Acta Cryst A FOUNDATIONS ADVANCES

Volume 76 (2020)

Supporting information for article:

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

Alessandro Genoni

Supporting Information for “On the use of the Obara-Saika recurrence relations for the calculation of structure factors in quantum crystallography”

Authors

Alessandro Genoni[a*]

[a] Université de Lorraine & CNRS, Laboratoire de Physique et Chimie Théoriques, 1 Boulevard Arago, Metz, F-57078, France

Correspondence email: Alessandro.Genoni@univ-lorraine.fr

S1. Further theoretical details.

In this section we provide some theoretical details concerning the derivation of equation (30) in the main text.

Let us start from equation (25) in the main text:

$$I_x(a_x|b_x) = \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x-i_x} (P_x - B_x)^{b_x-j_x} \, e^{ik_x P_x} \quad \text{(S1)}$$

where

$$\Upsilon_{i_x+j_x} = \sqrt{\frac{\pi}{\alpha_i + \beta_j}} \left(\frac{i}{2\sqrt{\alpha_i + \beta_j}} \right)^{i_x+j_x} H_{i_x+j_x}\left(\frac{k_x}{2\sqrt{\alpha_i + \beta_j}} \right) e^{-\frac{k_x{}^2}{4(\alpha_i+\beta_j)}} \quad \text{(S2)}$$

Since $\Upsilon_{i_x+j_x}$ and the binomial coefficients do not depend on the nuclear coordinates, the derivative of equation (S1) with respect to nuclear coordinate A_x can be written as follows:

$$\begin{aligned}\frac{\partial I_x(a_x|b_x)}{\partial A_x} &= \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (a_x - i_x)(P_x - A_x)^{a_x-i_x-1} \left(\frac{\partial P_x}{\partial A_x} - 1 \right) (P_x - B_x)^{b_x-j_x} \, e^{ik_x P_x} \\ &+ \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (b_x - j_x)(P_x - B_x)^{b_x-j_x-1} \frac{\partial P_x}{\partial A_x} (P_x - A_x)^{a_x-i_x} \, e^{ik_x P_x} \\ &+ \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x-i_x} (P_x - B_x)^{b_x-j_x} \, e^{ik_x P_x} \, ik_x \frac{\partial P_x}{\partial A_x} \quad \text{(S3)}\end{aligned}$$

Considering that

$$P_x = \frac{\alpha_i \, A_x + \beta_j \, B_x}{\alpha_i + \beta_j} \quad \text{(S4)}$$

we obtain

$$\frac{\partial P_x}{\partial A_x} = \frac{\alpha_i}{\alpha_i + \beta_j} \quad \text{(S5)}$$

and equation (S3) becomes:

$$\begin{aligned}\frac{\partial I_x(a_x|b_x)}{\partial A_x} &= \left(\frac{\alpha_i}{\alpha_i + \beta_j} - 1 \right) \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (a_x - i_x)(P_x - A_x)^{a_x-i_x-1} (P_x - B_x)^{b_x-j_x} \, e^{ik_x P_x} \\ &+ \frac{\alpha_i}{\alpha_i + \beta_j} \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (b_x - j_x)(P_x - B_x)^{b_x-j_x-1} (P_x - A_x)^{a_x-i_x} \, e^{ik_x P_x} \\ &+ \frac{\alpha_i}{\alpha_i + \beta_j} \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x} \Upsilon_{i_x+j_x} \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x-i_x} (P_x - B_x)^{b_x-j_x} \, e^{ik_x P_x} \, ik_x \quad \text{(S6)}\end{aligned}$$

Now, since it is easy to show that

$$\binom{a_x}{i_x}\ (a_x - i_x) = a_x \binom{a_x - 1}{i_x} \quad \text{(S7)}$$

and, in analogous way, that

$$\binom{b_x}{j_x}\ (b_x - j_x) = b_x \binom{b_x - 1}{j_x} \quad \text{(S8)}$$

we can write:

$$\begin{aligned}\frac{\partial I_x(a_x|b_x)}{\partial A_x} &= \left(\frac{\alpha_i}{\alpha_i + \beta_j} - 1\right) a_x \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x}\ \Upsilon_{i_x+j_x}\ \binom{a_x - 1}{i_x} \binom{b_x}{j_x}\ (P_x - A_x)^{a_x - i_x - 1} (P_x - B_x)^{b_x - j_x}\ e^{ik_x P_x} \\ &+ \frac{\alpha_i}{\alpha_i + \beta_j}\ b_x\ \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x}\ \Upsilon_{i_x+j_x}\ \binom{a_x}{i_x} \binom{b_x - 1}{j_x}\ (P_x - B_x)^{b_x - j_x - 1}\ \ (P_x - A_x)^{a_x - i_x}\ e^{ik_x P_x} \\ &+ ik_x\ \frac{\alpha_i}{\alpha_i + \beta_j} \sum_{i_x=0}^{a_x} \sum_{j_x=0}^{b_x}\ \Upsilon_{i_x+j_x}\ \binom{a_x}{i_x} \binom{b_x}{j_x} (P_x - A_x)^{a_x - i_x} (P_x - B_x)^{b_x - j_x}\ e^{ik_x P_x} \qquad \text{(S9)}\end{aligned}$$

Therefore, considering equation (S1), equation (S9) can be rewritten as follows:

$$\begin{aligned}\frac{\partial I_x(a_x|b_x)}{\partial A_x} &= \left(\frac{\alpha_i}{\alpha_i + \beta_j} - 1\right) a_x\ I_x(a_x - 1|b_x) + \frac{\alpha_i}{\alpha_i + \beta_j}\, b_x I_x(a_x|b_x - 1) \\ &+ ik_x\ \frac{\alpha_i}{\alpha_i + \beta_j}\ I_x(a_x|b_x) \qquad \text{(S10),}\end{aligned}$$

which is exactly equation (30) in the main text.