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RELATIVISTIC THEORY OF LOW ENERGY
ELECTRON DIFFRACTION

by

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Abstract

In view of investigating the role of spin polarization and further relativistic effects in the diffraction of low energy electrons (LEED) by crystals composed of heavy atoms, a relativistic dynamical theory is developed for calculating LEED intensities and spin polarizations. The presentation of the general framework of solving the boundary value problem for the mixed-representation Dirac equation is followed by the construction of a relativistic KKRZ-type electron-ion-core pseudopotential. The solution of the Dirac equation inside a model crystal that consists of this potential plus a bulk and surface optical potential is then derived in an algebraic form. Provision is made for taking into account thermal lattice effects.

The computational application of this relativistic LEED theory to the (001) and the (110) surface of tungsten firstly yields intensity results that are found to be in good agreement with experimental data. Secondly, appreciable spin polarization features are predicted, in particular in the specular beam for large angles of incidence on W(001) at very low energies. It is concluded that measurement of spin polarization in LEED can be expected to be a valuable tool for obtaining additional information about the surface region.

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1. Introduction

1.1 Low Energy Electron Diffraction

Amongst the various techniques currently in use for the investigation of solid surfaces on an atomic level, the diffraction of low energy electrons — usually referred to by the acronym LEED — appears to be one of the most promising. Electrons in the energy range from zero up to several hundred eV are scattered very strongly by ion cores and valence electrons and, therefore, penetrate only a few atomic layers into the solid. Measurement of the intensities of elastically and inelastically diffracted electrons as functions of primary energy and of polar and azimuthal angles of incidence ^{*)} hence can provide — via comparison with results from theoretical model calculations — information about a variety of physical properties of the surface region, in particular as regards atomic and electronic structure, lattice-vibrational and magnetic properties.

As for the general background of LEED, we can refer to comprehensive review articles (May 1965, Lander 1965, Estrup and McRae 1971) and hence content ourselves with a brief survey of the highlights in the development of the field. The history of LEED starts in the early days of quantum mechanics with the experiments of Davisson and Germer (1927). Bethe (1928) subsequently developed a theory of electron diffraction, in which a solution of Schrödinger's equation inside the crystal is obtained with the aid of a three-dimensional plane-wave expansion

^{*)} The most widely used form of presenting results is the "intensity-energy profile", in which, for fixed angles of incidence, the intensities of the diffracted beams are plotted against energy.

Bauer 1961, Gafner 1964, McRae and Caldwell 1964) *). The beginning of a new era in LEED theory, which is characterized by a gradual reconciliation of the two "complementary" requirements of theoretical adequacy and computational feasibility **), is marked by McRae's (1966) self-consistent multiple scattering approach and by the mixed-representation approach of Hirabayashi and Takeishi (1966), which were shortly followed by a variety of alternative "dynamical" methods (Kambe 1967a,b, Boudreaux and Heine 1967, Hofmann and Smith 1967, Beeby 1968, Marcus and Jepsen 1968a,b, McRae 1968a,b, Ohtsuki 1968, Capart 1969, Duke and Tucker 1969a,b, Gafner 1969, Jones and Strozier 1969, Pendry 1969a,b,c). From the varying extent of agreement with experimental results, in particular intensity-energy profiles, that was achieved by computations using these methods and modifications and combinations thereof ***), it can be concluded that the following three basic ingredients are indispensable for an adequate LEED theory:

- (a) accurate description of ion core scattering,
- (b) adequate treatment of intra- and interlayer multiple scattering,
- (c) incorporation of the effect of inelastic processes on elastic quantities.

*) Recently, LEED from Xe single crystal films was found to form an exception to this (Ignatievs et al 1971). Also, it has been suggested (Lagally et al. 1971, Tucker and Duke 1972) that appropriate averaging over experimental results could eliminate multiple scattering features and therefore allow an interpretation of such averaged curves in terms of kinematic theory. A constructive criticism of "averaging methods" has been given by Pendry (1972).

**) An essential prerequisite for this reconciliation was the advent of high-speed digital computers.

***) For a survey cf. (Laramore 1972).

The accuracy of agreement between theory and experiment that has been reached lately, and the wealth of information about the surface region that can be extracted therefrom, are most impressive in the work of Jepsen et al. (1972a,b), who applied the "layer-KKR method" *) to several clean low index faces of Al, Ag and Cu for various angles of incidence, and of Andersson and Pendry (1973), who applied an essentially similar formalism to a system consisting of an epitaxial layer of Na on a Ni(001) substrate. The information retrieval through LEED at its present stage still proceeds in a trial and error manner, i.e. intensities for various trial structures are computed and compared with experimental data. This procedure is practicable for simple systems, but becomes uneconomical and even unmanageable in the case of more complicated structures. The more universal tool, which could also cope with the complicated cases, — the solution of the inverse scattering problem —, still remains to be found, but an important step towards this goal has been made recently by Gersten and McRae (1972) in a theoretically very appealing complex-analysis approach to LEED.

In conclusion of this brief survey on LEED, we wish to emphasize that very encouraging progress has been made during the rapid expansion of the field over the last seven years and that LEED is actually becoming a practically useful tool for detailed surface analysis.

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This approach combines an improved version of Kambe's (1967a,b) KKR-type Green's function method for the single-layer problem with the "propagation matrix method" (Marcus and Jepsen 1968) for the many-layer problem.

1.2 Spin Polarization and Relativistic Effects in Scattering of Slow *) Electrons by Atoms and Solids.

Spin polarization in electron scattering from atomic and solid targets manifests itself in essentially two forms. Firstly, given a completely polarized incident beam, the differential cross section depends on the direction of polarization of the incident beam, i.e. the differential cross section for 'spin-up' electrons differs from the one for 'spin-down' electrons. Secondly, given an unpolarized incident beam, the scattered beams become partially polarized. Since an unpolarized beam can be regarded as an incoherent superposition of an equal number of 'spin-up' and 'spin-down' electrons, the two forms of manifestation are theoretically equivalent. Due to the unavailability of intense sources of highly polarized electrons **), experiment has so far been mainly concerned with the second form, using an unpolarized primary beam and measuring intensity and degree of polarization of the scattered beams. As regards the physical origin of spin polarization in electron scattering, there are basically three different mechanisms, which could be responsible: spin-orbit coupling, exchange interaction between the incident electron and electrons in the target, and magnetic dipole-dipole interaction. It has been shown, however, that, as a consequence of the strength of the Coulomb interaction, the

*)

By "slow" we denote in the present context energies up to several keV.

**)

This situation has considerably improved over the last few years. Apart from scattering methods, which are discussed in the present Section, the following approaches appear most promising for the production of polarized electrons: field emission from ferromagnets (Chrobok et al. 1968, Obermair 1969), photo emission from ferromagnets (Busch et al 1971), photo emission from alkali atoms using either a spin-polarized target and unpolarized light (Raith 1969) or an unpolarized target and circularly polarized light (Heinzmann et al. 1970)

dipole-dipole mechanism is insignificant in comparison with the other two (Pepinski 1970). We give in the following a brief survey of theoretical and experimental results concerning spin polarization and further relativistic effects, with particular emphasis on spin-orbit-coupling-induced spin polarization effects.

