scatterings (either bulk Bragg peaks or crystal truncation rods) occurs at integer order positions and the calculation is more complicated since the two amplitudes will add together. This interference effect, which has been used to determine the registry of the layer on the bulk \[3.30\], does not exist for additional surface spots and, thus, their integrated intensity is still given by \(3.2.41\) and can be compared directly with experiment. However, if we want to compute the Patterson function, some Fourier components of the surface structure are missing. Nevertheless, a partial interpretation can still be done. It generates possible structures which should be checked by structure factor calculations.

An example is shown in Fig. 3.32 which gives the Patterson function calculated from fractional order reflections measured for a reconstructed InSb(111) surface which exhibits a \((2 \times 2)\) pattern \[3.31\]. The interatomic distances and directions of bonds deduced from the Patterson functions are consistent with a distortion of the hexagonal arrangement of atoms which would be the normal atomic structure of the unreconstructed \((111)\) face of a diamond cubic crystal. Moreover, one In atom is missing per \((2 \times 2)\) unit cell. The resulting calculated structure factors are in good agreement with experiment.

As a conclusion, we can say that X-ray scattering data are simpler to interpret than LEED data since they can be treated in the single scattering approximation. However, the experimental set up is much more involved.

### 3.2.3 Indirect Methods

**a) Photoelectron Diffraction (PhD)**

This technique relies on the photoelectric effect. In this type of experiment the surface of the sample is exposed to a beam of monochromatic photons of energy \(h \nu\) (\(h\): Planck constant, \(\nu\): photon frequency). When the photon interacts with the solid, it may transfer its energy to an electron initially at energy \(E_i\) which can escape into an analyzer if its final energy, \(E_f = E_i + h \nu\), is above the vacuum level (Fig. 3.33).

In a PhD experiment, the escaping electrons are collected in a given small solid angle around the direction determined by the polar and azimuthal angles \(\theta\) and \(\varphi\) (Fig. 3.34). The excited electrons can propagate either directly towards the analyzer or be scattered by the atoms of the solid before being collected (Fig. 3.35). The total spectrum contains not only elastic electrons at the energy \(E_f\), but also photoelectrons which have lost some energy on their way to the surface by electron–electron or electron–phonon interactions. These inelastic electrons are called the secondary electrons, they give rise to a continuous background which must be subtracted from the spectrum before any analysis. The elastic photoemitted current results from the interference of the wave functions of elastic electrons and, consequently, its modulation with \(\theta\) and \(\varphi\) contains information on the sample atomic structure. This information can be extracted most easily when the photoelectron originates from an inner shell
Fig. 3.32a–e. Grazing X-ray diffraction study of the \((2 \times 2)\) reconstruction of InSb(111). a Atomic structure of the unreconstructed surface. b Atomic structure of the reconstructed surface. c Patterson function calculated from fractional order reflections. The map shows equally spaced positive contours. The origin peak (shaded) rises 17 contour levels. The dashed lines are mirror planes surrounding the repeating asymmetric unit of the Patterson function. d Interpretation of the map in terms of a distorted hexagon of atoms. e Pair correlation peaks 1 to 4 derived from vectors 1 to 4 drawn in d) [3.31]

Fig. 3.33. Schematic energy diagram of photoelectric effect
since its initial wave function, being localized, is insensitive to the atomic structure. Therefore, the photon energies used lie in the soft X-ray or X-ray range. Moreover, if the aim of the experiment is the determination of surface structures, the kinetic energy of the outgoing electron should correspond to a rather small mean free path (see Fig. 3.23). The simplest system to analyze is an adsorbate covered surface since we can excite a given core level of the adsorbate whereas, in the case of clean surfaces, electrons are emitted not only from the surface but also from the sublayers. This is the reason why the first experiments were performed to determine the substrate–adsorbate registry on systems like the c(2 × 2) Se, S, O, CO . . . overlayers on Ni(100) [3.32].

A further simplification occurs if we choose the photon energy such that the diffusion factor \( f(\theta, k) \) (see Appendix A) is small at the kinetic energy of the outgoing electron. Then, we can neglect the multiple scattering events. However, we have just seen that this kinetic energy cannot be too large so as to avoid a large electron mean free path. The range of kinetic energies for which both conditions are fulfilled lies around 100 to 1000 eV. Of course, the lower energy limit depends on the system.

