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

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

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 $Q_{jk} = q_jq_k$. 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

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

The first integral is shown only for a consistent representation; actually it will be reconverted to a sum and evaluated in direct space. The first part of the second integral will be evaluated with Parseval's theorem and the second part in the limit as $|\mathbf{X}|$ approaches zero:

$$[1/2V_d\Gamma(n/2)]\int FT_3[P(\mathbf{X})] \times FT_3[|\mathbf{X}|^{-n}\gamma(n/2, \pi w^2|\mathbf{X}|^2)]\ \mathrm{d}\mathbf{H} - \lim_{\mathbf{X}\to 0}[1/2V_d\Gamma(n/2)][P(0)|\mathbf{X}|^{-n}\gamma(n/2, \pi w^2|\mathbf{X}|^2)].$$

The first Fourier transform (of the Patterson function) is the set of amplitudes of the structure factors and the second Fourier transform has already been discussed above; the method for obtaining the limit (for n equal to or greater than 1) was also discussed above. The result obtained is

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

The integral can be converted into a sum, since $|F[\mathbf{H}(\mathbf{h})]|$ is nonzero only at the reciprocal-lattice points:

$$[1/2V_d\Gamma(n/2)]\pi^{n-(3/2)}\sum_{\mathbf{h}}|F[\mathbf{H}(\mathbf{h})]|^2|\mathbf{H}(\mathbf{h})|^{n-3} \times \Gamma[(-n/2) + (3/2), \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2].$$

The term with $\mathbf{H}(\mathbf{h}) = 0$ is evaluated in the limit, for n greater than 3, as

$$[\Gamma(n/2)]^{-1}V_d^{-1}\pi^{n/2}w^{n-3}(n-3)^{-1}|F(0)|^2.$$

Since $|F(0)|^2 = \sum\sum q_j q_k$, this term is identical with the third term of $V(n, \mathbf{R}_j)$ as derived earlier. The case of $n = 1$ is handled in the same way as previously discussed, where the limit of this term is zero provided the unit cell has no net charge or dipole moment.

3.4.9. Evaluation of the incomplete gamma function

The incomplete gamma function may be expressed in terms of commonly available functions such as the exponential integral and the complement of the error function. The definition of the exponential integral is

$$E_1(x^2) = \int_{x^2}^{\infty} t^{-1}\exp(-t)\ \mathrm{d}t = \Gamma(0, x^2).$$

The definition of the complement of the error function is

$$\mathrm{erfc}(x) = \int_{x}^{\infty}\exp(-t^2)\ \mathrm{d}t = \pi^{-1/2}\Gamma(1/2, x^2).$$

Numerical approximations to these functions are given, for example, by Hastings (1955). The recursion formula for the incomplete gamma function (Davis, 1972)

$$\Gamma(n+1, x^2) = n\Gamma(n, x^2) + x^{2n}\exp(-x^2)$$

may be used to obtain working formulae starting from the special values of $\Gamma(0, x^2)$ and $\Gamma(1/2, x^2)$ which are defined above. Also we note that $\Gamma(1, x^2) = \exp(-x^2)$.

3.4.10. Summation over the asymmetric unit and elimination of intramolecular energy terms

Let us consider the case where the unit cell contains Z molecules which are related by Z symmetry operations, and it is desired to include only intermolecular distances in the summation. In the direct sum (1) the indices j and k will then run only over the asymmetric unit, and all terms with $\mathbf{d} = 0$ are eliminated. The calculated energy refers then to one molecule (or mole) rather than to one unit cell. The correction term (2) also refers to one molecule according to the range of j and k. Since the reciprocal-lattice sum refers to the entire unit cell, terms (3) and (4) need to be divided by Z to refer the energy to one molecule.

Both the direct and reciprocal sums must be corrected for the elimination of intramolecular terms. Using the convergence function $W(R)$, we have

$$V(n, \mathbf{R}_j) = \sum_{\text{inter}}|\mathbf{R}|^{-n}W(R) + \sum_{\text{intra}}|\mathbf{R}|^{-n}W(R) + \sum_{\text{inter}}|\mathbf{R}|^{-n}[1 - W(R)] + \sum_{\text{intra}}|\mathbf{R}|^{-n}[1 - W(R)].$$

As mentioned above, the second summation term, which is the intramolecular term in direct space, is simply left out of the calculation. When using the accelerated-convergence method the third and fourth summation terms are always obtained, evaluated in reciprocal space. The undesired inclusion of the intramolecular term (fourth term above) in the reciprocal-space sum may be compensated for by explicit subtraction of this term from the sum.

3.4.11. Reference formulae for particular values of n

In this section let $a^2 = \pi w^2|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2$ and $b^2 = \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2$. Let $T_0 = \sum Q_{jj} = \sum q_j^2$; $T_1 = \sum\sum Q_{jk} = T_0 + 2\sum\sum_{j>k} Q_{jk}$. If the geometric mean combining law holds, $T_1 = (\sum_j q_j)^2$; let

$$T_2(h) = \sum_j\sum_k Q_{jk}\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)] = T_0 + 2\sum_{j>k}\sum Q_{jk}\cos[2\pi\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)].$$

Then

$$T_2(\mathbf{h}) = |F(\mathbf{h})|^2 = |\sum_j q_j\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot\mathbf{R}_j]|^2 = A(\mathbf{h})^2 + B(\mathbf{h})^2,$$

where

$$A(\mathbf{h}) = \sum_j q_j\cos[2\pi\mathbf{H}(\mathbf{h})\cdot\mathbf{R}_j]$$

and

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

The formulae below describe $V(n, \mathbf{R}_j)$ in terms of T_0, T_1 and T_2; the distance $|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|$ is simply represented by R_{jkd}.

$$V(1, \mathbf{R}_j) = (1/2)\sum_j{\sum_k}' q_j\ q_k\sum_{\mathbf{d}}R_{jkd}^{-1}\ \mathrm{erfc}(a) + (1/2\pi V_d)\sum_{\mathbf{h}\neq 0}T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^{-2}\exp(-b^2) - wT_0$$

$$V(2, \mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}}R_{jkd}^{-2}\exp(-a^2) + (\pi/2V_d)\sum_{\mathbf{h}\neq 0}T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^{-1}\mathrm{erfc}(b) - (\pi/2)w^2T_0$$