Since the spin-orbit interaction is implicitly contained in the Dirac Hamiltonian, spin polarization effects can, together with further relativistic effects, be expected in 'Dirac scattering' from suitable electrostatic potentials. They were, in fact, first predicted by Mott (1929, 1932) for large-angle scattering of high-energy electrons (of about 100 keV) by large-Z Coulomb potentials, which were meant as approximations to large-Z atom potentials, and experimentally confirmed by Shull et al. (1943). The 'Mott effect' was predicted to decrease rapidly with decreasing energy, but calculations by Massey and Mohr (1941) and Mohr (1943), in which the screening of the nuclear Coulomb field by the atomic electrons was taken into account, indicated that appreciable polarization effects could be expected even at low energies (down to about 100 eV). This surprising result may be explained heuristically by viewing the slow-electron scattering as a diffraction process by an atom, whose effective radius is assumed to be spin-dependent due to the spin-orbit interaction (cf. Kessler 1969 p.8). For a detailed survey of the subsequent history and the achievements of the very flourishing field of elastic slow-electron-atom scattering we refer to comprehensive review articles (Kessler 1969, Walker 1971) and merely wish to emphasize the following results in view of their relevance for our own work. Very appreciable degrees of spin polarization have been measured for scattering by mercury and noble gas atoms at energies ranging from a few

eV to about 1 keV (e.g. Deichsel et al. 1966, Jost and Kessler 1966), and good agreement between experiment and theory (e.g. Weiss 1969) is obtained, provided that further relativistic corrections in addition to the spin-orbit coupling are taken into account (cf. Browne and Bauer 1966, Meister and Weiss 1968). As for spin polarization effects from solid targets, early experiments, e.g. by Davisson and Germer (1929), who used a double scattering set-up with 10-200 eV electrons incident on Ni(111), had failed *), and it was only fairly recently that successful measurements were reported from polycrystalline targets of Hg (Eckstein 1967) and W, Pt and Au (Loth 1967) with maximum degrees of polarization of 23% and 10%, respectively. In particular, Loth (1967) found that the polarization was sizeable only for high target temperatures, e.g. 1700 °C for W. Bearing in mind that under the poor vacuum conditions available (10^{-6} torr) the surfaces were rather contaminated and that the degree of contamination decreases with increasing temperature, it can be concluded firstly that spin polarization is very sensitive to foreign-atom adsorption, and secondly that higher degrees of polarization could be expected under ultra-high vacuum conditions as available in present-day LEED chambers.

The above positive results for scattering from large-Z atomic and polycrystalline targets strongly suggest that spin polarization and further relativistic effects should be of im-

*)

These failures could be due to various reasons, e.g. too small atomic numbers of the materials used, surface contamination by impurity atoms, insufficient energy and angular resolution, or, finally, multiple-scattering suppression of the effect at the arbitrarily chosen angles. More recently, Gervais et al. (1968) expressed their intention of conducting a double-scattering experiment with tungsten single crystals to investigate spin polarization effects. Since no positive results from this project have come to our attention, we suspect that it also failed.

portance in LEED. In fact they should, as has been pointed out by several authors (Maison 1966, McRae 1966, Kessler 1969) be even more pronounced in LEED as a consequence of multiple scattering processes. Measurement of spin polarization in LEED from large- Z solids should therefore be able to provide additional information about the surface region, which is not obtainable from pure intensity measurements, and might furthermore lead to a source of polarized electrons as well as a polarization detector that operates — in contrast to the conventional Mott detector — at low energies. In the absence of an adequate theoretical treatment *) **), we have, therefore, decided to develop a relativistic LEED theory and therefrom to obtain spin polarization predictions, which may serve as a guide for future experiments. ***)

*)

The relativistic electron diffraction theories by Halpern (1931), Hellmann (1931), Weisskopf (1935), Fujiwara (1961) and Terakura et al. (1966) are essentially relativistic versions of Bethe's (1928) nonrelativistic theory and are therefore equally unsuitable for LEED purposes (cf.p.2).

**)

While our present work was in progress, a LEED formalism that treats spin polarization and further relativistic effects (Jennings 1970) and numerical results (Jennings 1971) calculated by means of this formalism have come to our attention. For the moment, we merely note that the two approaches differ considerably from each other. A comparison of Jennings' theory and results with ours will be given in Chapters 8 and 10.4.

***)

Further, though less direct evidence for the importance of developing a relativistic LEED treatment is provided by results of energy band calculations for large- Z solids ($Z > 50$), where relativistic corrections (Johnson et al. 1963) and spin-orbit coupling (cf.e.g. Mattheiss 1965) have been found to play a significant role. In fact, most band structure calculations for large- Z metals that have been carried out since about 1965, employed the fully relativistic generalization of a nonrelativistic band structure method (mainly the relativistic orthogonalized plane wave method due to Soven (1965), the relativistic augmented plane wave method due to Loucks (1965a), the relativistic KKR methods due to Takada (1966) and Onodera and Okazaki (1966), and modifications of these methods). Since there is a close relation between LEED and energy bands — from a methodological point of view as well as with respect to the interpretation of LEED intensity-energy profiles —, the necessity of treating large- Z band structure problems relativistically suggests that the same should apply to large- Z LEED.

Before proceeding to give an outline of the present work, which mainly aims at incorporating spin-orbit-induced polarization effects, we find it pertinent to digress briefly on the polarization effects due to the second of the previously mentioned physical mechanisms, namely the exchange interaction between the incident electron and unpaired polarized electrons in the target. In the atomic domain, this mechanism has been harnessed for the production of polarized electrons by scattering unpolarized electrons from atoms with a preferential population of certain spin states, e.g. 'spin-up', which may be produced by a Stern-Gerlach experiment (Farago and Siegmann 1966). In LEED, pronounced effects are to be expected for target crystals with ordered spin structures. For antiferromagnets, the discrepancy between the magnetic and the chemical lattice periodicity leads to 'extra spots', which have actually been observed (Palmborg et al. 1969, Hayakawa et al. 1971, Suzuki et al. 1971). For ferromagnets, large spin polarization values have been predicted from kinematic theory (Vredevoe and DeWames 1968) and, recently, also from a dynamical approach (Feder 1973 b, Appendix B), but we are not aware of any experimental investigation of this effect.

1.3 Outline of the Present Work

The present work comprises two main parts: firstly the development of a relativistic LEED theory and secondly its application to LEED from clean low-index faces of tungsten.

