Chapter 3

Theory of Low Energy Electron Diffraction

Low Energy Electron Diffraction (LEED) is one of the first and one of the most successful surface science techniques for structure determination ever invented. For more than 50 years it has been the dominant method to study the structure and morphology of two dimensional plane surfaces. From its invention in 1927 by Davison and Germer [88] until today a vast variety of very different techniques and extremely sophisticated applications have been developed.

For the structure analysis of atomic positions in the surface unit cell, LEED I – V analysis has been developed with an accuracy of less than a few hundreds Å. Furthermore, the determination of complex surface structures has been automated [89]. Besides the intensities of the diffraction spots also the profile and position contain important information about the surface morphology, which can be analyzed by Spot Profile Analysis LEED (SPA-LEED) [90]. In the following, both the kinematic and dynamic theory of LEED will briefly be described since the SPA-LEED analysis is based on the kinematic theory whereas the tensor LEED analysis based on the dynamic theory and both will be used in this thesis.

3.1 Kinematic LEED Theory

The diffraction from surfaces may be described as a sum of electron wave functions scattered from the initial wave vector $\vec{k}_i$ of the incoming electron to the final wave vector $\vec{k}_f$ by all surface atoms at positions $\vec{r}(\vec{n})$.

$$\Psi(\vec{K}, \vec{k}_i) = \sum_n f(\vec{n}, \vec{K}, \vec{k}_i) e^{i\vec{K}\vec{r}(\vec{n})}$$

(3.1)

where $\vec{K} = \vec{k}_i - \vec{k}_f$ is the scattering vector and $f(\vec{n}, \vec{K}, \vec{k}_i)$ the structure factor, which depends both on the initial $\vec{k}_i$ and final electron wave vector $\vec{k}_f$. The structure factor combines the electron waves coming from the surface atom at $\vec{r}(\vec{n})$ and all underlying atoms in the column perpendicular to the surface.
The diffraction phenomena with the diffraction spot intensity
\[ I(\vec{K}, \vec{k}_i) = |\Psi(\vec{K}, \vec{k}_i)|^2 = \sum_{n,m} f(\vec{n}, \vec{K}, \vec{k}_i) f^*(\vec{m}, \vec{K}, \vec{k}_i) e^{i\vec{K}(\vec{r}(\vec{n}) - \vec{r}(\vec{m}))} \] (3.2)
are mainly determined by the scattering cross section, i.e. the values of the structure factor \( f(\vec{n}, \vec{K}, \vec{k}_i) \).

The infinite periodicity parallel to the surface results in extremely well defined reciprocal lattice vectors \( \vec{K}_\parallel \). On the contrary, in the direction perpendicular to the surface, electrons in a LEED experiment are elastically scattered within a depth of only a few atomic layers due to strong electron-electron interactions. The lack of a well defined periodicity perpendicular to the surface relaxes the selection rule for \( \vec{K}_\perp \), almost any value of \( \vec{K}_\perp \) is possible. Therefore the reciprocal lattice in a LEED experiment is well described by a periodic arrangement of lattice rods.

The finite penetration depth of the electrons together with the dominating multiple scattering effects influences the intensity via the structure factor \( f(\vec{n}, \vec{K}, \vec{k}_i) \) as a function of the initial \( \vec{k}_i \) and the final scattering vector \( \vec{k}_f \).

Dynamic LEED theory is necessary to describe the dependence between the geometric atomic structure in the unit cell and the intensities \( I(\vec{K}, \vec{k}_i) \) of the diffraction spots as a function of electron energy and incidence angle. This whole field of atomic structure determination by LEED \( I-V \) analysis for smooth and homogeneous surface will be described in section 3.2.

For simplicity reasons the kinematic approximation is used for the spot profile analysis of rough or stepped surfaces. Pendry et al. [91] have discussed multiple scattering effects of disordered surfaces. However, up to now, it is still too complicated to consider different structure factors \( f(\vec{n}, \vec{K}, \vec{k}_i) \) for the diffraction from disordered step edges of rough surfaces.

