

Chapter 31

PERIODIC SYSTEMS

For most solids, the atomic arrangement of maximum stability (and therefore the equilibrium atomic configuration at zero temperature) is that of a perfect crystal, defined as a system that has long-range order in all its dimensions. The essential properties of crystals depend upon the microscopic arrangements of their atoms, and for the most part persist even when an overall, macroscopic sample does not have the full crystal symmetry. Loosely speaking, a crystal is a regular array of **cells**, each of which contains an identical distribution of atoms, and **long-range order** refers to the notion that even cells which are far apart are located (to high precision) at the points corresponding to the ordered array. Systems with long-range order in one, two, or all three dimensions are referred to as **periodic** (with 1-D, 2-D, or 3-D periodicity); the periodicity invokes a requirement of symmetry in the wave functions describing them, and also provides opportunities for specialized methods of computation.

The consequences of periodicity and long-range order are pervasive and influence phenomena ranging from the reflective properties of sample surfaces to the angular distribution of scattered radiation (exemplified by the importance of x-ray crystallography as an identification tool). Long-range order and symmetry also have a profound influence on the electronic states of periodic systems, and thereby on important properties such as electric conductivity. A good survey of a wide range of these topics must be reserved to a text on condensed-matter physics. Here we limit consideration to some of the mathematical methods that have been developed for the study of periodic systems.

31.1 LATTICES

In one dimension, a **lattice** (assumed infinite in extent) can be formed by taking a first lattice point (the origin), then identifying additional points by adding all integer multiples (both plus and minus) of a length h called either the **cell size** or the **lattice constant**. Thus, the lattice points constitute a set at positions nh , with $n = \dots, -2, -1, 0, 1, 2, \dots$. This recipe obviously identifies an equally spaced set of points, and can also be thought of as defining cells the n -th of which is bounded by nh and $(n+1)h$. With cells defined in this way, they form a “space-filling” set with each cell identified by its value of n ; all points of the space are within a cell or on a cell boundary.

In two dimensions, we can define a lattice as the origin point plus the vectors $n_1\mathbf{h}_1 + n_2\mathbf{h}_2$, where \mathbf{h}_1 and \mathbf{h}_2 are any two fixed vectors that are not collinear, and

n_1, n_2 can assume arbitrary positive, negative, or zero integer values. This prescription defines a set of cells, each bounded by a parallelogram with sides \mathbf{h}_1 and \mathbf{h}_2 . Significant differences from one-dimensional periodicity are (1) the vectors \mathbf{h}_1 and \mathbf{h}_2 may or may not have the same magnitude, and (2) they may or may not be perpendicular to each other. Providing only that \mathbf{h}_1 and \mathbf{h}_2 are not collinear, they define a space-filling set of 2-D cells indexed by n_1 and n_2 .

In three dimensions, lattices are defined by three vectors $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ that are not coplanar, and have lattice points at $n_1\mathbf{h}_1 + n_2\mathbf{h}_2 + n_3\mathbf{h}_3$. These lattices have unit cells that are parallelepipeds, with edges that may either have the same or different magnitudes, and which form angles with each other that may or may not be perpendicular. In any case, the parallelepipeds form a space-filling array of cells indexed by n_1, n_2 , and n_3 .

Whatever the number of dimensions, the cell defined by the \mathbf{h}_i is called the **primitive unit cell**.

BRAVAIS LATTICES

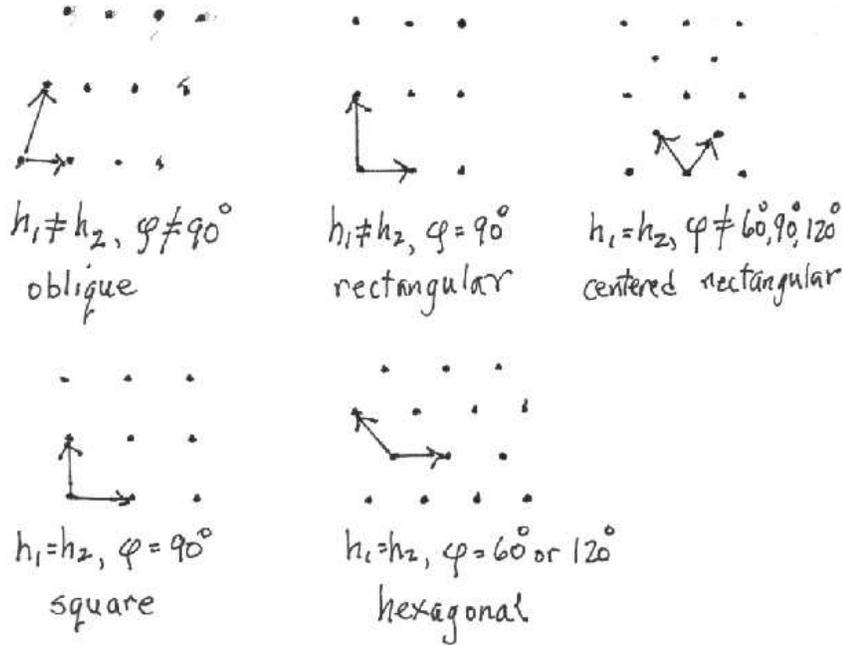
It may happen that the points defining a lattice have symmetry elements in addition to those describing the translational symmetry. For example, a two-dimensional lattice with $|\mathbf{h}_1| = |\mathbf{h}_2|$ and with \mathbf{h}_1 and \mathbf{h}_2 perpendicular is called **square**; there will be four-fold symmetry axes through all the lattice points and at the cell centers. The term **Bravais lattice** is used to identify lattices according to their symmetry elements. In one dimension, there is only one possibility, hence one Bravais lattice. In two dimensions, it turns out that there are five Bravais lattices (i.e., five distinct lattice symmetry types). They are shown in Fig. 31.1. In 3-D, the number of Bravais lattices is 14.

In many cases a lattice with oblique (i.e. nonperpendicular) lattice vectors can make an overall lattice with rectangular symmetry. An example in two dimensions occurs when \mathbf{h}_1 and \mathbf{h}_2 have the same length but are not perpendicular. Then, as shown in the panel of Fig. 31.1 labeled “centered rectangular”, the overall result is an array with a rectangular grid of lattice points, but with an extra point at the center of each rectangle. The area needed to create a rectangular repeating unit is twice the primitive cell size, and the resulting composite unit cell is sometimes called the **Bravais cell**. When the primitive and Bravais cells differ, the Bravais cell more completely reflects the symmetry of the periodic system and will be preferred for some types of computation. Moreover, when the Bravais cell has higher symmetry than the primitive cell, the symmetry of the Bravais cell is used when naming the corresponding Bravais lattice.

SPACE GROUPS

Having now defined space-filling arrays of cells, we consider periodic systems in which each cell is assigned the same content. If the cell content has nontrivial symmetry elements that are compatible with that of the Bravais lattice, the overall system will have a symmetry group that is the direct product of the lattice symmetry group and that of the unit cell (its **point-group** symmetry). This overall symmetry is identified as the **space group** of the system. Since there are 32 3-D point groups that are consistent with one or more of 14 lattice symmetries, it is not surprising that the number of possible space groups is large. A detailed enumeration finds 230 3-D space groups.

Figure 31.1: The five two-dimensional Bravais lattices. Lattice vector lengths: h_1 , h_2 ; angle between lattice vectors: φ .



PERIODICITY AND DIMENSIONALITY

Before leaving our discussion of lattices, we need to observe that there is a big difference between a 1-D system and a 3-D system with 1-D periodicity. Most of the physics applications of 1-D-periodic systems are to situations such as stereoregular polymers, where each monomer is a 3-D object, with all monomers connected together in a line (assumed straight). Then the overall symmetry of the system must include the internal symmetry of all the objects in the unit cell, which may include angular-momentum and spin variables. These additional complications arise, for example, when studying the electronic states of linear polymers, where each atom, even if centered on a line, may be described in terms of orbitals that are distributed in 3-D space and which may have nonzero angular momenta. A common case is that of a polymer which consists of a 3-D chain of atoms most of which are not on a common straight line, and which may have additional 3-D symmetry elements.

A similar situation is encountered with 2-D periodicity, which is appropriately used to describe the surfaces of solid (3-D) materials. The layers of atoms below the surface have different values of a coordinate perpendicular to the plane of periodicity, and may introduce elements (both with and without significant symmetry) in addition to that of the 2-D periodic structure. These issues are important to physics, but are outside the scope of the present discussion.

RECIPROCAL LATTICE

Given a Bravais lattice consisting of points \mathbf{r}_q (where q identifies the points in an arbitrary way), one can construct another Bravais lattice whose points are \mathbf{k}_p , such

that, for all p and q ,

$$e^{i\mathbf{k}_p \cdot \mathbf{r}_q} = 1. \quad (31.1)$$

Each of these lattices is said to be the **reciprocal lattice** of the other (and the reciprocal of the reciprocal recovers the original lattice). If a lattice has arisen as a quantity describing a phenomenon in physical space (as for example positions in a crystal), it is conventionally identified as a **direct-space** lattice, with its reciprocal partner then referred to as in **reciprocal space**.

The connection between the direct-space and reciprocal lattices depends crucially upon the periodicity of the complex exponential as a function of \mathbf{r}_q and \mathbf{k}_p . The essential behavior is already apparent for 1-D lattices (with $\mathbf{r} \rightarrow x$ and $\mathbf{k} \rightarrow k$). It is obvious that with $x = 0$ a point of the direct-space lattice, then $k = 0$ is a reciprocal-lattice point. If the direct-space and reciprocal lattice have the respective cell sizes h and g , then typical values of x and k are respectively nh and mg , with n and m integers, and Eq. (31.1) requires $(nh)(mg) = 2\pi N$, with N integral for all choices of m and n . This is only possible if $g = 2\pi/h$, showing that there is indeed a reciprocal relationship between the cell sizes of the direct-space and reciprocal lattices.