Chapter 2 introduces the first part by exposing the basic assumptions underlying our theory. After a brief discussion of the one-electron approximation, the necessity of using the full

four-component Dirac equation is established and general features of the crystal model are outlined. In Chapter 3 we present the framework of our relativistic LEED theory. Starting from the mixed-representation Dirac equation, we formulate the boundary value problem with the aid of a 'propagation matrix' and develop a method for solving it and calculating intensities and spin polarizations of the LEED beams, without yet having specified an effective electron-solid interaction potential. This is done in the following two following chapters. The interaction of the incident electron with the ion core lattice is represented, in Chapter 4, by means of a pseudopotential that is the relativistic analogue of the KKRZ pseudopotential. We first derive this potential in configuration space and then transform it, via a momentum space representation, into the mixed representation, in which it is required in our LEED formalism. In Chapter 5 we select an imaginary optical potential to take into account the effect of inelastic bulk and surface processes and discuss briefly the real inner potential and its transition from the crystal into the vacuum. As for spin-dependent contributions to the optical potential, it is found that such are not required in the absence of a long range magnetic order. Having established a crystal potential model, we proceed, in Chapter 6, to derive a method for solving the mixed-representation Dirac equation and obtaining the propagation matrix across the crystal. Since the potential is 'factorized', the original system of integro-differential equations can be reduced to an inhomogeneous system of algebraic equations. In addition, we derive propagation matrices for continuous local surface potential barriers and for one-dimensional Delta function potentials. After having combined the relevant individual propagation ma-

trices to form the propagation matrix for the whole crystal, our formalism is complete except for taking into account the effect of thermal lattice vibrations. This is done, in Chapter 7, in an approximation, which treats the atomic motions as independent, by introducing effective phase shifts that replace the actual ones in the pseudopotential. Chapter 8 is devoted to a critical comparison between the present theory and a spin-polarized LEED formalism due to Jennings (1970, 1971bc) which is found to be a different, but essentially equivalent method.

The second part of our work, in which we apply the LEED formalism presented in the first part to clean low-index faces of tungsten, starts with introducing, in Chapter 9, several specific assumptions, which we require for performing numerical computations. In particular, we decide to obtain the phase shift input for the relativistic ion-core pseudopotential from a band structure potential. As for imaginary potential contributions that represent inelastic effects, we deduce qualitative features from experimental electron energy-loss data. A specification of the beams taken into account in the computations concludes Chapter 9. In Chapter 10, we present and discuss numerical intensity and spin polarization results obtained for the (001)- and the (110)-face of tungsten. Comparing our theoretical intensity-energy profiles with the available experimental ones, we notice generally good agreement, even for nonspecular beams and off-normal incidence. Relativistic intensity results are found to differ noticeably from their nonrelativistic counterparts that we calculated by means of a nonrelativistic analogue of our relativistic formalism. Appreciable spin polarization features are predicted under various conditions. In particular we wish

to draw attention to the fairly large spin polarization values (of about 40%) found in the specular beam from W(001) in connection with surface state resonances in the intensity-energy profiles. The effect of inelastic surface and bulk processes — as described by an imaginary δ -potential and a uniform imaginary potential contribution — on spin polarization features is subsequently investigated. A brief comparison with results predicted by an alternative spin-polarized LEED method terminates Chapter 10. In Chapter 11 we draw conclusions regarding specific applications of spin-polarization in LEED.

In order to make the mainstream of the presentation more coherent, we have relegated some parts of the work to Appendices A to G. In Appendix A, we give a brief outline of the Schrödinger-equation-based analogue of our relativistic formalism, which can be considered as a LEED method in its own right. In Appendix B, this nonrelativistic method is applied to ferromagnetic iron ^{*)}, where the exchange interaction is found to produce very appreciable spin polarization values over a fairly wide energy range. Appendices C and D are of a purely ancillary nature, mainly to Chapters 3 and 6. A practical method for calculating relativistic phase shifts for electron scattering by a central potential is outlined in Appendix E. In Appendix F, we study the scattering of electrons by a one-dimensional imaginary Delta-function potential in the relativistic and the nonrelativistic case in view of employing such a potential in our relativistic LEED formalism. Finally, a description of the computer programmes, which we used to obtain the numerical results presented in Chapter 10 and Appendix B, is given in Appendix G.

^{*)}

For reasons that are given in Appendix B, this problem, although it involves spin polarization, can be treated by means of a Schrödinger-equation-based LEED theory.

In conclusion of this 'Outline of the Present Work', we would like to mention that part of this work has already been published in scientific journal articles (Feder 1971, 1972 α , 1973 a and b).

2. Basic Assumptions

Before developing our relativistic LEED formalism, we present the theoretical model assumptions, on which it is based, with particular emphasis on the necessity of making use of the Dirac equation.

2.1 One-Electron Approximation

The interaction of an external electron with the nuclei and electrons of a solid constitutes an extremely complicated many-body problem. A rigorous application of quantum field theoretical methods, which have proved most successful for a variety of many-body problems, appears — although it can be formulated in principle (cf. eg. Feibelman et al. 1972) — at present beyond the limits set by practicality. Since we are, however, concerned only with "on the energy-shell" scattering — i.e. we restrict our attention to electrons that leave the solid without having lost or gained energy —, the "one-electron approximation", which considers the incident electron as moving in an average self-consistent electrostatic field is justified, provided that many-body and in particular inelastic effects are adequately incorporated into the one-electron Hamiltonian. We defer the discussion of how these effects can be incorporated until later (Chapter 5), and proceed to a point, which is vital for our relativistic LEED formalism, namely the justification of an effective field for electrons described by the Dirac equation. A relativistic generalization of the Hartree-Fock self-consistent field equations was first derived by Swirles (1935) and reformulated in a manner allowing the practical application to large- Z atoms by Grant (1961). Actual calculations of relativistic Hartree-Fock atomic fields were first

carried out by Coulthard (1967). For further references and a general review of relativistic atomic structure calculations we refer to (Grant 1970). An extension of the relativistic self-consistent field beyond the Hartree-Fock approximation has been given by Pratt (1963), who derived a generalized form of the Dirac equation, which includes correlation corrections. The application of a generalized single-electron Dirac equation to our problem is thus theoretically possible. Since it is bound to entail a substantial increase both in "theoretical effort" and in computational labour as compared to a Schrödinger-equation-based LEED formalism (cf. Chapter 1.1 and Appendix A), which already tends to reach the limits of the capacity of present-day computers, the question arises, however, whether the use of a two-component approximation to the full Dirac equation would not produce identical results while reducing the labour required.

Before discussing this issue, we briefly digress to state an assumption — shared with all nonrelativistic LEED theories we know of — concerning the electron beams, in particular the primary beam in the vacuum. We describe them in terms of plane waves, i.e. attribute to them infinite lateral and longitudinal coherence.*)

2.2 Dirac Equation

We discuss now, whether the treatment of spin polarization and further relativistic effects in LEED requires the four-component Dirac equation or whether adequate results could also be achieved by means of a two-component approximation.

*)

For a discussion of the consequences of a departure from this idealized assumption we refer to (Estrup and McRae 1971 p.10) and further work referenced therein.