All structure factors are replaced by their spatial average (3.3)
\[ f = f(\vec{K}, \vec{k}_i) = \langle f(\vec{n}, \vec{K}, \vec{k}_i) \rangle_n \] (3.3)
independent on the site of a particular unit cell and the arrangement of the neighboring unit cells. This approximation is strictly valid for a smooth and flat surface. However, small deviations may be expected at crystal positions without translational symmetry, i.e. at step edges. Considering the unit cell columns just at the step edge, it becomes clear that the surrounding atomic configurations are different as shown in Fig. 3.1. Electrons scattered directly from below and above the step edge undergo different structure factors. Due to the very limited electron penetration depth of less than 5 Å only such a small band around a step edge may show up a different structure factor. Electrons scattered from unit cells further away than 5 Å from the step edge are simply insensitive to it and exhibit all the same structure factor \( f \). Therefore, this approximation is the better, the larger the separation between steps. With decreasing
3.1. Kinematic LEED Theory

![Diagram of a step edge showing structure factors](image)

**Fig. 3.1:** At a step edge the structure factor $f$ deviates from its average value. $f_u$ and $f_d$ may show different scattering amplitudes and scattering phases.

The intensity splits up

$$ I(\vec{K}, \vec{k}_i) = F(\vec{K}, \vec{k}_i)G(\vec{K}) $$

into the dynamical form factor, which depends on the initial and final wave vector

$$ F(\vec{K}, \vec{k}_i) = |f(\vec{K}, \vec{k}_i)|^2 $$

and the well known lattice factor, which is only determined by the surface morphology and the scattering vector $\vec{K}$

$$ G(\vec{K}) = \left| \sum_n e^{i\vec{K}\cdot\vec{r}(n)} \right|^2 $$

The lattice factor $G(\vec{K})$ does not modify the integral intensity of the spots, it influences the intensity distribution in reciprocal space. A perfectly smooth, flat surface shows up with perfectly sharp diffraction spots, which are only instrumentally broadened. However, any deviation from a perfect translational symmetry such as a step edge or an island results in a redistribution of intensity from the sharp fundamental diffraction spots into diffuse intensity between the LEED spots [92, 93]. For a rough surface spot broadening is observed, for a regular step train spot splitting, and for facets new fundamental spots [94].

The total intensity of the diffuse and peaked part of a particular spot $i, j$ is conserved and normalized to 1 by the number $N$ of surface unit cells and is independent on the surface morphology and independent on $K_\perp$:

$$ \int_{B_z} d\vec{K} ||G_{ij}(\vec{K}) = 1 $$
This is of very special importance for the spot profile analysis and is essential for the practical data evaluation. The lattice factor $G_{ij}(\vec{K})$ is obtained from the intensity $I_{ij}(\vec{K})$ of LEED spot $i, j$. The absolute value of the spot intensity is not evaluated, only the variation of the spot profile with $\vec{K}$. The lattice factor $G_{ij}(\vec{K})$ is obtained by normalization of the experimentally measured intensity profile $I_{ij}(\vec{K})$ with the total integral intensity of the spot $i, j$.

\[
\frac{I_{ij}(\vec{K})}{\int d\vec{K}|I_{ij}(\vec{K})|} = \frac{F(\vec{K}, \vec{k}_i)G(\vec{K})}{\int_{Bz} d\vec{K}|F(\vec{K}, \vec{k}_i)G(\vec{K})|} \approx \frac{F(\vec{K}, \vec{k}_i)G(\vec{K})}{\bar{F}_{ij}(\vec{k}_i) \int_{Bz} d\vec{K}|G(\vec{K})|} \sim F(\vec{K}, \vec{k}_i)G(\vec{K}) (3.8)
\]

This intensity profile is also modulated by the dependence of the dynamic form factor $F(\vec{K}, \vec{k}_i)$ on the electron energy $E$, the angle of incidence $\varphi$ of the electron beam and the scattering vector $\vec{K}$. Recording a spot profile usually only the scattering vector $\vec{K}$ is varied. For the analysis it is usually assumed that the variation of $F(\vec{K}, \vec{k}_i)$ with $\vec{K}$ is much smoother than that of the lattice factor $G_{ij}(\vec{K})$, i.e. that $F(\vec{K}, \vec{k}_i) = \bar{F}_{ij}(\vec{k}_i)$ is constant with respect to $\vec{K}$ around the spot $i, j$ in reciprocal space, where diffuse intensity is observed.

This approximation is the better, the larger the observed morphological features are, because the diffuse intensity will be confined to a smaller region around the spot $i, j$. The kinematic approximation works best for large morphological structures. However, the observation of such large structures requires a high resolution instrument.

