Low-energy electron diffraction with signal electron carrier-wave number modulated by signal exchange-correlation interaction

John Rundgren, Bo E Sernelius and Wolfgang Moritz

1 Department of Physics, KTH Royal Institute of Technology, 10691 Stockholm, Sweden
2 Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden
3 Department of Earth and Environmental Sciences, Ludwig-Maximilians-University, Theresienstrasse 41, 80333 Munich, Germany

* Author to whom any correspondence should be addressed.

E-mail: jru@kth.se, bo.e.sernelius@liu.se and wolfgang.moritz@lrz.uni-muenchen.de

Keywords: surface physics, low-energy electron diffraction, elastic electron-atom scattering in solids and surface slabs, signal electron self-energy in solids, signal electron exchange-correlation interaction

Abstract
Low-energy electron diffraction (LEED) is considered as elastic electron-atom scattering (EEAS) operating in a target crystal waveguide, where a signal electron carrier wave is wavenumber modulated by signal exchange-correlation (XC) interaction. A carrier potential is designed using a KKR (Korringa-Kohn-Rostoker) muffin-tin (MT) model built on overlapping MT spheres that implement atoms with double degree of freedom, radius and potential level. An XC potential is constructed using Sernelius’s many-particle theory on electron self-energy. EEAS phase shifts are derived from Dirac’s differential equations, and four recent LEED investigations are recalculated: Cu(111) + (3√3 × √3) R30° - TMB, TMB = 1,3,5-tris(4-mercaptophenyl)-benzene with chemical formula C24H15S3; Ag(111) + (4 × 4) - O; Ag(111) + (7 × √3) recr-SO4; and Ru(0001) + (3 × 3) R30° - Cl. Our EEAS phase shifts generate substantially improved reliability factors, and we report the first confirmation of electron self-energy by LEED experiment.

1. Introduction

A common effort in surface structure investigations by LEED (low-energy electron diffraction) is to measure interatomic distances reliably with 0.001 nm accuracy. LEED uses electrons in the energy range of about 20–500 eV. The limited attenuation length of 0.1–1 nm in this energy range allows the study of the structures of crystal surfaces. Figure 1 shows a frequently used experimental setup together with two diffraction patterns. The back-scattered diffraction picture is made visible on a fluorescent screen. The intensities of the diffracted beams depend on the energy of the primary beam and can be measured with a video camera. The analysis of the diffracted intensities allows the determination of the atomic arrangement of adsorbate atoms and their bond lengths. The direct images obtained for example with scanning probes like STM or AFM provide additional information about the structure model, the homogeneity of the surface, and existence of domains etc, but allow only estimates of the atomic coordinates. The precise knowledge of the structure is required for the detailed understanding of chemical reactions taking place at surfaces, for example in catalytic processes.

LEED experience shows that the accuracy is determined by the elastic electron-atom scattering (EEAS) phase shifts injected as input to the diffraction code [2–4]. There exist, of course, effects that limit the accuracy of the surface structure determined by LEED, which does not quite reach the accuracy obtained by x-ray diffraction in the 3-D crystal. This is due to atomic displacement in point defects, domain boundaries in adsorbate structures, steps in the substrate surface, or other defects not included in the multiple scattering program. Another source of error is also the inadequate treatment of thermal vibrations. The multiple scattering program for anisotropic or anharmonic atomic displacements for all point groups is not yet available, and most structure analyses up to now have been performed with isotropic displacements. This study investigates how the crystal potential model influences calculated LEED intensities.
In a new study of EEAS we set up a KKR (Korringa-Kohn-Rostoker) muffin-tin (MT) potential with overlapping MT spheres corresponding to \( N_{\text{eq}} \) symmetrically inequivalent atoms in the surface structure unit cell. The inequivalence with respect to symmetry opens \( 2 \times N_{\text{eq}} \) degrees of freedom due to overlapping MT spheres with freely variable radii together with freely adaptable energy shifts of atomic potentials. Unfortunately, the traditional KKR approach of Mattheiss [5–7] fixes each touching atom potential on the energy axis by superposition of the neighbor potential tails onto each particular atom potential. The MT sphere potentials are then fixed, and only \( N_{\text{eq}} \) nonoverlapping MT radii are accessible for the optimization of a crystal potential. We consider that the KKR overlap model with \( 2 \times N_{\text{eq}} \) radial and potential parameters satisfactorily describes LEED for incident electron energy \( E_{\text{inc}} \) greater than the plasmon threshold energy \( E_{\text{ph}} \) which is of the order of \( 20 \) eV on metallic surfaces. In conclusion we illustrate the overlap KKR potential model on four complicated LEED investigations and report noticeably improved theoretical–experimental LEED agreement compared with recent publications. The energy region \( 0 - E_{\text{pl}} \) belongs to VLEED (very-low-energy electron diffraction) using meV electrons in experiments that are interpreted by full-potential band structure theory and complex electron self-energy theory [8]; not treated in the present paper.

We design EEAS with similar terminology as used for electromagnetic scattering like teletransmission and radar [9], with waveguide, carrier-wave, and wavenumber modulation, with flowchart (a)–(d):

(a) The target propagating the incident electron serves as a waveguide for the signal-electron flow. A low-energy incident electron excerts atomic spin and charge repulsion about herself, weakening local nuclear screening. Resulting additional nuclear attraction contributes negative self-energy \( \Sigma \) that scatters the signal electron by her own exchange–correlation (XC) potential; see the excellent review by L. Hedin and S.O. Lundqvist [10].

(b) We compose a KKR overlap diffraction model using Coulombic atomic mass-and-charge potentials added up on atomic sites. The Coulombic crystal potential created in this way, designated carrier potential, is taken to be invariant with respect to signal electron energy \( E \) in the range beyond VLEED, \( E > E_{\text{ph}} \). It constitutes the major scatterer in LEED.

(c) The electron self-energy is taken to be a potential built on central atomic charge densities when \( E > E_{\text{ph}} \). The Rayleigh-Schrödinger many-particle balance between the crystal’s chemical potential at rest and the one under one-electron excitation makes the XC interaction a function of incident energy \( E \). The XC interaction is transient, first running through a minimum about \( \sim 10 \) eV about the plasmon threshold \( E_{\text{pl}} \sim 20 \) eV, then gradually approaching zero due to the finite relaxation time of the crystal’s electron gas. In terms of the signal electron wavevector \( \mathbf{k} = \sqrt{E} \) (atomic Rydberg units) the X interaction vanishes as \(-1/k^2\) [11] and the C interaction continues to high energy as \(-1/k\) [12]. We consider very high energy \( E \) to be a limit where C interaction is treated as negligible.

(d) How to sum up carrier and XC potential to a total scattering potential? Two implementations are done, (1) addition of carrier potential and XC potential, and (2) determination of MT radii of a given potential. The order in which the implementations are applied is significant. Either (1) sums up the existing carrier and the existing XC potential to a total potential, and (2) generates the energy dependent MT radii of the total potential. Or, (2) generates the MT radii of the carrier potential, and (1) sums up the XC potential and the carrier potential of the known MT radii to a total potential. We establish a KKR-MT model by the latter alternative that takes least computing time. This approach separates the full scattering potential into an energy-invariant carrier potential with fixed MT radii and an energy transient XC potential. The fact that the two scatterers are decoupled with respect to signal electron energy is the motivation for the title of the paper. The carrier potential is predominant relative to the XC potential, which is shallow compared with the deep atomic cores. The total potential and the carrier potential guide electron waves of wavevector \( q \) and \( k \), respectively, where the wavevector displacement \( q - k > 0 \) is determined by the self-energy part of the inner potential. We refer to \( q - k \) as wavevector modulation of the carrier wave. The qualifications of our KKR
diffraction model are later tested against actual LEED investigations. Quantitative LEED determining atomic positions in crystals is currently combined with density functional theory [13, 14] contained in computer program suites not considered here.