The issue has been investigated for the scattering of low energy electrons from heavy atoms by Meister and Weiss (1968), who compared predictions forthcoming from the Dirac equation with those from the two-component approximation obtained by means of the Foldy-Wouthuysen transformation (including all terms of order α^2). From theoretical considerations these authors deduced that, as a consequence of the Coulomb (Z/r) behaviour of the atomic potential for $r \rightarrow 0$, a discrepancy should exist, which should increase with increasing atomic number Z and decreasing radial quantum number ℓ . This was subsequently explicitly confirmed by numerical results. To demonstrate the magnitude of the discrepancy, we find it appropriate to reproduce (in table 2.1) phase shifts obtained by Meister and Weiss for the scattering of 45eV electrons by Hg ($Z = 80$) atoms.

ℓ	<u>relativistic</u>		<u>nonrelativistic</u>	
	$\delta_{\ell-1}$	δ_{ℓ}	$\delta_{\ell-1}$	δ_{ℓ}
0	-1.304		-0.361	
1	-1.364	-0.981	-0.568	-0.192
2	-0.746	-1.010	-0.719	-0.641
3	0.730	-1.104	0.798	0.810
4	0.255	0.080	0.296	0.296

Table 2.1

Comparison of phase shifts calculated by means of the Dirac equation and a nonrelativistic approximation to it for scattering of 45 eV electrons by Hg atoms (Meister and Weiss 1968)

We note that the relativistic δ_0 differs very substantially from the nonrelativistic one and that the difference between corresponding phase shifts decreases with increasing ℓ . The spin polarization and the cross section calculated from the above phase shifts show a considerable discrepancy.

Since diffraction of electrons from a solid can be viewed as a superposition of scattering events from its constituent atoms

and since the effective one-electron potential at each of the atomic sites shows the same behaviour in the vicinity of the nucleus as an atomic potential, namely Z/r , we conclude from the above results that LEED from large Z solids requires indeed the use of the full four-component Dirac equation.

2.3 General Features of the Crystal Model

In the spirit of the one-electron approximation, which we have discussed in Chapter 2.1, we describe the target crystal, as seen by an incident electron, in terms of an electrostatic potential. (Although we are using the Dirac equation, there is no need for introducing magnetic potentials, since the Dirac equation is covariant with respect to Lorentz transformations and we choose as our reference system the laboratory system, which is identical with the rest frame of the crystal.). This effective electron-solid potential can be regarded as consisting of two main ingredients: firstly, a potential describing the interaction of the incident electron with the ion cores inside the solid, and secondly, a contribution representing the effect of the interaction with the valence electrons of the solid. Both contributions have been realized to be of importance in LEED and are — in more or less accurate approximations and with different relative weighting — actually incorporated in current dynamical LEED theories (for references cf. Chapter 1.1). The specific forms, in which the potential contributions enter in our relativistic LEED theory, will be presented later (in Chapters 4 and 5), and we now merely discuss three general assumptions which we make regarding the effective potential.

Firstly we assume the potential as being of infinite extension in planes parallel to the surface and of perfect two-

dimensional periodicity in such planes. This implies in particular that we disregard random structural features, such as steps and surface roughness, which are present on real crystal surfaces. The effect of such features on LEED patterns and intensity results has been investigated (cf. e.g. Heckingbottom 1969, Houston and Park 1971) and it appears that, as long as the scale of the imperfections is considerably larger than the coherence width of the primary electron beam, the assumption of an ideal surface is reasonable. An 'a posteriori' justification of this assumption — as well as of the plane-wave description of the electron beams — is provided by the agreement between experimental data and results predicted by the leading theories of LEED (cf. Chapter 1.1), which all share these assumptions.

Our second general assumption about the effective crystal potential is that we consider it as having only finite extension in the direction perpendicular to the surface, i.e. we assume the crystal as consisting only of a finite number of atomic layers. This appears justified by the fact that the penetration depth of low energy electrons into the solid is, as a consequence of inelastic scattering processes and of the strength of the ion-core scattering, very limited (of the order of 3 to 10 Å) (cf. Duke and Tucker 1969, Bauer 1970). The validity of this assumption has also been explicitly confirmed by numerical calculations of LEED intensities from aluminium (Jepsen et al. 1971a), in which the specular beam intensity-energy profile produced by four atomic layers was already very close to the one produced by a semi-infinite crystal. *)

*)

From a practical computational point of view, a finite-crystal assumption may give rise to difficulties (D.W. Jepsen 1971 private communication, R. Feder 1972 unpublished result). As soon as — for a given number of layers — the number of evanescent

Thirdly, we specify the crystal further by distinguishing between a "selvedge" and a "substrate" (cf. Mc Rae 1968). The substrate consists of a number L_2 of equidistant layers of identical geometrical structure and identical atomic scattering properties such that the surface projections of the atomic sites of adjacent layers may differ by a fixed translation vector $\mathbf{q}$. Designating by $\tilde{L}_2$ the number of consecutive layers such that $\tilde{L}_2 \mathbf{q}$ is a plane lattice vector, we note that the finite crystal assumption may entail $L_2 < \tilde{L}_2$. The selvedge^{**)} consists of a surface optical potential (cf. Chapter 5) and of L_1 layers, whose geometrical structure, atomic scattering properties and inter-layer spacing may differ from the corresponding bulk properties. Allowing for different atomic scattering properties, we make provision for chemically "foreign" atoms and for atoms, which are of the same chemical species as those in the bulk, but are inequivalent as a result of the modification of the electronic environment near the surface.

*) (continued from page 18)

waves —which are exponentially increasing or decreasing — exceeds a certain limit, round-off errors introduced by the computer lead to a divergence of the numerical results. Since the semi-infinite crystal model, on the other hand, requires a matrix diagonalization, which is more time-consuming than the solution of the finite-crystal problem, we give, in view of the appreciable increase in computing time expected as a consequence of the relativistic treatment, preference to the finite-crystal assumption.

**)

Although the model crystal is finite, we assume only one selvedge — on the 'reflection side' — since the 'transmission side' surface is only a theoretical artifact, the detailed properties of which should not significantly affect numerical LEED results. If they do, this is an indication that the number of layers was chosen too small.

3. Framework of Relativistic LEED Formalism

Having established the necessary basic assumptions, we now proceed to develop the general framework of a relativistic LEED formalism. Without yet assuming a specific crystal potential, we derive general expressions for the intensities and spin polarizations of the diffracted beams as functions of the energy, the orientation and the polarization vector of the primary beam.

