

3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

 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				

 Table 3.4.12.2. The reciprocal-lattice results (kJ mol^{-1} , Å) 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

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

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

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 (kJ mol^{-1} , Å); 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 (kJ mol^{-1} , Å) 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 \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 \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

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Table 3.4.12.5. Approximate time (s) required to evaluate the dispersion sum ($n = 6$) for crystalline benzene within $0.001 \text{ kJ mol}^{-1}$ truncation error

w	Direct terms	Reciprocal terms	Time, direct	Time, reciprocal	Total time
0.0	(not yet converged at 20 \AA summation limit)				>107
0.1	15904	0	77	0	77
0.15	4718	34	23	6	29
0.2	2631	78	13	14	27
0.3	1313	246	7	46	53
0.4	524	804	3	149	152

slightly better than one-figure accuracy. The accelerated-convergence technique therefore yielded nearly five orders of magnitude improvement in accuracy, even without evaluation of the reciprocal-lattice sum.

The column showing $w = 0.15$ shows an example of how the reciprocal-lattice sum can also be neglected if lower accuracy is required. Table 3.4.12.2 shows that the reciprocal-lattice sum is still only 0.003. But now the direct-lattice sum only needs to be evaluated out to 14 \AA , with further savings in calculation effort. For w values larger than 0.15 the reciprocal sum is needed. For $w = 0.4$ this sum must be evaluated out to 0.8 \AA^{-1} to obtain six-figure accuracy.

Table 3.4.12.3 illustrates an application for the ($n = 6$) dispersion sum. When $w = 0.1 \text{ \AA}^{-1}$ five figures of accuracy can be obtained without consideration of the reciprocal sum. The direct sum is required out to 18 \AA . If $w = 0.15$, better than four-figure accuracy can still be obtained without evaluating the reciprocal-lattice sum. In this case, the direct lattice needs to be summed only to 12 \AA , and there is a saving of an order of magnitude in the length of the calculation. As with the Coulombic sum, if w is greater than 0.15 the reciprocal-lattice summation is needed; Table 3.4.12.4 shows the values.

The time required to obtain a lattice sum of given accuracy will vary depending on the particular structure considered and of course on the computer and program which are used. An example of timing for the benzene dispersion sum is given in Table 3.4.12.5 for the PCK83 program (Williams, 1984) running on a VAX-11/750 computer. In this particular case direct terms were evaluated at a rate of about 200 terms s^{-1} and reciprocal terms, being a sum themselves, were evaluated at a slower rate of about 5 terms s^{-1} .

Table 3.4.12.5 shows the time required for evaluation of the dispersion sum using various values of the convergence constant, w . The timing figures show that there is an optimum choice for w ; for the PCK83 program the optimum value indicated is $0.15\text{--}0.2 \text{ \AA}^{-1}$. In the program of Pietila & Rasmussen (1984) values in the range $0.15\text{--}0.2 \text{ \AA}^{-1}$ are also suggested. For the WMIN program (Busing, 1981) a slightly higher value of 0.25 \AA^{-1} is suggested. Trial calculations can be used to determine the

optimum value of w for the situation of a particular crystal structure, program and computer.

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