Continuing to three dimensions, we consider first the case that the three direct-space lattice vectors are mutually perpendicular, in the respective directions $\hat{\mathbf{e}}_i$. Equation (31.1) can then be satisfied individually in each dimension, and the reciprocal lattice can be characterized by lattice vectors \mathbf{g}_i , where for each i

$$\mathbf{g}_i = \frac{2\pi}{|\mathbf{h}_i|} \hat{\mathbf{e}}_i. \quad (31.2)$$

If the lattice vectors \mathbf{h}_i are not mutually perpendicular, we can still satisfy Eq. (31.1) by choosing each \mathbf{g}_i so that

$$\mathbf{h}_i \cdot \mathbf{g}_j = 2\pi\delta_{ij}, \quad (31.3)$$

thereby causing the scalar products of Eq. (31.1) to have the form

$$(n_1\mathbf{h}_1 + n_2\mathbf{h}_2 + n_3\mathbf{h}_3) \cdot (m_1\mathbf{g}_1 + m_2\mathbf{g}_2 + m_3\mathbf{g}_3) = 2\pi(n_1m_1 + n_2m_2 + n_3m_3),$$

i.e., integer multiples of 2π .

Given the \mathbf{h}_i , determination of the corresponding \mathbf{g}_i was the topic of Example 3.2.1; in the present notation (and at the present scaling), that result is

$$\mathbf{g}_1 = 2\pi \frac{\mathbf{h}_2 \times \mathbf{h}_3}{\mathbf{h}_1 \cdot \mathbf{h}_2 \times \mathbf{h}_3}, \quad \mathbf{g}_2 = 2\pi \frac{\mathbf{h}_3 \times \mathbf{h}_1}{\mathbf{h}_1 \cdot \mathbf{h}_2 \times \mathbf{h}_3}, \quad \mathbf{g}_3 = 2\pi \frac{\mathbf{h}_1 \times \mathbf{h}_2}{\mathbf{h}_1 \cdot \mathbf{h}_2 \times \mathbf{h}_3}. \quad (31.4)$$

An alternative to Eqs. (31.4) is to notice that the requirement of Eq. (31.1) corresponds to the matrix equation

$$\begin{pmatrix} \mathbf{g}_1 \\ \mathbf{g}_2 \\ \mathbf{g}_3 \end{pmatrix} \begin{pmatrix} \mathbf{h}_1 & \mathbf{h}_2 & \mathbf{h}_3 \end{pmatrix} = 2\pi \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (31.5)$$

which can be solved for the \mathbf{g}_i after forming the matrix containing the columns \mathbf{h}_i . The formulation corresponding to Eq. (31.5) can be generalized to an arbitrary number of dimensions.

Equation (31.5) enables us to establish a relationship between the volumes of the direct- and reciprocal-space unit cells. As found in Section 4.4, the determinants of

the matrices on the left-hand side of Eq. (31.5) are the respective volumes of these cells, and the product of these two volumes is equal to the determinant of the matrix on the right-hand side, which evaluates to $(2\pi)^3$. Thus,

$$(\text{reciprocal unit-cell volume}) = \frac{(2\pi)^3}{(\text{direct-space unit-cell volume})}. \quad (31.6)$$

In applications other than crystallography, it is usually most convenient to work with the Bravais cell, but to ignore the additional symmetries associated with, e.g., face-centered or body-centered lattice features. However, for crystallographic applications, we note that (1) the factor 2π , important for using Eq. (31.1), is often omitted from the definition of the reciprocal lattice, and (2) advantage is taken of the additional lattice symmetries. In particular, it can be shown that the lattice reciprocal to a body-centered cubic lattice is face-centered cubic and vice versa. Verification of this property is left to Exercise 31.1.3.

RECIPROCAL SPACE AND DELTA FUNCTION

The reciprocal space concept appears in formulas involving the Dirac delta function. In our study of angular momentum eigenfunctions, we already found (Exercise 15.5.4) that sums of products of azimuthal eigenfunctions could be used to generate a discrete representation of the delta function. If we extend the formula of that exercise to an arbitrary angular range, we have the important formula

$$\frac{1}{2\pi} \sum_{m=-\infty}^{\infty} \exp(imx) = \sum_{n=-\infty}^{\infty} \delta(x - 2n\pi). \quad (31.7)$$

The qualitative features of this result are as expected: if x is any integer multiple of 2π (including zero), every term in the m summation becomes unity and they add to an infinite result; any other value of x produces terms of regularly differing phase that combine to yield a negligible result.

To make Eq. (31.7) more generally applicable, we can change x to $2\pi x/h$ and regroup terms:

$$\frac{1}{2\pi} \sum_m e^{[2\pi im/h]x} = \sum_n \delta\left(\frac{2\pi}{h}[x - nh]\right) = \frac{h}{2\pi} \sum_n \delta(x - nh). \quad (31.8)$$

The last member of Eq. (31.8) uses the property of the delta function given in Eq. (1.158). We can now reinterpret Eq. (31.8), identifying its left-hand summation as one over a lattice of dimension $2\pi/h$, while the right-hand sum is over a lattice of dimension h . But a lattice of dimension $2\pi/h$ is the 1-D lattice reciprocal to a direct-space lattice of dimension h , so what we actually have is a formula that can be written

$$\sum_m e^{ik_m x} = h \sum_n \delta(x - r_n). \quad (31.9)$$

Here $r_n = nh$ and $k_m = 2\pi m/h$, so this formula connects a sum of exponentials over a reciprocal lattice to a sum of delta functions on the corresponding direct-space lattice, with the only constant in the formula being the direct-space lattice constant.

The three-dimensional analog of Eq. (31.9) is also needed frequently. It is

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x}} = v_{\text{cell}} \sum_{\mathbf{r}} \delta(\mathbf{x} - \mathbf{r}), \quad (31.10)$$

where \mathbf{r} and \mathbf{k} are respectively summed over corresponding direct-space and reciprocal-space lattices, with v_{cell} the volume of the direct-space unit cell.

Exercises

- 31.1.1.** Why is there no centered square 2-D Bravais lattice?
- 31.1.2.** For a primitive cubic lattice with cell constant h , show that if k_0 is a point of its reciprocal lattice, then so also is

$$k_0 + \frac{2\pi m_1}{h} \hat{e}_1 + \frac{2\pi m_2}{h} \hat{e}_2 + \frac{2\pi m_3}{h} \hat{e}_3 ,$$

where the m_i are integers.

- 31.1.3.** (a) Show that the lattice reciprocal to a face-centered cubic (fcc) Bravais lattice with cell dimension h is a body-centered cubic (bcc) lattice with cell dimension $4\pi/h$.
- (b) Show that the lattice reciprocal to this bcc lattice is the original fcc lattice.

31.2 LATTICE SUMS

As a first task in our analysis of periodic systems, let's consider the problem of evaluating the electrostatic energy of an ionic lattice. We assume the ions to be held at fixed positions in a lattice and our present interest is in computing their mutual electrostatic energy when the ions are treated as point charges. The actual ion positions will be determined in part by this electrostatic energy, but also by short-range repulsive forces that will arise when their electron distributions overlap (and which we do not consider here).

We start by examining a simple case for a 1-D lattice with cell dimension h . Let's place a charge q_A at the origin of each cell (i.e., at the lattice point), and place another charge q_B in each cell at the fractional position α_B , where $0 < \alpha_B < 1$, meaning that in an overall coordinate system the charges in Cell n are: q_A at position nh , and q_B at position $(n + \alpha_B)h$. Our first step in analyzing the electrostatic energy will be to compute the potential at the origin (the position of a charge q_A), due to the charges at all other points. In units such that the potential of a charge q at a distance r is just q/r , this potential $\psi(0)$ is

$$\psi(0) = \lim_{N \rightarrow \infty} \left[\sum'_{n=-N}^N \frac{q_A}{|n|h} + \sum_{n=-N}^N \frac{q_B}{|n + \alpha_B|h} \right] , \quad (31.11)$$

where the prime on the first summation indicates that $n = 0$ is to be omitted from the sum. Notice that the limits of both summations are the same; this is necessary because if independently extended to $n = \infty$ each sum would diverge. We will also have divergence unless $q_A + q_B = 0$; if this condition is violated our unit cell will not be neutral, causing an infinite long-range contribution to the potential.

Assuming $q_B = -q_A$, what we have in Eq. (31.11) is a conditionally convergent series; the physical situation (namely that we keep terms corresponding to a physically realizable sample) determines the way in which the series is to be evaluated. Without this need to correspond to the physics, we could manipulate our summation to get an arbitrary result. Another, equivalent way of writing Eq. (31.11) is

$$\psi(0) = \frac{q_A}{h} \left(-\frac{1}{\alpha_B} + \sum'_{n=-\infty}^{\infty} \left[\frac{1}{|n|} - \frac{1}{|n + \alpha_B|} \right] \right) . \quad (31.12)$$

The potential given by Eq. (31.11) is that for a finite, but macroscopic 1-D “crystal” which is terminated by a charge q_A at $-Nh$ and a charge q_B at $(N + \alpha_B)h$. Note, however, that our result is not sensitive to the termination. For example, if we added a charge q_A at the origin of Cell $N+1$ (so that the terminating charge becomes q_A instead of q_B), the value of $\psi(0)$ would, if N is large enough, not change.

The conditional convergence of lattice sums of a $1/r$ potential is an indication that the Coulomb potential is **long-range**. We will need to keep this in mind as we continue to more complicated situations.

To obtain the electrostatic energy of our 1-D lattice, we return to Eq. (31.11) and make the following observations:

1. The total electrostatic energy of an infinite lattice will be infinite. It is more relevant to compute the energy **per unit cell**.
2. The product $q_A\psi(0)$ is the interaction energy of the entire lattice with the charge q_A at the origin. But half of each contribution to this energy should be assigned to the other charge involved, so the total electrostatic energy per cell will be $[q_A\psi(0) + q_B\psi(\alpha_B h)]/2$.

