International Tables for Crystallography (2006). Vol. B, Section 3.4.5, pp. 388–389.

$$\begin{aligned} S'(n,0) = {} & [\Gamma(n/2)]^{-1}\sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d})|^{-n}\Gamma(n/2,\pi w^2|\mathbf{X}(\mathbf{d})|^2) \\ & - [\Gamma(n/2)]^{-1}2\pi^{n/2}w^n n^{-1} \\ & + [\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3} \\ & \times \Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2] \\ & + [\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}. \end{aligned}$$

3.4.5. Extension of the method to a composite lattice

Define a general lattice sum over direct-space points $\mathbf{R}_j$ which interact with pairwise coefficients Q_{jk}, where $Q_{jk} = Q_{kj}$:

$$V(n,\mathbf{R}_j) = (1/2)\sum_j\sum_k{}' Q_{jk}\sum_{\mathbf{d}}|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^{-n},$$

where the prime indicates that when $\mathbf{d}=0$ the self-terms with $j=k$ are omitted. For convenience the terms may be divided into three groups: the first group of terms has $\mathbf{d}=0$, where j is unequal to k; the second group has $\mathbf{d}$ not zero and j not equal to k; and the third group had $\mathbf{d}$ not zero and $j=k$. (A possible fourth group with $\mathbf{d}=0$ and $j=k$ is omitted, as defined.)

$$\begin{aligned} V(n,\mathbf{R}_j) = {} & (1/2)\sum_{j\neq k} Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n} \\ & + (1/2)\sum_{j\neq k} Q_{jk}S'(n,|\mathbf{R}_j-\mathbf{R}_k|) + (1/2)\sum_j Q_{jj}S'(n,0). \end{aligned}$$

By expanding this expression we obtain

$$\begin{aligned} V(n,\mathbf{R}_j) = {} & (1/2)\sum_{j\neq k} Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n} && (1) \\ & + \Big\{[1/2\Gamma(n/2)]\sum_{j\neq k} Q_{jk}\sum_{\mathbf{d}\neq 0}|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^{-n} \\ & \quad \times \Gamma(n/2,\pi w^2|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^2)\Big\} && (2) \\ & - \Big\{[1/2\Gamma(n/2)]\sum_{j\neq k} Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n} \\ & \quad \times \gamma(n/2,\pi w^2|\mathbf{R}_k-\mathbf{R}_j|^2)\Big\} && (3) \\ & + \Big\{[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_{j\neq k} Q_{jk}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3} \\ & \quad \times \Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2] \\ & \quad \times \exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k-\mathbf{R}_j)]\Big\} && (4) \\ & + [1/2\Gamma(n/2)]V_d^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}\sum_{j\neq k} Q_{jk} && (5) \\ & + \Big\{[1/2\Gamma(n/2)]\sum_j Q_{jj}\sum_{\mathbf{d}\neq 0}|\mathbf{X}(\mathbf{d})|^{-n} \\ & \quad \times \Gamma(n/2,\pi w^2|\mathbf{X}(\mathbf{d})|^2)\Big\} && (6) \\ & - [1/\Gamma(n/2)]\pi^{n/2}w^n n^{-1}\sum_j Q_{jj} && (7) \\ & + \Big\{[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_j Q_{jj}\sum_{\mathbf{h}\neq 0}|\mathbf{H}(\mathbf{h})|^{n-3} \\ & \quad \times \Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2]\Big\} && (8) \\ & + [1/2\Gamma(n/2)]V_d^{-1}\pi^{n/2}w^{n-3}2(n-3)^{-1}\sum_j Q_{jj}. && (9) \end{aligned}$$

This expression for V has nine terms, which are numbered on the right-hand side. Term (3) can be expressed in terms of Γ rather than γ:

$$\begin{aligned} (3) = {} & -(1/2)\sum_{j\neq k} Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n} \\ & + [1/\Gamma(n/2)]\sum_{j\neq k} Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n}\Gamma(n/2,\pi w^2|\mathbf{R}_k-\mathbf{R}_j|^2). \end{aligned}$$

It is seen that cancellation occurs with term (1) so that

$$\begin{aligned} (1)+(3) = {} & [1/\Gamma(n/2)]\sum_{j\neq k} Q_{jk}|\mathbf{R}_k-\mathbf{R}_j|^{-n} \\ & \times \Gamma(n/2,\pi w^2|\mathbf{R}_k-\mathbf{R}_j|^2), \end{aligned}$$

which is the $\mathbf{d}=0$, j unequal to k portion of the treated direct-lattice sum. The $\mathbf{d}$ unequal to 0, j unequal to k portion corresponds to term (2) and the $\mathbf{d}$ unequal to 0, $j=k$ portion corresponds to term (6). The direct-lattice terms may be consolidated as

$$\begin{aligned} (1)+(2)+(3)+(6) = {} & [1/2\Gamma(n/2)]\sum_j\sum_k{}' Q_{jk}\sum_{\mathbf{d}}|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^{-n} \\ & \times \Gamma[n/2,\pi w^2|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^2]. \end{aligned}$$