3.1 Dirac Equation in Mixed Representation

As motivated in Chapter 2.2, we choose as the dynamical basis of our formalism a generalized version of the time-independent Dirac equation in its covariant form (cf. Pratt 1963)*)

$$(-i\gamma^0 w + \sum_{k=1}^3 \gamma^k \partial_k + 1) \psi(\underline{r}) = -i\gamma^0 \int d^3 \underline{r}' v(\underline{r}, \underline{r}') \psi(\underline{r}'), \quad (3.1)$$

where w is the energy of the incident electron and $v(\underline{r}, \underline{r}')$ is a complex potential operator involving γ -matrices, that describes the effective electron-solid interaction. The perfect periodicity of the crystal model, and therefore of $v(\underline{r}, \underline{r}')$, in planes parallel to the surface — which is taken as the (x, y) -plane — suggests the following two-dimensional Fourier expansions (cf. Laue 1931, Hirabayashi and Takeishi 1966, Marcus and Jepsen 1968) of the potential and the four-spinor $\psi(\underline{r})$:

$$v(\underline{r}, \underline{r}') = \sum_{k\ell} v_{k\ell}(z, z') \exp(-i g_k \cdot \underline{r}' + i g_\ell \cdot \underline{r}) \quad , \quad (3.2a)$$

*)

We use natural units $\hbar = c = m_e = 1$ (where m_e is the electron mass) and the metric tensor $g^{\mu\nu}$ as given in Appendix C. Some pertinent remarks on our use of the Dirac γ -matrices may also be found in Appendix C.

$$\psi(\underline{r}) = \sum_{\underline{l}} \psi_{\underline{l}}(z) \exp(i \underline{k}_{\underline{l}} \cdot \underline{r}), \quad \underline{k}_{\underline{l}} = \underline{k}_0^{\parallel} + \underline{g}_{\underline{l}}, \quad (3.2b)$$

where $\underline{k}_0^{\parallel}$ is a surface-plane wave vector, which is still to be defined and $\underline{k}, \underline{l}$ enumerate the plane reciprocal lattice vectors $\underline{g}_{\underline{l}}$ in an arbitrary, but definite order, in principle up to infinity, in practice up to a finite N , the value of which depends on the convergence properties of the potential and on the degree of accuracy desired for the intensity and spin polarization results. To obtain a more concise notation, we introduce the column vector $\psi(z) = (\psi_1(z), \dots, \psi_2(z))^T$, the $(N \times N)$ diagonal matrices K^X and K^Y with elements $k_{\underline{l}}^X$ and $k_{\underline{l}}^Y$, respectively, and the $(4N \times 4N)$ -matrix $V(z, z')$ with elements $v_{\underline{k}\underline{l}}(z, z')$. *) Substitution of eqs.(3.2) into eq.(3.1) then yields

$$[\partial_z + i\gamma^0 \gamma^3 W + \gamma^3 (1 + i\gamma^1 \otimes K^X + i\gamma^2 \otimes K^Y)] \hat{\psi}(z) = i\gamma^0 \gamma^3 \int dz' V(z, z') \hat{\psi}(z'), \quad (3.3)$$

where " $\otimes$ " denotes the tensor product between γ -matrices and $(N \times N)$ -matrices. Eq.(3.3) constitutes in general a system of $4N$ integro-differential equations, the method of solution of which will depend on the properties of $V(z, z')$.

3.2 Boundary Value Problem

In accordance with the finite-crystal assumption (cf. Chapter 2.3) we now specify the diffraction problem as follows. A monochromatic electron beam, characterized by a four-spinor u_i and a wave vector $\underline{k}_0 = (\underline{k}_0^{\parallel}, k_0^z)$, is incident from $z = -\infty$ on the potential $v(\underline{r}, \underline{r}')$, which is confined between z_1 and z_2 . **) Denoting the solutions $\psi(\underline{r})$ of eq.(3.1) by $\psi_I(\underline{r})$ for $z < z_1$, $\psi_{II}(\underline{r})$ for $z_1 \leq z \leq z_2$ and $\psi_{III}(\underline{r})$ for $z > z_2$, and using eq.(3.2b), we find

*) Since the original potential operator contains γ -matrices, each $v_{\underline{k}\underline{l}}(z, z')$ is actually a (4×4) -matrix.

**) i.e. z_1 and z_2 are chosen such that $V(z, z') = 0$ for $z, z' < z_1$ and $z, z' > z_2$.

$$\psi_X(\underline{r}) = \sum_{\ell} \psi_{X\ell}(z) \exp[i(\underline{k}_X^{\parallel} + \underline{q}_{\ell}) \cdot \underline{r}] \quad , \quad (3.4)$$

where $X = I, II, III$ and $\underline{k}_I^{\parallel} = \underline{k}_0^{\parallel}$. Since the solutions $\psi(\underline{r})$ have to be continuous at the boundaries z_1 and z_2 for arbitrary x and y , it follows that $\underline{k}_{III}^{\parallel} = \underline{k}_{II}^{\parallel} = \underline{k}_I^{\parallel} = \underline{k}_0^{\parallel}$, and the continuity equations can be written in the form

$$\hat{\psi}_I(z_1) = \hat{\psi}_{II}(z_1) \quad , \quad \hat{\psi}_{II}(z_2) = \hat{\psi}_{III}(z_2) \quad . \quad (3.5)$$

The solutions in the vacuum have the plane wave components

$$\psi_{I\ell}(z) = u_i \delta_{i\ell} e^{ik_{\ell}^z(z-z_1)} + u_{r\ell} e^{-ik_{\ell}^z(z-z_1)} \quad , \quad \psi_{III\ell}(z) = u_{t\ell} e^{ik_{\ell}^z(z-z_1)} \quad , \quad (3.6)$$

where k_{ℓ}^z is determined from energy conservation as

$$k_{\ell}^z = \sqrt{w^2 - (\underline{k}_0^{\parallel} + \underline{q}_{\ell})^2 - 1} \quad (3.7)$$

and the spinors u_i , $u_{r\ell}$, $u_{t\ell}$ characterize the incident beam, the ℓ th reflected and the ℓ th transmitted beam, respectively. From eq.(3.7) one can see that for a given energy w only a limited number of solutions will have real k_{ℓ}^z , i.e. actually emerge from the crystal and represent observable LEED beams. These solutions are referred to as 'propagating', those with imaginary k_{ℓ}^z as 'evanescent' waves.