These considerations lead us to the final formula for the electrostatic energy per unit cell, E :

$$E = \frac{1}{h} \left(\frac{q_A q_B}{\alpha_B} + \sum_{n=-\infty}^{\infty}{}' \left[\frac{q_A^2 + q_B^2}{2|n|} + \frac{q_A q_B}{|n + \alpha_B|} \right] \right). \quad (31.13)$$

Example 31.2.1. Some 1-D Lattice Sums

Consider first a unit lattice of equally spaced unit charges (all of the same sign of charge), and we desire the potential half way between any two lattice points. Allowing for the fact that we sum in both directions from the point where the potential is evaluated, we have

$$\psi = 2 \left[\frac{1}{1/2} + \frac{1}{3/2} + \frac{1}{5/2} + \cdots \right] = 2 \left[\frac{2}{1} + \frac{2}{3} + \frac{2}{5} + \cdots \right], \text{ which is divergent.}$$

Next, look at a unit lattice with positive unit charges at the lattice points and unit negative charges at the cell midpoints. Now let's evaluate the potential at any lattice point from all charges not at that point:

$$\psi = 2 \left[-\frac{1}{1/2} + \frac{1}{1} - \frac{1}{3/2} + \cdots \right] = 4 \left[-\frac{1}{1} + \frac{1}{2} - \frac{1}{3} + \cdots \right] = -4 \ln 2.$$

Finally, consider the more typical situation in which the negative charges are at the fractional point α of each cell, with $\alpha \neq 1/2$:

$$\psi = 2 \left[-\frac{1}{\alpha} + \frac{1}{1} - \frac{1}{1+\alpha} + \frac{1}{2} - \frac{1}{2+\alpha} + \cdots \right]. \quad (31.14)$$

This summation does not have a simple closed evaluation, and if summed directly will converge extremely slowly. This situation is typical of electrostatic lattice sums, and indicates a need for more sophisticated summation methods. In the present 1-D case, a simple strategy is to expand the terms $1/(n + \alpha)$ in the series

$$\frac{1}{n + \alpha} = \frac{1}{n} \left(\frac{1}{1 + \alpha/n} \right) = \frac{1}{n} - \frac{\alpha}{n^2} + \frac{\alpha^2}{n^3} + \cdots.$$

When this expression is inserted in Eq. (31.14) the $1/n$ terms all cancel and we have

$$\begin{aligned}\psi &= 2 \left[-\frac{1}{\alpha} + \sum_{n=1}^{\infty} \frac{\alpha}{n^2} - \sum_{n=1}^{\infty} \frac{\alpha^2}{n^3} + \cdots \right] \\ &= 2 \left[-\frac{1}{\alpha} + \alpha\zeta(2) - \alpha^2\zeta(3) + \cdots \right].\end{aligned}\quad (31.15)$$

Since we can always define our lattice to make $\alpha \leq 1/2$ and the zeta function is tabulated, Eq. (31.15) will be both convenient and rapidly convergent. ■

MADELUNG SUMS

We continue now to the more important case of 3-D periodicity, where summations corresponding to the electrostatic energy are known as **Madelung sums**. Here the consequences of conditional convergence are more severe, as the energetic contributions of individual charges fall off as r^{-1} while the number of charges in a shell at distance r increases proportionally to r^2 . In fact, unlike the 1-D case, the potential at interior points of a macroscopic (3-D) crystalline sample depends on the way in which the sample is terminated. To see this, consider a spherical sample of neutral material surrounded by a monolayer of atomic charges (all of the same sign). The potential within the sphere will diverge as the sample size increases (the total charge involved increases as r^2 while the potential produced by each element of charge only decreases as $1/r$). Arrays of dipoles (e.g., dipolar unit cells) produce shape and size-dependent potentials at interior points, as can be expected since the potential of a dipole decays as r^{-2} while their number on a surface scales as r^2 . Finally, even unit cells with nonzero second moments will affect the evaluation of a Madelung sum, as the decay of their contributions (net r^{-1}) is too slow to yield absolute convergence.¹

We illustrate the techniques and limitations of direct evaluation of lattice sums with the following example.

Example 31.2.2. CsCl Lattice Sum

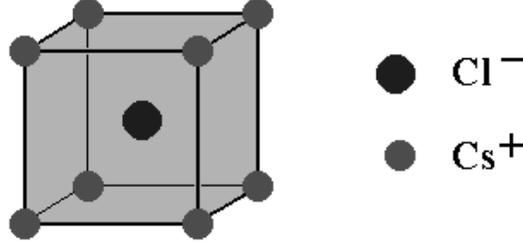
The CsCl structure (Fig. 31.2) has a unit cell in which Cs^+ ions are at the corners of a cube, with a Cl^- charge at the center. To make the unit cell neutral, we can assign $1/8$ -th of a Cs^+ to each corner, and if we build a larger structure by arranging these cubes in a 3-D array, the fractional Cs ions will combine to make unit-charged Cs^+ everywhere except on the surface of the array. Notice that alternatively and equivalently we could take unit-cell cubes of the same size in which the Cl^- ions are at the corners, with Cs^+ ions at the cell centers.

Let's use a coordinate system with the origin at a unit-cell center, with charge q_0 at that point; its cube corners are at positions $(\pm h, \pm h, \pm h)$. Then the unit cell will be neutral, with one CsCl unit and volume $(2h)^3$, and will have zero dipole moment:

$$\sum_i q_i x_i = \sum_i q_i y_i = \sum_i q_i z_i = 0.$$

¹For discussions of this, see R. N. Euwema and G. T. Surratt, *J. Phys. Chem. Solids* **36**, 67 (1975); and F. E. Harris, in *Theoretical Chemistry, Advances and Perspectives*, Vol. 1, H. Eyring and D. Henderson, eds. New York: Academic Press (1975), pp. 147–218.

Figure 31.2: CsCl structure and a possible choice for its unit cell.



Moreover, all components of its quadrupole moment will also vanish:

$$\sum_i q_i x_i y_i = \sum_i q_i x_i z_i = \sum_i q_i y_i z_i = \sum_i q_i (x_i^2 - y_i^2) = \sum_i q_i (2z_i^2 - x_i^2 - y_i^2) = 0 ;$$

the last two of these summations vanish because

$$\sum_i q_i x_i^2 = \sum_i q_i y_i^2 = \sum_i q_i z_i^2 = -q_0 h^2 . \quad (31.16)$$

Let's now attempt to evaluate the energy of interaction of a charge q_0 at the origin with all other charges of the lattice. We obtain this energy, $q_0\psi(0)$, as a sum of contributions from successive shells of ions, where we take the n -th shell to be the ions on the surface of a cube of side $2nh$ centered at the origin. If we keep the contributions through Shell N , we take the charges on Shell N to be the fractional values they would have for an $N \times N \times N$ array of unit cells (so our entire sample will be neutral and will have vanishing dipole and quadrupole moments). The charges in Shell n will be at coordinate points (jh, lh, mh) such that one or more of j, l, m equals n , and all of j, l, m must have the same parity as n . Moreover, j, l, m sets that differ only by a permutation will make the same contribution to the electrostatic energy.

The above considerations lead to the enumeration of contributions to $q_0\psi(0)$ listed in Table 31.2. In that table, V_{jlm} is the contribution from one charge at (jh, lh, mh) , the number multiplying it is the number of equivalent charges in the shell, and the contributions are grouped (under E_F , E_E , or E_C) to indicate whether they are on a face, an edge, or a corner of the shell. This classification is needed to deal with fractional charges for the outermost Shell N . Tabulated are the full energy contributions from the shell (E_{full}) and also those that would result from partial charges on a surface shell, which are for the shell faces $E_F/2$, for its edges $E_E/4$, and for its corners $E_C/8$.

If we now add the full contributions for the first $N - 1$ shells and the surface contribution for Shell N , we get through $N = 6$ the results shown in Table 31.1. The results oscillate and do not seem to be converging to a single value. That is in fact the case; if we extend to large enough values of N , we find that the even- N and odd- N values of $\psi(0)$ converge to different values. We include in Table 31.1 values that are just about converged to five decimal places at $N = 149$ and $N = 150$. Thus, in addition to the oscillation we have rather slow convergence.

The existence of two different values for $q_0\psi(0)$ is due to the fact that the second-moment tensor of the charge distribution has different values for termination after odd- N and even- N shells. This affects the result even when the low-order multipole

moments all vanish. As shown in the publications cited in the footnote on page 8, the potential at interior points of a crystal is shifted by an amount $-4\pi T/3$, where T is (per unit volume) the trace of the second-moment tensor of the charge distribution. When our CsCl sample is terminated after $2N + 1$ shells (corresponding to an array of unit cells with q_0 at their centers), its second moment per unit volume, which can be computed from Eq. (31.16), is

$$T = \frac{1}{2} \frac{1}{(2h)^3} \sum_i q_i (x_i^2 + y_i^2 + z_i^2) = -\frac{3q_0}{16h}, \quad (31.17)$$

while termination of $2N$ shells (an array built from unit cells with $-q_0$ at their centers) will lead to $T = +3q_0/16h$. Thus, the two terminations will cause $q_0\psi(0)$ to differ by

$$\Delta[q_0\psi(0)] = \frac{4\pi}{3} \frac{3q_0^2}{8h} = \frac{\pi}{2} \frac{q_0^2}{h}.$$

In units of q_0^2/h , this energy difference is $\pi/2 \approx 1.57080$. We note that this is approximately the difference between the large- N even- and odd-shell results in Table 31.1: $-1.80307 + 0.23229 = 1.57078$. The small difference arises from the incomplete convergence of the data in the table.

If our objective was to compute the entire electrostatic energy, we would need to add to our present result an equal contribution $q\psi$ for the ions of the other sign, and also to divide our entire energy by 2, to allow for the fact that every interaction is counted twice.

■

POISSON SUMMATION THEOREM

In addition to the complications associated with the need to specify the termination (surface definition) of our sample, we noticed that the Coulombic contributions (even when taken in appropriate combinations) converge very slowly. A first step toward addressing this problem is provided by a relation known as the **Poisson summation theorem**. This theorem states that if $f(\mathbf{r})$ is a function possessing a Fourier transform, denoted $g(\mathbf{k})$, then the sum of $f(\mathbf{r})$ over a direct-space lattice is related to the sum of $g(\mathbf{k})$ over the corresponding reciprocal-space lattice by

$$\sum_{\mathbf{k}} g(\mathbf{k}) = \frac{v_{\text{cell}}}{(2\pi)^{3/2}} \sum_{\mathbf{r}} f(\mathbf{r}). \quad (31.18)$$

Table 31.1: Electrostatic energy (units $q_0^2 h^{-1}$) as a function of number of shells included.