Let us assume that the analyzer is at position \( \mathbf{R} \). In PhD we have to calculate the current, \( dI \), through an elementary surface, \( dS \), normal to the direction of
observation $\hat{R} = R/R$

$$dI = j \cdot dS = j \cdot \hat{R} R^2 d\Omega = j_R R^2 d\Omega \ ,$$  

(3.2.56)

$j_R$ is the radial component of the current density which is given by

$$j_R = \frac{\hbar}{m} \left[ \text{Im} \psi^*(R) \frac{\partial \psi(R)}{\partial R} \right] ,$$  

(3.2.57)

where $\psi(R)$ is the wave function of the photoelectrons at the detector. In the single scattering approximation $\psi(R)$ is the superposition of a wave emerging directly from the emitter atom and waves which have been scattered once by the neighbouring atoms $p$ (Fig. 3.36):

$$\psi(R) = \psi_{\text{dir}}(R) + \sum_p \psi_{\text{scat}}^{(p)}(R) \ .$$  

(3.2.58)

Let us assume that the potential of each atom is spherically symmetric for $r < a$ and vanishes when $r \geq a$. We denote the angular momentum quantum numbers of a final state of the excited core electron by $(l, m)$. Far from the emitter, and in any direction $\hat{r} = r/r$, the outgoing wave $\psi_{\text{dir}}^{lm}(r)$ can be written

$$\psi_{\text{dir}}^{lm}(r) = \frac{D_l \exp \left[ i \left( kr - \frac{l\pi}{2} + \delta_0^l \right) \right]}{2ikr} Y_{lm}(\hat{r}) \ ,$$  

(3.2.59)

$$= \frac{D_l}{2} (-i)^{l+1} \exp(i\delta_0^l) \frac{\exp(ikr)}{kr} Y_{lm}(\hat{r}) \ ,$$

$\delta_0^l$ is the $l$ phase shift due to the emitter potential and $D_l$ is a normalization constant.

Note that the radial function in $\psi_{\text{dir}}^{lm}(r)$ is the outgoing part of $\mathcal{R}_l(r \to \infty)$ given by (A.8) in Appendix A. This is rather intuitive and can be fully justified with the help of Green functions [3.33–36].

In order to compute $\psi_{\text{scat}}^{(p)}(R)$ we assume that $\psi_{\text{dir}}^{lm}(r)$ can be approximated by a plane wave, of amplitude $\psi_{\text{dir}}^{lm}(R_p)$ and wavevector $k\hat{R}_p$, when reaching the scatterer $p$ at $R_p$ ($\hat{R}_p = R_p/R$). Then, the wave scattered by atom $p$ in direction

![Diagram](image)

**Fig. 3.36.** Single scattering description in photoelectron diffraction
\( \theta_p \) (Fig. 3.36) can be written (Appendix A):

\[
\psi_{\text{scat}}^{lm(p)}(R) = \frac{D_i}{2} (-i)^{l+1} \exp(i\delta_p^0) \exp\left(\frac{ikR_p}{kR_p}\right) \frac{Y_{lm}(\hat{R}_p)f_p(\theta_p, k)}{\left|R - R_p\right|} \exp\left[\frac{ik|R - R_p|}{R_p}\right],
\]

(3.2.60)

where \( f_p \) is the atomic diffusion factor of atom \( p \), and, since \( R \gg R_p \), we have:

\[
\left|R - R_p\right| \approx R - R_p \cdot \hat{R} = R - R_p \cos \theta_p,
\]

so that (3.2.60) becomes

\[
\psi_{\text{scat}}^{lm(p)}(R) = \frac{D_i}{2} (-i)^{l+1} \exp(i\delta_p^0) \frac{\exp(ikR)}{kR} \frac{Y_{lm}(\hat{R}_p)f_p(\theta_p, k)}{\left|R_p\right|} \exp\left[\frac{ikR_p(1 - \cos \theta_p)}{R_p}\right].
\]

We obtain for the total \((l, m)\) wave function

\[
\psi^{lm}(R) = \frac{D_i}{2} (-i)^{l+1} \exp(i\delta_p^0) \frac{\exp(ikR)}{kR} \left[Y_{lm}(\hat{R}) + \sum_p \frac{\exp[ikR_p(1 - \cos \theta_p)]}{R_p} f_p(\theta_p, k) Y_{lm}(\hat{R}_p)\right],
\]

(3.2.61)

Thus, summing over all possible \((l, m)\) states

\[
\psi(R) = \sum_{lm} M_{i,m_i,m} \psi^{lm}(R)
\]

where \( M_{i,m_i,m} \) is the optical transition matrix element between an initial core state of energy \( E_i \) and angular momentum \((l_i, m_i)\) and a state of energy \( E_f = E_i + \hbar \nu > 0 \) and angular momentum \((l, m)\). Using (3.2.56), (3.2.57) and (3.2.61), we get [3.33, 34], summing over all (incoherent) initial states

\[
\frac{dI}{d\Omega} \propto \sum_{m_i} \left| \sum_{lm} M_{i,m_i,m} \left[Y_{lm}(\hat{R}) + \sum_p \frac{\exp[ikR_p(1 - \cos \theta_p)]}{R_p} f_p(\theta_p, k) Y_{lm}(\hat{R}_p)\right] \right|^2,
\]

(3.2.62)

because, in practice, the experiment is performed for an initial state with a given value of \( l_i \). We have dropped all multiplicative constants since we are interested only in the relative modulation of the current with \( \hat{R} \).