The solution $\hat{\psi}_{II}(z)$ inside the crystal is obtained from the system of integro-differential equations eq.(3.3). Since the method of actually solving this system depends strongly on the type of potential that one has chosen —e.g. straightforward numerical integration in the case of a local potential or some iterative method for a highly non-local potential —, this item will be treated later (in Chapter 6), after a particular potential mo-

del has been adopted. There is, however, a general feature of the solution, which allows us to proceed with the formulation of our theory without yet specifying a potential. Since eq.(3.3) comprises $4N$ first-order linear equations, we can relate the solution $\hat{\psi}_{II}(z_2)$ to an arbitrary initial solution $\psi_{II}(z_1)$ by means of a $(4N \times 4N)$ 'propagation matrix' $\hat{M}(z_2, z_1)$ (cf. Marcus and Jepsen 1968, Feder and Meister 1969):

$$\hat{\psi}_{II}(z_2) = M(z_2, z_1) \hat{\psi}_{II}(z_1) \quad (3.8)$$

The columns of $\hat{M}(z_2, z_1)$ can be obtained by solving eq.(3.3) successively with the columns of $\hat{M}(z_1, z_1) = 1_{4N}$ as initial values. Since any (4×4) -matrix can be represented as a linear combination of the 16 basis elements of the Dirac algebra (cf. Appendix C), we can write $\hat{M}(z_2, z_1)$ in the form

$$\hat{M}(z_2, z_1) = \sum_{\epsilon=\pm} \sum_{\mu=1}^8 (\Gamma_{\mu} \otimes D_{\epsilon}^{\mu}(z_2, z_1)) P_{\epsilon}, \quad (3.9)$$

where the set $\{\Gamma_{\mu}\}$ is the sub-algebra

$$\{1, \gamma^1, \gamma^2, \gamma^1\gamma^2, \gamma^3, \gamma^1\gamma^3, \gamma^2\gamma^3, \gamma^1\gamma^2\gamma^3\}. \quad (3.10)$$

The $D_{\epsilon}^{\mu}(z_2, z_1)$ are $(N \times N)$ -matrices, the n^{th} columns of which result from the n^{th} beam initial value problem, and the projection operator P_{ϵ} is given, together with its essential properties, by

$$P_{\epsilon} = \frac{1}{2} (1 + \epsilon \gamma^0 \gamma^3), \quad P_{\epsilon}^2 = P_{\epsilon}, \quad P_{\epsilon} P_{-\epsilon} = 0; \quad (3.11a)$$

$$P_{\epsilon} \Gamma = \Gamma P_{\epsilon} \text{ for } \Gamma = \gamma^1, \gamma^2, \gamma^1\gamma^2 \text{ and } P_{\epsilon} \gamma^3 = \gamma^3 P_{-\epsilon}, \quad (3.11b)$$

$$P_{\epsilon} (A + \gamma^0 \gamma^3 B) = P_{\epsilon} (A + \epsilon B), \quad (3.11c)$$

where A, B are arbitrary $(N \times N)$ -matrices and $\epsilon = \pm$.

Assuming the propagation matrix $\hat{M}_C = \hat{M}(z_2, z_1)$ as known, we now present a formal solution to the boundary value

problem as given by eq.(3.5). With the aid of eqs.(3.6) and (3.8) we obtain

$$\hat{u}_t = \hat{M}_c (\hat{u}_i + \hat{u}_r) \quad , \quad (3.12)$$

from which we proceed to express the "reflected hyper-spinor" $\hat{u}_r$, which contains the information about the intensities and polarization vectors of the LEED beams, and the "transmitted hyper-spinor" $\hat{u}_t$ in terms of the "incident hyper-spinor" $\hat{u}_i$, which represents the primary beam and is therefore assumed as known. At first sight, the problem appears to be undetermined, consisting of $4N$ equations for $8N$ unknowns. However, of the four components of each spinor u_s — $s = i, r, t$ — only two are independent; the other two can be determined by means of the Dirac equation in momentum space

$$\gamma^3(1 + i\gamma^1 K_s^x + i\gamma^2 K_s^y) \hat{u}_s = -i(K_s^z + \gamma^0 \gamma^3 w) \hat{u}_s \quad , \quad (3.13)$$

where $s = i, r, t$. The $(N \times N)$ -diagonal matrices K_s^x , K_s^y and K_s^z are defined with elements k_{sl}^x , k_{sl}^y and k_{sl}^z , respectively, so that the following relations hold between them

$$K_i^{x,y} = K_r^{x,y} = K_t^{x,y} \quad , \quad K_r^z = -K_i^z \quad , \quad K_t^z = K_i^z \quad . \quad (3.14)$$

In order to solve eq.(3.12), we require an explicit relation between the dependent and the independent components of each of the spinors $\hat{u}_s$. To this end we decompose these spinors by means the projectors operators P_ϵ (cf. eq.(3.11)) as follows:

$$\hat{u}_s = \sum_{\epsilon=\pm} P_\epsilon u_s =: \hat{u}_s^+ + \hat{u}_s^- \quad . \quad (3.15)$$

Multiplication of eq.(3.13) by P_+ readily yields a connection between $\hat{u}_s^+$ and $\hat{u}_s^-$:

$$\hat{u}_s^+ = (w + K_s^z)^{-1} \otimes \gamma^3 \left(\sum_{\mu=1}^3 \gamma_\mu I_s^\mu \right) \hat{u}_s^- \quad , \quad (3.16a)$$

where the Γ_μ are Dirac matrices as given by eq. (3.10), and

$$I_S^1 = i 1_N, \quad I_S^2 = -K_S^x, \quad I_S^3 = -K_S^y. \quad (3.16b)$$

Expressing the propagation matrix $\hat{M}(z_2, z_1)$ according to eq. (3.9), we obtain from eq. (3.12) through multiplication by $P_\pm$

$$\hat{u}_t^- = \left(\sum_{\mu=1}^4 \Gamma_\mu D_-^\mu \right) (\hat{u}_i^- + \hat{u}_r^-) + \left(\sum_{\mu=5}^8 \Gamma_\mu D_+^\mu \right) (\hat{u}_i^+ + \hat{u}_r^+), \quad (3.17a)$$

$$\hat{u}_t^+ = \left(\sum_{\mu=1}^4 \Gamma_\mu D_+^\mu \right) (\hat{u}_i^+ + \hat{u}_r^+) + \left(\sum_{\mu=5}^8 \Gamma_\mu D_-^\mu \right) (\hat{u}_i^- + \hat{u}_r^-). \quad (3.17b)$$

Using eq. (3.16) and eliminating $\hat{u}_t^-$ one obtains

$$\left(\sum_{\mu=1}^4 \Gamma_\mu B_r^\mu \right) \hat{u}_r^- = - \left(\sum_{\mu=1}^4 \Gamma_\mu B_i^\mu \right) \hat{u}_i^-, \quad (3.18)$$

where the $(N \times N)$ -matrices $B_{r,i}^\mu$ are sums of products between the $I_{i,r}^\mu$ and D_6^μ . The inverse of the $(4N \times 4N)$ -matrix $\left(\sum_{\mu=1}^4 \Gamma_\mu B_r^\mu \right)$ has the form $\left(\sum_{\mu=1}^4 \Gamma_\mu X_\mu \right)$, the matrices X_μ being determined by the equation

$$\left(\sum_{\mu=1}^4 \Gamma_\mu X_\mu \right) \left(\sum_{\mu=1}^4 \Gamma_\mu B_r^\mu \right) = 1, \quad (3.19)$$

which is — because of the linear independence of the Γ_μ — equivalent to a set of four equations for the X_μ . Multiplication of eq. (3.18) by $\sum_{\mu=1}^4 \Gamma_\mu X_\mu$ yields

$$\hat{u}_r^- = \left(\sum_{\mu=1}^4 \Gamma_\mu A_\mu \right) \hat{u}_i^- \quad (3.20)$$

where the A_μ are bilinear forms in X_μ and B_i^μ . The reflected spinor $\hat{u}_r$ is obtained from eq. (3.20) with the aid of eq. (3.15) and eq. (3.16a):

$$\hat{u}_r = \left(\sum_{\mu=1}^8 \Gamma_\mu A_\mu \right) P_- \hat{u}_i \quad (3.21)$$

with

$$A_5 = \sum_{\mu=1}^3 I_r^\mu A_\mu, \quad A_6 = -I_r^1 A_2 - I_r^2 A_1 + I_r^3 A_4,$$

$$A_7 = -I_r^1 A_3 - I_r^2 A_4 - I_r^3 A_1, \quad A_8 = I_r^1 A_4 + I_r^2 A_3 - I_r^3 A_2.$$