Of special importance are conditions, when the structure factor equals zero: the different scattering amplitudes from atoms of the unit cell annihilate each other (complete destructive interference). Small changes of the initial or final wave vector will immediately disturb the cancellation: intensity is observed and may strongly vary by orders of magnitude for small variations of the scattering vector $\vec{K}$. This effect does not happen for strong intensity conditions, when the scattering amplitudes of most atoms of the unit cell interfere constructively. Changes of the energy and scattering vector will also affect this situation and may also modify the intensity. However, the relative changes of the structure factor with $\vec{K}$ or $\vec{k}_i$ will be small, and will only become large, if the structure factor varies strongly or is close to zero.

The lattice factor could also be expressed by the absolute square of the two-dimensional Fourier transform

\[
G(\vec{K}) = \frac{1}{2\pi} \left| \sum_n e^{i\alpha K_1 \vec{n}} \varphi(K_\perp, \vec{n}) \right|^2 (3.10)
\]

of the surface phase function

\[
\varphi(K_\perp, \vec{n}) = e^{idK_\perp h(\vec{n})} (3.11)
\]
This equation highlights the maximum obtainable morphological information: The surface height function \( h(\vec{n}) \) is in principal not accessible, only its projection on the unit circle of complex numbers could be determined. Due to the modulo properties of the complex exponential with \( 2\pi \) this causes some ambiguous results, if the spot profile is determined only for a single value of \( K_\perp \). For an unambiguous determination of the surface morphology \( h(\vec{n}) \) the lattice factor \( G(\vec{K}) \) must be known for different values of \( K_\perp \).

The scattering phase \( S \) replaces the vertical scattering vector as dimensionless value (independent on the particular material)

\[
S = K_\perp / 2\pi \tag{3.12}
\]

\[
\varphi(S, \vec{n}) = e^{i2\pi S h(\vec{n})} \tag{3.13}
\]

The scattering phase \( S \) describes the phase difference in numbers of the electron wavelength \( \lambda \), when electrons are scattered from adjacent terraces with a height difference of one atomic step \( d \).

\[
\lambda = (h^2 / 2m_e eE)^{-1/2} \tag{3.14}
\]

Electrons interfere constructively for integer \( S \), i.e. the Bragg or ”in-phase” condition of scattering. For this conditions they are not sensitive to any surface roughness. Therefore, a sharp LEED spot is expected for electrons with an energy corresponding to a Bragg condition.

For the ”out-of-phase” or anti-Bragg condition the electrons interfere destructively and are most sensitive to surface roughness. The electrons are not annihilated from the sharp LEED spot, but redistributed into a diffuse part surrounding the sharp spot. The shape or profile of such a broadened spot is determined by the lattice factor \( G(\vec{K}) \).

For the (00) spot, i.e. \( \vec{K}_\parallel = 0 \), and an arbitrary incidence angle the scattering phase \( S \) depends as follows on the electron wavelength

\[
S = 2d \cos(\vartheta) / \lambda \tag{3.15}
\]

or electron energy

\[
S = 2d \cos(\vartheta) \sqrt{E(/eV)/150.4} \tag{3.16}
\]

Though the electrons gain energy during the scattering process due to the inner potential \( V_0 \) of the crystal, the interference conditions described by the scattering phase \( S \) are not affected. Each electron undergoes the same constant phase shift due to the inner potential.

Therefore, the accurate and absolute determination of vertical layer distances is possible for a rough surface via the position of the ”in-phase” conditions, i.e. the three dimensional Bragg conditions [94].

3.2 Dynamic LEED Theory

**Standard Dynamic Intensity Calculation.** As mentioned above, dynamic LEED theory is necessary for the determination of atomic structures. The computation of diffraction intensities must consider multiple scattering due to the large cross section for electron-atom scattering. Though the total of scattering events is complex the calculations can be organized in a clear way by following the hierarchical scheme as displayed in Fig. 3.2: First, the scattering of the electrons by a single atom is calculated. Then the atoms are arranged to form an atomic layer for which layer diffraction matrices are computed. Finally, the layers are stacked to a crystal to yield the total reflection matrix of the surface.