The paper continues with the following content: the design of a KKR overlap MT model and the construction of the carrier potential; the derivation of an XC potential from Sernelius’s signal electron self-energy [15, 16]. Together these potentials constitute the central potential in Dirac’s bispinor differential equations; we initiate their orbital solutions. In the interstice the big Dirac bispinor satisfies a Schrödinger equation of electron wavenumber $q$ in terms of the signal energy and an energy dependent XC potential; we recognize the difference between $q$ and carrier wavenumber $k$ as signal electron wavenumber modulation. Finally, when EEAS phase shifts are derived from the Dirac equations, we apply particular numerics for determining the phase shift accuracy. The advantage of overlap atomic potentials relative to touching ones is confirmed by LEED surface structure search governed by Pendry’s reliability factor [17]. As test cases we use four complex surface structures published recently: Cu(111) + ($3 \sqrt[3]{3} \times \sqrt[3]{3}$)R30° -TMB [18], TMB = 1,3,5-mercaptophenyl)-benzene with chemical formula C$_{32}$H$_{15}$S$_{6}$Ag(111) + (4 × 4) -O [19]; Ag(111) + (7 × 3)rect-SO$_{4}$ [20]; and Ru(0001) + ( $3 \sqrt[3]{3} \times \sqrt[3]{3}$)R30° -Cl [1].

2. Carrier wave

We consider the framework of a surface unit cell of $N_{uc}$ atoms built by $N_{ieq}$ symmetrically inequivalent atoms of interatomic distance $d_{NN,i}, i = 1, 2, \ldots, N_{ieq}$; Radii of MT sphere and of its next neighbor MT sphere are $R_i$ and $R_{NN,i}$, respectively. In particular, when these radii fulfill the inequality $R_i + R_{NN,i} \leq d_{NN,i}$, they form a prototype of touching atoms [7]. In this work we use overlapping MT spheres defined by the inequality

$$R_i + R_{NN,i} \leq d_{NN,i} \times (1 + S_i), \quad S_i \geq 0,$$

where the parameter $S_i$ of site $i$ defines overlap relative to interatomic distance. Experimentally adjusted LEED conditions on the overlap radii are $R_i > 0.3 \times d_{NN,i}$ and $R_i < 0.9 \times d_{NN,i}$ see appendix B.

We initiate the EEAS theory by constructing the carrier potential. Assigned to each site $i$ is an atom of electron density $\rho(r)$ and nucleus $Z_i$. We utilize computer code available from National Institute of Standards and Technology [21, 22] 4 using $\rho(r)$ and $Z_i$ for calculating Coulombic potentials $V_{NIST}(r)$ with standard normalization, zero at large radius. Given $V_{NIST}(r)$, we wish to build a KKR carrier crystal potential $V_c(r), r \leq R_0$, where $R_0$ signifies MT radius. Standard normalization is arbitrary with respect to crystalline potential levels $V_c(r)$. Differential evolution (DE) [23] is an appropriate method for shifting $V_{NIST}(R_i)$ onto actual crystal level $V_c(R_i)$. We specify a spatially constant interstitial potential $V_0$ as the unit cell average over the carrier potentials, each $V_i(r)$ with its value at its MT radius $R_i$ and $N_{ieq}$ counting equivalent atoms of kind $i$,

$$V_0 = N_{uc}^{-1} \sum_{i=1}^{N_{ieq}} N_{ieq} V_i(R_i)$$

(2)

Here a signal electron scattering argument comes in. Signal electron reflection at potential steps between the interstitial potential $V_0$ and peripheral values of MT potential $V_c(R_i)$ would excite alien standing-wave resonances in the MT spheres. Removal of potential steps $V_c(R_i) - V_0$ is therefore a necessary condition on clean signal electron EEAS in the crystal. The requirement corresponds to a DE fitness number $\epsilon$ of $N_{ieq}$ parameters $V_i(R_i)$, each depending on two unknowns, MT radius $R_i$ and energy shift of potential $V_i(r)$, in addition to the interstitial potential $V_0$, unknown too,

$$\epsilon = \min_i \left[ \max_j \left( V_i(R_i) - V_0 \right) \right], \quad i = 1, 2, \ldots, N_{ieq}$$

(3)

DE applied on equations (1)-(3) is initiated from $V_i(r) = V_{NIST}(r), i = 1, 2, \ldots, N_{ieq}$. A first DE calculation creates sets $R_i$ and $V_i(r)$ with a coarse fitness number $\epsilon = O(1)$ in units of eV. We make a substitution that keeps $V_0$ invariant,

$$V_i(r) - V_0 \rightarrow V_0,$$

(4)

In a second iteration DE finishes with $\epsilon = O(10^{-15})$ in a computer of 64 bit precision. The KKR model with overlapping MT spheres refined by DE makes the crystal potential exactly continuous with respect to potential values, while minor scattering perturbations remain due to steps of potential gradients. DE starts from a random set of radii $R_i$ enclosed by lower–upper values in a $N_{ieq}$-dimensional parallelepiped

$$R_{min,i} < R_i < R_{max,i}, \quad i = 1, 2, \ldots, N_{ieq}$$

(5)

4 Supplemental Material: E Shirley, Hartree–Fock program, SM1.tgz.
The inequalities are kept sufficiently open for the optimum to remain detached from the parallelepiped, or they be restricted so that the optimum is moved in some thought direction. The second method is used in the paragraph below for adjusting the interstitial potential of the surface unit cell to the one of the bulk. Approximate values \( R_{\text{min},i} \) and \( R_{\text{max},i} \) are indicated in appendix B, section 1, 4th paragraph.

The interstitial potential \( V_0 \) of the surface structure will be determined by our connecting the unit cell of the surface slab to the crystal bulk. Fortunately, a slab-to-bulk boundary condition is inherent in the DE method. We force the MT radii of the innermost layers of the surface unit cell to optimize in minute intervals fitted to known MT radii of the bulk; in this way DE optimization lifts \( V_0 \) to the inner potential of the bulk. In next paragraph we learn that electron self-energy is currently normalized to zero at very high energy. Correspondingly, standard carrier potential \( V(r) \), \( i = 1,2,\ldots,N_{\text{eq}} \) is normalized to \( V_0 = \text{MTZ} \) (muffin-tin zero) = 0.

3. Electron self-energy and wave number modulation

The advantage of energy dependent XC interaction in LEED investigations was published in 1982 [24]. L Hedin and B I Lundqvist [25, 26] had shortly before put one-electron excitation equal to the sum of incident energy and electron-gas chemical potential. Later Sernelius applied Rayleigh-Schrödinger many-particle theory and identified electron self-energy and electron gas ground-state [15, 16] and appendix A,

\[
p^2 + \Sigma(p/p_F, r_s) = E + E_F + \Sigma(1, r_s)
\]

Left-hand member of equation (6) creates kinetic energy and self-energy potential of an excited signal electron, while right-hand member provides available energy sources, incident energy and chemical potential of ground-state electron gas. Designations are: \( p = \) signal electron momentum, equal to wavenumber in atomic Rydberg units; \( \Sigma = \) signal electron self-energy, of which \( \Sigma(1, r_s) \) is the XC part of the chemical potential; \( p_F(r_s) = \) Fermi momentum; \( E_F(r_s) = \) Fermi energy; with \( r = \) atomic radius, \( r_s(r) = \) electron-space radius, and \( \rho(r) = \) electron gas density; \((4\pi/3)r_s^3\rho = 1\), where \( r_s = 0 - 6d_0 \) for most crystals. Momentum \( p/p_F \) in one-electron excitation equation (6) is solved as a function of incident energy \( E \) by means of Sernelius’s data base \( \text{sdat}^5 \) illustrated in figure 2,

\[
(p/p_F)^2 = (E/E_F) + 1 + r_s[\text{sdat}(1, r_s) - \text{sdat}(p/p_F, r_s)]
\]

\[
\text{sdat}(p/p_F, r_s) = \Sigma(p/p_F, r_s)/E_F/r_s
\]