Note that \( kR_p(1 - \cos \theta_p) \) is nothing but the difference of path lengths between the direct and scattered waves. In the dipolar approximation, which neglects the spatial dependence of the vector potential of the electromagnetic field \((A(r) = A_0\hat{\ell}, \hat{\ell} \) being the polarization vector), it can be shown that (Sect.
\[ M_{i,m_i,m} \propto \langle f|\hat{e} \cdot \mathbf{r}|i \rangle \]  

(3.2.63)

where \(i\) and \(f\) are the initial and final state wave functions for an isolated atom which can be written \(R_i(r)Y_{i,m_i}(\hat{r})\) and \(R_f(r)Y_{m}(\hat{r})\), respectively. Consequently

\[ M_{i,m_i,m} \propto \int Y^*_{m}(\hat{r})\hat{e} \cdot \hat{r} Y_{i,m_i}(\hat{r})d\Omega \int R^*_f(r)R_i(r)r^2dr \]  

(3.2.64)

Using the relation

\[ \hat{e} \cdot \hat{r} = \frac{4\pi}{3} \sum_{m=-1}^{1} Y^*_{m}(\hat{e})Y_{1m}(\hat{r}) , \]  

(3.2.65)

we find

\[ M_{i,m_i,m} \propto \rho_{li} \frac{4\pi}{3} \sum_{m=-1}^{1} Y^*_{m}(\hat{e})\int Y^*_{m}(\hat{r})Y_{1m}(\hat{r})Y_{i,m}(\hat{r})d\Omega \]  

(3.2.66)

where \(\rho_{li}\) is the radial integral in (3.2.64). The integral in (3.2.66) is known in the literature as a Gaunt coefficient and vanishes except when:

\[ l = l_i \pm 1 , \]

\[ m = m_i + m_e , \]  

(3.2.67)

which are the dipolar selection rules.

Consequently, the number of \((l,m)\) terms in \(dI/d\Omega\), see (3.2.62), is very limited. When the initial wave function is an s wave the expression of \(dI/d\Omega\) becomes very simple since the only allowed transitions are to p states \((l = 1)\). Using (3.2.62, 66 and 67), we find [3.35]

\[ \frac{dI}{d\Omega} \propto |\hat{e} \cdot \hat{R} + \sum_{p \neq 0} \frac{f_p(\theta_p,k)}{R_p} \exp[ikR_p(1 - \cos \theta_p)]\hat{e} \cdot \hat{R}_p|^2 . \]  

(3.2.68)

We note that here the matrix element \(\rho_{li}\) appears just as a multiplicative factor.

Finally, the introduction of the photoelectron mean free path, which gives rise to a damping factor, limits the summation over all scatterers \(p\) to a small cluster around the emitter [3.34, 35]. One can also add a Debye–Waller factor which accounts for the thermal vibrations of the atoms (Sect. 4.6.2b).

Some work has also been done taking into consideration the spherical nature of \(\psi_{dir}\), near the scatterer or the multiple scattering [3.36, 37]. However, the calculations become much more involved and less physically transparent.

In practice, the photoemission current is measured as a function of one of the two variables, \(\varphi, \theta\), the other one being fixed. The calculation is performed for given geometries and compared with the experimental results. Note that the azimuthal pattern (i.e., measured at a given value of \(\theta\)) directly reflects the symmetry of the emitter sites.
In Fig. 3.37 we compare an azimuthal experimental scan for a $c(2 \times 2)$ overlayer of S on Ni(001) with calculation for several adsorption positions of the adatoms [3.32]. The best agreement is found for a fourfold position at 1.35 Å from the surface, in good agreement with LEED experiments.

As already noted, the case of clean surfaces is more complicated since the emission comes from several layers. However, such experiments [3.34] have been performed with success on W(100) and W(110) (Fig. 3.38) attempting, in addition, to separate the surface and sublayer emission by taking advantage of the surface core level binding energy shift which depends itself on the geometry (Sect. 5.11). However, this new technique must be improved in order to get interatomic distances reliably.

We can also study $dI/d\Omega$ as a function of the photon energy for a given collection direction of the photoelectrons [3.38] and, for the sake of simplicity, we limit ourselves to the excitation of a s core level. In these experiments, the comparison of the results with the theoretical calculations needs the computation of the variation of the optical matrix element with $h\nu$. We can avoid this computation by considering the quantity

$$\chi(k) = \frac{dI(k)/d\Omega - dI^0(k)/d\Omega}{dI^0(k)/d\Omega},$$  \hspace{1cm} (3.2.69)
Fig. 3.38. Experimental azimuthal photoelectron diffraction patterns $4f_{7/2}$ core level emission in W(110) and W(100), compared with single scattering calculations ($hv = 65$ eV, $\Theta = 30^\circ$, $\alpha = 22.5^\circ$) [3.34]

where $dI^0(k)/d\Omega$ is the emission of an isolated atom. From (3.2.68), we find immediately that, to first order in $f_p(\theta_p, k)$:

$$\chi(k) = 2 \sum_p \frac{\hat{\varepsilon} \cdot \hat{R}_p}{\hat{\varepsilon} \cdot \hat{R}} \frac{|f_p(\theta_p, k)|}{R_p} \cos[kR_p(1 - \cos \theta_p) + \phi_p(\theta_p, k)] , \quad (3.2.70)$$

with

$$f_p(\theta_p, k) = |f_p(\theta_p, k)| \exp[i\phi_p(\theta_p, k)] .$$

The quantity $dI^0(k)/d\Omega$, i.e., the non-oscillatory part of $dI(k)/d\Omega$, is deduced from experimental spectra by a fitting procedure. This type of experiment is often called ARPEFS (Angle Resolved Photoemission Extended Fine Structure).

