

Effective calculation of LEED intensities using symmetry-adapted functions

W Moritz

Institut für Kristallographie und Mineralogie der Universität München, Theresienstrasse 41, D-8000 München 2, West Germany

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Abstract. The calculation of LEED intensities in a spherical-wave representation can be substantially simplified by symmetry relations. The wave field around each atom is expanded in symmetry-adapted functions where the local point symmetry of the atomic site applies. For overlayer systems with more than one atom per unit cell symmetry-adapted functions can be used when the division of the crystal into monoatomic subplanes is replaced by a division into subplanes containing all symmetrically equivalent atomic positions.

1. Introduction

The quantitative evaluation of LEED spectra is still limited to relatively simple surface structures. The calculational effort required increases rapidly with the size of the surface unit cell and very soon reaches the capacity of present-day computers. The reason is that the solution of the multiple-scattering problem within the crystal requires the solution of very large systems of linear equations. These occur in all formulations of the multiple-scattering problem. The size of the matrices to be inverted can be considerably reduced by making proper use of symmetry relations. Symmetries are nearly always present when adsorbate structures are investigated on low-index surfaces of highly symmetric crystals. The adsorbate structure itself may have a lower symmetry than the clean surface but usually at least some of the symmetry elements of the bulk structure are retained. The full symmetry of the surface unit cell can be used in the calculation for normal incidence of the primary beam, while at oblique incidence only a mirror plane or glide plane is maintained when the primary beam lies within this plane of symmetry. Most frequently experiments are performed at normal incidence and at incidence within a mirror plane since the orientation of the probe is easily controlled by the symmetry of the diffraction picture. It is therefore most desirable to develop theoretical methods to simplify the calculation for these two cases.

The calculation of LEED intensities is usually divided into two parts. One part solves the multiple-scattering problem within a single plane or within two or more layers having a small interlayer distance; a spherical-wave representation is used. The second part uses a plane-wave expansion and is employed for interlayer multiple scattering with larger interlayer spacings. How symmetries can be used in the latter part where the wave field inside the crystal is described in terms of plane waves has been shown in detail by Rundgren and Salwén (1974) and by Van Hove and Pendry (1975). Pendry (1974) also

gives some applications of symmetry. In the spherical-wave representation of the wave field the use of symmetries is also possible and a description for that has also been given, by Rundgren and Salwén (1976); however, their formulation is only applicable to monoatomic layers. The purpose of this paper is to show how symmetries can be effectively used in cases where the unit cell contains more than one atom and the multiple-scattering amplitudes have to be calculated in a spherical-wave representation. This can be done in several ways—the direct matrix inversion method first described by Beeby (1968) and Pendry (1971), and an iterative method given by Zimmer and Holland (1975), Tong (1975), Tong and Van Hove (1977) and Van Hove and Tong (1979) and a transfer matrix method given by Jepsen (1980). The formulation that will be used here is the direct matrix inversion method. An application to other methods causes no problems.

The appropriate way to take into account symmetries in connection with spherical harmonics is to use symmetry-adapted functions. These are linear combinations of spherical harmonics that are either invariant or have the required transformation properties under symmetry operations. The scattered wave from each atom can be expanded in terms of symmetry-adapted functions where the local point symmetry of the atom applies. Although it is possible to develop the multiple-scattering formalism in angular momentum space starting with symmetry-adapted functions, this method will not be described here. It is more convenient to introduce symmetries into the well known general case. The first step is to perform the sum over equivalent atomic sites as well as the sum over equivalent beams in the system of equations defining the T -matrices and the reflection and transmission matrices. This will be shown in § 2. The symmetrisation in angular momentum space is only briefly described, in § 3, since group theoretical methods and tables of symmetry-adapted functions can be found in the literature (Bradley and Cracknell 1972). Some details of the calculation of interlayer propagator matrices are discussed in § 4.