Iteration of \( p/p_F \) is done with bivariate interpolation [27] in \( \text{sdat} \). Extrapolation of the data base \( \text{sdat} \) to high momentum simulates the Hartree–Fock exchange potential \( \propto -(p/p_F)^2 [11] \) together with the Lindhard correlation potential \( \propto -(p/p_F)^{-1} [12] \). The former rapidly vanishes with energy; the latter does not converge to zero but is considered negligible at very high energy. The result is a set of atomic XC potentials \( \iota \) in terms of variables \( r, E, p \), and \( p \) together with materials data \( p_F, E_F, \) and \( r_s \).

\[5\] Supplemental Material: B. E. Sernelius, Electron self-energy database, SM2.tgz.
4. Elastic electron-atom scattering phase shifts

Relativistic EEAS with central potential is determined by Dirac equation $W\psi = H\psi$ [28], where $\psi$ is a two-component spinor and $W$ is the eigenvalue $E + mc^2$ with $E$ = signal energy, $m = \text{mass}$, and $c =$ speed of light $2/\alpha$, $\alpha$ being fine structure constant $1/137$ (atomic Rydberg units). Eigenstates are $G_\kappa = u_{1\kappa}/r$ and $F_\kappa = u_{2\kappa}/r$ with spin–orbit quantum number $\kappa$, total angular momentum $j$, and atomic orbital $l$,

\[
\kappa = \begin{dcases} 
- l - 1 & \text{for } j = l + \frac{1}{2}, \ l = 0, 1, 2 \ldots \\
\ l & \text{for } j = l - \frac{1}{2}, \ l = 1, 2, \ldots 
\end{dcases} \tag{10}
\]

$\kappa$ is negative or positive corresponding to spin $1/2$ parallel or $-1/2$ antiparallel to electron’s direction of flight [29]. $u_{1\kappa}$ and $u_{2\kappa}$ are solutions of two Dirac differential equations with central potential,

\[
\frac{du_{1\kappa}}{dr} = -\frac{\kappa}{r} u_{1\kappa} + \{c + c^{-1}[E - V_T(r, E)]\} u_{2\kappa}
\]
\[
\frac{du_{2\kappa}}{dr} = \frac{\kappa}{r} u_{2\kappa} - c^{-1}[E - V_T(r, E)] u_{1\kappa} \tag{11}
\]

where $V_T(r, E) = V(r) + V_{XC}(r, E)$ signifies total atomic potential. Boundary conditions at the origin are [28],

\[
u_{1\kappa} = Ar^\gamma \quad \text{and} \quad u_{2\kappa} = Ar^\gamma(\kappa + \gamma)/\xi \tag{12}
\]

with $A = \text{const.}$, $\gamma = \kappa^2 - \zeta^2$, $\zeta = \alpha Z$, and $Z =$ atomic number; $\gamma > 0$ corresponds to regular solutions of the Dirac equations. We use an exponential radial grid $r_n = n = 1, 2, \ldots$, where $\tau_1 = 10^{-16}$, a current initial radius for atomic calculations [21]. With increasing orbitals $l$, angular momenta displace the electron waves $u_{1\kappa}$, $u_{2\kappa}$ away from the origin. Correspondingly, initiation radii $r_\kappa = (\tau_1)^{2/\gamma}$ move so that wave factors $A(r_\kappa)^\gamma$ in condition (12)

\[V_{XC}(r, E) = \text{s\_data}(p/p_E, r_i) E_k r_\kappa, \ i = 1, 2, \ldots N_{\text{seq}} \tag{8}\]

The atomic self-energy potentials are added up to a spatially flat interstitial XC potential,

\[
V_{XC0}(E) = \sum_{i=1}^{N_{\text{seq}}} N_{\text{seq}} V_{XC}(R_i, E) \tag{9}\]

Substitution similar to expression (4) makes XC potentials $V_{XC0}(R_i, E)$ equal to interstitial $V_{XC0}(E)$. Following the normalization convention of s\_data in figure 2 we shift the field of XC potentials to MTZ = 0 at very high energy. The $V_{XC0}(E)$ curve in figure 3 turns out to have universal shape given by a four-coefficient approximation [24], whose increasing part almost identically fits the calculated XC potential.

In an attempt to confirm the theoretical self-energy $V_{XC0}(E)$ by experimental LEED data, we attach a multiplier $f_{XC}$ to the right-hand member of equation (8). The purpose is to consider $f_{XC}$ as an adjustable structural parameter and to record an r-factor versus $f_{XC}$ curve during the LEED investigation. $f_{XC}$ close to unit would indicate confirmation (Appendix B and section V).

Figure 3. Interstitial XC potential of surface Cu(111) $+(3\sqrt{3} \times \sqrt{3})$R30° on TMB (black) and 4-coefficient approximation $V_{SCF}(E) \approx \max [p_0 + p_1/r |E + p_2, p_3 |(red). It is extractable from LEED experiment by r-factor optimization of $p_0 - p_4$.
remain constant $A$. We initiate with $u_{1c} = r_{1}$ and $u_{2c} = r_{1}(\kappa + \gamma)/\zeta$, $A = 1$. The Dirac equations are integrated using Shampine and Gordon’s ODE (ordinary differential equation) solver built on Adams predictor-corrector method with automatic initiation and step size control [30].

In the interstice of spatially constant $V_{XC}^{(0)}(E)$ elimination of $u_{2c}$ from the first-order Dirac equations (11) gives rise to a second-order Schrödinger equation for $u_{1c}$,

$$
\frac{d^2u_{1c}}{dr^2} + \left( q^2 - \frac{\kappa(\kappa + 1)}{r^2} \right) u_{1c} = 0,
q^2 = E - V_{XC}^{(0)}(E) + e^{-2}[E - V_{XC}^{(0)}(E)]^2
$$

(13)
The difference between wavenumbers $q$ and $k = \sqrt{E}$ constitutes the XC modulation of the carrier wave $\kappa(\kappa + 1)$ equals $k(l + 1)$ for both spins, and the eigenvectors are $r_1(qr)$ and $r_2(qr)$ with spherical Bessel functions $j_1$ and $y_1$. The signal electron in the interstice is expressed in terms of scattering phase shifts $\delta_{1c}$,

$$
u_{1c}(r) = \mathcal{C} [r_1(qr) \cos \delta_{1c} - r_2(qr) \sin \delta_{1c}]$$

(14)
$C = \text{const.} \, \kappa$ takes a single subscript $-1$ for orbital $l = 0$ and two subscripts, $-1$ and $l$, for orbitals $l \geq 1$. The phase shifts $\delta_{1c}$ determine the phase shifts $\delta_{1c}$ by equating logarithmic derivatives belonging to $u_{1c}$, inside and outside MT radius $R_l$, of relative magnitude $e^{-1}$ is neglected. With prime for differentiation with respect to $r$, phase shifts are obtained from

$$
\tan \delta_{1c} = \left[ \left( u_{1c}(r) \right)' r_1(qr) - u_{1c}(r) \left( r_1(qr) \right)' \right] / \left[ \left( u_{1c}(r) \right)' r_2(qr) - u_{1c}(r) \left( r_2(qr) \right)' \right] \bigg|_{r = R_l}
$$

(15)

The phase shift spin states define two sets of scattering amplitudes, $q^{-1}e^{i\delta_{1c} - \delta_{1c}}$, $q^{-1}e^{i\delta_{1c} - \delta_{1c}}$, of spin $\frac{1}{2}$ and $-\frac{1}{2}$, respectively. LEED without spin combines the above scattering amplitudes with orbital weights $l + 1$ and $l$ divided by $2l + 1$.