No. of shells	$q_0\psi(0)$	No. of shells	$q_0\psi(0)$
1	-0.57735	5	-0.23994
2	-1.76947	6	-1.79775
3	-0.25384	149	-0.23229
4	-1.79117	150	-1.80307

Table 31.2: Energy contributions of shells to $q_0\psi(0)$, CsCl structure, units $q_0^2h^{-1}$. ^a

		E_{full}	E_{surface}
Shell 1	$E_F = 0$	0.00000	0.00000
	$E_E = 0$	0.00000	0.00000
	$E_C = -8V_{111}$	-4.61880	-0.57735
Shell 2	$E_F = 6V_{200}$	3.00000	1.50000
	$E_E = 12V_{220}$	4.24264	1.06066
	$E_C = 8V_{222}$	2.30940	0.28868
Shell 3	$E_F = -24V_{311}$	-7.23627	-3.61814
	$E_E = -24V_{331}$	-5.50598	-1.37649
	$E_C = -8V_{333}$	-1.53960	-0.19245
Shell 4	$E_F = 6V_{400} + 24V_{420} + 24V_{422}$	11.76554	5.88277
	$E_E = 12V_{440} + 24V_{442}$	6.12132	1.53033
	$F_C = 8V_{444}$	1.15470	0.14434
Shell 5	$E_F = -24V_{511} - 48V_{531} - 24V_{533}$	-16.39225	-8.19612
	$E_E = -24V_{551} - 24V_{553}$	-6.48521	-1.62130
	$E_C = -8V_{555}$	-0.92376	-0.11547
Shell 6	$E_F = 6V_{600} + 24V_{620} + 24V_{622}$ $+24V_{640} + 48V_{642} + 24V_{644}$	21.06577	10.53288
	$E_E = 12V_{660} + 24V_{662} + 24V_{664}$	6.72561	1.68140
	$E_C = 8V_{666}$	0.76980	0.09623

a. $V_{jlm} = 1/\sqrt{j^2 + l^2 + m^2}$; E_{full} is the full contribution of the shell.

E_{surface} is the contribution using fractional charges to make the overall sample neutral.

Here v_{cell} is the volume of the direct-space unit cell. Notice that we can make this formula completely symmetric relative to direct vs. reciprocal space by rewriting it in the form

$$v_{\text{RS}}^{1/2} \sum_{\mathbf{k}} g(\mathbf{k}) = v_{\text{cell}}^{1/2} \sum_{\mathbf{r}} f(\mathbf{r}), \quad (31.19)$$

where v_{RS} is the volume of the reciprocal-lattice unit cell; the passage from Eq. (31.18) to Eq. (31.19) is easily checked using Eq. (31.5). The 1-D equivalent of Eq. (31.19) is

$$\left(\frac{2\pi}{h}\right)^{1/2} \sum_{m=-\infty}^{\infty} g(2\pi m/h) = h^{1/2} \sum_{n=-\infty}^{\infty} f(nh), \quad (31.20)$$

where h is the direct-space cell dimension.

The proof of Eq. (31.18) is straightforward. We simply write the basic formula

for the Fourier transform of $f(\mathbf{r})$ and sum \mathbf{k} over the reciprocal lattice:

$$\begin{aligned} \sum_{\mathbf{k}} g(\mathbf{k}) &= \frac{1}{(2\pi)^{3/2}} \int \left(\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}'} \right) f(\mathbf{r}') d^3 r' \\ &= \frac{1}{(2\pi)^{3/2}} \int \left(v_{\text{cell}} \sum_{\mathbf{r}} \delta(\mathbf{r}' - \mathbf{r}) \right) f(\mathbf{r}') d^3 r' \\ &= \frac{v_{\text{cell}}}{(2\pi)^{3/2}} \sum_{\mathbf{r}} f(\mathbf{r}). \end{aligned} \quad (31.21)$$

The Poisson summation theorem is often used for lattice sums of functions that are not centered at the lattice points. If a function $f(\mathbf{r})$ is centered at a point \mathbf{s} in each cell, so the quantity being summed is $f(\mathbf{r} - \mathbf{s})$, then, applying the translation formula, Eq. (20.48), Eq. (31.18) becomes

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{s}} g(\mathbf{k}) = \frac{v_{\text{cell}}}{(2\pi)^{3/2}} \sum_{\mathbf{r}} f(\mathbf{r} - \mathbf{s}). \quad (31.22)$$

When used for sums of charges at various points in each cell, Eq. (31.22) has the desirable feature that, irrespective of the various values that may be assumed by \mathbf{s} , the same function $g(\mathbf{k})$ enters the formula.

The value of the Poisson summation theorem rests in part on the fact that a series of Fourier transforms may converge more rapidly than the series of the original functions. Alternatively, one of the two equivalent series may be summed more easily than the other, providing yet another method for the summation of series. We illustrate with an example.

Example 31.2.3. Use of Poisson Formula

Let's suppose that we want to evaluate the sum

$$S = \sum_{n=-\infty}^{\infty} \frac{1}{n^2 + a^2}.$$

This is a 1-D sum, with the function $f(n) = 1/(n^2 + a^2)$ evaluated on a unit lattice. To convert it using the Poisson summation theorem, we need the Fourier transform of f , which is (compare the first transform of Example 20.2.1)

$$g(\omega) = \frac{\sqrt{2\pi}}{2a} e^{-a|\omega|}.$$

Since the lattice reciprocal to a unit lattice has cell constant 2π , our alternate expression for S is

$$S = \sqrt{2\pi} \sum_{m=-\infty}^{\infty} \frac{\sqrt{2\pi}}{2a} e^{-2\pi a|m|}. \quad (31.23)$$

Notice that we wrote $2\pi|m|$ in the exponential so that the m summation could be over integers.

The summation in Eq. (31.23) is (for each sign of m) a geometric series, and its evaluation proceeds as follows:

$$\begin{aligned} S &= \frac{\pi}{a} \left[2 \sum_{m=0}^{\infty} e^{-2\pi am} - 1 \right] = \frac{\pi}{a} \left(\frac{2}{1 - e^{-2\pi a}} - 1 \right) = \frac{\pi}{a} \frac{1 + e^{-2\pi a}}{1 - e^{-2\pi a}} \\ &= \frac{\pi \coth(\pi a)}{a}. \end{aligned} \quad (31.24)$$

This result agrees with that we found in Example 11.9.1 using contour integration. ■

EWALD METHOD

By itself, the Poisson formula is difficult to use for electrostatic lattice sums because of the problems associated with their conditional convergence. However, it opens the door for an ingenious approach to such sums that was published by P. P. Ewald in 1921. Ewald considered lattice sums giving the potential $\psi(0)$ at the origin of a 3-D periodic system in which there was a charge q_0 at each point of a direct-space lattice and additional charges q_i ($i = 1, 2, \dots, M$) at the respective points \mathbf{s}_i of each cell (with the q_i required to satisfy the condition that each cell have zero net charge, a condition necessary for convergence). Thus,

$$q_0 + \sum_{i=1}^M q_i = 0. \quad (31.25)$$

Ewald's approach is based on the following integral representation of the Coulomb potential:

$$\begin{aligned} \frac{1}{r} &= \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-r^2 z^2} dz \\ &= \frac{2}{\sqrt{\pi}} \int_0^Z e^{-r^2 z^2} dz + \frac{2}{\sqrt{\pi}} \int_Z^{\infty} e^{-r^2 z^2} dz \\ &= \frac{\operatorname{erf}(Zr)}{r} + \frac{\operatorname{erfc}(Zr)}{r}. \end{aligned} \quad (31.26)$$

Equation (31.26), which is true for any value of Z in the range ($0 \leq Z < \infty$), follows directly from the definition of the error functions, Table 1.2, and the fact that for all x , $\operatorname{erf}(x) + \operatorname{erfc}(x) = 1$. The motivation for this division of the integral representation into two parts is that in the large- z interval, summations over an r lattice will converge exponentially, while the convergence of lattice sums for small z can be improved using the Poisson summation formula.

After dividing the integration interval but before any further manipulations, we

have the following initial formula for $\psi(0)$:

$$\psi(0) = \sum_{i=0}^M \sum'_{\mathbf{r}} \frac{q_i}{|\mathbf{r} + \mathbf{s}_i|} = \sum_{i=0}^M q_i (S_i + T_i), \quad \text{where} \quad (31.27)$$

$$S_0 = \frac{2}{\sqrt{\pi}} \sum'_{\mathbf{r}} \int_0^Z e^{-z^2 \mathbf{r}^2} dz, \quad (31.28)$$

$$T_0 = \sum'_{\mathbf{r}} \frac{\operatorname{erfc}(Z|\mathbf{r}|)}{|\mathbf{r}|} \quad (31.29)$$

$$S_i = \frac{2}{\sqrt{\pi}} \sum'_{\mathbf{r}} \int_0^Z e^{-z^2 |\mathbf{r} + \mathbf{s}_i|^2} dz, \quad (i \neq 0), \quad (31.30)$$

$$T_i = \sum'_{\mathbf{r}} \frac{\operatorname{erfc}(Z|\mathbf{r} + \mathbf{s}_i|)}{|\mathbf{r} + \mathbf{s}_i|}, \quad (i \neq 0). \quad (31.31)$$

In these equations the \mathbf{r} sum is over the direct-space lattice. However, notice that for charge q_0 we needed to exclude the potential from the charge at the origin; this exclusion is indicated by the primes on the summations.

Though Eqs. (31.27)–(31.31) clearly contain the separation parameter Z , the ultimate result cannot depend upon its value. We can choose Z to have any value that is convenient for actual computation.

The above equations show that the formulas for the contributions T_i converge exponentially because that is the behavior of the erfc function. Notice that the larger the value we assign to Z , the more rapid will be the convergence of the T_i summations.