2. Interlayer multiple scattering

In the layer KKR method the crystal is divided into layers or subplanes with identical translational symmetry. When the interlayer distance is large enough multiple scattering between subplanes can be calculated in k -space, which is usually more efficient than the calculation in angular momentum space. Nevertheless, it occurs quite frequently that an adsorbate layer or reconstructed surface layer contains several subplanes with small interplanar distances. Then the calculation has to be done in angular momentum space. Only this case will be considered here. The surface unit cell then contains several atoms which may or may not be coplanar. The reflection and transmission matrices for the whole layer are given by

$$M_{g'g} = \frac{8\pi^2 i}{|K_g|A|K_{g'}|} \sum_{lm} \sum_{l'm'} \sum_{\nu} i^{-l} Y_{lm}(\Omega_{K_g}) \exp(-iK_g \cdot d_{\nu}) T_{\nu,lm,l'm'}(K_g) \\ \times \exp(iK_g \cdot d_{\nu}) i^l (-1)^m Y_{l'-m'}(\Omega_{K_{g'}}) \quad (1)$$

where the notation of Pendry (1974) has been used with the exception that the scattering matrices $T_{\nu}(K_g)$ are denoted differently there. K_g and $K_{g'}$ are the sets of incoming and outgoing waves respectively. The sum over ν runs over all atoms in the unit cell, which

means over all subplanes. The vectors d_ν give the positions of the atoms with respect to the origin of the unit cell. The matrices $T_\nu(K_g)$ describe the scattered wave around the ν th atom. They are defined by a set of linear equations:

$$T_\nu(K_g) = t_\nu(E) + t_\nu(E) \sum_\mu G_{\nu\mu}(K_0) \exp[iK_g(d_\mu - d_\nu)] T_\mu(K_g). \quad (2)$$

The indices lm and $l'm'$ have been dropped here. The propagator matrices $G_{\nu\mu}(K_0)$ describe the transport of a spherical wave from point μ to point ν and are here defined without the phase factors $\exp[iK_g(d_\mu - d_\nu)]$; they depend therefore on the incoming wave K_0 only. The quantities $t_\nu(E)$ are diagonal matrices describing a single scattering event. The size of the matrix to be inverted to solve (2) is $N(l_{\max} + 1)^2 \times N(l_{\max} + 1)^2$, where N is the number of atoms in the unit cell and $l_{\max} + 1$ is the number of angular momentum components. The size of the matrix can be reduced considerably when symmetry can be used. It is clear that the matrix $M_{g'g}$ must be invariant under any symmetry operation that leaves the crystal together with the incident beam unchanged. Unfortunately this symmetry property cannot be used in the present form of (1) and (2).

When there is only a single atom in the unit cell the origin can be chosen such that the phase factors $\exp[i(K_g - K_g)d_\nu]$ in (1) vanish. It then becomes immediately clear that symmetry-adapted functions can be used. This is still possible when the origin of the layer is chosen to be at special points in the unit cell that have the full symmetry. A symmetry operation transforms point ν into point ν' , which has to be a lattice point too in that case. The phase factors then remain unchanged:

$$\exp(iK_g d_\nu) = \exp(iK_g d_{\nu'}) \quad \text{when } d_{\nu'} - d_\nu = r_n$$

where r_n is a translation vector and K_g is a vector of the reciprocal net. Here only the totally symmetric representation, the so-called unit representation, is needed. When K_g is a superlattice beam the phase factors may change sign and one of the other representations has to be used. This formalism is needed for bulk subplanes and has been described in detail by Rundgren and Salwén (1976) and will not be repeated here. In the following it is assumed that all the vectors K_g and K_g belong to the reciprocal net of the surface lattice.

When there are atoms at general positions in the unit cell the phase factors are no longer invariant under a symmetry operation and the T -matrices no longer contain symmetries. Also the propagator matrices $G_{\nu\mu}(K_0)$ are in general not invariant under a symmetry operation. That means for an atom in a general equivalent position in the unit cell no symmetries can be used. The local symmetry of that atom is 1 and the wave field around this atom is also without any symmetries. This fact and the flexibility wanted for arbitrary angles of incidence has prevented the use of symmetries in angular momentum space in most LEED calculations. Nevertheless, each general point in the unit cell has several symmetrically equivalent points, the number depending on symmetry, and the matrices $T_\nu(K_g)$ can be transformed into each other by simple symmetry operators.