ODE is managed by two error tolerances $\text{redera}$ and $\text{abserrr}$ and responds with errors

$$
\epsilon_1 \leq \text{redera} \left| u_{1c}(r') \right| + \text{abserrr} \left| r_{1c} \right| \text{on Adams predictor-corrector radial grid. Continued calculation transmits these errors to error bars on the EEAS phase shifts $\delta_{1c}(E)$. Since the phase shifts provide preliminary data for reliability estimation of theoretical LEED spectra [17], we wish to work with known phase shift accuracy. Using the benchmark technique from earlier LEED work [31], we accompany Dirac representation (11) by a representation that is analytically equivalent and is at once computationally different with respect to algorithms and initiation conditions. We apply the substitutions,

$$
u_{1c} = \gamma_{1c} r^\gamma \text{ and } u_{2c} = \gamma_{2c} r^{\gamma} \left( \kappa + \gamma \right)/\zeta $$

(16)
to equations (11) and find a new Dirac representation, overlooked by Dirac equation treatise [28],

$$
\begin{align*}
\frac{dy_{1c}}{dr} &= \left( \kappa + \gamma \right) \left[ \frac{-\kappa}{r} y_{1c} + \left\{ c + e^{-1}[E - V_{g1}(r, E)] \right\} y_{2c} \right]/\zeta \\
\frac{dy_{2c}}{dr} &= \left( \kappa - \gamma \right) \left[ \frac{\kappa}{r} y_{2c} - e^{-1}[E - V_{g1}(r, E)] y_{1c} \right]/\zeta 
\end{align*}
$$

(17)

Equations (17) integrate twice as fast as equations (11) and are initiated from boundary conditions $\gamma_{1c} = \gamma_{2c} = \text{unity at the origin, distinct from initiation by equations (12), } u_{1c} = r_{1}$ and $u_{2c} = r_{1}(\kappa + \gamma)/\zeta$ with $r_{1} = 10^{-10}$. The Dirac representations (11) and (17) of phase shifts $\delta_{1c}$ and $\delta_{2c}$, respectively, determine the phase shift accuracy

$$
\epsilon = \max_{i, l, E, \kappa} \left| (\delta_{1c}(E) - \delta_{2c}(E)) \right|
$$

(18)
with respect to spin, energy, orbitals, and atoms. For example, with $\text{redera} = 1 \cdot E - 6$ and $\text{abserrr} = 1 \cdot E - 9$ atoms S, C, H, and Cu of the surface structure Cu(111) + (3 3 0 3 × 3 3) R30°-TMB [18] attain phase shift accuracy 2. E = 5.

5. Result

Moritz implemented the EEAS method of section 2–4 for surface structure determination using the LEEDFIT program packet [32, 33]. Appendix B gives an account of the successive LEEDFIT iterations determining Pendry’s r-factor [17]. Table 1 illustrates LEED investigations of four complicated surface structures on large unit cells, which were carried out in earlier publications using touching MT spheres, and are now recalculated using overlapping MT spheres. Column T (touching) of the table lists structures with $N_{req}$ varied MT radii, while column O (overlapping) counts structures given $N_{req}$ simultaneously varied MT radii and potential shifts. The O result shows an r-factor reduction in value by 0.015, 0.062, 0.072, 0.018 [1, 18–20], and in percent by 11, 20, 22, 8.
In LEED the I only finite reciprocal space and is not taken as an independent data point for each peak. In Pendry KKR-T one and DFT comparison presently not available to the authors. The r-factor, probably larger. To make the r-factors of T and O comparable, we calculate the expectation value of the T r-factor for LEED the number of peaks is estimated as determines the limits of trustworthy reliability and identity in the range 0.4.<ref>

Table 2. Comparing the r-factors of the models T and O supposing that both models have the same number of internal parameters. Data: ∆E = total energy range, N = total number of data points, p = number of structural parameters, pO = number of internal parameters of the O model, rT and rO r-factors of T and O models, and ⟨rT⟩ = expected r-factor of a T model supposed to have pO internal parameters.

| Surface structure | ∆E (eV) | N  | p  | pO  | rT  | ⟨rT⟩ | rO  | S   |
|-------------------|---------|----|----|-----|-----|------|-----|-----|
| Cu(111) + (3 √ 3 × 3)R30°-TMB | 11–200  | 344 | 50 | 12  | 0.32 | 0.314 | 0.252 |
| Ag(111) + (4 × 4)-O | 25–250  | 248 | 26 | 10  | 0.34 | 0.332 | 0.26 |
| Ag(111) + (7 × 3)rect-SO₄ | 10–150  | 60  | 107| 12  | 0.235| 0.229 | 0.211 |
| Ru(0001) + (3 √ 3 × 3)R30°-Cl | 20–300  | 154 | 10 | 12  | 0.137| 0.131 | 0.116 |

Table 1. LEED reliability [17] with touching (T) and overlapping (O) MT spheres; E is energy of incidence; O parameter is S ~ [(R + R_{SO})/(interatomic distance)] − 1 [cf equation (1)].

consider the KKR-O model an interesting method for LEED evaluations. To which degree the KKR-O scattering model improves the physical-chemical picture of the surface structures in Table 1 is a task of systematic LEED and DFT comparison presently not available to the authors.

In a statistical study of the result we follow Pendry’s theory for LEED intensity spectra [17]. A reduction of the r-factor is expected when the number of parameters is increased. For the structures discussed in Table 2 we only find a marginal reduction of the T r-factors, when we temporarily apply the internal parameters of model O. In LEED the I(V) curves can be considered as a superposition of Lorentzian peaks. The number of independent data points is given by the number of peaks and their intensity. The width of the peaks is approximately constant in reciprocal space and is not taken as an independent data point for each peak. In Pendry’s definition of the r-factor for LEED the number of peaks is estimated as N = ∆E/(4 × |V_i|), where ∆E is the total energy range and V_i is the optical potential, assumed to be −4 eV. This is a conservative estimate and the real number of peaks is probably larger. To make the r-factors of T and O comparable, we calculate the expectation value of the T r-factor, ⟨r_T⟩, where the T model is given the same number of parameters as the O model,

\[
⟨r_T⟩ = r_T \sqrt{N - p - p_O}/(N - p)
\]

The 7th and 8th columns of Table 2 mark that the KKR-O potential model is more efficient for LEED than the KKR-T one.

A single MT overlap parameter S per structure is found to give similar reliability as atomic S. Appendix B, figure 7, shows S varied from zero to saturated MT overlap; for two curves saturation occurs giving rise to constant r-factors beyond S = 0.7 and 0.8.

For searching an experimental confirmation of the electron self-energy V_{SCD}(E), Moritz included the multiplier f_{SC} in the set of structural parameters. During S variation the r-factor is recorded as a function of f_{SC} in the range 0.4–1.4, see appendix B, figure 8. Pendry’s statistical RR measure [17] on the LEED experiment determines the limits of trustworthy reliability and identifies error bars on the r-factor versus f_{SC} diagram. The four structures in table 1 are found to give self-energy multipliers gratifyingly close to unity [1, 18–20]: 0.89 ± 0.2, 1.00 ± 0.1, 0.94 ± 0.1, 1.06 ± 0.1. This is the first LEED confirmation of the electron self-energy potential.

Introduced in LEED is the technique of signal carrier-wave, guided by a spin- and energy-independent electrostatic potential (Coulombic) that is wavenumber modulated by a transient self-energy potential. The self-
energy referred to as XC interaction is due to the repulsion of the signal electron by the spin and charge of the crystal’s electron gas opened up for increased nuclear attraction. At very low LEED incidence $\sim 20$ eV the modulation amounts to $\sim -10$ eV from XC interaction, at a few tens of eV the X interaction vanishes, and the C interaction continues like $\propto (-1/\sqrt{E})$.

**Acknowledgments**

J R conceptualised, B E S determined electron self-energy, and W M conducted LEED investigations. The work came up at the International Workshop of Quantitative LEED Analysis organised by Professor E W Plummer, Louisiana State University, April 18–20, 2016. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

**Appendix A. Electron self-energy determination**

**A.1. System of interacting electrons**

Our calculation of the electron self-energy is based on the Rayleigh-Schrödinger (RS) perturbation theory or on the mass-shell-perturbation-theory. The starting point is the energy, $E$, of the system of interacting electrons. The Hamiltonian is written with a variable coupling constant, $\lambda$,

$$H(\lambda) = H_0 + \lambda V,$$

$$H(1) = H,$$

$$H(0) = H_0,$$  \hspace{1cm} (A1)

where $H_0$ the non-interacting Hamiltonian and $V$ is the interaction part, in our present case the Coulomb interaction between the electrons.