The single atom scattering results from solving the Schrödinger equation assuming an atomic potential of spherical symmetry and finite spatial extension. The radius of the sphere is usually defined so that neighboring spheres touch each other. Electron orbitals extending over the sphere are redistributed inside the sphere. In the area between atomic spheres the potential is kept constant described by the real part of the inner potential $V_0$. It adds to the electron energy when the electron enters the solid, so its total kinetic energy within the surface is $E_i = E + V_0$. For an atomic layer the potential looks like an arrangement of a muffin tin, from which the expression muffin-tin potential arises. Of course, the spherical symmetry of the atomic scattering potential is an approximation only, as the atom is embedded in an arrangement of non-spherical symmetry. However, this approximation works well for LEED energies, because they are so much above the Fermi energy that scattering is dominated by the spherically symmetric inner electron shells and the nucleus of the atom. Due to the spherical symmetry the scattering is best described in the angular momentum.

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Fig. 3.2: Hierarchy of dynamical LEED intensity evaluation. [95].
presentation resulting in a set of phaseshifts $\delta_l$ with $l$ cut off at a certain maximum value $l_{\text{max}}$. For higher values of $l$ the phaseshifts are assumed to be negligible, thus

$$l_{\text{max}} \approx kR$$

with $R$ the radius of the atomic sphere is usually a good approximation. By solving the Schrödinger equation, the phaseshifts fully describe the multiple scattering within the atom.

The scattering within an atomic layer is also described in the angular momentum presentation. Scattered spherical waves outgoing from a certain atom are expanded to spherical waves with respect to the atomic position of a neighboring atom in order to account for multiple scattering. As this neighbor may scatter back to the original atom a self-consistent solution of the total sum of the scattering processes is required. This is equivalent to the inversion of a matrix whose dimension scales with $l_{\text{max}}^2$. Calculation and inversion of this matrix usually requires the major part of the computing time. For the total diffraction from a layer of atoms a representation in momentum space is appropriate because of translational symmetry. Therefore, the sum over all dynamical atomic scattering amplitudes is developed in a set of plane waves with surface parallel momenta $(\vec{k}_{\parallel} + \vec{g})$ producing layer diffraction amplitudes $M_{gg}^{\pm\pm}$ where the $\pm$ signs indicate the direction of incoming and outgoing plane waves. Eventually, the matrices $M_{gg}^{\pm\pm}$ are used to stack the layers in order to produce the full surface diffraction. Multiple diffraction between layers has to be accounted for, which again leads to the inversion of a matrix. It is sufficient, to couple neighboring layers step by step so that by each matrix inversion the number of layers can be doubled (layer doubling scheme). The dimension of the matrix is determined by the number of propagating plane waves, for which a natural cut-off is the Ewald sphere, so that $|\vec{g}| < k$ results. However, as attenuated waves also couple between neighboring layers, more beams have to be considered. When the layer spacings are well above about 1 Å one can avoid the matrix inversion and profit from the fact that forward diffraction of a layer (described by $M_{gg}^{++}$ or $M_{gg}^{--}$) normally dominates over back diffraction (described by $M_{gg}^{+-}$ or $M_{gg}^{-+}$). The corresponding approximative procedure is known as Renormalized Forward Scattering (RFS) [96].

While travelling within a solid an electron undergoes inelastic processes dominated by plasmon excitation by which it disappears from the elastic channel. This can be described by the imaginary part of the inner potential, the so called optical potential $V_{0i}$, which is of the order of 4-5 eV at 100 eV and is slightly energy dependent ($V_{0i} \propto E^{1/3}$ is usually a good approximation [97]). So, the total inner potential is complex

$$V_0 = V_{0r} + iV_{0i}$$

This with

$$\frac{1}{2}k^2 = E + V_0$$
results in an imaginary part of the wavenumber,

\[ k_i \approx V_{0i}/k_r \]  

(3.20)

with

\[ k_r \approx (2E + 2V_{0r})^{1/2} \]  

(3.21)

for \( V_{0i} \ll (E + V_{0r}) \). Consequently, spherical and plane waves described by \( \exp(ikr) \) and \( \exp(i\vec{k} \cdot \vec{r}) \), respectively, are attenuated whilst travelling. Quasielastic scattering by phonons also removes electrons from the coherent elastic channel. This can be described by a Debye-Waller factor, which reduces the atomic scattering factor for a finite temperature to

\[ t(E, T) = t(E, 0) \exp\left(-\frac{1}{2}\Delta k^2 < u^2 >\right) \]  

(3.22)

with \( \Delta k \) the modulus of the electron’s momentum transfer and

\[ <(u(T))^2> = <u^2> \]  

(3.23)

the mean square atomic displacement due to atomic vibrations at temperature \( T \). The simple relation between \( t \) and \( \delta_l \)

\[ t(E, T) = (k)^{-1} \sum_l (2l + 1) \sin \delta_l \exp(i\delta_l) P_l(\cos \vartheta) \]  

(3.24)

with \( \vartheta \) the scattering angle, allows simulation of the Debye-Waller factor by complex phasishifts \( \delta_l(T) \). This is a simple way to consider thermal vibrations also for multiple scattering processes, although this description is not fully exact.