We have still to deal with the summations in the quantities S_i . As already indicated, the convergence of these summations can be improved by application of the Poisson summation theorem. The key formula needed for this purpose is the Fourier transform given in Eq. (20.47),

$$\left[e^{-z^2 |\mathbf{r}^2|} \right]^T(\mathbf{k}) = \frac{1}{2^{3/2} z^3} e^{-|\mathbf{k}|^2 / 4z^2}. \quad (31.32)$$

For $i \neq 0$, the direct-space lattice sum is complete (it includes the lattice point at the origin), and Eq. (31.21) is directly applicable:

$$\begin{aligned} S_i &= \frac{2}{\sqrt{\pi}} \frac{(2\pi)^{3/2}}{v_{\text{cell}}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{s}_i} \int_0^Z \frac{dz}{2^{3/2} z^3} e^{-|\mathbf{k}|^2 / 4z^2} \\ &= \frac{\pi}{v_{\text{cell}}} \left[\sum'_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{s}_i} \int_{1/Z^2}^{\infty} e^{-|\mathbf{k}|^2 t / 4} dt + 2 \int_0^Z \frac{dz}{z^3} \right]. \end{aligned} \quad (31.33)$$

Here the \mathbf{k} summation is over all points of the reciprocal lattice; when a prime is attached to the summation the point $\mathbf{k} = 0$ is to be omitted. Thus, we see that in Eq. (31.33) we have separated off the $\mathbf{k} = 0$ term, and for $\mathbf{k} \neq 0$ we made a change of variables $t = 1/z^2$ (so $dt = -dz/2z^3$). Both the integrals in Eq. (31.33) are elementary. The second (which is the $\mathbf{k} = 0$ term of the sum) is divergent at $z = 0$, but when all the S_i are combined, the divergence cancels because of our assumption

that the cell is charge-neutral. We therefore retain only the upper limit from the second integral, reaching

$$S_i = \frac{4\pi}{v_{\text{cell}}} \sum'_{\mathbf{k}} \frac{e^{-|\mathbf{k}|^2/4Z^2 + i\mathbf{k}\cdot\mathbf{s}_i}}{|\mathbf{k}|^2} - \frac{\pi}{v_{\text{cell}}Z^2}, \quad (i \neq 0). \quad (31.34)$$

The treatment of S_0 is similar to that of the other S_i except that one term of the lattice sum is missing. We therefore add it so as to be able to proceed as for the other S_i (its value is $2Z/\sqrt{\pi}$) but then need to subtract it from the final result. The result is

$$S_0 = -\frac{2Z}{\sqrt{\pi}} + \frac{4\pi}{v_{\text{cell}}} \sum'_{\mathbf{k}} \frac{e^{-|\mathbf{k}|^2/4Z^2}}{|\mathbf{k}|^2} - \frac{\pi}{v_{\text{cell}}Z^2}. \quad (31.35)$$

Equations (31.34) and (31.35) show that the S_i are now written in terms of summations which will converge exponentially, at a rate that is faster for smaller Z .

One final observation: In the \mathbf{k} summations, the positions of the charges within the unit cell appear only as a complex exponentials, and these exponentials can be combined to form a **structure factor** $S(\mathbf{k})$, leaving the \mathbf{k} sum (and the factors multiplying it) in the form

$$\sum_{i=0}^M \frac{4\pi q_i}{v_{\text{cell}}} \sum'_{\mathbf{k}} \frac{e^{-|\mathbf{k}|^2/4Z^2 + i\mathbf{k}\cdot\mathbf{s}_i}}{|\mathbf{k}|^2} = \frac{4\pi}{v_{\text{cell}}} \sum'_{\mathbf{k}} S(\mathbf{k}) \frac{e^{-|\mathbf{k}|^2/4Z^2}}{|\mathbf{k}|^2}, \quad (31.36)$$

where

$$S(\mathbf{k}) = \sum_{i=0}^M q_i e^{i\mathbf{k}\cdot\mathbf{s}_i}. \quad (31.37)$$

Notice that the summation yielding $S(\mathbf{k})$ is over the unit cell, not the entire crystal. In crystals with high symmetry $S(\mathbf{k})$ will often evaluate to values as simple as zero or a signed integer.

Summarizing, we have found that our Ewald formulas contain the T_i summations, most rapidly convergent for large Z , and the S_i summations, most rapidly convergent for small Z . In all cases the convergence is exponential. There will be an intermediate range of Z that will give good convergence for both sets of lattice sums.

Because of its importance, we now collect the various components of the Ewald lattice sum into a single equation (in which it is understood that $\mathbf{s}_0 = 0$):

$\psi(0) =$

$$\frac{4\pi}{v_{\text{cell}}} \sum'_{\mathbf{k}} S(\mathbf{k}) \frac{e^{-|\mathbf{k}|^2/4Z^2}}{|\mathbf{k}|^2} + \sum_{i=0}^M q_i \left[\sum'_{\mathbf{r}} \frac{\text{erfc}(Z|\mathbf{r} + \mathbf{s}_i|)}{|\mathbf{r} + \mathbf{s}_i|} - \frac{\pi}{v_{\text{cell}}Z^2} \right] - \frac{2Zq_0}{\sqrt{\pi}}. \quad (31.38)$$

Here the prime on the \mathbf{r} sum excludes only the term for which the denominator vanishes, i.e. for $\mathbf{r} = 0$ when $i = 0$. In Eq. (31.38) as written above, the term containing $1/Z^2$ will cancel due to charge neutrality. We retained it because our derivation could have been carried out with different Z for different q_i .

The Ewald formula has an important and interesting feature: its use has converted a conditionally convergent (and slowly converging) summation into two summations, each of which is not only absolutely convergent but converges at an exponential rate.

The values of these summations, therefore, do not seem to depend explicitly on the termination conditions of the crystal. That smacks of magic, since our original lattice sum had a value that depended upon the way our sample was terminated. A close examination (absent in most discussions of the method) reveals that the manipulations involving the Poisson summation theorem carried the implicit assumption that the order of the summation and integration could be interchanged. It is now known that this interchange is legitimate only if all components of the second moment of the charge distribution vanish. This is a stronger condition than vanishing of the monopole (net charge), dipole, and quadrupole moments, as it also implies the vanishing of the spherically symmetric part of the second moment tensor.

The observations of the foregoing paragraph imply that the Ewald result is not the unique “right answer” to the electrostatic energy problem in ionic crystals, and that it might not even be the correct answer for any physically attainable crystal. What can be concluded is that

The Ewald result is the rapidly convergent answer to a well-defined (but often unrealistic) physical situation, but it can be modified (using macroscopic notions of electrostatics) to describe physically realizable crystalline samples.

Example 31.2.4. Ewald Sum, CsCl

We return to the CsCl structure to apply the Ewald method and to take note of the rapidity of its convergence. We use the notation and coordinate system of Example 31.2.2. For illustrative purposes we will make calculations for the two Z values $Z = 1/h$ and $Z = 1.4/h$. In actual practice one should use a value of Z that causes the exponentials $e^{-Z^2 r^2}$ (arising from the erfc functions) and $e^{-k^2/4Z^2}$ to decay at comparable rates as one takes steps in the \mathbf{r} or \mathbf{k} lattices.

For the direct-space sum, we may use the formulas for E_F , E_E , and E_C from Table 31.2, but since our summations converge exponentially we need not worry about surface effects, and we can simply evaluate $E_F + E_E + E_C$ for each shell. What is different from the earlier example is that the potential V_{jlm} is no longer that given in Table 31.2 but is instead of the form

$$V_{jlm} = \frac{\operatorname{erfc}(Z\eta)}{\eta}, \quad \text{with } \eta = \sqrt{j^2 + l^2 + m^2}. \quad (31.39)$$

The direct-space contributions from the first few shells of the CsCl structure are given for each Z , labelled as E_n in Table 31.3. Because they cancel when summed, the $\pi/v_{\text{cell}}Z^2$ terms are omitted.

The reciprocal-space sum is best approached by first computing the structure factors $S(\mathbf{k})$. The charge q_0 is at the cell origin, and its contribution to $S(\mathbf{k})$ is just q_0 for all \mathbf{k} . The other charge, $q_1 = -q_0$, is at the position $\mathbf{s}_1 = (h, h, h)$. Because the unit cell is of dimension $2h \times 2h \times 2h$, the \mathbf{k} lattice is at points $(\pi/h)(j, l, m)$, and $\mathbf{k} \cdot \mathbf{s}_1 = \pi(j + l + m)$. Since

$$e^{i\mathbf{k} \cdot \mathbf{s}_1} = e^{i\pi(j+l+m)} = (-1)^{j+l+m},$$

the contribution to $S(\mathbf{k})$ from q_1 is $+q_1$ if $j + l + m$ is even and $-q_1$ if $j + l + m$ is odd, so the overall evaluation of $S(\mathbf{k})$ becomes

$$S(\mathbf{k}) \equiv S_{jlm} = \begin{cases} q_0 + q_1 = 0, & j + l + m \text{ even,} \\ q_0 - q_1 = 2q_0, & j + l + m \text{ odd.} \end{cases} \quad (31.40)$$

Table 31.3: Contributions to the Ewald value of $q_0\psi(0)$ for the CsCl structure for two values of the separation parameter Z . Data in units q_0^2/h .