Let,

$$H(\lambda)\Psi_0(\lambda)) = E(\lambda)\Psi_0(\lambda)),$$

$$\langle \Psi_0(\lambda)\Psi_0(\lambda)\rangle = 1,$$

$$E(\lambda) = \langle \Psi_0(\lambda)\mid H(\lambda)\mid \Psi_0(\lambda)\rangle,$$  \hspace{1cm} (A2)

where $|\Psi_0(\lambda)\rangle$ is the interacting ground state of the system at coupling strength $\lambda$.

$$\frac{d}{d\lambda}E(\lambda) = \left\{ \frac{d\Psi_0(\lambda)}{d\lambda} \left| H(\lambda)\Psi_0(\lambda)\right\rangle + \langle \Psi_0(\lambda)\right| H(\lambda) \left| \frac{d\Psi_0(\lambda)}{d\lambda}\right\rangle \right\}$$

$$+ \langle \Psi_0(\lambda)\right| \frac{dH(\lambda)}{d\lambda} \left| \Psi_0(\lambda)\rangle \right. \right\}$$

$$= E(\lambda) \frac{d}{d\lambda} \langle \Psi_0(\lambda)\mid \Psi_0(\lambda)\rangle + \langle \Psi_0(\lambda)\mid V\mid \Psi_0(\lambda)\rangle = \langle \Psi_0(\lambda)\mid V\mid \Psi_0(\lambda)\rangle.$$  \hspace{1cm} (A3)

Integrating this equation with respect to the coupling constant from 0 to 1 gives

$$E_{int} = E - E_0 = \int_0^1 \frac{d\lambda}{\lambda} \langle \Psi_0(\lambda)\mid \lambda V\mid \Psi_0(\lambda)\rangle.$$  \hspace{1cm} (A4)

Equation (A4) is the starting point for diagrammatic perturbation theory. The result of rather cumbersome derivations is

$$E_{xc} = +i \int_0^1 \frac{d\lambda}{\lambda} \sum\int \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \hbar \left[ \frac{1}{\varepsilon^{\lambda}(q, \omega)} - 1 \right] \right\} \frac{N\lambda_0}{iv\kappa} \right\}$$  \hspace{1cm} (A5)

where the second term in the momentum summand is a subtraction of the self-interaction contributions of the $N$ number of electrons in the system. The prime indicates that the $q = 0$ term should be omitted. To be noted is that this expression is formally exact. The approximations lie in the approximations of the dielectric function, $\varepsilon^{\lambda}(q, \omega)$. The dielectric function is the longitudinal version on time-ordered form. Please note that here we let
the exchange and correlation energy, $E_{xc}$, denote the whole interaction energy, not the energy per electron which is usually the case.

A nice reformulation of the self-interaction in terms of the dielectric function of the system, $\varepsilon_\lambda(q, \omega)$, in case all electrons are responding completely independent of each other leads to a more symmetric expression,

$$
E_{xc} = + i \int_0^1 \frac{d\lambda}{\lambda} \frac{1}{2} \sum_q \left\{ \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\hbar}{\omega} \left[ \frac{1}{\varepsilon_\lambda(q, \omega)} - 1 \right] - \frac{1}{\varepsilon_\lambda(q, \omega)} - 1 \right\}.
$$

We use the Random Phase Approximation (RPA) in the diagrammatic perturbation theory. Then the dielectric function is the so-called Lindhardt dielectric function [12] and it can be expressed in terms of the polarizability, $\alpha_0(q, \omega)$,

$$
\varepsilon_\lambda(q, \omega) = 1 + \lambda \alpha_0(q, \omega).
$$

We may perform the integration over coupling constant with the result:

$$
E_{xc} = - i \frac{1}{2} \sum_q \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\hbar}{\omega} \ln \left[ \frac{\varepsilon(q, \omega)}{\varepsilon_0(q, \omega)} \right].
$$

Now, the integrand is rather complex and complex valued. It is favourable to perform integration along the imaginary axis in the complex frequency plane. We deform the integration path along the contour in figure A1. All poles are outside the contour. This means that the result of the integration is zero. Now the contributions from integration along the two curved parts of the contour cancel. This means that integration along the real axis gives the same result as integration along the imaginary axis in positive direction.

Thus,

$$
E_{xc} = \frac{1}{2} \sum_q \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\hbar}{\omega} \ln \left[ \frac{\varepsilon(q, i\omega)}{\varepsilon_0(q, i\omega)} \right].
$$

It is interesting to point out that exactly the same result is obtained from the summation of the zero-point energies [36] of the longitudinal normal modes of the system. This alternative derivation is much simpler. Here we also find contributions from transverse modes with the result.

Figure A1. Integration contour in the complex frequency plane. The crosses indicate the positions of the poles of the integrand when the functions are on the time-ordered form.
where the extra factor 2 in front of the right-hand-side is due to the two polarization directions of the transverse normal modes.

These results turn out to be negligible [36]. For the interaction between objects the first type, that comes from longitudinal modes, is responsible for the van der Waals interactions while the other type, that comes from transverse modes, gives rise to Casimir interactions. The dielectric function, from longitudinal modes, is responsible for the van der Waals interactions while the other type, that comes from transverse modes, gives rise to Casimir interactions. The dielectric function, \( \varepsilon(q, i\omega) \), in equation (A10) is the transverse version. It coincides with the longitudinal version, \( \varepsilon(q, \omega) \), as used in equation (A9), for small \( q \) but differs for large \( q \).

Why did we not obtain this contribution using the diagrammatic perturbation theory? The reason is that we did not include the whole interaction part in equation (A5), only the part representing the Coulomb interaction between the electrons. There are also \( \mathbf{p} \cdot \mathbf{A} \) - and \( \mathbf{A} \cdot \mathbf{p} \)-terms, where \( \mathbf{A} \) is the vector potential.

Our derivation of the electron self-energy is based on the results in equation (A9).

### A.2. The self-energy

In the calculation of the interaction energy of an electron gas the energy can be viewed as getting contributions from processes where electrons are scattered out of occupied states into unoccupied states.

In RS the self-energy for a state above the chemical potential is the change in the total interaction energy of the system when an electron is placed in this state. Placing the electron in that state adds new possible processes where the electron is scattered out from the state; it also reduces other processes where electrons otherwise could have been scattered into the state. These processes are now forbidden due to the Pauli exclusion principle.

Now, to get the energy of state \((\mathbf{p}, \sigma)\), what one really does is to take the variational derivative of the total energy \( E \) of the system with respect to the occupation number \( n_{\mathbf{p},\sigma} \) of state \((\mathbf{p}, \sigma)\),

\[
\varepsilon_{\mathbf{p},\sigma} = \frac{\delta E}{\delta n_{\mathbf{p},\sigma}} = \varepsilon_{\mathbf{p},\sigma}^0 + \hbar \Sigma_{\mathbf{p},\sigma}.
\]

Tim Rice [15] was the first to point this out. The self-energy is then

\[
\hbar \Sigma_{\mathbf{p},\sigma} = \frac{\delta E_{\text{xc}}}{\delta n_{\mathbf{p},\sigma}} \quad \text{(A12)}
\]

Germanium is a many-valley semiconductor. Heavily \( n \)-doped germanium has four equivalent Fermi-volumes in the Brillouin Zone. When a stress is applied to the system some valleys move up in energy and some move down; this results in shrinking and growing Fermi-volumes. This has effects on optical and transport properties. How the valleys move is closely related to the real part of the self-energy. The most straight forward test of the real part of the self-energy is found in the optical birefringence experiment and the agreement between theory [37] and experiment is striking.

GaAs is a direct-band-gap semiconductor. Heavily \( p \)-doped GaAs can be used to produce spin-polarized electrons by using polarized light. The excited electrons in the conduction band will then recombine with the holes in the two valence bands. The comparison [38] between theory and experiment on the resulting luminescence polarization gives a thorough test of both the real and imaginary parts of the self-energy. The RS self-energy well passed the test.

More recent tests have been made. The imaginary part of the self-energy has successfully been tested [39] in the dynamics of highly photo-excited electrons and holes in silicon.

