International Tables for Crystallography (2010). Vol. B, Section 3.4.5, pp. 452–453.

$$+[\Gamma(n/2)]^{-1}V_{\rm d}^{-1}\pi^{n/2}w^{n-3}[2/(n-3)].$$

The final result for S' is

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

The significance of the terms is as follows. The first term represents the convergence-accelerated direct sum, which does not include the origin term; the next term, also in direct space, corrects for the remainder resulting from the subtraction of the origin term; the third term comes from Parseval's theorem and is a sum over the nonzero **h** reciprocal-lattice points; and the last term is the reciprocal-lattice $\mathbf{h}=0$ term.

If $\mathbf{R}=0$ the second term becomes an indeterminate form 0/0. The limit can be found with use of L'Hospital's rule again, this time for the 0/0 form. We need the limit of $f(x)/g(x)$, where $f(R)=\gamma(n/2,\pi w^2R^2)$ and $g(R)=R^n$. To differentiate the incomplete gamma function, we can again use Leibnitz's formula. In this case only the second term of the formula is nonzero and we obtain for the ratio of the first derivatives

$$\frac{2\pi^{n/2}w^n|\mathbf{R}|^{n-1}\exp(-\pi w^2|\mathbf{R}|^2)}{n|\mathbf{R}|^{n-1}},$$

so that the limiting value for this term as $|\mathbf{R}|$ approaches zero is

$$-[\Gamma(n/2)]^{-1}2\pi^{n/2}w^n n^{-1}.$$

Therefore, the value of the sum when $\mathbf{R}=0$ is

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

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 **d** not zero and j not equal to k; and the third group had **d** not zero and $j=k$. (A possible fourth group with $\mathbf{d}=0$ and $j=k$ is omitted, as defined.)

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

By expanding this expression we obtain

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

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:

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

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

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

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

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

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

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

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

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

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.

$$\begin{aligned} V(n,\mathbf{R}_j) &= [1/2\Gamma(n/2)]\sum_j\sum_k{}' Q_{jk}\sum_{\mathbf{d}}|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^{-n} \\ &\quad \times \Gamma(n/2, \pi w^2|\mathbf{R}_k + \mathbf{X}(\mathbf{d}) - \mathbf{R}_j|^2) \qquad (1)\\ &\quad - [1/\Gamma(n/2)]\pi^{n/2}w^n n^{-1}\sum_j Q_{jj} \qquad (2)\\ &\quad + [1/2\Gamma(n/2)]V_{\mathrm{d}}^{-1}\pi^{n-(3/2)}\sum_{\mathbf{h}}|\mathbf{H}(\mathbf{h})|^{n-3} \\ &\quad \times \Gamma[(-n/2)+(3/2), \pi w^{-2}|\mathbf{H}(\mathbf{h})|^2] \\ &\quad \times \sum_j\sum_k Q_{jk}\exp[2\pi i\mathbf{H}(\mathbf{h})\cdot(\mathbf{R}_k - \mathbf{R}_j)] \qquad (3)\\ &\quad + [\Gamma(n/2)]^{-1}V_{\mathrm{d}}^{-1}\pi^{n/2}w^{n-3}(n-3)^{-1}\left(\sum_j\sum_k Q_{jk}\right). \qquad (4) \end{aligned}$$

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

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

and for term (9) is

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

Combining these two sums of integrals into one integral sum gives

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

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

references