Appendix A

Brillouin zone summations

Many types of equations can be solved, and infinite lattice summations can be evaluated efficiently using spatial Fourier transform and reciprocal space techniques (as in §2.3.3, §4.3.2 and Appendix D). In the following, some of these techniques (and in particular the methods of evaluating summations over reciprocal lattice sites) are outlined.

A lattice vector $\mathbf{r}$ is defined in terms of the set of primitive vectors $\boldsymbol{a}_i$ as

$$\mathbf{r} = \sum_{i=1}^{d} \lambda_i \boldsymbol{a}_i, \tag{A.1}$$

where the λ_i are integers, d is the dimension of the lattice and $|\boldsymbol{a}_i| = a$, the lattice parameter. The spatial Fourier transform of a function $f(\mathbf{r})$ is defined to be

$$F(\boldsymbol{q}) = \sum_{\mathbf{r}} f(\mathbf{r}) \exp(i\boldsymbol{q} \cdot \mathbf{r}), \tag{A.2}$$

where the sum is over all lattice vectors. The reciprocal lattice vector is

$$\boldsymbol{q} = \sum_{j=1}^{d} q_j \boldsymbol{b}_j, \tag{A.3}$$

where the primitive vectors of the reciprocal lattice, $\boldsymbol{b}_j$, are defined by $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = a\delta_{i,j}$ and the q_j have dimensions of reciprocal length. The inverse Fourier transform is then

$$f(\mathbf{r}) = \frac{1}{N} \sum_{\boldsymbol{q}} F(\boldsymbol{q}) \exp(-i\boldsymbol{q} \cdot \mathbf{r}), \tag{A.4}$$

where N is the number of lattice sites and the sum is over all reciprocal lattice vectors.

An example of importance is where $f(\mathbf{r}) = \exp(-i\boldsymbol{q}'\cdot\mathbf{r})$, and the Fourier transform of $f(\mathbf{r})$ vanishes by symmetry for all values of $\boldsymbol{q}$ except $\boldsymbol{q} = \boldsymbol{q}'$, in which case $F(\boldsymbol{q}) = N$; that is,

$$F(\boldsymbol{q}) = N\delta_{\boldsymbol{q},\boldsymbol{q}'}. \tag{A.5}$$

The Kronecker delta function is

$$\delta_{\boldsymbol{q},\boldsymbol{q}'} \doteq \prod_{j=1}^{d} \delta_{q_j,q_j'} \tag{A.6}$$

where $\delta_{q_j,q_j'} = 1$ if $q_j = q_j'$ and is zero otherwise. It is straightforward to confirm that the inverse Fourier transform (equation (A.4)) of $N\delta_{\boldsymbol{q},\boldsymbol{q}'}$ is the original function $f(\mathbf{r}) = \exp(-i\boldsymbol{q}'\cdot\mathbf{r})$.

It is possible to define a finite region of reciprocal space, called the first Brillouin zone, which simplifies the summation over all possible reciprocal lattice vectors in the inverse Fourier transform. From the definition of the Fourier transform (equation (A.2)), $F(\boldsymbol{q})$ is periodic so that for any reciprocal space vector $\boldsymbol{q}$ there is an equivalent vector, $\boldsymbol{q}'$, that can be written

$$\boldsymbol{q}' = \boldsymbol{q} + \frac{2\pi}{a}\sum_{j=1}^{d} n_j\boldsymbol{b}_j, \tag{A.7}$$

where the n_j are integers, so that $F(\boldsymbol{q}) = F(\boldsymbol{q}')$ for any n_j. In particular, any vector $\boldsymbol{q}$ has an equivalent vector, $\boldsymbol{q}'$, in the first Brillouin zone, which is the region in reciprocal space of vectors whose components satisfy the inequality $a|q_j'| \leq \pi$. This region of reciprocal space is sufficient to completely specify $F(\boldsymbol{q})$ for any vector $\boldsymbol{q}$ since the period of the exponential of a purely imaginary number is 2π.