In [37] one applied a mechanical stress on a heavily doped many-valley semiconductor to move the conduction band valleys up or down in energy. An alternative way is to apply a strong magnetic field. Then spin-up and spin-down valleys move up or down in energy. Fermi-volumes of one type grow and of the other type shrink, leading to a change in transport properties. Both silicon [40] and germanium [41] show negative magnetoresistance. The comparison between experiment and theory means a test of the real part of the self-energy. The results show qualitative agreement with a negative magnetoresistance in both the experimental and theoretical results.

Let us now return to the actual calculation of the self-energy in equation (A12). We should note that when the change in occupation numbers has been made the system is no longer in its ground state; it is unstable and decays; the signature of an unstable system is a complex-valued energy.
The occupation numbers are found in the polarizabilities entering the expression for the energies. Now,

\[
\alpha_0(q, \omega) = -\frac{1}{\hbar^2} \sum_\sigma q^2 \int \frac{d^3k}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi i} G_\sigma^{(0)}(k, \varepsilon) G_\sigma^{(0)}(k + q, \varepsilon + \omega),
\]

(A13)

\[
G_\sigma^{(0)}(k, \varepsilon) = \frac{m_{k,\sigma}}{\varepsilon - \hbar^2 k^2/2m^* - i\eta} + \frac{1 - n_{k,\sigma}}{\varepsilon - \hbar^2 k^2/2m^* + i\eta};
\]

(A14)

where \(k_F\) is the Fermi wave number and \(G_\sigma^{(0)}(k, \varepsilon)\) the Green’s function.

We introduce the following dimensionless quantities:

\[
Q = q/2k_F, \quad K = k/2k_F; \quad k_F = (3\pi^2n)^{1/3}
\]

\[
W = \hbar \omega/4E_F, \quad E = \hbar \varepsilon/4E_F; \quad E_F = \hbar^2 k_F^2/2m^*
\]

\[
\tilde{G}_\sigma^{(0)} = 4E_F G_\sigma^{(0)}/\hbar
\]

\[
y = m^* e^2/\hbar^2 k_F,
\]

(A15)

where \(E_F, n,\) and \(v\) are the Fermi energy, the electron density, and volume of the system, respectively.

Substitution of these in equation (A13) gives

\[
\alpha_0(Q, W) = -\frac{4\pi}{Q^2} \sum_\sigma \int \frac{d^3K}{(2\pi)^3} \int_{-\infty}^{\infty} \frac{dE}{2\pi i} \tilde{G}_\sigma^{(0)}(K, E) \tilde{G}_\sigma^{(0)}(K + Q, E + W)
\]

(A16)

One can prove the following general relation:

\[
\frac{\partial}{\partial n_{P,\sigma}} \sum_\sigma \int_{-\infty}^{\infty} \frac{dE}{2\pi i} \tilde{G}_\sigma^{(0)}(K, E) E_F(K, E) = E_F(P, P^2),
\]

(A17)

which gives

\[
\frac{\delta \alpha_0(Q, W)}{\delta n_{P,\sigma}} = -\frac{4\pi}{Q^2} \frac{1}{\nu(2k_F)^3} \left[ \tilde{G}_\sigma^{(0)}(P + Q, P^2 + W) + \tilde{G}_\sigma^{(0)}(P - Q, P^2 - W) \right].
\]

(A18)

Now, the electron self-energy can be written on two alternative forms depending on from which of the two equivalent versions of the interaction energy in equation (A5) or equation (A6) we start from. The two versions are

\[
h \Sigma_{P,\sigma} = -16\pi y E_F \int \frac{d^3Q}{(2\pi)^3} \left[ \int_{-\infty}^{\infty} \frac{dW}{2\pi i} \tilde{G}_\sigma^{(0)}(P + Q, P^2 + W)/Q^2 \tilde{G}^{(0)}(Q, W) + \frac{1}{2Q^2} \right],
\]

(A19)

and

\[
h \Sigma_{P,\sigma} = -16\pi y E_F \int \frac{d^3Q}{(2\pi)^3} \left[ \int_{-\infty}^{\infty} \frac{dW}{2\pi i} \tilde{G}_\sigma^{(0)}(P + Q, P^2 + W)/Q^2 \tilde{G}^{(0)}(Q, W) \right.
\]

\[
\left. - \frac{1}{2Q^2} \left( W - [(P + Q)^2 - P^2] + i\eta \right) - \frac{1}{W + [(P + Q)^2 - P^2] - i\eta} \right] \right].
\]

(A20)

In equation (A19) the contribution from the electron self-interaction is outside the \(W\)-integral but inside the \(Q\)-integral. In equation (A20) it is inside both.

We will now deform the integration path in the same way as we did to obtain equation (A8). In this case we will have poles from the Green’s function inside the contour; if we use equation (A20) we will also have poles from the second term. We will get two contributions to the integral; one from the integration along the imaginary axis and one from the residue contributions. These contributions are named the line- and residue-parts, respectively. The line-part is real-valued while the residue-part is complex-valued. Thus the imaginary part of the self-energy comes entirely from the residue-part. One point to notice is that there is no unique separation in line- and residue-parts. This is obvious since in our two approaches the self-interaction term gives contributions to the residue-part in one of the approaches but not in the other.
Let us treat the line-part first. This contribution is

$$\hbar \Sigma_{\text{line}}^{P,\sigma} = -16\pi\gamma E_F \int d^3Q \left[ \int_{-\infty}^{\infty} dW \left( \frac{1}{2\pi} \ln \left( \frac{(Q - iW)^2}{(Q + W)^2} \right) + \frac{1}{2Q^2} \right) \right],$$

where we have let the self-interaction term be included in the line-part. We use spherical coordinates and perform the angular integrations in the momentum integral. Then we make the substitution $W \rightarrow WQ$ and end up with the final result,

$$\hbar \Sigma_{\text{line}}^{P,\sigma} = \frac{\gamma E_F}{\pi^2} \int_0^\infty dQ \left\{ \int_{-\infty}^{\infty} dW \frac{1}{P \varepsilon(Q, iWQ)} \times \ln \left| \frac{(Q + 2P)^2 + W^2}{(Q - 2P)^2 + W^2} \right| + 4\pi \right\}.$$  \hspace{1cm} (A22)

The residue-part has contributions if the poles of the Green’s function happen to be inside the contour. This happens in two cases:

A.3. $P < |P + Q| < 1/2$

The residue contribution to the self-energy for a hole is

$$\hbar \Sigma_{\text{res}}^{P,\sigma} = -\frac{2\gamma E_F}{\pi^2} \int_{P < |P + Q| < 1/2} d^3Q \frac{1}{\varepsilon(Q, P + Q^2 - P^2)}.$$  \hspace{1cm} (A23)

This integral can be reformulated in a way that makes the physics more transparent. This is achieved with the substitution $W \rightarrow (P + Q)^2 - P^2$. Then $d^3Q \rightarrow -\frac{(\pi / P)}{Q\varepsilon(Q, W)} QdQdW$ and

$$\hbar \Sigma_{\text{res}}^{P,\sigma} = -\frac{2\gamma E_F}{\pi P} \int dWdQ \frac{1}{\varepsilon(Q, W)},$$

where the double integral is performed over the shaded area in figure A2. The physics is the following: The hole in state $P$ can fall upwards in energy. The energy and momentum is conserved via emission of electron-hole pairs; the conservation of energy only holds for actual transitions; these appear in the calculation of the imaginary part of the self-energy, which is closely connected to the life-time of the state. The shaded area shows which possible excitations (characterized by $(W, Q)$) are involved in the relaxation of the particular hole state. We realize that there is no possibility for plasmon excitations when the hole relaxes since the shaded area always stays within region 2.

Figure A2. The regions in the WQ-plane where the electron gas can gain energy and a hole in $P$ can loose energy. Regions 1 and 2 are the regions of electron-hole pair excitations. The curved line in the left part of region 3 shows possible plasmon excitations. The shaded area shows where a hole in $P$ can loose energy, $W$, and momentum, $Q$. 