Zh	1.0	1.4
E_1	-0.06608	-0.00280
E_2	0.01430	0.00023
E_3	-0.00002	0.00000
F_1	0.16197	0.54235
F_3	0.00052	0.02226
F_5	0.00000	0.00001
$-2Zh/\sqrt{\pi}$	-1.12838	-1.57973
Sum	-1.01769	-1.01768

Now, returning to Eq. (31.36), we see that the terms of the \mathbf{k} sum have (when multiplied by q_0) the form

$$\begin{aligned}
 U_{jlm} &= \frac{4\pi q_0}{v_{\text{cell}}} S_{jlm} \frac{e^{-\pi^2 \eta^2 / 4Z^2 h^2}}{\pi^2 \eta^2 / h^2} \\
 &= \frac{q_0}{2\pi h} S_{jlm} \frac{e^{-\pi^2 \eta^2 / 4Z^2 h^2}}{\eta^2}, \quad \text{with } \eta = \sqrt{j^2 + l^2 + m^2}. \quad (31.41)
 \end{aligned}$$

Inserting the value we have found for S_{jlm} , we have (in units of q_0^2/h)

$$U_{jlm} = \begin{cases} 0, & j+l+m \text{ even,} \\ \frac{e^{-\pi^2 \eta^2 / 4Z^2 h^2}}{\pi \eta^2}, & j+l+m \text{ odd.} \end{cases} \quad (31.42)$$

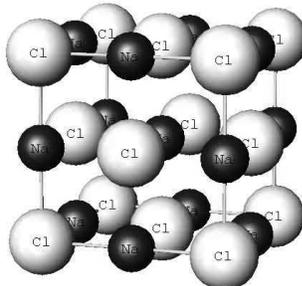
These contributions can now be organized into shells in which the n -th will have $j+l+m = n$. It is obvious that nonzero terms will result only from odd n . Counting equivalent contributions for $n = 1$, $n = 3$, and $n = 5$ (and remembering that this time we do not require j , l , and m to be odd; only their sum) we have shell energies F_i given by

$$\begin{aligned}
 F_1 &= 6U_{100}, & F_3 &= 6U_{300} + 24U_{210} + 8U_{111}, \\
 F_5 &= 6U_{500} + 24(U_{410} + U_{320} + U_{311} + U_{221}). \quad (31.43)
 \end{aligned}$$

These quantities are evaluated for the two chosen Z values, with the results shown in Table 31.3.

Finally, we taulate the unsummed energy contribution $-2Zq_0^2/\sqrt{\pi}$, which in units of q_0^2/h becomes $-2Zh/\sqrt{\pi}$, and then sum all contributions to form the Ewald value of $q_0\psi(0)$. We note that, as expected, the results are (apart from round-off) independent of Z and that for both Z values the convergence is remarkably rapid. Moreover, the Ewald energy is consistent with the average of the two values found by direct-lattice summation in Example 31.2.2. This average corresponds to the adjustment of the values from that example to second-moment $T = 0$, which is the termination condition implied by the Ewald method. ■

Figure 31.3: NaCl structure



Exercises

31.2.1. Consider the summation $S = \sum_{n=-\infty}^{\infty} e^{-an^2}$, with $a = 0.01$.

- Find the smallest $|n|$ for which the individual terms of this sum are smaller than 10^{-6} .
- Obtain an alternate summation for S using the Poisson summation theorem, and use this alternate formula to evaluate S to six decimal places. How many terms did this require?

31.2.2. Set up a direct-space evaluation for the NaCl structure (see Fig. 31.3). In a cubic Bravais cell of dimension $2h$, the Na^+ ions are at $(0, 0, 0)$, $(h, h, 0)$, $(h, 0, h)$, and $(0, h, h)$; the Cl^- ions are at $(h, 0, 0)$, $(0, h, 0)$, $(0, 0, h)$, and (h, h, h) . Proceed as follows:

- Letting V_{jlm} stand for the interaction of unit charges (of the same sign), one at the origin and the other at (jh, lh, mh) , make a table similar to Table 31.2 for the first three shells of ions. For each entry, compute (to five decimal places) numerical values of E_{full} and E_{surface} .
- Construct a table similar to Table 31.1 for the value of $q_0\psi(0)$ for the inclusion of 1, 2, and 3 shells of ions.

31.2.3. Set up an Ewald calculation for the NaCl structure. Use the Bravais unit cell from Exercise 31.2.2. Make computations only for $Z = 1/h$. Proceed as follows:

- Compute the direct-space contributions ($E_n = E_{\text{full}}$ only) for Shells 1, 2, and 3.
- Compute the structure factor $S(\mathbf{k}) \equiv S_{jlm}$ for general reciprocal lattice points (j, l, m) .
- Compute the reciprocal-space contributions F_n for Shells 1, 2, and 3.
- Complete the Ewald sum and explain any similarities and differences between it and the result obtained in Exercise 31.2.2.

31.3 ELECTRONIC STATES

PLANE WAVES

The simplest way to describe electrons in solids is to represent them as **plane waves**, with wave functions of the functional form

$$\psi(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} . \quad (31.44)$$

Here \mathbf{r} is the position vector for the wave function, and \mathbf{k} is a parameter. If we include a time dependence $e^{-i\omega t}$, the wave function $\psi(\mathbf{k}, \mathbf{r})$ describes waves that are moving in the direction of \mathbf{k} at angular frequency ω and with wavelength $2\pi/k$. The wave fronts (lines of constant phase) are at \mathbf{r} values that satisfy the equation $\mathbf{k}\cdot\mathbf{r} = \text{constant}$, so if both \mathbf{r} and \mathbf{r}' satisfy this condition, with $\mathbf{r}' = \mathbf{r} + \mathbf{p}$, then we must have $\mathbf{k}\cdot\mathbf{p} = 0$, showing that the wave fronts are perpendicular to \mathbf{k} .

Plane waves are adequate as descriptions of electrons when they are not actually bound to individual nuclei, and therefore are often used to represent electrons in metals.

Example 31.3.1. Thomas-Fermi Model

An important early application of plane-wave states was their use by Thomas and Fermi to describe the **uniform electron gas**, which consists of electrons in the presence of a uniform and static background of compensating positive charge. This fictitious system (which becomes relevant in the limit that specific electron-nuclear interactions can be neglected) is sometimes referred to as **jellium**. Electrons are **fermions**, but Thomas and Fermi included this property only to the extent that they assigned each electron a different orthogonal wave function, ignoring all effects that arise from the interaction of the electrons. Based on this model, the goal was to compute the ground-state quantum-mechanical electronic kinetic energy as a function of the uniform electron density.

Considering a macroscopic cube of jellium of dimensions $L \times L \times L$ containing N electrons, an orthogonal set of plane waves (equivalent to the terms of a Fourier series for this 3-D region) is defined by the \mathbf{k} values $\mathbf{k}_{lnp} = (2\pi/L)(l\mathbf{e}_x + n\mathbf{e}_y + p\mathbf{e}_z)$, or

$$\psi_{lnp}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} = e^{2\pi i(lx+ny+pz)/L} , \quad (31.45)$$

where l, n, p are integers (of either sign, including zero).

The kinetic energy associated with ψ_{lnp} is computed from

$$T\psi_{lnp}(\mathbf{r}) = -\frac{1}{2m}\nabla^2\psi_{lnp}(\mathbf{r}) = \frac{2\pi^2}{mL^2}(l^2 + n^2 + p^2)\psi_{lnp}(\mathbf{r}) ,$$

with m the electron mass, yielding

$$T_{lnp} = \frac{2\pi^2}{mL^2}(l^2 + n^2 + p^2) = \frac{|\mathbf{k}_{lnp}|^2}{2m} . \quad (31.46)$$

As we have previously noted in several places, \mathbf{k} can be identified as the momentum of the electron described by $\psi(\mathbf{k}, \mathbf{r})$.

The ground-state kinetic energy will be the sum of the T_{lnp} for the N distinct states of smallest T , keeping in mind that because of the electron spin, there are two states for given l, n , and p . Since the value of T_{lnp} is proportional to the magnitude

squared of \mathbf{k}_{lnp} , we must use the $N/2$ states \mathbf{k}_{lnp} of smallest $|\mathbf{k}|$, namely those for which the point (l, n, p) falls within a sphere of volume $N/2$ centered at the origin of nlp space:

$$\frac{4\pi}{3} (l^2 + n^2 + p^2)^{3/2} \leq \frac{N}{2}, \quad (31.47)$$

equivalent to

$$\frac{kL}{2\pi} \leq \left(\frac{3N}{8\pi} \right)^{1/3}. \quad (31.48)$$

Equation (31.47) is necessarily only approximate, as there is for most N no sphere that includes exactly $N/2$ integer points. However, it, and also Eq. (31.48) approach exactness asymptotically as N is increased, so these formulas become quantitatively valid in the limit of large N and L .

Equation (31.48) assumes a more useful form if we identify L as $V^{1/3}$, where V is the sample volume, and then observe that $N/V = \rho$, the electron density of the sample. We can now note that electrons will be assigned states for which $k \leq k_F$, where k_F is called the **Fermi level** and is given for this system by

$$k_F = (3\pi^2\rho)^{1/3}. \quad (31.49)$$

At this point the easiest way to compute the average kinetic energy per electron is to use the fact that the electron states are uniformly distributed in \mathbf{k} space and so close together in \mathbf{k} that sums over l , n , and p can be replaced by an integral over \mathbf{k} . We therefore get

$$\frac{T}{N} = \frac{\int_{k \leq k_F} \frac{k^2}{2m} d^3k}{\int_{k \leq k_F} d^3k} = \frac{1}{2m} \frac{4\pi k_F^5/5}{4\pi k_F^3/3} = \frac{3k_F^2}{10m} = \frac{3}{10m} (3\pi^2\rho)^{2/3}. \quad (31.50)$$

■

BLOCH ORBITALS

The plane-wave functions of the previous subsection carry the inherent assumption that the electron density is uniform throughout the sample, since $|e^{i\mathbf{k}\cdot\mathbf{r}}| = 1$ everywhere. For systems in which the electron-nuclear interactions are significant, this assumption is inadequate and we will need to take a more detailed approach. We proceed by observing that an electron in a periodic solid can be expected to be a state consistent with the translational symmetry, which does not mean that its wave function will be the same at all translationally equivalent points, but that it will exhibit a symmetric probability distribution. Since probability is obtained from a wave function by squaring its absolute value, the necessary symmetry condition is that if \mathbf{r} is a member of the solid's direct-space Bravais lattice and \mathbf{s} is an arbitrary point, then

$$|\psi(\mathbf{s} + \mathbf{r})|^2 = |\psi(\mathbf{s})|^2. \quad (31.51)$$

If, in addition, we choose to describe the electronic wave function as a linear combination of atomic orbitals centered in the individual cells of the periodic lattice (lattice

points at \mathbf{r}_n), our symmetry requirements can be met by taking a wave function of the form (illustrated for a 1-D lattice with lattice constant h)

$$\psi_\alpha(k, x) = \frac{1}{(2N + 1)^{1/2}} \sum_{n=-N}^N \varphi_\alpha(x - nh - s_\alpha) e^{iknh} . \quad (31.52)$$

We plan to use Eq. (31.52) in the limit of large N , and we assume that for the overwhelming majority of n values the atomic orbital φ_α will have become negligible within Cells N and $-N$ (i.e., we will neglect end effects). The subscript α indicates the particular functional form chosen for φ_α and the position s_α of the orbital within each unit cell of the periodic lattice. A wave function of this type is called a **Bloch orbital**. It is evident that ψ_α is a sum of atomic orbitals of the same functional form (φ_α) centered at the same point, s_α , of each cell, with the individual orbitals at phases determined by the complex exponential factor e^{iknh} . We see that k is a parameter determining the extent of the phase change as we move from cell to cell (varying n), while x is the coordinate at which the wave function is evaluated.