It is important to note that the sum over equivalent positions can be done prior to inversion of the matrix. To do that it is necessary to perform the sum over equivalent beams in (1). There are n_g equivalent beams K_{gi} generated by all symmetry operations acting on K_g ; K_{gi} ($i = 1, \dots, n_g$) is the beam star of K_g . K_g denotes here and always in the following the set of symmetrically equivalent beams, saving a further subscript. As has been already shown by Van Hove and Pendry (1975) and by Rundgren and Salwén (1974), only for these beams are the reflection and transmission matrices needed. It is

convenient to define vectors $a_{\nu,lm}(K_g)$ and $b_{\mu,lm}(K_g)$:

$$a_{\nu,lm}(K_{g'}) = (n_{g'})^{1/2} \sum_{i=1}^{n_{g'}} \exp(-iK_{g'i}d_{\nu}) i^{-l} Y_{lm}(\Omega_{K_{g'i}}) \tag{3a}$$

$$b_{\mu,lm}(K_g) = (n_g)^{-1/2} \sum_{i=1}^{n_g} \exp(iK_{gi}d_{\mu}) i^l (-1)^m Y_{l-m}(\Omega_{K_{gi}}) \tag{3b}$$

and a vector $Z_{\nu,lm}(K_g)$

$$Z_{\nu,lm}(K_g) = (n_g)^{-1/2} \sum_{i=1}^{n_g} \sum_{l'm'} T_{\nu,lm,l'm'}(K_{gi}) \exp(iK_{gi}d_{\nu}) i^l (-1)^m Y_{l-m}(\Omega_{K_{gi}}). \tag{3c}$$

The equation for the reflection and transmission matrices then reads

$$M_{g'g} = \frac{8\pi^2 i}{|K_g|A|K_{g'\pm}|} \sum_{lm} \sum_{\nu} a_{\nu,lm}(K_{g'}) Z_{\nu,lm}(K_g). \tag{4}$$

The matrices $T_{\nu}(K_g)$ are not explicitly needed to calculate $M_{g'g}$ and (2) is solved directly for the vectors $Z_{\nu}(K_g)$:

$$Z_{\nu}(K_g) = t_{\nu}(E) b_{\nu}(K_g) + t_{\nu}(E) \sum_{\mu} G_{\nu\mu}(K_0) Z_{\mu}(K_g). \tag{5}$$

The vectors $a_{\nu}(K_g)$ and $b_{\nu}(K_g)$ are vectors in angular momentum space. They are not invariant under a symmetry operation but simple transformation rules exist. A symmetry operation of a space group may be denoted by $\{\alpha|r_n + v(\alpha)\}$ (Koster 1957) where α is a point group operation, r_n is a translation vector and $v(\alpha)$ indicates here a glide vector in a two-dimensional group. $v(\alpha)$ is zero for the point operations. The operation $\{\alpha|r_n + v(\alpha)\}$ acting on a vector d_{ν} transforms it into $d_{\nu'}$; also the vector $a_{\nu}(K_g)$ is transformed into $a_{\nu'}(K_g)$. The operator here acts only on d_{ν} since $a_{\nu}(K_g)$ depends on the beam star K_g which is invariant under a symmetry operation, but for which a phase factor occurs for a glide operation:

$$\{\alpha|r_n + v(\alpha)\} a_{\nu}(K_g) = a_{\nu'}(K_g) \exp(iK_g v(\alpha)). \tag{6}$$

The transformation operator can be explicitly expressed as a matrix. From the definitions given above and the properties of the spherical harmonics it follows directly that a rotation about an n -fold axis with rotation angle $\varphi_n = 2\pi/n$ implies

$$a_{\nu',lm}(K_g) = a_{\nu,lm}(K_g) \exp(im\varphi_n). \tag{7a}$$

A mirror line at an angle γ to the x axis leads to

$$a_{\nu',lm}(K_g) = a_{\nu,l-m}(K_g) (-1)^m e^{2im\gamma}. \tag{7b}$$

A glide plane is connected with a phase factor in the reflected amplitude and therefore

$$a_{\nu',lm}(K_g) = a_{\nu,l-m}(K_g) (-1)^m \exp(2im\gamma) \exp(iK_g v(\alpha)). \tag{7c}$$