The inverse Fourier transform of $F(\boldsymbol{q})$ (equation (A.4)) includes a summation over all reciprocal lattice sites, $\boldsymbol{q}$, and can, by the periodicity of the argument, be written as a summation over the equivalent vectors in the first Brillouin zone. The summation over a finite volume involves a quasi-infinite number of terms and can therefore be well approximated by an integral of the continuum over the first Brillouin zone, multiplied by the density of reciprocal lattice vectors, $v/(2\pi)^d$ where v is the volume (area) of the primitive cell of the real lattice. The following notations are then equivalent:

$$\frac{1}{N}\sum_{\boldsymbol{q}} \equiv \frac{v}{(2\pi)^d}\int_{BZ} d\boldsymbol{q} \tag{A.8}$$

where $v = V/N$ and V is the total volume (area) of the lattice. In three-dimensional lattices $v = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$ and

$$\frac{v}{(2\pi)^3}\int_{BZ} d\boldsymbol{q} \doteq \frac{v}{(2\pi)^3}\iiint_{-\pi/a}^{\pi/a} \frac{a^3}{v}\, dq_1\, dq_2\, dq_3 \tag{A.9}$$

since $\boldsymbol{b}_1 \cdot (\boldsymbol{b}_2 \times \boldsymbol{b}_3) = a^3/v$, and a similar relation holds for two-dimensional lattices, where $v = |\boldsymbol{a}_1 \times \boldsymbol{a}_2|$. Expression (A.9) is valid only for lattices where the condition $|\boldsymbol{a}_i| = a$ for $1 \leq i \leq d$ holds. The above finite, one-dimensional integrals can be evaluated numerically using the Gauss-Legendre technique (Abramowitz and Stegun 1972) to high accuracy in most cases.

The Kronecker delta function notation, $N\delta_{\boldsymbol{q},\boldsymbol{q}'}$, used with the summation notation in the above example becomes the delta function

$$(2\pi)^d \delta(\boldsymbol{q} - \boldsymbol{q}') \doteq \left(\frac{2\pi}{a}\right)^d \prod_{j=1}^{d} \delta(q_j - q_j') \tag{A.10}$$

in the integral approximation since

$$F(\boldsymbol{q}') = \frac{1}{N}\sum_{\boldsymbol{q}} N\delta_{\boldsymbol{q},\boldsymbol{q}'} F(\boldsymbol{q}) = \frac{v}{(2\pi)^d}\int_{BZ} (2\pi)^d \delta(\boldsymbol{q} - \boldsymbol{q}') F(\boldsymbol{q})\, d\boldsymbol{q}. \tag{A.11}$$

Some types of integrals over the Brillouin zone of the the cubic lattices, particularly lattice generating functions, are especially time consuming to calculate accurately using the Gauss-Legendre technique. In these cases it is advantageous to use the special points integration technique of Chadi and Cohen (1973) which makes use of the 48 symmetry operators R_i of the cubic point group (see, for example, Burns and Glazer 1990) to define the function

$$F_1(\boldsymbol{q}) = \sum_{i=1}^{48} F(R_i \boldsymbol{q}) \tag{A.12}$$

which has the complete symmetry of the lattice. The Brillouin zone integral can then be written

$$\int_{BZ} F(\boldsymbol{q})\, d\boldsymbol{q} = \int_{IR} F_1(\boldsymbol{q})\, d\boldsymbol{q} \tag{A.13}$$

where the integral of $F_1(\boldsymbol{q})$ is over the irreducible Brillouin zone which is 1/48 of the Brillouin zone volume and which generates the whole (first) Brillouin zone by the application of the 48 symmetry opperators R_i. The irreducible Brillouin zones of the

simple-cubic (s.c.), face-centred-cubic (f.c.c.) and body-centred-cubic (b.c.c.) lattices are

$$\begin{aligned} &0 \le q_3 \le q_2 \le q_1 \le \frac{\pi}{a}, && \text{(s.c.)} \\ 0 \le q_3 \le q_2 \le q_1 \le \frac{\pi}{a} \quad &\text{and} \quad q_1 + q_2 + q_3 \le \frac{3\pi}{2a}, && \text{(f.c.c.)} \\ 0 \le q_3 \le q_2 \le q_1 \le \frac{\pi}{a} \quad &\text{and} \quad 0 \le q_1 + q_2 \le \frac{\pi}{a}. && \text{(b.c.c.)} \end{aligned} \tag{A.14}$$

