$$V(3,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-3}[\mathrm{erfc}(a) + 2a\pi^{-1/2}\exp(-a^2)] + (\pi/V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})E_1(b^2) - (2\pi/3)w^3T_0$$

$$V(4,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-4}(1+a^2)\exp(-a^2) + (\pi^{5/2}/V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})| \times [-\pi^{1/2}\mathrm{erfc}(b) + b^{-1}\exp(-b^2)] + (\pi^2/V_d)wT_1 - (\pi^2/4)w^4T_0$$

$$V(5,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-5} \times [\mathrm{erfc}(a) + 2\pi^{-1/2}a(1+2a^2/3)\exp(-a^2)] + (2\pi^3/3V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^2 \times [b^{-2}\exp(-b^2) - E_1(b^2)] + (2\pi^2/3V_d)w^2T_1 - (4\pi^2/15)w^5T_0$$

$$V(6,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-6}[1+a^2+(a^4/2)]\exp(-a^2) + (\pi^{9/2}/3V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^3 \times [\pi^{1/2}\mathrm{erfc}(b) + [(1/2b^3) - (1/b)]\exp(-b^2)] + (\pi^3/6V_d)w^3T_1 - (\pi^3/12)w^6T_0$$

$$V(7,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-7} \times [\mathrm{erfc}(a) + 2\pi^{-1/2}a[1+(2/3)a^2+(4/15)a^4] \times \exp(-a^2)] + (2\pi^5/15V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^4 \times [(-b^{-2}+b^{-4})\exp(-b^2) + E_1(b^2)] + (2\pi^3/15V_d)w^4T_1 - (8\pi^3/105)w^7T_0$$

$$V(8,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-8} \times [1+a^2+(a^4/2)+(a^6/6)]\exp(-a^2) + (2\pi^{13/2}/45V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^5 \times [-\pi^{1/2}\mathrm{erfc}(b) + [(1/b) - (1/2b^3) + (3/4b^5)] \times \exp(-b^2)] + (\pi^4/30V_d)w^5T_1 - (\pi^4/48)w^8T_0$$

$$V(9,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-9} \times [\mathrm{erfc}(a) + 2\pi^{-1/2}a[1+(2/3)a^2+(4/15)a^4 + (8/105)a^6]\exp(-a^2)] + (4\pi^7/315V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^6 \times [(b^{-2}-b^{-4}+2b^{-6})\exp(-b^2) - E_1(b^2)] + (8\pi^4/315V_d)w^6T_1 - (16\pi^4/945)w^9T_0$$

$$V(10,\mathbf{R}_j) = (1/2)\sum_j{\sum_k}' Q_{jk}\sum_{\mathbf{d}} R_{jkd}^{-10} \times [1+a^2+(a^4/2)+(a^6/6)+(a^8/24)]\exp(-a^2) + (\pi^{17/2}/315V_d)\sum_{\mathbf{h}\neq 0} T_2(\mathbf{h})|\mathbf{H}(\mathbf{h})|^7 \times [\pi^{1/2}\mathrm{erfc}(b) + [(-1/b) + (1/2b^3) - (3/4b^5) + (15/8b^7)]\exp(-b^2)] + (\pi^5/168V_d)w^7T_1 - (\pi^5/240)w^{10}T_0.$$

3.4.12. Numerical illustrations

Consider the case of the sodium chloride crystal structure (a face-centred cubic structure) as a simple example for evaluation of the Coulombic sum. The sodium ion can be taken at the origin, and the chloride ion halfway along an edge of the unit cell. The results can easily be generalized for this structure type by using the unit-cell edge length, a, as a scaling constant.

First, consider the nearest neighbours. Each sodium and each chloride ion is surrounded by six ions of opposite sign at a distance of $a/2$. The Coulombic energy for the first coordination sphere is $-(1/2)(12)(2/a)(1389.3654) = -16672.385/a$ kJ mol^{-1}. Table 3.4.2.1 shows that the converged value of the lattice energy is $-4855.979/a$. Thus the nearest-neighbour energy is over three times more negative than the total lattice energy. In the second coordination sphere each ion is surrounded by 12 similar ions at a distance of $a/2^{1/2}$. The energy contribution of the second sphere is $+(1/2)(24)(2^{1/2}/a)(1389.3654) = +23578.313/a$. Thus, major cancellation occurs and the net energy for the first two coordination spheres is $+6905.928/a$ which actually has the wrong sign for a stable crystal. The third coordination sphere again makes a negative contribution. Each ion is surrounded by eight ions of opposite sign at a distance of $a/3^{1/2}$. The energy contribution is $-(1/2)(16)(3^{1/2}/a)(1389.3654) = -19251.612/a$, now giving a total so far of $-12345.684/a$. In the fourth coordination sphere each ion is surrounded by six others of the same sign at a distance of a. The energy contribution is $+(1/2)(12)(1/a)(1389.3654) = +8336.19/a$ to yield a total of $-4009.491/a$.

It is seen immediately by examining the numbers that the Coulombic sum is converging very slowly in direct space. Madelung (1918) devised a method for accurate evaluation of the sodium chloride lattice sum. However, his method is not generally applicable for more complex lattice structures. Evjen (1932) emphasized the importance of summing over a neutral domain, and replaced the sum with an integral outside of the first few shells of nearest neighbours. But the method of Ewald remained as the

Table 3.4.12.1. *Accelerated-convergence results for the Coulombic sum (n = 1) of sodium chloride (kJ mol^{-1}, Å): the direct sum plus the constant term*

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
6.0	−779.087	−838.145	−860.393	−924.275	−1125.372
8.0	−818.549	−860.194	−863.764	−924.282	−1125.372
10.0	−865.323	−862.818	−863.811	−924.282	
12.0	−861.183	−862.824	−863.811		
14.0	−862.717	−862.828			
16.0	−862.792	−862.828			
18.0	−862.810				
20.0	−862.825				

references