The transformation properties can be formally written as

$$a_{\nu'}(K_g) = a_{\nu}(K_g) D_{\nu\nu'}. \tag{8a}$$

The matrices $D_{\nu\nu'}$ are unitary matrices in angular momentum space. They are diagonal for a rotation and change the sign of the m indices for a mirror or glide plane. For the point groups they are independent of the wavevectors K_g or $K_{g'}$, while for groups with

a glide plane they contain a phase factor $u_g = \exp(iK_g v(\alpha))$, which makes the calculation for propagator matrices somewhat more complicated as will be discussed below.

For the vectors $b_\nu(K_g)$ the same relations apply for the inverse matrices:

$$b_{\nu'}(K_g) = D_{\nu'\nu}^{-1} b_\nu(K_g). \quad (8b)$$

The reflection and transmission matrices must remain unchanged under a symmetry operation of the crystal and this leads to equivalent relations for the vectors $Z_\nu(K_g)$:

$$Z_{\nu'}(K_g) = D_{\nu'\nu}^{-1} Z_\nu(K_g). \quad (8c)$$

These relations enable us to perform the sum over equivalent positions in (5). For this purpose it is necessary to split the sum over subplanes or over all atoms in the unit cell into two parts. Summation indices ν, μ refer to all atoms in the unit cell, where ν_0, μ_0 designate only symmetrically independent positions. Finally ν', μ' designate the set of equivalent positions generated by the symmetry operations. A summation index ν' includes the position ν_0 unless it is explicitly indicated otherwise under the summation sign. It should be kept in mind that at oblique incidence all rotation axes are lost and only mirror or glide planes coinciding with the plane of incidence are retained. The symmetry of the unit cell is then only one of the groups pm, cm and pg.

With these definitions one obtains from (5)

$$Z_{\nu_0}(K_g) = t_{\nu_0}(E) b_{\nu_0}(E) + t_{\nu_0}(E) \sum_{\mu_0} \sum_{\mu \neq \mu_0} G_{\nu_0\mu}(K_0) D_{\mu'\mu_0}^{-1} Z_{\mu_0}(K_g) \quad (9)$$

where use has been made of (8c).

We define new interlayer propagators G^s

$$G_{\nu_0\mu_0}^s(K_0) = \sum_{\mu'} G_{\nu_0\mu'}(K_0) D_{\mu'\mu_0}^{-1} \quad (10)$$

and (9) can then be written as

$$Z_{\nu_0} = t_{\nu_0} b_{\nu_0} + t_{\nu_0} \sum_{\mu_0} G_{\nu_0\mu_0}^s Z_{\mu_0}. \quad (11)$$

this equation is completely equivalent to (5); the only difference is that the interlayer propagators $G_{\nu_0\mu_0}^s$ describe the transport of a spherical wave from a subplane ν_0 to a subplane μ_0 , where the latter contains all symmetrically equivalent positions and is no longer a subplane within the former definition. The index μ_0 in (11) runs now over all points in the asymmetric unit of the surface unit cell, i.e., only for these points do the scattering matrices T_ν or the vectors Z_ν have to be calculated. Now the reflection and transmission matrices are simply given by

$$M_{g'g} = \sum_{\nu} a_\nu(K_{g'}) Z_\nu(K_g) = \sum_{\nu_0} n_{\nu_0} a_{\nu_0}(K_{g'}) Z_{\nu_0}(K_g) \quad (12)$$

where n_{ν_0} is the multiplicity of point ν_0 .

This is not the only consequence of symmetry that can be used. Equation (2) has now been brought into a form suited for the introduction of symmetry-adapted functions. The symmetrisations in angular momentum space and in k -space are coupled in that sense that symmetries in angular momentum space can only be used when the corresponding sum over equivalent beams and the sum over equivalent atomic positions are also performed. That means that (11) has to be solved instead of (5); otherwise the symmetry in angular momentum space is destroyed.

