Reciprocal Space and Irreducible Representations of Space Groups

VI.1 Introduction

Many aspects of the physics and chemistry of crystalline solids require the use of group theory, for example, the study of band theory, of phonon theory and infra-red and Raman active modes, of soft modes and of the Landau theory of phase transitions are all based fundamentally upon the theory of space groups and their irreducible representations. The set of pure translational symmetry operations \( \{e/T\} \) is a subgroup of the space group of a three dimensional crystalline solid, and this leads naturally to an initial search for the irr. reps. of this subgroup. A representation is a set of matrices which are associated with the symmetry operations (in this case the pure transitions) of the group and which multiply like the operations, i.e., if \( \psi_1 \) is a matrix associated with \( T_1 \) and \( \psi_2 \) is associated with \( T_2 \) then \( \psi_2 \psi_1 \) is associated with \( T_1 + T_2 \). It is not necessary that \( \psi_1 \neq \psi_2 \).

There is a theorem of group theory that says that if all of the operations of a group commute then the irr. reps. of the group are one dimensional i.e., the sets of basis functions contain only one function each and this function transforms into itself multiplied by a constant under the symmetry operations of the group. The pure translations do commute (vector addition is commutative) and thus the search for basis function (and irr. reps.) of the pure translational subgroup is the search for functions which change by a multiplicative constant under a translational symmetry operation.

VI.2 Reciprocal Lattice

For example, we first seek a function which transforms into itself under the translational symmetry operations i.e., a function which has the periodicity of the lattice. This function is a basis function for the “totally symmetric” representation and its representation is a string of 1’s, one for each \( T \).

For the purpose of finding a basis function for the totally symmetric representation of the pure translations it is useful to know a function of \( r \) that is incremented by an integer when \( r \) is incremented by \( T \). That is, it would help to have available a vector \( K \) such that

\[
K \cdot (r + T) = K \cdot r + K \cdot T = K \cdot r + \text{integer},
\]

\[(VI.1) \quad (VI.2)\]
for with such a vector, for example

\[ \sin 2\pi K \cdot (r + T) = \sin 2\pi[K \cdot r + K \cdot T] \] (VI.3)

\[ = \sin 2\pi K \cdot r \] (VI.4)

and we would have found, as desired, a function with the periodicity of the lattice. Thus we seek a \( K \) such that \( K \cdot T = \text{integer} \). We know that \( T = ma + nb + pc \) and therefore \( K = m^*a^* + n^*b^* + p^*c^* \) with \( m^*, n^*, p^* \) integers and \( a^* \cdot a = 1, \ a^* \cdot b = a^* \cdot c = 0, \ b^* \cdot b = 1, \ b^* \cdot a = b^* \cdot c = 0, \) and \( c^* \cdot c = 1, \ c^* \cdot b = c^* \cdot a = 0 \) has the desired property since, with these definitions,

\[ K \cdot T = m^*m + n^*n + p^*p \] (VI.5)

which is an integer. The definitions mean that \( a^* \) is perpendicular to \( b \) and \( c \), i.e., is proportional to \( b \times c \). Taking the proportionality constant to be \( \alpha \),

\[ a^* = \alpha(b \times c), \] (VI.6)

and determining the value of \( \alpha \) by \( a^* \cdot a = a \cdot a^* = 1 \) yields

\[ \alpha(a \cdot b \times c) = \alpha V_{\text{cell}} = 1, \] (VI.7)

or \( \alpha = V_{\text{cell}}^{-1} \). Proceeding similarly for \( b^* \) and \( c^* \) yields

\[ a^* = \frac{b \times c}{V_{\text{cell}}}, \quad b^* = \frac{c \times a}{V_{\text{cell}}}, \quad c^* = \frac{a \times b}{V_{\text{cell}}}, \] (VI.8)

and with \( K = m^*a^* + n^*b^* + p^*c^* \) the functions \( \sin 2\pi K \cdot r \), \( \cos 2\pi K \cdot r \) and \( \exp 2\pi i K \cdot r \) all have the periodicity of the lattice (each is a basis function for the totally symmetric irreps.). The definition of \( K \) is such that \( K \cdot r \) is dimensionless, thus \( K \) has the dimension of reciprocal length and is called a reciprocal vector or, since \( m^* \), \( n^* \) and \( p^* \) can be allowed all integral values thereby generating a lattice (a reciprocal lattice), \( K \) is called a reciprocal lattice vector.

The essential feature used in the definition of the reciprocal lattice vector is that \( K \cdot T = \text{integer} \) (note: it is also common to define \( K \) such that \( K \cdot T \) is an integral multiple of \( 2\pi \), and this reciprocal vector is obtained from that defined here by multiplication by \( 2\pi \)). It follows that if \( \beta \ | \ t \) is a symmetry operation of a crystalline solid then \( K \cdot \beta T \) is an integer if \( K \cdot T \) is. However if \( K \cdot \beta T \) is an integer then so too is \( \beta^{-1}K \cdot T \). This is true for a given \( T \) and all of the reciprocal vectors generated by the rotational part of the symmetry operations of the space group. Thus if \( K \) is a reciprocal lattice vector so too is \( \beta K \) and the reciprocal lattice has the same rotational symmetry as the real lattice.