In the special points technique the integral is evaluated using the approximation

$$\int_{IR} F_1(\boldsymbol{q})\, d\boldsymbol{q} = \sum_{i=1}^{n} \alpha_i F_1(\boldsymbol{q}_i') \tag{A.15}$$

where the α_i are weights and the $\boldsymbol{q}_i'$ are n distinct special points in the irreducible Brillouin zone, generated from two reciprocal space vectors, $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, using the equation

$$\boldsymbol{q}_i = \boldsymbol{k}_1 + R_i \boldsymbol{k}_2. \tag{A.16}$$

These $\boldsymbol{q}_i$ are then transformed, using the R_i opperators, into the irreducible Brillouin zone to the vectors $\boldsymbol{q}_i'$ and the α_i are the numbers of $\boldsymbol{q}_i$ equivalent to each distinct $\boldsymbol{q}_i'$, normalised to unity. The $\boldsymbol{q}_i'$ so generated can then be used as seed vectors, $\boldsymbol{k}_1$, to generate an additional group of special points and this process can be repeated to improve the accuracy of the integral approximation. The base special-points sets are

$$\boldsymbol{k}_1 = \frac{\pi}{2a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \quad \boldsymbol{k}_2 = \frac{\pi}{4a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \tag{A.17}$$

with successive values of $\boldsymbol{k}_2$ for generating additional groups of points given by

$$\boldsymbol{k}_2 = \frac{\pi}{2^{m+1}a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \qquad m = 2, 3, \ldots \tag{A.18}$$

for the Brillouin zone of the s.c. lattice, and

$$\boldsymbol{k}_1 = \frac{\pi}{a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \quad \boldsymbol{k}_2 = \frac{\pi}{2a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \tag{A.19}$$

with successive values of $\boldsymbol{k}_2$ for generating additional groups of points given by

$$\boldsymbol{k}_2 = \frac{\pi}{2^m a}(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3), \qquad m = 2, 3, \ldots \tag{A.20}$$

for the Brillouin zones of the f.c.c. and b.c.c. lattices.

Appendix B

Transformation of $\mathrm{T}_p(\mathbf{q},\mathbf{j},z)$ and $\mathrm{T}_p(\mathbf{q})$

The functions $T_p(\boldsymbol{q},\boldsymbol{j},z)$ and $T_p(\boldsymbol{q})$ are the spatial Fourier transforms of $Y_{2p}(\Omega)/r^3$ in two- and three-dimensional systems respectively, where $\mathbf{r} = (r,\Omega)$. The transformations of these functions are each treated separately in the following two sections.

B.1 The two-dimensional case

The function $T_p(\boldsymbol{q},\boldsymbol{j},z)$ is defined by (see §2.3.3)

$$T_p(\boldsymbol{q},\boldsymbol{j},z) = \sum_{\boldsymbol{l}} \frac{Y_{2p}(\Omega_\alpha)}{r_\alpha^3} \exp(i\boldsymbol{q}\cdot\mathbf{r}_\alpha) \tag{B.1}$$

where $\mathbf{r}_\alpha$ are the vectors $\boldsymbol{l}+\boldsymbol{j}+z\hat{\boldsymbol{k}}$ and where the summation is over the lattice vectors in an infinite plane. In terms of basis vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, where $|\boldsymbol{a}_i| = a$, and two-dimensional reciprocal lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, defined by $\boldsymbol{a}_i\cdot\boldsymbol{b}_j = a\delta_{ij}$, the vectors $\mathbf{r}_\alpha$ and $\boldsymbol{q}$ are

