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

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

w	Direct terms	Reciprocal terms	Time, direct	Time, reciprocal	Total time
0.0	(not yet converged at 20 Å 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 Å, 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 Å^{-1} to obtain six-figure accuracy.

Table 3.4.12.3 illustrates an application for the $(n = 6)$ dispersion sum. When $w = 0.1$ Å^{-1} five figures of accuracy can be obtained without consideration of the reciprocal sum. The direct sum is required out to 18 Å. 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 Å, 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 0.15–0.2 Å^{-1}. In the program of Pietila & Rasmussen (1984) values in the range 0.15–0.2 Å^{-1} are also suggested. For the *WMIN* program (Busing, 1981) a slightly higher value of 0.25 Å^{-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.

References

Arfken, G. (1970). *Mathematical Methods for Physicists,* 2nd ed. New York: Academic Press.

Bertaut, E. F. (1952). *L'énergie électrostatique de réseaux ioniques. J. Phys. (Paris)*, **13**, 499–505.

Bertaut, E. F. (1978). *The equivalent charge concept and its application to the electrostatic energy of charges and multipoles. J. Phys. (Paris)*, **39**, 1331–1348.

Busing, W. R. (1981). *WMIN, a computer program to model molecules and crystals in terms of potential energy functions.* Oak Ridge National Laboratory Report ORNL-5747. Oak Ridge, Tennessee 37830, USA.

Cummins, P. G., Dunmur, D. A., Munn, R. W. & Newham, R. J. (1976). *Applications of the Ewald method. I. Calculation of multipole lattice sums. Acta Cryst.* A**32**, 847–853.

Davis, P. J. (1972). *Gamma function and related functions. Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, edited by M. Abramowitz & I. A. Stegun, pp. 260–262. London, New York: John Wiley. [Reprint, with corrections of 1964 Natl Bur. Stand. publication.]

DeWette, F. W. & Schacher, G. E. (1964). *Internal field in general dipole lattices. Phys. Rev.* **137**, A78–A91.

Evjen, H. M. (1932). *The stability of certain heteropolar crystals. Phys. Rev.* **39**, 675–694.

Ewald, P. P. (1921). *Die Berechnung optischer und elektrostatischer Gitterpotentiale. Ann. Phys. (Leipzig)*, **64**, 253–287.

Fortuin, C. M. (1977). *Note on the calculation of electrostatic lattice potentials. Physica (Utrecht)*, **86A**, 574–586.

Glasser, M. L. & Zucker, I. J. (1980). *Lattice sums. Theor. Chem. Adv. Perspect.* **5**, 67–139.

Hastings, C. Jr (1955). *Approximations for digital computers.* New Jersey: Princeton University Press.

Madelung, E. (1918). *Das elektrische Feld in Systemen von regelmässig angeordneten Punktladungen. Phys. Z.* **19**, 524–532.

Massidda, V. (1978). *Electrostatic energy in ionic crystals by the planewise summation method. Physica (Utrecht)*, **95B**, 317–334.

Nijboer, B. R. A. & DeWette, F. W. (1957). *On the calculation of lattice sums. Physica (Utrecht)*, **23**, 309–321.

Pietila, L.-O. & Rasmussen, K. (1984). *A program for calculation of crystal conformations of flexible molecules using convergence acceleration. J. Comput. Chem.* **5**, 252–260.

Widder, D. V. (1961). *Advanced Calculus*, 2nd ed. New York: Prentice-Hall.

Williams, D. E. (1971). *Accelerated convergence of crystal lattice potential sums. Acta Cryst.* A**27**, 452–455.

Williams, D. E. (1984). *PCK83, a crystal molecular packing analysis program.* Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA.

Williams, D. E. (1989a). *Accelerated convergence treatment of R^{-n} lattice sums. Crystallogr. Rev.* **2**, 3–23.

Williams, D. E. (1989b). *Accelerated convergence treatment of R^{-n} lattice sums. Corrections. Crystallogr. Rev.* **2**, 163–166.