Now let us combine terms (4) and (8), carrying out the $\mathbf{h}$ summation first:

$$\begin{aligned} (4)+(8) = {} & [1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}}|\mathbf{H}(\mathbf{h})|^{n-3} \\ & \times \Gamma[(-n/2)+(3/2),\pi w^{-2}|\mathbf{H}(\mathbf{h})|^2] \\ & \times \sum_j\sum_k Q_{jk}\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k-\mathbf{R}_j)]. \end{aligned}$$

Terms (5) and (9) may be combined:

$$(5)+(9) = [\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n/2}w^{n-3}(n-3)^{-1}\left(\sum_j Q_{ij} + \sum_{j\neq k} Q_{jk}\right).$$

The final formula is shown below. The significance of the four terms is: (1) the treated direct-lattice sum; (2) a correction for the difference resulting from the removal of the origin term in direct space; (3) the reciprocal-lattice sum, except $\mathbf{h}=0$; and (4) the $\mathbf{h}=0$ term of the reciprocal-lattice sum.

$$\begin{aligned} & V(n,\mathbf{R}_j) \\ & = [1/2\Gamma(n/2)]\sum_j\sum_k{}' Q_{jk}\sum_{\mathbf{d}}|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^{-n} \\ & \quad \times \Gamma(n/2,\pi w^2|\mathbf{R}_k+\mathbf{X}(\mathbf{d})-\mathbf{R}_j|^2) && (1) \\ & \quad - [1/\Gamma(n/2)]\pi^{n/2}w^n n^{-1}\sum_j Q_{jj} && (2) \end{aligned}$$

$$+ [1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}}|\mathbf{H}(\mathbf{h})|^{n-3} \times \Gamma[(-n/2)+(3/2), \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2] \times \sum_j\sum_k Q_{jk}\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)] \quad (3)$$

$$+ [\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n/2}w^{n-3}(n-3)^{-1}\left(\sum_j\sum_k Q_{jk}\right). \quad (4)$$

3.4.6. The case of $n = 1$ (Coulombic lattice energy)

As taken above, the limit of the reciprocal-lattice $\mathbf{h} = 0$ term of $S'(n, \mathbf{R})$ or $S'(n, 0)$ existed only if n was greater than 3. The corresponding contributions to $V(n, \mathbf{R}_j)$ were terms (5) and (9) of Section 3.4.5. To extend the method to $n = 1$ we will show in this section that these $\mathbf{h} = 0$ terms vanish if conditions of unit-cell neutrality and zero dipole moment are satisfied.

The integral representation of the term (5) is

$$[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_{j\neq k} Q_{jk}\int\delta(0)|\mathbf{H}|^{n-3} \times \Gamma[(-n/2)+(3/2), \pi w^{-2}|\mathbf{H}|^2] \times \exp[2\pi i\mathbf{H}\cdot(\mathbf{R}_k - \mathbf{R}_j)]\,\mathrm{d}\mathbf{H}$$

and for term (9) is

$$[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\sum_j Q_{jj}\int\delta(0)|\mathbf{H}|^{n-3} \times \Gamma[(-n/2)+(3/2), \pi w^{-2}|\mathbf{H}|^2]\,\mathrm{d}\mathbf{H}.$$

Combining these two sums of integrals into one integral sum gives

$$[1/2\Gamma(n/2)]V_d^{-1}\pi^{n-(3/2)}\int\delta(0)|\mathbf{H}|^{n-3} \times \Gamma[(-n/2)+(3/2), \pi w^{-2}|\mathbf{H}|^2]\sum_j\sum_k Q_{jk} \times \exp[2\pi i\mathbf{H}\cdot(\mathbf{R}_k - \mathbf{R}_j)]\,\mathrm{d}\mathbf{H}.$$

For $n = 1$, suppose q_j are net atomic charges so that the geometric combining law holds for $Q_{jk} = q_j q_k$. Then the double sum over j and k can be factored so that the limit that needs to be considered is

$$\lim_{|\mathbf{H}|\to 0}\frac{\left[\sum_k q_k\exp(2\pi i\mathbf{H}\cdot\mathbf{R}_k)\right]\left[\sum_j q_j\exp(-2\pi i\mathbf{H}\cdot\mathbf{R}_j)\right]}{|\mathbf{H}|^2}.$$