$$\mathbf{r}_\alpha = z\hat{\boldsymbol{k}}+\boldsymbol{j}+\boldsymbol{l} = z\hat{\boldsymbol{k}}+(j_1\boldsymbol{a}_1+j_2\boldsymbol{a}_2)+(\lambda_1\boldsymbol{a}_1+\lambda_2\boldsymbol{a}_2), \tag{B.2}$$

$$\boldsymbol{q} = q_1\boldsymbol{b}_1+q_2\boldsymbol{b}_2. \tag{B.3}$$

The summation over $\boldsymbol{l}$ in equation (B.1) then corresponds to λ_1 and λ_2 summed over integers from $-\infty$ to ∞. This two-dimensional sum can be transformed into a

sum over two-dimensional reciprocal lattice co-ordinates μ_1 and μ_2, using the Poisson summation formula in a similar way to the case $\boldsymbol{q} = 0$ considered by Sholl (1966). The result is, for $p \geq 0$,

$$T_p(\boldsymbol{q},\boldsymbol{j},z) = A_p \sum_{\mu_1,\mu_2=-\infty}^{\infty} F_p(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2} \exp\{-2\pi(z/a) f_{\mu_1,\mu_2}\} \tag{B.4}$$

where

$$A_p = \frac{4\pi^2(-i)^p}{a|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\left[\frac{5}{4\pi(2-p)!\,(2+p)!}\right]^{1/2},$$

$$F_p(\mu_1,\mu_2,j_1,j_2) = \exp\Big\{i[p\omega_{\mu_1,\mu_2} - 2\pi(j_1\mu_1 + j_2\mu_2)]\Big\},$$

$$f_{\mu_1,\mu_2} = |(\mu_1 + a\rho_1)\boldsymbol{b}_1 + (\mu_2 + a\rho_2)\boldsymbol{b}_2|,$$

$$\omega_{\mu_1,\mu_2} = \arctan\left[\frac{-a_{2x}(\mu_1 + a\rho_1) + (\mu_2 + a\rho_2)}{a_{2y}(\mu_1 + a\rho_1)}\right],$$

$a_{2x} = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2/a^2$, $a_{2y} = \sqrt{1 - a_{2x}^2}$ and $\boldsymbol{q} = 2\pi\boldsymbol{\rho}$. The values of $T_p(\boldsymbol{q},\boldsymbol{j},z)$ for $p < 0$ can be obtained from

$$T_{-p}(\boldsymbol{q},\boldsymbol{j},z) = (-1)^p T_p^*(-\boldsymbol{q},\boldsymbol{j},z). \tag{B.5}$$

The expression (B.4) is not valid for $z = 0$. In this case the transformation can be made to a rapidly converging form by using an auxiliary function (Nijboer and DeWette 1957). The results are

$$T_0(\boldsymbol{q},\boldsymbol{j},0) = \frac{-\sqrt{5}}{2\pi a^3}\left[\sum_{\lambda_1,\lambda_2}{}' \frac{\exp(i\boldsymbol{q}\cdot\boldsymbol{\sigma}_{\lambda j})}{\sigma_{\lambda j}^3}\Gamma\left(\frac{3}{2},\pi\sigma_{\lambda j}^2\right) - \frac{2}{3}\pi^{3/2}\delta_{\boldsymbol{j},0}\right.$$
$$\left. + \frac{\pi^2 a^2}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\sum_{\mu_1,\mu_2} F_0(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2}\Gamma\left(-\frac{1}{2},\pi f_{\mu_1,\mu_2}^2\right)\right], \tag{B.6}$$