J. Phys. Commun. 5 (2021) 105012 J. Rundgren et al.
The residue contribution to the self-energy for an electron is

$$\hbar \Sigma^{\text{res}}_{\nu, p} = -\frac{2yE_p}{\pi^2} \int_{1/2|P+Q|<P} d^3Q \frac{1}{Q^2\varepsilon(Q, P^2 - (P + Q)^2)}.$$  \hspace{1cm} (A25)

The physics is more transparent by using again equation (A24) where now the double integral is performed over the shaded area in figure A3.

Here we see that the integration region extends outside the single-particle continuum. If the electron is high enough in energy, plasmons can be excited. We should notice that the electron must have an energy somewhat larger than $\hbar\omega_{pl}$ above the Fermi energy to be able to excite plasmons; large-momentum plasmons are excited first (when the electron energy is gradually increased) and these have higher energy than the zero-momentum ones due to the dispersion of the plasmon line. This is also what is found in photo-emission experiments. The shaded area is the region that contains all possible energy and momentum pairs an electron in state $p$ may give away when it relaxes towards equilibrium. It can only give away this combination if at the same time the rest of the system can absorb it. For the calculation of the imaginary part of the self-energy this limits the active part of the integration region to the union between the shaded area on the one hand and regions 1 and 2 and the plasmon line on the other. The integrand is basically the dynamical structure factor which is closely related to the possible excitations of the system. With the above form of the integral we can actually separate out the various contributions to the decay of the electron.

Now we have completed the derivation of the electron self-energy from electron-electron interactions. However the integrals in the line-part is rather slowly converging. This is improved if we use the approach with the artificial dielectric function.

We have used RS to calculate the electron self-energy. A competing approach is the so-called Brillouin-Wigner (BW) perturbation theory. It has the benefit of being self-consistent. However, our experience is that RS, although not being self-consistent, is still to be preferred.

As the last example we give one where the RS theory has been applied to real metals. We used the imaginary part of the RS electron self-energy to find the inelastic electron-mean-free-path in metals. In figure 9 of [42] we compared our theoretical results for Li and Na with the corresponding experimental photoemission data presented in [43]. Also, here the agreement was good.

Appendix written by B.E.S.

Appendix B. Surface structure search by multiple scattering program LEEDFIT

B.1. Crystal potential with overlapping MT spheres

The phase shift program EEASISSF is combined with the LEED multiple scattering program LEEDFIT. The phase shifts are calculated for the specific structure model defined in the LEED input file. The combination of the two programs performs the optimisation of the muffin-tin (MT) potential model in the LEED-I(V) analysis, and also to check the validity of the Sernelius’s model for energy dependent exchange-correlation (XC) potential.
understood that phase shifts are referred to atoms. In order to limit the number of active phase shifts, the set of potential minimum and maximum MT radii, type is given in the LEEDFIT input. Each atom type comprises three parameters for the construction of the MT symmetrically different bonds, C-H, C-C, and C-S. The assignment of each atom to the corresponding atom variable between 0.0 to 1.0 and is maximum radius is limited by the NN distance. The four surface structures investigated in a LEED investigation there are in principle 3 instances during the structural r-factor minimization, LEEDFIT delivers iterated MT parameters to EEASISSS. This cannot be done when the MT parameters are changed, then the bulk backscattering matrices have to be recalculated. The LEEDFIT program is here reorganized in such a way that MT parameters and structural parameters are optimizable simultaneously or separately. Each iteration of phase shifts gives rise to a new set of scattering matrices, and a special flow chart of LEED calculation is required in order to maintain bearable calculation times.

Lower and upper limits of MT radii are chosen automatically by LEEDFIT from the structure data. From interatomic distance $d_{\text{NN},i}$, the minimal radius is set somewhat smaller than the midpoint radius, while the maximum radius is limited by the NN distance. The four surface structures investigated in figure B1 indicate approximate limits for the MT radii: $R_{\text{min},i} = 0.3 \times d_{\text{NN},i}$ and $R_{\text{max},i} = 0.9 \times d_{\text{NN},i}$. The overlap parameter $S_i$ is chosen variable between 0.0 to 1.0 and is fitted by r-factor minimization. $S_i$ can be chosen either as a single parameter common to all atom types or as separate overlap parameter for each different atom type. At repeated instances during the structural r-factor minimization, LEEDFIT delivers iterated MT parameters to EEASISSS that correspondingly generates iterated phase shifts.

Figure B1 shows r-factors a function of overlap S for four surface structures investigated in this work; the I(V) curves are available from best fit structure data; a common overlap turned out sufficient in each case. The results for three of four cases show minimum r-factor in $S$ range 0.2 − 0.4. Ag(111)- (4 × 4) -O is an exception, where the minimum occurs at $S = 0.75$. Its r-factor remains constant at larger overlaps due to the maximum MT radius. The same situation appears for Ru(0001)- (6 × 3)R30°-Cl at $S = 0.7$.

We conclude that for initial structure search and refinement a value of $S = 0.3$ can be chosen for most atoms. Changing MT parameters requires a subsequent refinement of structural parameters. When a good model is found, an optimum overlap parameter is determined in a final refinement by a grid search or a fit. In the case of Ag(111)- (4 × 4) -O with minimum r-factor at $S = 0.75$, the difference to the r-factor at $S = 0.3$ is fairly small so

**Figure B1.** R-factor as function of the overlap parameter for Cu(111)- (3 √ 3 × √ 3)R30°-TMB [18], Ag(111)- (4 × 4) -O [19], Ag(111)- (7 × √ 3)R30°-SO$_4$ [20], Ru(0001)- (6 × 3)R30°-Cl [11], TMB stands for 1,3,5-tris(4-mercaptophenyl)-benzene with chemical formula C$_{24}$H$_{15}$S$_3$.\[32\]
that only minor structural differences are expected from a final refinement. The influence of the overlap parameter on the structural result has been found to be relatively small as discussed in the last section.

B.2. First LEED confirmation of electron self-energy potential

To check whether the energy dependent exchange and correlation potential meets quantitatively the experimental data a factor $f_{XC}$ was introduced to $V_{XC0}$. The influence of this variable factor on the $r$-factor in the LEED-I(V) analysis is shown in figure B2. The error bar of the minimum $r$-factor defines a range for $f_{XC}$. For the error bar the RR-factor defined by Pendry was used [17] which depends on the minimum $r$-factor and the total energy range of the I(V) curves. A minimum around 1.0 was found in three cases. For Ru(0001) - ($\sqrt{3} \times \sqrt{3}$) R30°-Cl only few data could be measured due to the small unit cell. The minimum $r$-factor occurs here at a slightly lower value but the $r$-factor curve is very flat and the value $f_{XC} = 1.0$ lies in any case within the confidence interval. It appears sufficient to start the analysis with $f_{XC} = 1.0$ and to find the optimum with the final result.

It should be noted that the experimental data include potential shifts from polarized adsorbates and further experimental errors due to measurement of the energy of the incident beam. Therefore, the parameters which are fitted in the I(V) analyses describe the energy dependence of the inner potential, which is the difference between the external energy and the internal energy. These parameters deviate necessarily from the parameters for $V_{XC}$ which are determined from Sernelius’s model for the electron exchange and correlation potential. The experimental determined energy dependence of the inner potential does not directly proof the correctness of the model of $V_{XC}$. The scattering inside the crystal takes place at energies given by the MT zero and $V_{XC}(E)$. Nevertheless, the finding that the minimum $r$-factor occurs at values $f_{XC} \sim 1.0$ confirm the validity of Sernelius’s model for the XC interaction.