If the unit cell does not have a net charge, the sum over the q's goes to zero in the limit and this is a 0/0 indeterminate form. Let $|\mathbf{H}|$ approach zero along the polar axis so that $\mathbf{H}\cdot\mathbf{R}_k = H_3R_{3k}$, where subscript 3 indicates components along the polar axis. To find the limit with L'Hospital's rule the numerator and denominator are differentiated twice with respect to H_3. Represent the numerator of the limit by the product (uv) and note that

$$\frac{\mathrm{d}^2(uv)}{\mathrm{d}x^2} = u\frac{\mathrm{d}^2v}{\mathrm{d}x^2} + v\frac{\mathrm{d}^2u}{\mathrm{d}x^2} + 2\frac{\mathrm{d}u}{\mathrm{d}x}\frac{\mathrm{d}v}{\mathrm{d}x}.$$

It is seen that in addition to cell neutrality the product of the first derivatives of the sums must exist. These sums are

$$\left[2\pi i\sum_k q_kR_{3k}\exp(2\pi iH_3R_{3k})\right]$$

and

$$\left[-2\pi i\sum_j q_jR_{3j}\exp(-2\pi iH_3R_{3j})\right],$$

which vanish if the unit cell has no dipole moment in the polar direction, that is, if $\sum q_jR_{3j} = 0$. Since the second derivative of the denominator is a constant, the desired limit is zero under the specified conditions. Now the polar direction can be chosen arbitrarily, so the unit cell must not have a dipole moment in any direction for the limit of the numerator to be zero. Thus we have the formula for the Coulombic lattice sum

$$V(1, \mathbf{R}_j) = [1/2\Gamma(1/2)]\sum_j\sum_k{}' Q_{jk}\sum_{\mathbf{d}}|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-1} \times \Gamma(1/2, \pi w^2|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2)$$
$$+ [1/2\Gamma(1/2)V_d^{-1}\pi^{-1/2}\sum_{\mathbf{h}}|\mathbf{H}(\mathbf{h})|^{-2} \times \Gamma(1/2, \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2)\sum_j\sum_k Q_{jk} \times \exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)]$$
$$- [1/\Gamma(1/2)]\pi^{1/2}w\sum_j q_j^2,$$

which holds on conditions that the unit cell be electrically neutral and have no dipole moment. If the unit cell has a dipole moment, the limiting value discussed above depends on the direction of $\mathbf{H}$. For methods of obtaining the Coulombic lattice sum where the unit cell does have a dipole moment, the reader is referred to the literature (DeWette & Schacher, 1964; Cummins *et al.*, 1976; Bertaut, 1978; Massidda, 1978).

3.4.7. The cases of $n = 2$ and $n = 3$

If $n = 2$ the denominator considered for the limit in the preceding section is linear in $|\mathbf{H}|$ so that only one differentiation is needed to obtain the limit by L'Hospital's method. Since a term of the type $\sum q_j\exp(2\pi i\mathbf{H}\cdot\mathbf{R}_j)$ is always a factor, the requirement that the unit cell have no dipole moment can be relaxed. For $n = 2$ the zero-charge condition is still required: $\sum q_j = 0$. When $n = 3$ the expression becomes determinate and no differentiation is required to obtain a limit. In addition, factoring the Q_{jk} sums into q_j sums is not necessary so that the only remaining requirement for this term to be zero is $\sum\sum Q_{jk} = 0$, which is a further relaxation beyond the requirement of cell neutrality.

3.4.8. Derivation of the accelerated convergence formula *via* the Patterson function

The structure factor with generalized coefficients q_j is defined by

$$F[\mathbf{H}(\mathbf{h})] = \sum_j q_j\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot\mathbf{R}_j].$$

The corresponding Patterson function is defined by

$$P(\mathbf{X}) = V_d^{-1}\sum_{\mathbf{h}}|F[\mathbf{H}(\mathbf{h})]|^2\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot\mathbf{X}].$$

The physical interpretation of the Patterson function is that it is nonzero only at the intersite vector points $\mathbf{R}_k + \mathbf{X}(\mathbf{h}) - \mathbf{R}_j$. If the origin point is removed, the lattice sum may be expressed as an integral over the Patterson function. This origin point in the Patterson function corresponds to intersite vectors with $j = k$ and $\mathbf{H}(\mathbf{h}) = 0$:

$$S_n = (1/2V_d)\int|\mathbf{X}|^{-n}[P(\mathbf{X}) - P(\mathbf{X})\delta(\mathbf{X})]\,\mathrm{d}\mathbf{X}.$$

Using the incomplete gamma function as a convergence function, this formula expands into two integrals

references