$$T_1(\boldsymbol{q},\boldsymbol{j},0) = 0, \tag{B.7}$$

$$T_2(\boldsymbol{q},\boldsymbol{j},0) = \frac{\sqrt{5}}{\sqrt{6}\pi a^3}\left[\sum_{\lambda_1,\lambda_2}{}' \frac{\exp[i(2\phi_{\lambda j} + \boldsymbol{q}\cdot\boldsymbol{\sigma}_{\lambda j})]}{\sigma_{\lambda j}^3}\Gamma\left(\frac{5}{2},\pi\sigma_{\lambda j}^2\right)\right.$$
$$\left. - \frac{\pi^2 a^2}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\sum_{\mu_1,\mu_2}{}' F_2(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2}\Gamma\left(\frac{1}{2},\pi f_{\mu_1,\mu_2}^2\right)\right] \tag{B.8}$$

where the prime on the summation over λ_1, λ_2 denotes the exclusion of the $\lambda_1 = \lambda_2 = 0$ term when $\boldsymbol{j} = 0$, and the prime on the summation over μ_1, μ_2 denotes the exclusion of the $\mu_1 = \mu_2 = 0$ term if $\boldsymbol{q} = 0$, and where $\boldsymbol{\sigma}_{\lambda j}$ is the projection of the vector $\mathbf{r}_\alpha$ on to the xy-plane; that is, $\boldsymbol{\sigma}_{\lambda j} = \mathrm{r}_\alpha - z\hat{\boldsymbol{k}} = \boldsymbol{l} + \boldsymbol{j}$. $\Gamma(x,\pi\sigma^2)$ is the incomplete gamma function.

B.2 The three-dimensional case

The function $T_p(\boldsymbol{q})$ is defined by (see §4.3.2)

$$T_p(\boldsymbol{q}) = \sum_{\boldsymbol{m}} \frac{Y_{2p}(\Omega_\alpha)}{r_\alpha^3} \exp(i\boldsymbol{q}\cdot\mathbf{r}_\alpha) \tag{B.9}$$

where the $Y_{2p}(\Omega)$ are spherical harmonics, and where the $\mathbf{r}_\alpha$ are the vectors $\boldsymbol{m}+\boldsymbol{j}$, where $\boldsymbol{m}$ are lattice vectors, and $\boldsymbol{j}$ is the nonzero relative displacement between the two sublattices in the crystal structure. The summation is over all the lattice vectors in the three-dimensional lattice. In terms of basis vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$, where $|\boldsymbol{a}_i| = a$ and which need not be orthogonal, and reciprocal lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ and $\boldsymbol{b}_3$, defined by $\boldsymbol{a}_i\cdot\boldsymbol{b}_j = a\delta_{ij}$, the vectors $\mathbf{r}_\alpha$ and $\boldsymbol{q}$ are

$$\mathbf{r}_\alpha = \boldsymbol{m}+\boldsymbol{j} = (\lambda_1\boldsymbol{a}_1+\lambda_2\boldsymbol{a}_2+\lambda_3\boldsymbol{a}_3)+(j_1\boldsymbol{a}_1+j_2\boldsymbol{a}_2+j_3\boldsymbol{a}_3), \tag{B.10}$$

$$\boldsymbol{q} = q_1\boldsymbol{b}_1+q_2\boldsymbol{b}_2+q_3\boldsymbol{b}_3. \tag{B.11}$$

The summation over $\boldsymbol{m}$ in equation (B.9) then corresponds to λ_1, λ_2 and λ_3 summed over integers from $-\infty$ to ∞. This summation can be transformed into a rapidly converging two-dimensional sum over reciprocal space co-ordinates μ_1 and μ_2, using the planewise summation technique developed by Nijboer and DeWette (1957) and discussed by Barton and Sholl (1980) for the case of orthogonal basis vectors. The result is, for $p \geq 0$ and $j_3 \neq 0$,

$$T_p(\boldsymbol{q}) = A_p \sum_{\mu_1,\mu_2=-\infty}^{\infty} F_p(\mu_1,\mu_2,j_1,j_2) f_{\mu_1,\mu_2} \left[(-)^p h(j_3,\mu_1,\mu_2) + h^*(1-j_3,\mu_1,\mu_2)\right] \tag{B.12}$$