**Reliability Factor.** In order to measure the agreement between curves quantitatively, so called reliability factors (R-factors) are widely used today. Due to the complex structure of the spectra, different concepts for the construction have been followed in the past leading to a variety of different R-factors [88]. Today, the relative mean square deviations of intensities (\( R_2 \)) or the Pendry R-factor (\( R_P \)) are mostly used. In both cases the summation is over all intensities \( I_g(E_i) \) taken for different beams \( g \) and at different energies \( E_i \). So \( R_2 \) simply results by

\[ R_2 = \frac{\sum_{i,g} (cI_{cal} - I_{exp})^2}{\sum_{i,g} (I_{exp})^2} \]  

(3.25)

where \( c \) is the average normalization constant between experimental and calculated spectra. The Pendry R-factor [98] is more sophisticated and follows the idea that maxima and minima in the spectra are the important features. Their positions come by constructive or destructive interference, which depends both on the electron wavelength and the pathlength difference between different interfering diffraction processes. Therefore, emphasis is on the positions of maxima and minima rather than on the
absolute height of intensities. So, instead of the intensities their logarithmic derivative
with respect to energy is used

\[ L = (\partial I / \partial E) / I \]  

(3.26)

As for small intensities this is very sensitive to experimental errors, the bounded
function

\[ Y = L / [1 + (LV_0)^2] \]  

(3.27)

is used instead of \( L \). The Pendry \( R \)-factor then simply results as the mean square
deviations of \( Y \) functions rather than of the intensities as in the case of \( R_2 \). i.e.

\[ R_P = \sum_{i,g} (Y_{cal} - Y_{exp})^2 / \sum_{i,g} (Y_{cal}^2 + Y_{exp}^2) \]  

(3.28)

Ideal agreement corresponds to \( R_P = 0 \), uncorrelated spectra yield \( R_P = 1 \) and
anticorrelated curves produce \( R_P = 2 \). The variance of the Pendry \( R \)-factor

\[ \text{var}(R_P) = R_{P,\text{min}} (8V_{0i} / \Delta E)^{1/2} \]  

(3.29)

with \( \Delta E \) the energy width of the total data base, allows estimation of the error limits
for the model parameters determined [98].

**Tensor LEED Approximation.** As described above the theory of dynamical
low energy electron diffraction has been well developed since the 1970s. It allows the
reliable calculation of intensities for structures in principle of any complexity. How-
ever, though for clean and low index surfaces the calculation can even be performed
on a minicomputer, the necessary computer efforts grow considerably with increasing
complexity. They scale, depending on the approximations used, with \( n^2 - n^3 \) where \( n \)
is the number of atoms in the unit cell. Though the calculations could be speeded up
by the use of symmetry adapted functions in angular momentum expansion [99,100]
this remained fatal for the retrieval of the correct values of structural parameters
when a scan of the parameter space is used to find the best theory-experiment fit
in a trial-and-error procedure. This is because the number of trial structures grows
exponentially with the dimensionality of the parameter space, i.e. the complexity of
the structure.

Therefore, the strategy to solve complex structures by LEED must be twofold. On
one hand the computer efforts to calculate the intensities for a certain structure have
to be reduced. On the other hand, the scan of the parameter space has to be given
up in favor of directed search procedures or direct methods. In fact, both strategies
were followed during the last decade. The substantial reduction of computer time for
the intensity calculation was made possible by the introduction of the perturbation
method tensor LEED.

Of course, any reduction of computer time for the calculation of intensities of a
trial structure must use certain approximations instead of applying the full dynamical
theory. In the latter approximations are also used, which, however, can be iterated

Fig. 3.3: Scattering of a plane wave by an atom into a spherical wave centered at the atom’s origin (left) and by a displaced atom (right) with the scattering expressed in terms of spherical waves centered at the original position. [102].

to yield accuracy. Such approximations have been tried since the early days of LEED calculations [88]. All of them consider only a subset of the total of the multiple scattering processes, which is, of course, at the cost of accuracy. Nevertheless, these approximate schemes proved to be useful in a number of cases. However, they were made largely superfluous with the development of the powerful tensor LEED method. The underlying theory was developed by the London Imperial College group. It marks the most important progress in LEED theory made during the 1980s [91,101]. Its essentials are presented below.