3. Symmetrisation in angular momentum space

Symmetry-adapted functions for all crystallographic point groups have been tabulated by Bradley and Cracknell (1972); the irreducible representations for the point symmetries and the character tables can be found there. However, only the 17 two-dimensional space groups are needed here and the index selection rules may be repeated briefly. The ten two-dimensional point groups are considered first since for these groups the transformation matrices do not depend on the wavevector K_g or $K_{g'}$. Consequently only the unit representation is needed, provided the wavevectors K_g belong to the reciprocal net of the unit cell. When the point ν is on an n -fold axis, (7a) implies that

$$a_{\nu,lm} = a_{\nu,lm} e^{im2\pi/n} \quad (13a)$$

and m should satisfy the condition

$$m = 0(\text{mod } n).$$

It is unimportant whether point ν is at the origin or not, provided that the origin is chosen properly at the principal axis as usual; then the condition for m holds true for all other axes. It should be noted that this is only true for point groups and symmorphic groups; a glide operation can add a phase factor and m can take other values. When ν lies on a mirror line it follows from (7b) that

$$a_{\nu,lm} = a_{\nu,l-m} (-1)^m e^{2im\gamma} \quad (13b)$$

where γ is the angle between the x axis and the mirror line. For all atoms on a mirror line the spherical harmonics and similarly the vectors a_ν , b_ν and Z_ν can be replaced by the symmetry-adapted function

$$Y_{lm}^s = 2^{-1/2} [Y_{lm} + (-1)^m e^{2im\gamma} Y_{l-m}] \quad (14)$$

and only positive values of m are needed.

These selection rules for the spherical waves remain unaltered for the vectors Z_ν and consequently also for the propagator matrices $G_{\nu_0\mu_0}^s$.

For (10) and the properties of the transformation matrices it follows that for an atom ν_0 on an n -fold axis

$$G_{\nu_0lm, \mu_0l'm'}^s = 0 \quad (15)$$

unless

$$m = 0(\text{mod } n).$$

This is a consequence of the fact that $G_{\nu_0\mu_0}^s$ is a propagator from a subplane containing all symmetrically equivalent atoms. It is easy to show that for the indices $l'm'$ on the right-hand side the local point symmetry of atom μ_0 has to be taken. For an atom in a general equivalent position all spherical waves are needed and no reduction is possible. Here the reduction is given by the fact that the sum over equivalent positions can be performed before inverting the matrix. For each atom a different set of indices lm has to be defined, according to its local symmetry, in such a way that the matrix to be inverted is reduced to its minimum size. The interlayer propagator matrices $G_{\nu_0lm, \mu_0l'm'}^s$ are now rectangular matrices, where the left-hand side indices lm take values belonging to the local symmetry of point ν_0 and the right-hand side indices $l'm'$ refer to the local symmetry of point μ_0 .

The index selection rules given above apply for the point groups and symmorphic groups, which are here the groups cm and cmm . The propagators for the centred lattices can be calculated choosing the primitive unit cell and retaining the mirror plane. For the other groups containing glide planes the calculation becomes more complicated. As mentioned above a glide operation changes the sign of the reflected amplitudes for those beams having an odd-order index parallel to the glide plane. The consequence is that different representations are required for different beams. A glide plane parallel to the x axis implies that

$$a_{v',lm}(K_g) = a_{v,l-m}(K_g)(-1)^m e^{i\pi h} \quad (16)$$

where $K_g = K_0 + ha^* + kb^*$ and h, k are indices of the beam K_g . Consequently the propagator matrices have to be calculated twice for the two beams sets (i.e. the set with index h even and the set with h odd), each having a different set of symmetry-adapted functions.

A combination of a rotation axis with a glide plane (symmetry groups pmg , pgg and $p4g$) requires even more computational effort. In general different representations are needed for the beam sets h, k and $h+k$, even or odd. The representation that applies can be found in the character tables of the corresponding point groups. However, in the computer program it is convenient to find the allowed values of the index m by using the condition that

$$\sum_{\alpha \in G(\alpha)} \{\alpha | r_n + v(\alpha)\} \exp(iK_{g_i} d_v) \exp(im\varphi_{K_{g_i}}) \neq 0 \quad (17)$$

where $G(\alpha)$ is the symmetry group and K_{g_i} is any one of the beams belonging to the beam star K_g .

