

3. DUAL BASES IN CRYSTALLOGRAPHIC COMPUTING

 Table 3.4.2.2. Untreated lattice-sum results for the dispersion energy ($n = 6$) of crystalline benzene (kJ mol^{-1} , \AA)

Truncation limit	Number of molecules	Number of terms	Calculated energy
6.0	26	524	-69.227
8.0	51	1313	-76.007
10.0	77	2631	-78.179
12.0	126	4718	-79.241
14.0	177	7531	-79.726
16.0	265	11274	-80.013
18.0	344	15904	-80.178
20.0	439	22049	-80.295
Converged value			-80.589

the original sum, which contains the difference terms, is not increased.

$$V_n = (1/2) \sum_j^{\text{one cell}} \sum_k^{\text{all cells}} Q_{jk} R_{jk}^{-n} W(R) + (1/2) \sum_j^{\text{one cell}} \sum_k^{\text{all cells}} Q_{jk} R_{jk}^{-n} [1 - W(R)].$$

In the accelerated-convergence method the difference terms are expressed as an integral of the product of two functions. According to Parseval's theorem (described below) this integral is equal to an integral of the product of the two Fourier transforms of the functions. Finally, the integral over the Fourier transforms of the functions is converted to a sum in reciprocal (or Fourier-transform) space. The choice of the convergence function $W(R)$ is not unique; an obvious requirement is that the relevant Fourier transforms must exist and have correct limiting behaviour. Nijboer and DeWette suggested using the incomplete gamma function for $W(R)$. More recently, Fortuin (1977) showed that this choice of convergence function leads to optimal convergence of the sums in both direct and reciprocal space:

$$W(R) = \Gamma(n/2, \pi w^2 R^2) / \Gamma(n/2),$$

where $\Gamma(n/2)$ and $\Gamma(n/2, \pi w^2 R^2)$ are the gamma function and the incomplete gamma function, respectively:

$$\Gamma(n/2, \pi w^2 R^2) = \int_{\pi w^2 R^2}^{\infty} t^{(n/2)-1} \exp(-t) dt$$

and

$$\Gamma(n/2) = \Gamma(n/2, 0).$$

The complement of the incomplete gamma function is

$$\gamma(n/2, \pi w^2 R^2) = \Gamma(n/2) - \Gamma(n/2, \pi w^2 R^2).$$

3.4.4. Preliminary derivation to obtain a formula which accelerates the convergence of an R^{-n} sum over lattice points $\mathbf{X}(\mathbf{d})$

The three-dimensional direct-space crystal lattice is specified by the origin vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . A general vector in direct space is defined as

$$\mathbf{X}(\mathbf{x}) = x_1 \mathbf{a}_1 + x_2 \mathbf{a}_2 + x_3 \mathbf{a}_3,$$

where x_1, x_2, x_3 are the fractional cell coordinates of \mathbf{X} . A lattice vector in direct space is defined as

$$\mathbf{X}(\mathbf{d}) = d_1 \mathbf{a}_1 + d_2 \mathbf{a}_2 + d_3 \mathbf{a}_3,$$

where d_1, d_2, d_3 are integers (specifying particular values of x_1, x_2, x_3) designating a lattice point. V_d is the direct-cell volume which is equal to $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$. A general point in the direct lattice is $\mathbf{X}(\mathbf{x})$; the contents of the lattice are by definition identical as the components of \mathbf{x} are increased or decreased by integer amounts.

The reciprocal-lattice vectors are defined by the relations

$$\begin{aligned} \mathbf{a}_j \cdot \mathbf{b}_k &= 1 & j &= k \\ &= 0 & j &\neq k. \end{aligned}$$

A general vector in reciprocal space $\mathbf{H}(\mathbf{r})$ is defined as

$$\mathbf{H}(\mathbf{r}) = r_1 \mathbf{b}_1 + r_2 \mathbf{b}_2 + r_3 \mathbf{b}_3.$$

A reciprocal-lattice vector $\mathbf{H}(\mathbf{h})$ is defined by the integer triplet h_1, h_2, h_3 (specifying particular values of r_1, r_2, r_3) so that

$$\mathbf{H}(\mathbf{h}) = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3.$$

In other sections of this volume a shortened notation \mathbf{h} is used for the reciprocal-lattice vector. In this section the symbol $\mathbf{H}(\mathbf{h})$ is used to indicate that it is a particular value of $\mathbf{H}(\mathbf{r})$.

The three-dimensional Fourier transform $g(\mathbf{t})$ of a function $f(\mathbf{x})$ is defined by

$$g(\mathbf{t}) = FT_3[f(\mathbf{x})] = \int f(\mathbf{x}) \exp(2\pi i \mathbf{x} \cdot \mathbf{t}) d\mathbf{x}.$$

The Fourier transform of the set of points defining the direct lattice is the set of points defining the reciprocal lattice, scaled by the direct-cell volume. It is useful for our purpose to express the lattice transform in terms of the Dirac delta function $\delta(x - x_0)$ which is defined so that for any function $f(\mathbf{x})$

$$f(\mathbf{x}_0) = \int \delta(\mathbf{x} - \mathbf{x}_0) f(\mathbf{x}) d\mathbf{x}.$$

We then write

$$FT_3\left\{\sum_{\mathbf{d}} \delta[\mathbf{X}(\mathbf{x}) - \mathbf{X}(\mathbf{d})]\right\} = V_d^{-1} \sum_{\mathbf{h}} \delta[\mathbf{H}(\mathbf{r}) - \mathbf{H}(\mathbf{h})].$$

First consider the lattice sum over the direct-lattice points $\mathbf{X}(\mathbf{d})$, relative to a particular point $\mathbf{X}(\mathbf{x}) = \mathbf{R}$, with omission of the origin lattice point.

$$S'(n, \mathbf{R}) = \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d}) - \mathbf{R}|^{-n}.$$

The special case with $\mathbf{R} = 0$ will also be needed:

$$S'(n, 0) = \sum_{\mathbf{d} \neq 0} |\mathbf{X}(\mathbf{d})|^{-n}.$$