b) Surface Extended X-ray Absorption Fine Structure (SEXAFS)

The SEXAFS technique is an extension to surface studies of a bulk technique called Extended X-ray Absorption Fine Structure (EXAFS) which is able to give the local environment of a given atom in a solid. This X-ray absorption fine
structure of solids was observed as early as 1920 by Fricke [3.39] and Hertz [3.40] and a first interpretation was proposed by Krönig in 1931–1932 [3.41]. However, it was only since the seventies that these observations became a powerful technique in material studies due to the advent of high flux tunable X-ray sources like the synchrotron radiation.

Let us first explain this technique. When a monochromatic beam of X-rays of frequency, \( \nu \), and intensity, \( I_0 \), passes through a crystal of thickness, \( x \), the transmitted intensity is given by:

\[
I = I_0 e^{-\mu x},
\]

(3.2.71)

\( \mu \) being the absorption cross-section of the material. This absorption occurs since some photons give their energy to a core electron which is excited from an occupied \( E_i \) (wave function \( |i> \)) to an unoccupied level \( E_f \) (wave function \( |f> \)). \( \mu \) is proportional to the optical transition probability given by the following Fermi golden rule in the dipolar approximation (Sect. F.1)

\[
\mu \propto \sum_f |<f|\hat{\mathbf{r}}|i>|^2,
\]

(3.2.72)

with \( E_f = E_i + \hbar \nu \).

When \( \nu \) varies, the absorption cross-section \( \mu \) of a free atom exhibits discontinuities, called absorption thresholds, due to the successive excitations of the discrete levels of this atom. Between two consecutive thresholds \( \mu \) reaches quickly a maximum and decreases (Fig. 3.39).

![Log |I| vs. E(eV) for solid and gas phases](image)

**Fig. 3.39.** Absorption spectrum at the Ne K edge, in the gas and in the solid, as a function of the photon energy
When this experiment is performed in a solid, \( \mu \) follows roughly the same average behaviour, however, oscillations can be observed (Fig. 3.39) which are due to the presence of the neighbouring atoms. Indeed, when an electron is excited from an emitter atom, its wave function can be represented by a spherical wave which is scattered by the neighbours, as we have already seen in PhD theory. The only non-vanishing contribution to the absorption matrix element in (3.2.72) comes from the region where the core state \(|i\rangle\) is non-zero, i.e., around the center of the emitter atom. When the kinetic energy of the photoelectron varies, i.e., when \( hv \) varies, the interference in this region between the outgoing and backscattered waves may be constructive or destructive producing the observed oscillations of \( \mu \) (Fig. 3.40). The analysis of these oscillations is greatly simplified if we neglect multiple scattering events, as in the photoemission case [3.42]. This assumption is certainly valid if we discard the region of the absorption spectrum extending over \( \sim 100 \text{ eV} \) above the threshold. In order to separate the variation of \( \mu \) due to free atom effects from that resulting from the presence of the neighbours, it is convenient to introduce a function \( \chi \) defined as follows

\[
\chi = \frac{\mu - \mu_0}{\mu_0}, \tag{3.2.73}
\]

\( \mu_0 \) being the free atom X-ray cross-section. If we assume that the potential of each atom is spherically symmetric for \( r < a \) and vanishes for \( r \geq a \), the final state wave function in a solid, with quantum numbers \((l, m)\), can be written as

\[
|f\rangle = \psi_{\text{dir}}^{lm} + \sum_p \psi_{\text{bscat}}^{lm(p)}, \tag{3.2.74}
\]

\( \psi_{\text{dir}}^{lm} \) and \( \psi_{\text{bscat}}^{lm(p)} \) being, respectively, the direct outgoing wave of angular momentum \((l, m)\) and the corresponding wave backscattered from the atom \( p \). Thus, to first order in \( \psi_{\text{bscat}}^{lm(p)} \)

\[
\chi = \frac{\sum_p \sum_{lm} 2\text{Re}[\langle \psi_{\text{dir}}^{lm} | \hat{\epsilon} \cdot \hat{r} | i \rangle \langle i | \hat{\epsilon} \cdot \hat{r} | \psi_{\text{bscat}}^{lm(p)} \rangle]}{\sum_{lm} |\langle \psi_{\text{dir}}^{lm} | \hat{\epsilon} \cdot \hat{r} | i \rangle|^2}. \tag{3.2.75}
\]
For the sake of simplicity, we will consider an s initial core state \( |i\rangle = \mathcal{R}_0(r)Y_{00}(\tilde{r}) \), i.e., a K edge. The computation of the matrix elements in (3.2.75) needs the knowledge of \( \psi_{\text{dir}}^{1m} \) and \( \psi_{\text{bscat}}^{1m(p)} \) in the core region \( r < a \) of the emitter. In this region, see (A.6),