4. Calculation of interlayer propagator matrices

The electron propagator function describing the transport of a spherical wave from one point to another point is given by (Pendry 1974)

$$G_{vlm,ul'm'}(K_0) = \sum_P \sum_{l''m''} \exp(iK_0 \cdot P) c(lm, l'm', l''m'') i^{l''} h_{l''}(|K_0||P + d_\mu - d_\nu|) \times (-1)^m Y_{l''-m''}(\Omega_{P-d_\mu-d_\nu}) \quad (18)$$

where

$$c(lm, l'm', l''m'') = 4\pi i^{l-l'-l''} \int Y_{lm} Y_{l'-m'} Y_{l''m''} d\Omega.$$

As shown by Tong *et al* (1973) the direct lattice sum in (18) can be replaced by a sum in k -space when $|d_{\nu\pm} - d_{\mu\pm}| \neq 0$:

$$G_{vlm,ul'm'}(K_0) = \frac{-8\pi^2 i}{A} \exp[-iK_{0-}(d_{\nu-} - d_{\mu-})] \times \sum_g \frac{1}{K_{g-}} \exp[iK_g(d_\nu - d_\mu)] Y_{l-m}(\Omega_{K_g}) Y_{l'm'}(\Omega_{K_g}). \quad (19)$$

Which sum is more convenient to evaluate depends on the magnitude of the normal component of the vector $d_\nu - d_\mu$.

In (10) the sum of propagator matrices from all symmetrically equivalent positions

to the atom ν_0 appears. This sum can often be simplified when some or all of the vectors $d_{\mu'} - d_{\nu_0}$ are obtained from $d_{\mu_0} - d_{\nu_0}$ by a symmetry operation. This is always satisfied when the multiplicity n_ν of point μ_0 is smaller than that of point ν_0 . Then the sum over μ' should be transformed into a sum over ν' :

$$\sum_{\mu'} G_{\nu_0\mu'} D_{\mu'\mu_0}^{-1} = \frac{n_{\mu_0}}{n_{\nu_0}} \sum_{\nu'} D_{\nu_0\nu'} G_{\nu'\mu_0} \quad (20)$$

since

$$G_{\nu'\mu'} = D_{\nu'\nu_0}^{-1} G_{\nu_0\mu_0} D_{\mu_0\mu'}. \quad (21)$$

The latter equation follows directly from the definitions in (18) and (19).

The sum on the left-hand side of (20) contains n_{μ_0} terms whereas the sum on the right-hand side contains a smaller number n_{ν_0} , or even only one term when the point ν_0 has the full symmetry of the unit cell. The calculation of interlayer propagators takes a large proportion of the total computational effort and a reduction of the number of lattice sums reduces the computing time considerably.

As mentioned above the indices l, m and l', m' do not take the same values since l, m are related to point ν_0 and the corresponding set of symmetry-adapted functions, whereas l', m' are related to point μ_0 and another set of symmetry-adapted functions.

Where the direct lattice sum is evaluated (equation (18)) both sets of symmetry-adapted functions are coupled via the coupling coefficients $c(lm, l'm', l''m'')$ and these have to be defined here for combinations of spherical harmonics when mirror or glide lines are involved. The third couple of indices l'', m'' is related to the vector $d_{\mu_0} - d_{\nu_0}$ and must obey the symmetry of point $d_{\mu_0} - d_{\nu_0}$ with respect to the origin. A formal treatment of all allowed combinations of indices and a definition of coupling coefficients for symmetry-adapted functions on the basis of group theoretical methods could in principle be made and would be mathematically elegant, but in practice this would be most inefficient. The number of coefficients is rather large and separate storage for each subgroup is not possible. It is therefore appropriate to use the coupling coefficients as defined above for spherical harmonics and not as defined for symmetry-adapted functions, which are combinations of spherical harmonics. The sum over positive and negative values of m and m' can be performed afterwards when necessary.

