

3.4. ACCELERATED CONVERGENCE TREATMENT OF  $R^{-N}$  LATTICE SUMS

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,  $T_1 = (\sum q_j)^2$ ; let

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

Then

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

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  $R_{jkd}$ .

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

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

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

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

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

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

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

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

### 3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

Table 3.4.12.1. Accelerated-convergence results for the Coulombic sum ( $n = 1$ ) of sodium chloride ( $\text{kJ mol}^{-1}$ ,  $\text{\AA}$ ): 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				

Table 3.4.12.2. The reciprocal-lattice results ( $\text{kJ mol}^{-1}$ ,  $\text{\AA}$ ) for the Coulombic sum ( $n = 1$ ) of sodium chloride

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
0.0	-277.872	-416.806	-555.742	-833.613	-1111.483
0.4	0.000	0.003	0.986	61.451	261.042
0.5		0.003	0.986	61.451	261.042
0.6				61.457	262.542
0.7				61.457	262.542
0.8					262.547
0.9					262.547

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

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

#### 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  $-(1/2)(12)(2/a)(1389.3654) = -16672.385/a \text{ kJ mol}^{-1}$ . 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 coordi-

Table 3.4.12.3. Accelerated-convergence results for the dispersion sum ( $n = 6$ ) of crystalline benzene ( $\text{kJ mol}^{-1}$ ,  $\text{\AA}$ ): the figures shown are the direct-lattice sum plus the two constant terms

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
6.0	-73.452	-77.761	-79.651	-61.866	76.645
8.0	-79.029	-80.374	-80.256	-61.870	76.645
10.0	-80.217	-80.571	-80.265	-61.870	
12.0	-80.527	-80.585	-80.265		
14.0	-80.578	-80.585			
16.0	-80.588				
18.0	-80.589				
20.0	-80.589				

Table 3.4.12.4. The reciprocal-lattice results ( $\text{kJ mol}^{-1}$ ,  $\text{\AA}$ ) for the dispersion sum ( $n = 6$ ) of crystalline benzene

Limit	$w = 0.1$	$w = 0.15$	$w = 0.2$	$w = 0.3$	$w = 0.4$
0.0	-5.547	-16.706	-32.326	-43.681	80.947
0.3	0.000	-0.004	-0.321	-16.792	-117.106
0.4	0.000	-0.004	-0.324	-18.656	-152.651
0.5			-0.324	-18.716	-155.940
0.6				-18.719	-157.102
0.7				-18.719	-157.227
0.8					-157.233
0.9					-157.234
1.0					-157.234

nation 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 only completely general and accurate method of evaluating the Coulombic sum for a general lattice. Although it was derived in a somewhat different way, Ewald's method is equivalent to accelerated convergence for the special case of  $n = 1$ .

In the reciprocal lattice of sodium chloride only points with indices  $(hkl)$  all even or all odd are permitted by the face-centred symmetry. The reciprocal cell has edge length  $1/a$  and the reciprocal-axis directions coincide with the direct-lattice axis directions. The closest points to the origin are the eight (111) forms at a distance of  $(1/a)/3^{1/2}$ . For sodium chloride this distance is  $0.3078 \text{ \AA}^{-1}$ .

Table 3.4.12.1 shows the effect of convergence acceleration on the direct-space portion of the ( $n = 1$ ) sum for the sodium chloride structure. The constant term  $-w \sum q_j^2$  is included in the values given. This constant term is always large if  $w$  is not zero; for instance, when  $w = 0.1$  this term is  $-277.872$  (Table 3.4.12.2). For  $w = 0.1$  the reciprocal-lattice sum is zero to six figures. Thus, only the direct sum (plus the constant term) is needed, evaluated out to  $20 \text{ \AA}$  in direct space, to obtain six-figure accuracy. As shown in Table 3.4.2.1 above, the same summation effort without the use of accelerated convergence gave 8% error, or only