\[
\psi_{\text{dir}}^{1m} = C_1 R_0(r) Y_{1m}(\tilde{r}) ,
\]

so that using (3.2.65)

\[
\langle \psi_{\text{dir}}^{1m}|\hat{\epsilon} \cdot \mathbf{r}|i\rangle = \frac{4\pi}{3} \sum_{m_1 = -1}^{1} \rho_{10} Y_{1m_1}(\hat{\epsilon}) \int Y_{00}(\tilde{r}) Y_{1m_1}(\tilde{r}) Y_{1m}(\tilde{r}) d\Omega ,
\]

or, since \( Y_{00}(\tilde{r}) = (4\pi)^{-1/2} \)

\[
\langle \psi_{\text{dir}}^{1m}|\hat{\epsilon} \cdot \mathbf{r}|i\rangle = \frac{\sqrt{4\pi}}{3} \rho_{10} Y_{1m}(\hat{\epsilon}) \delta_{11} ,
\]

with

\[
\rho_{10} = \int_0^a \mathcal{R}_0(r) C_1 R_0^*(r)r^2 dr .
\]

Thus, only \( \psi_{\text{dir}}^{1m} \) gives a non-vanishing matrix element in agreement with the dipolar selection rule (3.2.67) and the summation over \( l \) in (3.2.75) is restricted to the \( l = 1 \) term.

Consequently, using (3.2.65) we get

\[
\sum_m |\langle \psi_{\text{dir}}^{1m}|\hat{\epsilon} \cdot \mathbf{r}|i\rangle|^2 = \frac{|\rho_{10}|^2}{3} .
\]

Let us now calculate \( \psi_{\text{bscat}}^{1m(p)} \). The outgoing wave \( \psi_{\text{dir}}^{1m} \) gives rise to a scattered wave due to the neighbour \( p \) which, in the plane wave approximation and far from the scatterer, is given by (3.2.60)

\[
\psi_{\text{bscat}}^{1m(p)}(\mathbf{r}) = \frac{-D_1 \exp[i(kR_p + \delta_0)]}{2kR_p} Y_{1m}(\tilde{R}_p) f_p(\theta, k) \frac{\exp(ik|\mathbf{r} - \mathbf{R}_p|)}{|\mathbf{r} - \mathbf{R}_p|} ,
\]

with \( \theta = (\mathbf{R}_p, \mathbf{r} - \mathbf{R}_p) \).

We approximate the back-scattered wave \( \psi_{\text{bscat}}^{1m(p)}(\mathbf{r}) \) around the emitter by a plane wave propagating along the direction \( -\tilde{R}_p (\theta = \pi) \)

\[
\psi_{\text{bscat}}^{1m(p)}(\mathbf{r}) \approx \frac{-D_1 \exp[i(2kR_p + \delta_0)]}{2kR_p^2} Y_{1m}(\tilde{R}_p) f_p(\pi, k) \exp(-ik\tilde{R}_p \cdot \mathbf{r})
\]

\[
= A_{1m}^{(p)} \exp(-ik\tilde{R}_p \cdot \mathbf{r}) .
\]

This plane wave is scattered by the emitter and the resulting scattered wave has
the following asymptotic from (Appendix A)

\[
\psi_{\text{bscat}}^{1m(p)}(r \to \infty) = A_{1m}^{(p)} \left[ \exp(-ik\hat{R}_p \cdot r) + f_0(\theta, k) \frac{\exp(ikr)}{kr} \right]
\]

with \( \theta = (-R_p, r) \) and where \( f_0(\theta, k) \) is the atomic scattering factor of the emitter.

However, we need \( \psi_{\text{bscat}}^{1m(p)}(r) \) in the core of the emitter for the calculation of the matrix element involving the back-scattered wave in (3.2.75). We know, from Appendix A, that the solution of the Schrödinger equation for the emitter atom which behaves asymptotically as the above expression can be written

\[
\psi_{\text{bscat}}^{1m(p)}(r) = A_{1m}^{(p)} \sum_{l', m'} \beta_{l'm'} R_{l'}(r) Y_{l'm'}(\hat{r}) .
\]

Using the asymptotic form of \( R_{l'}(r) \)

\[
R_{l'}(r \to \infty) = D_{l'} \frac{\sin(kr - \frac{l'\pi}{2} + \delta_{l'})}{kr}
\]

it is shown in Appendix A, see (A.25), that

\[
\beta_{l'm'} = 4\pi i^{l'} Y_{l'm'}^*(\hat{R}_p) e^{ik_0 l'} D_{l'}^{-1} .
\]