Assume that a full dynamical calculation has been carried out for a certain structure, i.e. a reference structure, and that the electron wave field $|\Psi(k_\parallel)|$ inside the surface has resulted according to an incident electron beam with surface parallel momentum $k_\parallel$. Now some atoms at positions $\vec{r}_j$ with scattering $t$-matrix $t_j$ are displaced by $\delta\vec{r}_j$ to form a certain trial structure. If the atomic scattering of the displaced atom is still to be described by a $t$-matrix $t'_j$ located at its former position $\vec{r}_j$ one has to modify the old matrix according to

$$t'_j = t_j + \delta t_j(\delta\vec{r}_j) \quad (3.30)$$

the new matrix $t'_j$ can no longer be diagonal because, as illustrated in Fig. 3.3, the displacement introduces a non-spherical distortion of the scattering potential. In angular momentum basis using the abbreviation $L = (l,m)$ the change of the matrix can be calculated by

$$\delta t_{j,L'L'} = \sum_{LL'} G_{LL'}(\delta\vec{r}_j)t_{L'L'}G_{L'L'}(-\delta\vec{r}_j) - t_{jl}\delta l_l \quad (3.31)$$

whereby $G$ represents the spherical wave propagator, which converts a spherical wave centered at $\vec{r}_j$ to a set of spherical waves centered at $\vec{r}_j + \delta\vec{r}_j$. The atomic displacements
cause a change of the diffraction amplitude, which for the final direction with parallel
momentum $k_f \parallel$ can be calculated by first order perturbation

$$\delta A = \sum_j < \Psi(k_f \parallel) | \delta t_j | \Psi(k_\parallel) >$$

(3.32)

In angular representation this can be expressed by

$$\delta A = \sum_j \sum_{LL'} T_{j,LL'} \delta t_{j,LL'}$$

(3.33)

which eventually allows the calculation of the intensity of the new trial structure by

$$I = |A_0 + \delta A|^2$$

(3.34)

with $I_0 = |A_0|^2$ the intensity of the reference structure. The quantity $T$ is a tensor
in angular momentum representation and this explains the name tensor LEED or,
more precisely, as geometrical displacements cause the $t$-matrix changes, geometrical
tensor LEED. The tensor depends only on the reference structure and this mirrors the
main advantage of the method: Once the tensor has been computed the intensity of
any trial structure results very quickly using equations (3.31)-(3.34). This is similar
to a kinematic description of diffraction: in equation (3.33) the tensor represents the
form factor and the $\delta t$ stand for the structure factor. In fact, scattering processes
involving more than one $\delta t$, i.e. multiple scattering at changes of potentials, are
neglected in tensor LEED. In other words, the change of scattering due to the atomic
displacements is calculated kinematically.

Limitations of tensor LEED must exist with respect to the amount of $\delta \vec{r}_j$, by
which atoms can be displaced. Unfortunately, because of the complexity of multiple
scattering, no strict rules can be derived, though tensor LEED is exact in the kinematic
limit of diffraction. Experience tells that for displacements up to 0.2-0.5 Å tensor
LEED works well. This limit and the accuracy reached depend largely on the extent
of multiple scattering correlations of displaced atoms. In turn, this depends on the
scattering strengths of the atoms, the number of atoms displaced, the direction of
displacement and the electron energy. Consequently, tensor LEED retrieve the correct
structural data if the corresponding atomic displacements are not too large.

We have the impression that displacements of up to only a few tenths of an
Angstrom are not very helpful to scan a substantial part of the parameter space.
In fact it is true, that a good initial guess, i.e. the reference structure chosen being
near the true structure, is always of great advantage. If the perturbation of a chosen
reference fails to produce a satisfying fit to the experiment, one must try a new model
and start a new reference calculation. This procedure is advisable anyway, in order
to avoid landing in a local minimum of the $R$-factor and is applied in demanding
structure determinations.
Once the reference structure calculation has been carried out, tensor LEED is extremely fast to compute the intensities for neighboring structures. If there are \( n \) atoms per unit cell, the CPU time to calculate any new structure simply scales with \( n \), rather than with \( n^2 - n^3 \) in the full dynamical procedure. If only a small number of structures has to be calculated the overhead burden to perform the reference calculation might favor the full dynamical calculation. However, as soon as a large number of trial structures has to be checked, as is usually the case, dependent on the complexity of the structure tensor LEED is faster by orders of magnitude [103].