Denoting the elements of A_μ by $a_{\ell k}^\mu$ and replacing $\hat{u}_r$ and $\hat{u}_i$ by their components, eq.(3.21) is equivalent to

$$u_{r\ell} = \left(\sum_{\mu=1}^8 \Gamma_\mu a_{\ell 1}^\mu \right) P_- u_i. \quad (3.22)$$

The hyper-spinor $\hat{u}_t$ describing the transmitted beam could now be readily obtained by substituting eq.(3.21) into eq.(3.12) to yield the components $u_{t\ell}$ in a form analogous to eq.(3.22). Since the possibility of LEED in the transmission mode seems to be very remote at present — it would require thin films consisting only of a few atomic layers —, we concentrate exclusively on the reflected spinors $u_{r\ell}$, from which we are now going to obtain intensities and spin polarizations of the corresponding LEED beams.

3.3 Intensities and Spin Polarizations

We describe the spin polarization of electron beams with the aid of the covariant formalism suggested by Michel and Wightman (1955) and Michel (1959), in which the spin of an electron of four-momentum p^μ is described by a four-vector t^μ with $t^\mu t_\mu = 1$ and $t^\mu p_\mu = 0$.*) The actual spin direction is physically meaningfully identified with the spatial part of t^μ in the rest frame of the electron, where $t^0 = 0$. If we are dealing with a pure state with normalized spinor amplitude u , the statistical operator is

*)

A detailed presentation of this formalism has been given by Meister (1962). Although the covariant spin formalism shows its power mainly at relativistic energies, we prefer it, for the present low energy purpose, to an "ordinary" spin formalism (cf. e.g. Rose 1961) because of its greater mathematical elegance. As regards the work required for computing numerical results from the intensity and spin polarization expressions derived by means of the covariant formalism, it amounts to about the same as if one had used an "ordinary" spin formalism.

given by the projection operator *)

$$u \bar{u} = (1 + \gamma^5 \gamma^\mu t_\mu) (-i \gamma^\nu p_\nu + 1) / 4, \quad \bar{u} := u^\dagger i \gamma^0. \quad (3.23)$$

In order to provide in our formalism for LEED with partially polarized electrons, which includes a completely polarized and an unpolarized primary beam as limiting cases, we assume the incident beam as a statistical mixture, in which states with spin parallel and antiparallel to a given direction t_i^μ are represented with probabilities w_+ and w_- . The normalized statistical operator of the incident beam is then (cf. Meister (1962) p.103) given by

$$\rho_i := (1 + \gamma^5 \gamma^\mu t_i^\mu) (-i \gamma^\nu p_{iv} + 1) / 4, \quad (3.24)$$

where $t_i^\mu = (w_+ - w_-) t_i^\mu$ is referred to as the polarization vector of the incident beam and $(p_i^0, p_i^{1,2,3}) = (w, k_0^x, y, z)$. The (non-normalized) statistical operator ρ_{rl} that describe the l th reflected beam is obtained from eq.(3.22) by first calculating the adjoint spinor

$$\bar{u}_{rl} = \bar{u}_i P_+ \left(\sum_{\mu=1}^8 \Gamma_\mu \tilde{a}_l^\mu \right), \quad \tilde{a}_l^\mu = -(-1)^{\delta_{1\mu}} (-1)^{\delta_{8\mu}} a_l^{\mu*}. \quad (3.25)$$

We then denote the statistical operators relating to pure states of opposite spin alignment by ρ_{rl}^+, ρ_{rl}^- and ρ_{il}^+ and ρ_{il}^- , and use the relation

$$\rho_{xl} = w_+ \rho_{xl}^+ + w_- \rho_{xl}^-, \quad x = r, l, \quad (3.26)$$

which follows immediately from eq.(3.24). to obtain

$$\rho_{rl} = \left(\sum_{\mu=1}^8 \Gamma_\mu a_l^\mu \right) P_- \rho_i P_+ \left(\sum_{\mu=1}^8 \Gamma_\mu \tilde{a}_l^\mu \right), \quad (3.27)$$

*)

Our notation implies summation from 0 to 3 over co- and contra-gradient unspecified indices (in eq.(3.23) μ and ν).

where $\tilde{\alpha}_\ell^\mu$ is defined as in eq.(3.25).

The intensity R_ℓ of the ℓ th reflected beam (relative to the intensity of the incident beam, which has been chosen as unity) is now obtained by substituting eq.(3.24) into eq.(3.27) and calculating the trace of $\rho_{r\ell}$ (for details of this calculation cf. Appendix D.1).

$$R_\ell = \left\{ (w+k_0^z) \sum_{\mu=1}^4 |\alpha_\ell^\mu|^2 + 2[(w+k_0^z)\xi_i^x - k_0^x(\xi_i^0 + \xi_i^z)] \operatorname{Re} [\alpha_\ell^1 \alpha_\ell^{3*} + \alpha_\ell^2 \alpha_\ell^{4*}] + 2[(w+k_0^z)\xi_i^y - k_0^y(\xi_i^0 + \xi_i^z)] \operatorname{Re} [-\alpha_\ell^1 \alpha_\ell^{2*} + \alpha_\ell^3 \alpha_\ell^{4*}] + 2(\xi_i^0 + \xi_i^z) \operatorname{Im} [\alpha_\ell^1 \alpha_\ell^{4*} + \alpha_\ell^2 \alpha_\ell^{3*}] \right\} / (w - k_\ell^z). \quad (3.28)$$

We note that in this expression all the additive terms except the first one depend linearly on the components ξ_i^μ of the polarization vector of the incident beam. Therefore, for an unpolarized primary beam the intensities R_ℓ of the LEED beams are simply given by the first term in eq.(3.28), whereas for a partially polarized primary beam, the R_ℓ generally depend on the state of polarization of the primary beam. In particular we anticipate the intensities to be different for the two limiting cases of completely polarized initial beams of opposite spin alignment (i.e. $\xi_i^\mu = \pm t_i^\mu$, for $\mu = 0, 1, 2, 3$, where t_i^μ is a unit vector). Since an unpolarized primary beam can be regarded as a (50% : 50%) statistical mixture of two completely polarized ones of opposite spin alignment, this implies that the diffracted beams will be partially polarized.