Thus, in the core of the emitter, we have from (A.6)

\[
\psi_{\text{bscat}}^{1m(p)}(r) = A_{1m}^{(p)} \sum_{l'm'} 4\pi i^{l'} Y_{l'm'}^*(\hat{R}_p) e^{ik_0 l'} D_{l'}^{-1} C_{l'} R_{l'}(r) Y_{l'm'}(\hat{r}) .
\]

Let us now compute \( \langle i | \hat{\sigma} \cdot \hat{r} | \psi_{\text{bscat}}^{1m(p)}(r) \rangle \). If we replace \( \hat{\sigma} \cdot \hat{r} \) by the expression (3.2.65), it is straightforward to see by integrating over \( \hat{r} \) that the only non-zero contribution comes from \( l' = 1 \) and \( m' = m_z \). We get

\[
\langle i | \hat{\sigma} \cdot \hat{r} | \psi_{\text{bscat}}^{1m(p)}(r) \rangle =
\]

\[
\int \mathcal{R}_0(r) \frac{1}{\sqrt{4\pi}} r \frac{4\pi}{3} \sum_{m_z = -1}^{1} Y_{1m_z}(\hat{\xi}) A_{1m}^{(p)} 4\pi i^{l'} Y_{l'm'}^*(\hat{R}_p) e^{ik_0 l'} D_{l'}^{-1} C_{l'} R_{l'}(r) r^2 dr
\]

Substituting for \( A_{1m}^{(p)} \) from (3.2.79) and using (3.2.65) yields

\[
\langle i | \hat{\sigma} \cdot \hat{r} | \psi_{\text{bscat}}^{1m(p)} \rangle =
\]

\[
\frac{i}{2 \sqrt{4\pi \rho_{10}}} \frac{\exp[i(2kR_p + 2\delta_{l'})]}{k R_p^2} Y_{1m}(\hat{R}_p) f_p(\pi, k) \cos(\xi, \hat{R}_p) .
\]

Finally, we get using (3.2.75, 77, 78, 65 and 81)

\[
\chi(k) = - \sum_{p} 3 \cos^2(\xi, \hat{R}_p) \sin\left\{2kR_p + 2\delta_{l'} + \text{Arg}[f_p(\pi, k)]\right\} \frac{|f_p(\pi, k)|}{k R_p^2}
\]
If the light is unpolarized or for a polycrystalline sample, we must average over all possible directions of \( \vec{\varepsilon} \) or \( \vec{R}_p \), respectively. This leads to \( \cos^2(\varepsilon, \vec{R}_p) = 1/3 \). Thus
\[
\chi(k) = -\sum \frac{N_i \sin(2kR_i + 2\delta_i^0 + \text{Arg}[f_i(\pi, k)]) |f_i(\pi, k)|}{kR_i^2},
\]
(3.2.83)

\( N_i \) being the number of atoms at the distance \( R_i \) from the emitter which are to be of the same chemical species. Note that the argument of the sine function has a simple meaning: the phase shift, \( 2kR_i \), arises from the geometrical path-length difference, \( \text{Arg}[f_i(\pi, k)] \) is the phase shift due to the scattering by the neighbour \( i \) and \( 2\delta_i^0 \) is the phase shift caused by the absorbing atom. One can easily verify that this result is also valid for cubic crystals, even if the light is polarized. Finally, as in the PhD formula, a damping factor and a kind of Debye–Waller factor are introduced in order to take into account the finite mean free path of the electron and the relative thermal motion of the atoms involved (Sect. 4.6.2b) [3.42].

It follows from (3.2.83) that, when the phase shifts are known (from theory or from other experiments), the Fourier analysis of the observed oscillations gives access to the coordination number and interatomic distances of the emitter atoms, this information being limited to the first coordination spheres due to the finite mean free path. Unlike diffraction experiments, EXAFS can be used to investigate systems without long range order.

Unfortunately, this technique is not directly applicable to the study of the environment of surface atoms. Indeed, in the case of a clean surface, the contribution of surface atoms to the photon absorption is negligible compared to that of bulk atoms. This is not true if we excite a core level of an adsorbed atom. However the signal is too weak in that case. Therefore, we must find an observable quantity, differing from the transmitted photon intensity, but still proportional to \( \mu \) and giving a signal coming from the first layers of atoms. Three quantities have been used which fulfill this requirement: the fluorescence signals, the Auger signals and the total photoemission yield.

In the fluorescence and Auger experiments the core hole created by the incident photon is filled via an electronic transition: an electron of lower binding energy drops into the core hole created by the incident photon and the transition energy is released either by the creation of a photon which is detected (fluorescence signal), or by the ejection of an Auger electron which is collected (Auger signal) (Fig. 3.41).

If we assume that the creation of the core hole and its decay are independent processes, the collected signal is proportional to the probability of occurrence of the first process, i.e., to the absorption cross-section \( \mu \).