**Automatic Structure Search.** After the measurement the calculation of intensity spectra for a certain model is only the second step of the structural analysis. A task of substantial difficulty is still left, namely to find the correct model. This always starts with finding a reasonable model on the basis of some pre-knowledge about the surface under consideration. So, one generally knows the crystallographic face and the elemental composition of the substrate. In most cases the latter is also known for the adsorbate or it can be deduced from independent Auger measurements and/or from thermal desorption spectroscopy. Vibrational loss spectroscopy can be used to provide information about the orientation and bonding of molecules, and images obtained by the tunnelling microscope may even suggest a single atomic model or rule out models, which would be possible in principle. Last, but not least, experience from structure determination of related surface systems can be of great help, too.

Once a reasonable and promising model is established, the parameters of this model need to be adjusted. There are several ways for this procedure, which are based on a trial-and-error procedure, whereby scanning the parameter space is the most basic procedure. When a large number of parameters on a dense grid has to be scanned, the necessary computational efforts grow dramatically and an automated search to find the best fit structure is needed, i.e. a numerical procedure, which by built-in criteria finds the minimum of the \( R \)-factor automatically by a directed search. A number of such procedures were developed in recent years differing in requirements, strategies and efficiency, where experience from x-ray crystallography was very helpful [89]. Requirements can differ by the need to use derivatives of the \( R \)-factor with respect to parameters rather than only the intensities themselves. Derivatives in most cases are calculated numerically and so suffer from experimental noise and approximations used for the calculation of intensities [102]. Strategies differ by the numerical method to find the \( R \)-factor minimum and by the type of \( R \)-factor used.

The use of automated search procedures was frequently proposed [88] but first realized by the York group applying a form of steepest descent [105]. Starting with a certain reference structure the behavior of the \( R \)-factor in the surrounding part of the parameter space is explored to find the direction in which the \( R \)-factor decreases most and this procedure is iterated. Soon after, and in parallel, different other groups developed procedures of their own. The Munich and Berlin groups [106] use a non-
3.2. Dynamic LEED Theory

linear least-squares fit procedure whereby the expansion method is combined with the method of steepest descent [107].

Though the number of trial structures is dramatically reduced with the automated search mentioned above, there is a clear drawback. When the parameters are varied systematically in a grid search, one can make multiple use of costly energy-dependent quantities, such as, e.g., layer diffraction amplitudes, before this quantity is calculated for the next energy. This advantage has to be given up in the automated search because for a new set of parameters the data at all energies are needed for the comparison to experiment and for the decision, where to move next in parameter space. A way out of this situation is the use of tensor LEED together with a directed search as was accomplished by the Berkeley group [89,104] and is displayed by the flowchart given in Fig. 3.4. For a certain reference structure, which is chosen in a promising area of the parameter space, the tensor is calculated and stored for each energy and beam needed as well as for each atom to be displaced from the reference position. The intensities for a trial structure are calculated and compared to experiment by the Pendry $R$-factor. A steepest descent method is used to reach the next trial structure point in parameter space. For this the Rosenbrook algorithm is used, which does without derivatives. The procedure described is iterated until an $R$-factor minimum is reached. If on the way to the minimum the validity range of tensor LEED is left, a new reference calculation becomes necessary. Also, as the minimum eventually found

Fig. 3.4: Flowchart for the $R$-factor optimization using tensor LEED [104].
need not to be the global minimum, it is recommended to repeat the entire search pro-
cedure starting with different reference structures well separated in parameter space.
The deepest minimum found is believed to correspond to the correct model as long
as the $R$-factor level reached is satisfactory.

One can never be sure, that the best fit model found corresponds to the global best
fit. This is an intrinsic feature, because there is no mathematical criterion, whether a
minimum is local or global. Even with a grid search one can land in a local minimum,
if the span of the parameter space chosen was too small. Efforts to get around this
problem, e.g., by application of a simulated annealing procedure [108], which allows
large random jumps in parameter space, have only started. It should be emphasized,
that none of the automated search procedures described or in sight is push-button safe.
In spite of their high degree of automation, they need the investigator’s experience
with respect to the selection of the parameter space and proper starting points as well
as to the critical judgment of intermediate and final results.