We note also that the range of k yielding linearly independent wave functions is limited, as all k on the reciprocal lattice of our system will have (for all n) the same value of e^{iknh} as that for $k = 0$, namely $e^{iknh} = 1$. The space of k yielding linearly independent ψ_α will be a unit cell of the reciprocal lattice. Because our 1-D lattice was specified to have lattice constant h , its reciprocal lattice will have lattice spacing $2\pi/h$. It is usual to choose the reciprocal-lattice unit cell so that it is centered at $k = 0$, and therefore (in 1-D) is bounded by $\pm\pi/h$. A reciprocal-lattice unit cell chosen in this way is called the **Brillouin zone** of our periodic system.

A wavefunction of the form given in Eq. (31.52) is too simple to provide an exact description of electrons in periodic systems, but it is (usually with modifications in which φ_α is permitted also to depend upon k) adequate for many studies. The collection of wave functions corresponding to a range of k is called a **band**, and when such wave functions are adequate as approximations to eigenfunctions, they define energies associated with the wave functions in the band. One reason for defining the Brillouin zone as centered about $k = 0$ is that the phase changes associated with nonzero k increase the magnitude of the spatial derivatives of the wave function, so the wave function with $k = 0$ will have the smallest kinetic energy (and also the smallest total energy).² Since the total energy varies continuously with k , the energies are also collectively identified as an **energy band**.

ORTHOGONALITY

We start by considering 1-D periodicity, with Bloch orbitals of the form given in Eq. (31.52). Because the functions $\psi_\alpha(k, x)$ are linear combinations of $2N + 1$ atomic orbitals, different choices of the parameter k can only produce $2N + 1$ linearly independent ψ , and a convenient linearly independent set can be chosen by assigning k the values $k_p = 2\pi p/(2N + 1)h$, with p an integer in the range $-N \leq p \leq N$. Our present task is the evaluation of the **overlap integral** of a pair of Bloch orbitals, i.e.,

$$S_{\alpha\beta}(k_p, k_q) \equiv \langle \psi_\alpha(k_p, x) | \psi_\beta(k_q, x) \rangle , \quad (31.53)$$

where the angle brackets indicate integration over $-\infty < x < \infty$. On substitution of Eq. (31.52), and remembering that the bra half of the bracket is complex conjugated,

²This statement is an oversimplification; in particular, when the individual orbitals have nonzero angular momentum, the situation is more complicated and will not be considered here.

$S_{\alpha\beta}(k_p, k_q)$ becomes

$$S_{\alpha\beta}(k_p, k_q) = \frac{1}{2N+1} \sum_{n=-N}^N \sum_{m=-N}^N e^{i(-k_p n h + k_q m h)} \times \left\langle \varphi_\alpha(x - n h - s_\alpha) \middle| \varphi_\beta(x - m h - s_\beta) \right\rangle. \quad (31.54)$$

We now replace the integration variable x by $x + n h + s_\alpha$ and rearrange Eq. (31.54) to obtain

$$S_{\alpha\beta}(k_p, k_q) = \frac{1}{2N+1} \sum_{m=-N}^N e^{i(k_q - k_p) m h} \times \sum_{n=-N}^N e^{i k_p (m-n) h} \left\langle \varphi_\alpha(x) \middle| \varphi_\beta(x - (m-n) h - s_{\alpha\beta}) \right\rangle, \quad (31.55)$$

where $s_{\alpha\beta} = s_\beta - s_\alpha$. Next we replace $m - n$ by n in the second summation; this should cause its summation limits to become $-N + m$ and $N + m$, but we replace these limits by $\pm\infty$ because the bra-ket integral approaches zero as $|m - n|$ increases and extension of the integration limits has a negligible effect for large N . This is equivalent to the observation that end effects are negligible. These changes bring Eq. (31.55) to

$$S_{\alpha\beta}(k_p, k_q) = \frac{1}{2N+1} \sum_{m=-N}^N e^{i(k_q - k_p) m h} \times \sum_{n=-\infty}^{\infty} e^{i q_p n h} \left\langle \varphi_\alpha(x) \middle| \varphi_\beta(x - n h - s_{\alpha\beta}) \right\rangle. \quad (31.56)$$

An important feature of Eq. (31.56) is that the m and n sums are now completely decoupled, and the m summation can be recognized as of a type we encountered in discussing discrete Fourier transforms. Since $k_q - k_p = 2\pi(q - p)/(2N + 1)h$, the m sum is a case of Eq. (20.119), and has the value

$$\sum_{m=-N}^N e^{2\pi i(q-p)m/(2N+1)} = (2N+1)\delta_{pq}, \quad (31.57)$$

where p and q are restricted to the range $(-N, N)$, corresponding to \mathbf{k} values within the Brillouin zone. Applying Eq. (31.57), we find that $S_{\alpha\beta}$ vanishes unless $k_p = k_q$. Simplifying the notation accordingly, our final expression for the overlap integral is

$$S_{\alpha\beta}(k_q) = \sum_{n=-\infty}^{\infty} e^{2\pi i q m/(2N+1)} \left\langle \varphi_\alpha(x) \middle| \varphi_\beta(x - n h - s_{\alpha\beta}) \right\rangle. \quad (31.58)$$

We close this subsection by rewriting Eq. (31.58) in a more general notation that extends to 3-D periodicity:

$$S_{\alpha\beta}(\mathbf{k}) \equiv \left\langle \psi_\alpha(\mathbf{k}, \mathbf{r}') \middle| \psi_\beta(\mathbf{k}, \mathbf{r}') \right\rangle \quad (31.59)$$

$$= \sum_{\mathbf{r}_n} e^{i\mathbf{k}\cdot\mathbf{r}_n} \left\langle \varphi_\alpha(\mathbf{r}') \middle| \varphi_\beta(\mathbf{r}' - \mathbf{r}_n - \mathbf{s}_{\alpha\beta}) \right\rangle, \quad (31.60)$$

where \mathbf{r}' is the bra-ket integration variable, \mathbf{k} is a point in the Brillouin zone, \mathbf{r}_n ranges over the direct-space lattice, and $\mathbf{s}_{\alpha\beta} = \mathbf{s}_\beta - \mathbf{s}_\alpha$ depends upon the locations \mathbf{s}_α of the atomic-orbitals in each cell of the direct-space lattice. It is understood that if ψ_α and ψ_β have different \mathbf{k} values, the overlap integral vanishes. Thus,

Bloch orbitals of different \mathbf{k} are orthogonal, and the overlap of two Bloch orbitals of the same \mathbf{k} is given by Eq. (31.60).

BAND ENERGIES

Many computations on solids assume that the individual electrons are in states that can be adequately described by Bloch orbitals. Since each band of Bloch orbitals is built using a single orbital in each unit cell, the maximum assignment of electrons to the band (thereby making it “**fully occupied**”) will be two electrons per unit cell. If the number of electrons per cell in the band is zero or less than two, the band is said to be **unoccupied** or **partially occupied**. If thermal effects are ignored, bands will fill in the way that minimizes the energy associated with the occupied bands (or parts thereof). It is therefore relevant to be able to evaluate the kinetic and potential energy contributions from fully or partially occupied bands.

The kinetic energy can be computed in a manner similar to that employed for the overlap integral. We have

$$T_{\alpha\beta}(\mathbf{k}) \equiv \left\langle \psi_\alpha(\mathbf{k}, \mathbf{r}') \left| \frac{-\nabla_{\mathbf{r}'}^2}{2m} \right| \psi_\beta(\mathbf{k}, \mathbf{r}') \right\rangle \quad (31.61)$$

$$= \sum_{\mathbf{r}_n} e^{i\mathbf{k}\cdot\mathbf{r}_n} \left\langle \varphi_\alpha(\mathbf{r}') \left| \frac{-\nabla_{\mathbf{r}'}^2}{2m} \right| \varphi_\beta(\mathbf{r}' - \mathbf{r}_n - \mathbf{s}_{\alpha\beta}) \right\rangle. \quad (31.62)$$

If ψ_α and ψ_β have different \mathbf{k} , the integral vanishes. It must be remembered that the Bloch orbitals are not normalized, but have overlap integrals $S_{\alpha\beta}$ given by Eq. (31.60).

The potential energy contributions require further analysis, because they involve additional lattice sums and the electron-electron and electron-nucleus electrostatic energies are individually divergent. For the purposes of this text, we look now at one integral of this type, of the form

$$I = \left\langle \psi(\mathbf{k}, \mathbf{r})\psi(\mathbf{k}', \mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} - \sum_{\mathbf{C}} \frac{1}{|\mathbf{r} - \mathbf{C}|} \right| \psi(\mathbf{k}, \mathbf{r})\psi(\mathbf{k}', \mathbf{r}') \right\rangle, \quad (31.63)$$

where the bra-ket integrations are over \mathbf{r} and \mathbf{r}' . The \mathbf{C} summation is over nuclei; for simplicity we assume there to be only one nucleus per unit cell, at the lattice point, and that there is only one ψ , a Bloch orbital also centered on lattice points.

