munshi & Guru Row, 2006). Two different basis sets were used, cc-pVDZ and cc-pVTZ (Dunning, 1989). We computed the structure factors corresponding to the reflections deposited with the crystal structures (Destro *et al.*, 2000, 1988; Munshi & Guru Row, 2006). The values obtained using the OS method were compared with those resulting from the use of the MD approach in *Tonto* (Jayatilaka & Grimwood, 2003). The mean absolute discrepancies are shown in Table 1,

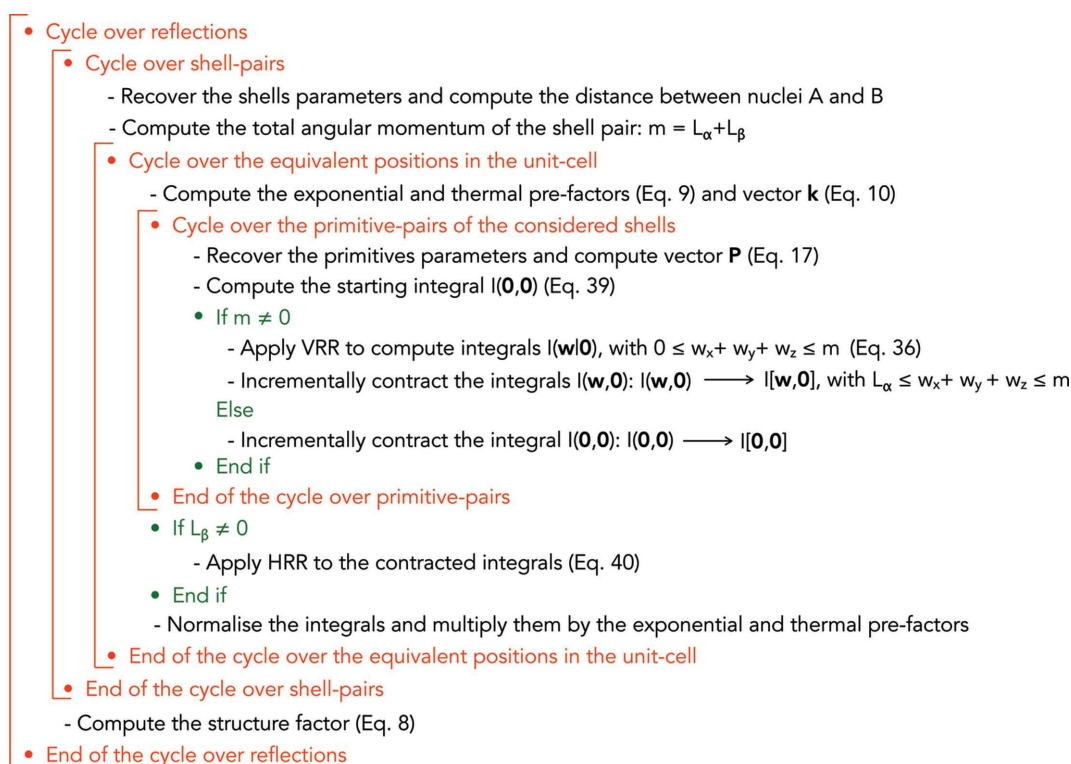


Figure 1

A schematic representation of the algorithm that implements the computation of structure factors through the use of the OS recurrence relations for Fourier integrals of Cartesian Gaussian products. The four nested loops of the algorithm are highlighted in red and by vertical lines at the side, while the 'if' constructs are highlighted in green. For the sake of simplicity and clarity, in this figure, the primitive integrals $I(\mathbf{a}|\mathbf{b})$ correspond to the primitive integrals $I_{ia}^{jb}(\mathbf{a}|\mathbf{b})$ in the text.

Table 2

Timings (in seconds) associated with the calculation of the structure factors by means of the OS recurrence relations: global CPU time for the complete set of reflections, and average time for the computation of a single structure factor.

The recorded timings were obtained running our in-house Fortran90 code (statically compiled with version 18.0.3 of the Intel Fortran Compiler) on an Intel Xeon Gold 6130 2.1 GHz processor. NBF is the number of basis functions. The numbers in parentheses in the leftmost column are the numbers of considered reflections.

	cc-pVDZ			cc-pVTZ		
	NBF	Global time (s)	Average time (s)	NBF	Global time (s)	Average time (s)
α -Glycine (3822)	100	62.808	0.016	250	298.316	0.078
L-Alanine (2519)	125	62.375	0.025	315	296.123	0.118
Salicylic acid (5704)	180	348.947	0.061	440	1238.053	0.217

while the values of the single structure factors obtained through the OS and MD approaches are provided in separate files in the supporting information. The two methods and the associated programs provide practically the same results.

For the sake of completeness, in Table 2 we also report the timings associated with the calculation of structure factors using the OS approach. The computation of single structure factors is already quite fast, but it is also worth noting that our current in-house program has not been optimized and, above all, has not been parallelized yet. Therefore, the speed of structure-factor calculations by means of the OS recurrence relations can be increased further.

4. Conclusions

We have shown that the Obara-Saika approach can easily be used for efficient analytical computation of structure factors in quantum crystallography. Unlike the pioneering techniques (McWeeny, 1953; Chandler & Spackman, 1978; Barua & Weyrich, 1986) based on case-by-case tabular enumerations of analytical results, the strategy described in this work makes use of recurrence relations and, for this reason, is conceptually close to the method relying on the extension of the McMurchie–Davidson recursion relationships introduced by Jayatilaka (1994). The difference between the OS and MD approaches is that the starting point of the latter consists of writing the products of Cartesian Gaussian-type functions as a linear combination of one-centre Hermite Gaussians, which enables the reduction of the integrations over two-centre functions to integrations over a set of one-centre functions. Recurrence relations are obviously advantageous from the computational point of view and nowadays are routinely used in modern quantum chemistry programs, although it is also worth bearing in mind that they may be subject to ‘digital erosion’ issues, as investigated by Barnett (2002) and, more recently, by Bailey & Borwein (2015).

Finally, it is important to note that, in this article, we have only shown how the OS method can be applied to the calculation of X-ray structure factors. However, the presented strategy can also be easily extended to the calculation of magnetic structure factors associated with polarized neutron

diffraction data and to the computation of Compton profiles. In other words, the applicability of the OS approach is not limited only to HAR or XCW methods, and in the future it could indeed be exploited in all those techniques of quantum crystallography that start from a wavefunction or density matrix *ansatz*. For example, it could be used in the context of the refinement strategies recently proposed by Gillet and coworkers (Guedidda, Yan & Gillet, 2018; Guedidda, Yan, Kibalin *et al.*, 2018; De Bruyne & Gillet, 2020) to obtain charge- or spin-resolved density matrices and densities, which could subsequently be analysed by means of the novel sophisticated approaches of quantum chemical topology (Gatti *et al.*, 2015, 2017; Macetti *et al.*, 2018).

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