where

$$A_p = \frac{4\pi^2(-i)^p}{a|\boldsymbol{a}_1\times\boldsymbol{a}_2|}\left[\frac{5}{4\pi(2+p)!\,(2-p)!}\right]^{1/2},$$

$$F_p(\mu_1,\mu_2,j_1,j_2) = \exp\Big\{i[p\omega_{\mu_1\mu_2} - 2\pi(j_1\mu_1+j_2\mu_2)]\Big\},$$

$$f_{\mu_1,\mu_2} = |(\mu_1+a\rho_1)\boldsymbol{b}_1' + (\mu_2+a\rho_2)\boldsymbol{b}_2'|,$$

$$\omega_{\mu_1\mu_2} = \arctan\left[\frac{a_{2x}(\mu_1+a\rho_1)-(\mu_2+a\rho_2)}{-a_{2y}(\mu_1+a\rho_1)}\right],$$

$$h(j,\mu_1,\mu_2) = \frac{\exp\{-2\pi j[a_{3z}f_{\mu_1,\mu_2} + i[t_1(\mu_1+a\rho_1)+t_2(\mu_2+a\rho_2)-a\rho_3]]\}}{1-\exp\{-2\pi[a_{3z}f_{\mu_1,\mu_2}+i[t_1(\mu_1+a\rho_1)+t_2(\mu_2+a\rho_2)-a\rho_3]]\}},$$

$$t_1 = \left(a_{3x} - \frac{a_{3y}a_{2x}}{a_{2y}}\right), \qquad t_2 = \frac{a_{3y}}{a_{2y}},$$

$a_{kx} = \boldsymbol{a}_k \cdot \boldsymbol{a}_1/a^2$ and $a_{ky} = \sqrt{1 - a_{kx}^2}$, for $k = 2$ and 3, and $2\pi\boldsymbol{\rho} = q_1\boldsymbol{b}'_1 + q_2\boldsymbol{b}'_2$ where the $\boldsymbol{b}'_i$ are the two-dimensional reciprocal lattice vectors defined by $\boldsymbol{a}_i \cdot \boldsymbol{b}'_j = a\delta_{ij}$ for i and $j = 1$, 2. The values of $T_p(\boldsymbol{q})$ for $p < 0$ can be obtained from

$$T_{-p}(\boldsymbol{q}) = T_p^*(-\boldsymbol{q}). \tag{B.13}$$

In the special case when $j_1 = j_2 = 0$ or $1/2$, as in the NaCl structure, $T_p(\boldsymbol{q}) = T_p(-\boldsymbol{q})$ in which case equation (B.13) becomes

$$T_{-p}(\boldsymbol{q}) = T_p^*(\boldsymbol{q}). \tag{B.14}$$

It is convenient to choose the basis vectors used to calculate the $T_p(\boldsymbol{q})$ for the NaCl structure to be the primitive lattice vectors of the f.c.c. lattice. The resulting spectral density functions, $g'_{pp'}(\omega\tau)$, will be for a magnetic field in the direction $\left(\arccos(1/\sqrt{3}), 3\pi/4\right)$ with respect to the crystallographic axes. The spectral density functions, $g_{pp'}(\omega\tau)$, corresponding to a magnetic field along the crystallographic axis are obtained from the spectral density functions for a magnetic field in the direction (β,α) using the rotation matrix $R(\alpha,\beta,0)$ as discussed by Sholl (1986) and where $\alpha = 3\pi/4$ and $\beta = \arccos(1/\sqrt{3})$. Crystal symmetry greatly simplifies the problem and the rotation can be achieved using the result, for $p = 0$ and 1,

$$g_{pp} = g'_{pp} + C_p(\sin^2 2\beta + \sin^4\beta \sin^2 2\alpha), \tag{B.15}$$

where

$$C_0 = \frac{3}{4}(g'_{11} - g'_{00}), \qquad \text{and} \qquad C_1 = \frac{1}{2}(g'_{00} - g'_{11}).$$