In a total photoemission yield experiment all the electrons emitted from the solid are collected: elastic photoelectrons and Auger electrons as well as the secondary electrons produced by these two processes. However, one can show that the signal is dominated by the secondary electrons produced by the Auger process. The signal is thus proportional to the elastic Auger current, which is itself proportional to \( \mu \).
The fluorescence detection applies only to adsorbate studies since on clean surfaces, the fluorescence photon has a long mean free path and, consequently, the surface signal is negligible compared to the bulk one. In the Auger and total photoemission yields, the collected electrons have a rather short mean free path and, thus, come from the first layers. However, since their kinetic energy does not usually correspond to the minimum of the electron mean free path (Fig. 3.23), the number of layers involved is large enough to make the surface signal difficult to extract. Therefore, this surface EXAFS technique has been almost exclusively used for the study of adsorbed layers.

The analysis of SEXAFS oscillations can be done with (3.2.82), since the signal is proportional to $\mu$, and can be put in a form similar to (3.2.83) by replacing the coordination number, $N_i$, by an effective coordination number, $N_i^*$, given by

$$N_i^* = \sum_{p=1}^{N_i} 3 \cos^2(\delta, \mathbf{R}_p), \quad (3.2.84)$$

in which the summation is performed over all atoms $p$ of the $i$th coordination sphere. $N_i^*$ varies with the orientation of the polarization relative to the surface. We can take advantage of this effect to enhance the contribution of a particular set of bonds.

Let us give, as an example, the case of a $\mathrm{c}(2 \times 2)$ sulphur overlayer on $\mathrm{Ni}(100)$ [3.43]. This experiment has been done using the sulphur K edge and Auger electron detection (Fig. 3.42). From the period of the oscillations one gets the $\mathrm{S}-\mathrm{Ni}$ distances of the first ($d_1 = 2.23 \pm 0.02 \, \text{Å}$) and next nearest ($d_2 = 4.15 \pm 0.10 \, \text{Å}$) neighbours in good agreement with the distance found in LEED and PhD. The distance $d_2$ is compatible with four-fold hollow adsorption sites. This is confirmed (see Table 3.1) from the comparison of experimental and calculated effective coordination numbers for various polarizations.

c) Other Methods

It is impossible to describe here in detail all the other experimental techniques from which structural information can be deduced. To complete this chapter, we will just briefly mention some of them.
ii) Atom Scattering

Some attempts have been made to use a Debye–Waller factor, $\exp(-2W)$, to account for the decrease of diffracted He beam intensities with increasing cryogenic temperature. Exactly as in LEED, we should find that $\ln I_b$ decreases linearly with $T$, in the high-temperature limit, where the mean square displacements of the atoms themselves are proportional to $T$. However, the experimental data, particularly for He scattered by metal surfaces, often give temperature dependencies of $\ln I_b$ which show considerable deviations from linear behaviour when $T \gtrsim 400$ K [4.33]. Indeed several complications occur:

- the atom turning point is located far from the surface and thus the long-range potential is not only determined by the position of one underlying atom but also by many of them, i.e., there is a multiple interaction.
- multiple scattering of the incident wave is generally not negligible.

These effects have been discussed by several authors [4.34, 35]. They have explained the nonlinear behaviour of $\ln I_b$ at high temperatures. However, $\ln I_b$ can no longer be expressed as a function of $\langle u^2 \rangle$ only. Consequently, the method is not well suited to the measurement of mean square displacement.

iii) X-ray Scattering at Grazing Incidence

As explained in Chap. 3, single scattering theory fully applies. The remaining problem is to get information coming from surface atoms only. When the first layer consists of identical atoms and has a unit cell multiple of the unit cell of the sublayers (reconstructed or adsorbate covered surfaces), this is achieved by choosing fractional order spots. In this case their intensity is given by

$$I = I_0 \exp(-2W) = I_0 \exp(-q^2 \langle u_q^2 \rangle)$$

where $I_0$ is the intensity obtained on a rigid lattice, $\langle u_q^2 \rangle$ is the mean square displacement in the direction of the momentum transfer, $q$, which, at grazing incidence and emergence, is parallel to the surface. This experiment has been performed on the reconstructed Au(110) surface and shows surface enhance thermal vibrations [4.36].

b) PhD and SEXAFS Experiments

Contrary to diffraction experiments in which only the phase factor due to the path length difference is modified by the displacements of atoms, in PhD and SEXAFS the other factors are also a function of these displacements and therefore the thermal average should, in principle, be determined using the full expression of the intensity. Such an average is not easy to calculate and it is usual to replace these factors by their values at equilibrium positions. This can be justified by noticing that they are a slowly varying function of the interatomic distances and diffusion angles, while rapid variations occur in the phase factor due to path length differences.
Another complication arises from the correlation of atomic motions on different sites. Indeed, contrary to diffraction experiments, in PhD and SEXAFS, the range of interatomic distances involved is limited. In other words, diffraction experiments are only sensitive to long range order, while SEXAFS and PhD probe short range order. Consequently, the correlation between motions of neighbouring atoms cannot be neglected in the latter experiments. Notice that this effect is not specific to the surface: it is well known that Debye–Waller factors are not the same in bulk X-ray diffraction and EXAFS experiments \[4.37, 38\].