We start our analysis of Eq. (31.63) by introducing the atomic-orbital expansions for the wave functions:

$$I = \frac{1}{N^2} \sum_{nn'mm'} e^{i\mathbf{k}\cdot(\mathbf{r}_{n'} - \mathbf{r}_n) + i\mathbf{k}'\cdot(\mathbf{r}'_{m'} - \mathbf{r}'_m)} \int d^3r d^3r' \\ \times \left[\varphi^*(\mathbf{r} - \mathbf{r}_n)\varphi(\mathbf{r} - \mathbf{r}_{n'}) \right] \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} - \sum_{\mathbf{C}} \frac{1}{|\mathbf{r} - \mathbf{C}|} \right] \left[\varphi^*(\mathbf{r}' - \mathbf{r}_m)\varphi(\mathbf{r}' - \mathbf{r}_{m'}) \right].$$

The factor $1/N^2$ arises because we have chosen to scale each ψ by $N^{-1/2}$, where N is the number of unit cells in our system. Making changes of variables $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{r}_n$, $\mathbf{r}' \rightarrow \mathbf{r}' + \mathbf{r}_m$ and renaming the lattice points so $\mathbf{r}_{n'} - \mathbf{r}_n \rightarrow \mathbf{r}_n$, $\mathbf{r}_{m'} - \mathbf{r}_m \rightarrow \mathbf{r}_m$, the expression for I reduces to

$$I = \frac{1}{N^2} \sum_{nn'mm'} e^{i\mathbf{k}\cdot\mathbf{r}_n + i\mathbf{k}'\cdot\mathbf{r}_m} \int d^3r d^3r' \left[\varphi^*(\mathbf{r})\varphi(\mathbf{r} - \mathbf{r}_n) \right] \\ \times \left[\frac{1}{|\mathbf{r} - \mathbf{r}' + \mathbf{r}_n - \mathbf{r}_m|} - \sum_C \frac{1}{|\mathbf{r} + \mathbf{r}_n - \mathbf{C}|} \right] \left[\varphi^*(\mathbf{r}')\varphi(\mathbf{r}' - \mathbf{r}_m) \right].$$

We now complete this portion of the evaluation of I by noticing that the n' and m' sums are vacant, so each simply contributes a factor N . Also renaming $C - \mathbf{r}_n \rightarrow \mathbf{C}$, we bring I to the form

$$I = \sum_{nm} \int d^3r d^3r' \left[e^{i\mathbf{k}\cdot\mathbf{r}_n} \varphi^*(\mathbf{r})\varphi(\mathbf{r} - \mathbf{r}_n) \right] \\ \times \left[\frac{1}{|\mathbf{r} - \mathbf{r}' + \mathbf{r}_n - \mathbf{r}_m|} - \sum_C \frac{1}{|\mathbf{r} - \mathbf{C}|} \right] e^{i\mathbf{k}'\cdot\mathbf{r}_m} \varphi^*(\mathbf{r}')\varphi(\mathbf{r}' - \mathbf{r}_m). \quad (31.64)$$

If we temporarily divide Eq. (31.64) into an electron-repulsion term I_{ee} and a nuclear-attraction term I_{ne} , we can identify I_{ee} as a triple convolution by writing it as

$$I_{ee} = \sum_{nm} \int f_n(\mathbf{r}) g_{nm}(\mathbf{r}' - \mathbf{r}) h_m(\mathbf{r}'' - \mathbf{r}') d^3r d^3r', \quad (31.65)$$

where $\mathbf{r}'' = 0$, $g_{nm}(\mathbf{t}) = 1/|\mathbf{t} + \mathbf{r}_n - \mathbf{r}_m|$, and

$$f_n(\mathbf{t}) = e^{i\mathbf{k}\cdot\mathbf{r}_n} \varphi(\mathbf{t})\varphi(\mathbf{t} - \mathbf{r}_n), \quad h_m(\mathbf{t}) = e^{i\mathbf{k}'\cdot\mathbf{r}_m} \varphi(-\mathbf{t})\varphi(-\mathbf{t} - \mathbf{r}_m).$$

Equation (31.65) is exactly of the form treated in Eqs. (20.86) and (20.87), and therefore can be evaluated as

$$I_{ee} = \sum_{nm} (2\pi)^{3/2} \int F_n(\mathbf{q}) G_{nm}(\mathbf{q}) H_m(\mathbf{q}) d^3q, \quad (31.66)$$

where F_n , G_{mn} , and H_m are the respective Fourier transforms of f_n , g_{mn} , and h_m . Notice that because we have already assigned a meaning to \mathbf{k} we are now calling the transform variable \mathbf{q} . The transform of $g_{nm}(\mathbf{t})$ is just that of $1/t$, except for a translation in the amount $\mathbf{r}_n - \mathbf{r}_m$, and therefore can be shown to have the form

$$G_{nm}(\mathbf{q}) = \left[\frac{1}{|\mathbf{t} + \mathbf{r}_n - \mathbf{r}_m|} \right]^T (\mathbf{q}) = e^{i\mathbf{q}\cdot(\mathbf{r}_n - \mathbf{r}_m)} \frac{1}{(2\pi)^{3/2}} \frac{4\pi}{q^2}. \quad (31.67)$$

The other transforms will in general be more difficult to evaluate and will depend upon the form of φ .

Inserting our expression for G_{nm} and combining the complex exponentials with F_n and H_m , we get the final formula

$$I_{ee} = 4\pi \int F(\mathbf{q}) H(\mathbf{q}) \frac{d^3q}{q^2}, \quad (31.68)$$

where

$$F(\mathbf{q}) = \sum_n e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}_n} \left[\varphi(\mathbf{t})\varphi(\mathbf{t}-\mathbf{r}_n) \right]^T(\mathbf{q}), \quad (31.69)$$

$$H(\mathbf{q}) = \sum_m e^{i(\mathbf{k}'-\mathbf{q})\cdot\mathbf{r}_m} \left[\varphi(-\mathbf{t})\varphi(-\mathbf{t}-\mathbf{r}_m) \right]^T(\mathbf{q}). \quad (31.70)$$

The remainder of I , which we denote I_{ne} , factors into separate integrals over \mathbf{r} and \mathbf{r}' . The \mathbf{r}' integral can be identified as an overlap integral, which we identify here as $S(\mathbf{k}')$, while the \mathbf{r} integral is a convolution, so we have

$$I_{\text{ne}} = S(\mathbf{k}') \sum_n \sum_C \int f_n(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{C}|} d^3r, \quad (31.71)$$

which, applying Eq. (20.72), and evaluating the transform of $1/|\mathbf{r}-\mathbf{C}|$, reduces to

$$I_{\text{ne}} = S(\mathbf{k}') \sum_C \int F(\mathbf{q}) \frac{4\pi}{(2\pi)^{3/2}q^2} e^{-i\mathbf{q}\cdot\mathbf{C}} d^3q. \quad (31.72)$$

Equations (31.66) and (31.72) can be seen to be parallel in structure if we rewrite $S(\mathbf{k}')$ to relate it to $H(\mathbf{q})$. The relation we need is that

$$S(\mathbf{k}') = (2\pi)^{3/2} H(0), \quad (31.73)$$

a result that can be verified by setting $\mathbf{q} = 0$ in Eq. (31.70). This substitution brings Eq. (31.72) to the form

$$I_{\text{ne}} = 4\pi \sum_C \int F(\mathbf{q}) H(0) e^{-i\mathbf{q}\cdot\mathbf{C}} \frac{d^3q}{q^2}. \quad (31.74)$$

If we now recombine I_{ee} and I_{ne} , the potentially divergent terms can be shown to offset each other, leaving a convergent result.

In addition to the form illustrated by Eq. (31.63), there are other combinations of \mathbf{k} values that lead to nonvanishing two-electron integrals. These combinations only give nonzero results because of the coupling produced by the factor $1/|\mathbf{r}-\mathbf{r}'|$. We illustrate the possibilities, but forego attempts at detailed evaluation. Most common is the so-called **exchange** integral,

$$X = \left\langle \psi(\mathbf{k}, \mathbf{r})\psi(\mathbf{k}', \mathbf{r}') \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \psi(\mathbf{k}', \mathbf{r})\psi(\mathbf{k}, \mathbf{r}') \right\rangle, \quad (31.75)$$

which arises in many solid-state computations. The most general two-electron integral that does not vanish as a requirement of the lattice symmetry has the form

$$\left\langle \psi(\mathbf{k}, \mathbf{r})\psi(\mathbf{k}', \mathbf{r}') \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \psi(\mathbf{k}+\mathbf{k}'', \mathbf{r})\psi(\mathbf{k}'-\mathbf{k}'', \mathbf{r}') \right\rangle. \quad (31.76)$$

It occurs in various high-level methods for treating the electronic structure of solids.

SUMMARY

The survey of this section should be regarded merely as an introduction that illustrates the mathematical techniques needed to study the band structure of periodic solids. The key concepts include the exploitation of lattice symmetry to demonstrate orthogonality of Bloch orbitals and the use of the Fourier convolution theorem to reduce the dimensionality and sometimes also the complexity of integrals. Current work in this active field also makes use of the Poisson summation theorem and generalization of the Ewald method to charge distributions more complicated than point charges.

Exercises

- 31.3.1.** Show how to obtain Eq. (31.49) from Eq. (31.48).
- 31.3.2.** Equation (31.60) is a lattice sum to which the Poisson summation theorem can be applied. Use that theorem to give $S_{\alpha\beta}(\mathbf{k})$ as a reciprocal-space summation.
Hint. You must call the reciprocal-space variable something other than \mathbf{k} , such as \mathbf{q} . Use the notation $g_{\alpha}(\mathbf{q})$ to denote the Fourier transform of φ_{α} . Your answer will have to depend upon this transform and the variables \mathbf{k} and $\mathbf{s}_{\alpha\beta}$.
- 31.3.3.** Show that the translational symmetry requirement for a periodic system is consistent with non-zero values for the expressions given in Eqs. (31.75) and (31.76).

Additional Readings

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