B.3. Influence of the upper and lower limit on the MT radii

The lower and upper limits for the MT radii are automatically determined in the LEED program from the average NN distance for all atom types. An influence on the result is only found if $R_{\text{min},i}$ has been chosen to small or too large. In the phase shift program the MT radius for each atom type is chosen to be within the lower and upper limit. Mostly the limits $R_{\text{min},i} = 0.3 \times d_{\text{NN},i}$ and $R_{\text{min},i} = 0.9 \times d_{\text{NN},i}$ are sufficient. The DE algorithm [23] in the phase shift program increases the actual MT radii by the overlap parameter for each atom type. The criterion is to find a step-free MT potential. The parameter $R_{\text{min},i}$ provided from the LEED program sets therefore a lower limit for the overlap parameter. There is a range for the overlap parameter $S$, where the actual MT radii remain within the limits and the $r$-factor remains at the minimum. It can nevertheless occur in some structure models that lower values for $R_{\text{min},i}$ should be chosen.

(i) If the lower limit is too small the MT spheres do not touch, the phase shifts are not correct and the $r$-factor for the comparison with experimental data becomes worse. The lower limit has to be increased.

(ii) If the lower limit is too large two cases can occur. Either the MT radius of at least one atom type cannot be chosen such that a step-free potential can be found. Then the phase shift program fails. Or the MT radius of at least one atom reaches the upper limit, the MT radii are not correctly chosen and the $r$-factor increases.

Figure B2. Influence of the self energy fitness factor $f_{XC}$ on the $r$-factor for the 4 structures investigated here. Labelling of the curves is same as in figure B1. The range of each $f_{XC}$ curve extends between the end points of the dash-dotted RR line. $f_{XC}$ value is measured at curve minimum and error bars from RR range: 1.00 ± 0.1 (red), 0.94 ± 0.1 (brown), 1.06 ± 0.1 (green), and 0.89 ± 0.2 (blue).
B.4. Influence of the potential model on the structural parameters

Different phases of the scattering factors lead to slightly different atomic positions if the structure is fitted. That means three sets of radial MT parameters add to the number of fit parameters in the structure analysis. Fortunately, it is not necessary to fit all parameters at once.

Usually, the phase shifts are not updated in each iteration of a fit or structure search procedure. If an optimum model is found the parameters for the phase shifts can be optimized separately keeping the structural parameters fixed. In a subsequent final fit the structure parameter are found with optimized phase shifts. In three of the four cases investigated here where 20 – 50 structural parameters were optimized we have found a noticeable improvement in the order of 0.02 up to 0.05 of Pendry’s r-factor.

Figure B3 shows the r-factor as function of the general overlap parameter with structural parameters from a previous analysis and the same calculation with the final structural parameters. The two curves are mainly parallel and show the same minimum for the overlap parameter. This demonstrates that the MT potential can be separately optimized in a final step, and a simultaneous refinement of all parameters including the MT potential seems not necessary.

The average change in the atomic positions is in the range of 0.02 – 0.05 Å. In several cases a change of a single coordinate of an oxygen atom in the order of 0.1 Å appeared. The structural changes remained in all cases within the error bars of the analysis.

ORCID iDs

John Rundgren https://orcid.org/0000-0002-7023-2603
Bo E Sernelius https://orcid.org/0000-0002-6281-868X
Wolfgang Moritz https://orcid.org/0000-0001-9036-1958

References

[1] Hofmann J P, Rohrlack S F, Hess E, Goritzka J C, Krause P P T, Seitzonen A P, Moritz W and Over H 2012 Surf. Sci. 606 297
[2] Saladin D K and Spence J C H 1994 Ultramicroscopy 55 397
[3] Walter S, Blum V, Hammer L, Müller S, Heinz K and Giesen M 2000 Surf. Sci. 458 155
[4] Vuorinen J, Pussi K, Diehl R D and Lindroos M 2012 J. Phys. Condens. Matter 24 015003
[5] Mattheiss L F 1964 Phys. Rev. 133 184
[6] Loucks T 1967 Augmented Plane Wave Method (New York, NY: Benjamin)
[7] Barbieri A and VanHove M A 2007 Phase Shift Package www.icts.hkbu.edu.hk/vanhove/VanHove_files/phshift2007.zip
[8] Krasovskii E E and Strocov V N 2009 J. Phys.: Condens. Matter 21 314009
[9] Briggs J N 2004 Target Detection by Marine Radar (London: The Institution of Engineering and Technology)
[10] Hedin L and Lundqvist S O 1969 Effects of Electron-Electron and Electron-Phonon Interactions on the One- Electron States of Solids (New York: Academic)
[11] Ashcroft N W and Mermin N D 1976 Solid State Physics (Philadelphia: Saunders College)
[12] Lindhard J 1954 Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd. 28 47
[13] Ebert H, Kedderitzsch D and Minár J 2011 Rep. Prog. Phys. 74 096501
[14] Gonis A and Butler W H 2012 Multiple Scattering in Solids (Berlin: Springer)
[15] Rice T M 1965 Ann. Phys. 31 100
[16] Shung K W K, Sernelius B E and Mahan G D 1987 Phys. Rev. B 36 4499
[17] Pendry J B 1980 J. Phys. C 13 937
[18] Sirtl T, Jelic J, Meyer J, Das K, Heckl W, Moritz W, Rundgren J, Schmittel M, Reuter K and Lackinger M 2013 Phys. Chem. Chem. Phys. 15 11054
[19] Reichelt R, Günther S, Winterlin J, Moritz W, Aballeb L and Mentes T O 2007 J. Chem. Phys. 127 134706
[20] Wyrwich R et al 2018 J. Global Opt. 11 341
[21] Shirley E L 1995 (private communication), eric.shirley@nist.gov
[22] Kotochigova S, Levine Z H, Shirley E L, Stiles M D and Clark C W 1997 Phys. Rev. A 55 191
[23] Sirtl T, Jelic J, Meyer J, Das K, Heckl W, Moritz W, Rundgren J, Schmittel M, Reuter K and Lackinger M 2013 Phys. Chem. Chem. Phys. 15 11054
[24] Storn R and Price K 1997 J. Global Opt. 11 341
[25] Neve J, Rundgren J and Westrin P 1982 J. Phys. C 15 4391
[26] Watson R E, Herbst J F, Hodges L, Lundqvist B I and Wilkins J W 1976 Phys. Rev. B 13 1463
[27] Abramowitz M and Stegun I A (ed) 1967 Handbook of Mathematical Functions (New York, NY: Dover)
[28] Mott N F and Massey H S W 1965 The Theory of Atomic Collisions (Oxford: Clarendon)
[29] Abramowitz M and Stegun I A (ed) 1967 Handbook of Mathematical Functions (New York, NY: Dover)
[30] Monteforte S, Caliari E and Gorini K M 1975 Computer Solutions of Ordinary Differential Equations (San Francisco: Freeman)
[31] Rundgren J 2007 Phys. Rev. B 76 195441
[32] Moritz W 2021 LEEDFIT program wolfgang.moritz@lrz.uni-muenchen.de
[33] Moritz W and VanHove M A 2022 Surface structure determination by LEED and X-rays In press (Cambridge: Cambridge University Press)
[34] Rundgren J 2003 Phys. Rev. B 68 125405
[35] Nascimento V B, Moore R G, Rundgren J, Zhang J, Cai L, Jin R, Mandrus D G and Plummer E W 2007 Phys. Rev. B 75 035408
[36] Sernelius B E 2018 Fundamentals of van der Waals and Casimir Interactions (Switzerland: Springer) (https://doi.org/10.1007/978-3-319-99831-2)
[37] Sernelius B E 1983 Phys. Rev. B 27 6234
[38] Sernelius B E 1986 Phys. Rev. B 34 8696
[39] Sernelius B E 1986 Phys. Rev. B 34 8696
[40] Meng F, Thomson M D, Sernelius B E, Jörgen M and Roskos H G 2015 Phys. Rev. B 91 075201
[41] da Silva A F, Levine A, Momtaz Z S, nd Bo H B and Sernelius B E 2015 Phys. Rev. B 91 214414
[42] da Silva A F, Sandoval M A T, Levine A, Levinson E, Boudinov H and Sernelius B E 2020 J. Appl. Phys. 127 045705
[43] Johansson L I and Sernelius B E 1994 Phys. Rev. B 50 16817
[44] Wertheim G K, Riffe D M, Smith N V and Citrin P H 1982 Phys. Rev. B 46 1955