The next problem to be solved is to isolate the fraction of the signal sensitive to the mean square relative displacements of pairs of atoms involving at least one surface atom. Up to now, this problem has not really been solved for clean surfaces and only experiments in which core levels of adatoms in adsorbed layers are excited have been performed.

\textit{i) PhD}

In PhD we have to calculate the thermal average of the intensity \((3.2.62)\) which can be written as

\[
I = \left| A_0 + \sum_j A_j \exp(i\Phi_j) \right|^2, \tag{4.6.14a}
\]

\[
= |A_0|^2 + \left[ A_0^* \sum_j A_j \exp(i\Phi_j) + c.c \right] + \sum_{jj'} A_j^* A_{j'} \exp[-i(\Phi_j - \Phi_{j'})] \tag{4.6.14b}
\]

with

\[
\Phi_j = k R'_{0j} (1 - \cos \theta_j),
\]

where \(R'_{0j}\) is the distance between the scatterer \(j\) and the emitter 0, and \(\theta_j\) the scattering angle. The phase shift \(\Phi_j\) can also be rewritten as

\[
\Phi_j = k |R_{0j} + u_j - u_0| - k \cdot (R_{0j} + u_j - u_0),
\]

where \(u_0\) and \(u_j\) are, respectively, the displacements of the emitter and scatterer. Expanding \(\Phi_j\) to first order in \((u_j - u_0)\), using \((4.1.21)\), we have

\[
\Phi_j = k R_{0j} \left( 1 + \frac{R_{0j} \cdot (u_j - u_0)}{R_{0j}^2} \right) - k \cdot (R_{0j} + u_j - u_0), \tag{4.6.15a}
\]

or

\[
\Phi_j = \Phi_j - q_j \cdot (u_j - u_0), \tag{4.6.15b}
\]

with

\[
q_j = k - k \hat{R}_{0j},
\]
$\Phi_j$ and $q_j$ are, respectively, the geometrical phase shift and the momentum variation of the photoelectron due to scattering in a rigid lattice.

The thermal average of the second term in (4.6.14b) is easily computed using (4.6.8)

$$
\langle \exp(i\Phi_j) \rangle = \exp(i\Phi_j) \exp\left\{ -\frac{1}{2} \langle [q_j \cdot (u_j - u_0)]^2 \rangle \right\}
$$

The second exponential in the above expression is a Debye–Waller factor, it can also be written

$$
\exp\left[ -\frac{1}{2} \langle [q_j \cdot (u_j - u_0)]^2 \rangle \right] = \exp\left[ -\frac{1}{2} q_j^2 \langle [\dot{q}_j \cdot (u_j - u_0)]^2 \rangle \right],
$$

$$
= \exp\left[ -k^2(1 - \cos \theta_j)\sigma_{0j}^2 \right], \tag{4.6.16a}
$$

with

$$
\sigma_{0j}^2 = \langle [\dot{q}_j \cdot (u_j - u_0)]^2 \rangle, \tag{4.6.16b}
$$

$\sigma_{0j}^2$ is, thus, the mean square relative displacement between the emitter 0 and scatterer j, projected on the direction of the momentum transfer due to the scattering on atom j.

If we assume that in the third term the thermal average of $\Phi_j$ and $\Phi_j'$, in (4.6.14b) can be decoupled, the thermal average of the intensity takes the form [4.39]

$$
I = \left| A_0 + \sum_j A_j \exp(i\Phi_j) \exp\left[ -k^2(1 - \cos \theta_j)\sigma_{0j}^2 \right] \right|^2. \tag{4.6.17}
$$

This last assumption is not rigorous, however it introduces only some errors in terms of the second order in $f(\theta_j, k)$, which are assumed to be small in single scattering theory.

In angular PhD experiments, even on adsorbed layers, the number of different $\sigma_{0j}^2$ involved is large and moreover each $\sigma_{0j}^2$ is a function of the angle of observation. Therefore, it seems hopeless to determine them from such measurements. This suggests performing the PhD experiment at a fixed observation angle and varying the photon energy (ARPEFS). If we use a s core level and take into account thermal vibrations, each term in $\chi(k)$ given by (3.2.70) is modulated by the corresponding Debye–Waller factor. This has been used to check sets of $\sigma_{0j}^2$ calculated using several models of lattice dynamics at a given temperature [4.39]. To our knowledge, no direct experimental determination with PhD of $\sigma_{0j}^2$ has been performed up to now. Nevertheless, by collecting the photoelectrons in the direction normal to the surface, the number of $\sigma_{0j}^2$ involved can be minimized. Furthermore, by Fourier transforming the spectrum, the contribution of each shell of neighbours can be isolated, and, by choosing appropriately the direction of polarization of the light, the contribution of some bonds can be enhanced. Then, the determination of at least some $\sigma_{0j}^2$ may become possible by means of ARPEFS.