Usually the coupling coefficients are stored in the sequence in which they are called in the routine that calculates the propagator matrices. This sequence can remain unchanged when no symmetries are used. It is no longer possible for the method described here since different sequences of l, m indices occur for the possible combinations of local symmetries. Therefore a direct addressing of coefficients with an index image function is needed. This is in practice possible if one makes use of the symmetry properties of the coefficients with respect to simultaneous change of signs and interchange of l, m and l', m' . It also has the advantage that the number of coefficients is minimised.

Where the lattice sum is performed in reciprocal space (equation (19)) the procedure is much easier since here no coupling coefficients occur and symmetry-adapted functions can be used directly.

5. Discussion

The full use of symmetries does not reduce the flexibility of the LEED program. For the

ten point groups the calculation becomes especially easy. Before starting the calculation of interlayer propagators the local symmetry of each atom needs to be labelled. This fixes the l, m sequence of the spherical harmonics for all atoms and the sequence can be stored in an index array. Any further reference to the indices l and m is done via this index image. The following calculation is then independent of the actual symmetry of each atom. The ten point groups and the groups cm and cmm can be handled that way. For the remaining groups containing glide planes the procedure requires more effort since an additional loop must be incorporated. The set of beams must be decomposed into two or more groups for which different symmetry-adapted functions are required. The propagator matrices have to be calculated again, but the sum over lattice points need not be repeated, since it can be stored and used again. There is still an important gain as regards computing time and memory space compared with the calculation made without using symmetries. All 17 two-dimensional space groups can be handled with the same program.

A further advantage of directly addressing the coupling coefficients lies in the fact that a different number of phaseshifts can be used for different atoms, i.e. for hydrogen only three or four phaseshifts are required at 150 eV while for a metal like iron seven are necessary. The following example may illustrate the efficiency of making full use of symmetries. The iridium (100) surface reconstructs to a (5×1) structure and in the surface structure model there are six atoms in the unit cell. Using nine phaseshifts a (486×486) matrix would have to be inverted for each point on the energy scale, a very costly or even impossible task for most computers. The introduction of symmetry-adapted functions reduces the matrix at normal incidence to (140×140) and this is a solvable problem.

There are in principle further symmetries that could be introduced using glide planes or mirror planes parallel to the surface. This would lead to a total of 80 plane groups. Of these only the case where the unit cell is a plane, i.e. when all atoms are within one plane, is easily combined with one of the 17 groups. This symmetry has been already described by Pendry (1971); it leads to a block-diagonalisation of the matrix since there are two irreducible representations that do not couple. Other cases can be handled too, of course, but they require a much more complicated computer code. Since these cases are very unlikely to occur on real surfaces they have not been discussed here.

The multiple-scattering problem can only be solved in angular momentum space when small interlayer spacings occur; otherwise a calculation in reciprocal space is in most cases more efficient. The calculation is then divided into two parts, one for the surface layer with a calculation in angular momentum space and another for the bulk with a calculation in k -space. The unit cell of bulk layers is usually smaller, leading to different sets of beams in k -space which are not coupled in the bulk. The calculation of reflection matrices for the bulk can then be done separately for each set of beams. However, for simple structures with a small unit cell, it may be advantageous to perform the total calculation in angular momentum space. Here the solution of the system of linear equations is only necessary for one vector (the incident beam), and all reflected beams are obtained by vector multiplications. In fact, this method has been chosen by Davis and Zehner (1980). For large unit cells the total calculation in angular momentum space is not attractive since it is not possible to change the basis vectors of the unit cell for bulk layers while this is possible in k -space. The number of atoms to be included then increases too much even at normal incidence where the full symmetry can be used.

Symmetry-adapted functions can be applied in all formulations of the multiple-scattering problem using a spherical-wave representation. They provide the most effec-

tive way of performing calculations; further improvements in calculational speed could only be achieved using a different theoretical approach. An n -fold axis at normal incidence multiplies the number of atoms per unit cell that can be treated with a given program size by a factor of approximately n , and an additional mirror plane doubles this number again. Since most experiments are performed under conditions where at least one symmetry plane is retained, the range of surface structures accessible for LEED calculations is enhanced by a factor of at least two.

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