The components ξ_ℓ^μ of the polarization (four-) vector of the ℓ th LEED beam can be determined from the statistical operator $\rho_{r\ell}$ (cf. eq.(3.27)) as (cf. Meister 1962 p.104)

$$\xi_\ell^\mu = \operatorname{tr} [\gamma^5 \gamma^\mu \rho_{r\ell}] / R_\ell, \quad (3.29)$$

with R_ℓ given by eq.(3.28). The evaluation of these traces proceeds in a similar manner as for the intensity and is relegated to Appendix D2. The result has the general form

$$\begin{aligned} \xi_\ell^\mu = & \left\{ (w+k_0^z) g_\ell^{\mu 1} + [(w+k_0^z) \xi_i^x - k_0^x (\xi_i^0 + \xi_i^z)] g_\ell^{\mu 2} + \right. \\ & \left. + [(w+k_0^z) \xi_i^y - k_0^y (\xi_i^0 + \xi_i^z)] g_\ell^{\mu 3} + (\xi_i^0 + \xi_i^z) g_\ell^{\mu 4} \right\} / R_\ell, \end{aligned} \quad (3.30)$$

where the coefficients $g_\ell^{\mu\nu}$, which are defined in terms of the coefficients $f_\ell^{\mu\nu}$ of eq.(D.8) in a manner that is obvious from comparison of eq.(3.31) with eq.(D.8), are simple algebraic functions of the coefficients a_ℓ^μ (i.e. the coefficients in the first rows of the result matrices A_μ of eq.(3.20)) and of k_ℓ^z . We note the structural analogy between eqs.(3.30) and eq.(3.28) as regards the dependence of the results on the momentum and spin polarization of the incident beam. Again, we obtain a particularly simple form for the case of an unpolarized incident beam. The degree of polarization P_ℓ of the ℓ^{th} reflected beam, which is more readily accessible to actual measurement than the polarization vector itself, is obtained from eq.(3.30) as

$$P_\ell = \sqrt{\xi_\ell^\mu \xi_{\ell\mu}} \quad (3.31a)$$

and thus in particular for the case of an unpolarized primary beam as

$$P_\ell = (w+k_0^z) \left(\sum_{k=1}^3 (g_\ell^{k1})^2 - (g_\ell^k)^2 \right)^{\frac{1}{2}} R_\ell^{-1}. \quad (3.31b)$$

From the above results we expect spin polarization effects in LEED. To obtain quantitative information, it is, however necessary to choose a crystal potential, which is adequate and yet not too intractable, to construct the propagation matrix explicitly and eventually to perform numerical computations.

4. Relativistic KKRZ-Type Pseudopotential for Ion Core Scattering

As stated earlier, a vital contribution to the effective electron-solid interaction consists in the interaction of the incident electron with the ion cores inside the solid. One-electron potentials that describe this interaction are extensively dealt with in the literature, mainly in connection with band structure calculations^{*)} and, more recently, also in connection with LEED (cf, e.g. Pendry 1969, Jones and Strozier 1970, Capart 1971, Pendry 1971). We can broadly classify them by distinguishing between 'actual' ion core potentials and 'pseudopotentials'. Actual ion core potentials are characterized by a Coulomb-type behaviour in the vicinity of the nuclei, as a consequence of which their plane wave expansions are very poorly convergent. Pseudopotentials^{**)} are defined as potentials that give rise to the same observable features as the actual potential under consideration, in particular to the same scattering properties, the plane wave expansions of which, however, are more rapidly convergent. Since our LEED formalism is based on a two-dimensional Fourier expansion of the potential (cf.eq.(3.2a)), it is clear that we have to employ a pseudopotential in order to make the method computationally viable^{***)}. In our search for an appropriate pseudopotential we note that, by definition, it has to produce

*)

The basic ideas of this vast area of solid state research and references to the 'classical' literature are part of standard textbooks on solid state physics (e.g. Harrison 1970, Ziman 1972). A comprehensive view of the current state of development of the field may be gained from the proceedings of a recent conference (Marcus et al. 1971).

**)

For a review of this subject cf. (Heine 1970).

***)

The use of a pseudopotential was also realized by Jepsen and Marcus as essential for the applicability of the original version of their propagation matrix method (Marcus and Jepsen 1968, Marcus et al. 1969) to real solids.

the same effect on a particle described by the Dirac equation as the actual potential ^{*}). This requirement rules out the numerous pseudopotentials described in the literature (cf. Heine 1970), since their dynamical basis is a nonrelativistic wave equation ^{**}).

We therefore proceed in the following to construct a 'relativistic' pseudopotential, i.e. a pseudopotential, which is derived with the aid of the Dirac equation. Adopting the widely used 'muffin-tin' approximation of the crystal potential, i.e. assuming the potential as spherically symmetric inside non-overlapping spheres drawn around each ion site and as constant in the interstitial regions, we first describe the relativistic scattering of an electron by a central potential and then construct an 'atomic' pseudopotential, which reproduces the scattering phase shifts of the actual ion core potential. Finally, we superimpose the individual atomic pseudopotentials at the lattice sites to obtain a crystal pseudopotential, which we transform into the mixed representation.

4.1 Scattering of a Dirac Electron by a Central Potential

Relativistic scattering of an electron by a spherically symmetrical electrostatic potential has been thoroughly investigated because of its importance in electron-atom scattering (cf. Chapter 1.2). For the general theoretical treatment, in particular by means of phase shift analysis, we can therefore refer to the literature (Rose 1961, Mott and Massey 1965) and

^{*})

We would like to emphasize that in the present work we are not concerned with setting up an actual ion core potential, but assume this to be known.

^{**})

Lately, a relativistic OPW pseudopotential was derived by Lin-Chung and Teitler (1972)

restrict ourselves to quoting results, which we require in view of our aim of obtaining a relativistic pseudopotential.

The symmetry of the potential $V(r)$ suggests that we start from the Dirac equation in polar coordinates ^{*)} (cf. Rose 1961):

$$\left[-i\beta_1 \otimes \sigma_r \left(\partial_r + \frac{1}{r} - \frac{1}{r} \beta_3 K \right) + V(r) + \beta_3 \otimes 1_2 \right] \psi(r, \vartheta, \varphi) = \omega \psi(r, \vartheta, \varphi),$$

$$\sigma_r = \underline{\sigma} \cdot \underline{r}/r, \quad K = \beta_3 \otimes (\underline{\sigma} \cdot \underline{l} + 1), \quad \underline{\sigma} = (\sigma_1, \sigma_2, \sigma_3) \quad (4.1)$$

where σ_k and β_k — $k = 1, 2, 3$ — are Pauli matrices (cf. Appendix C eq. (C.7)), and ' $\otimes$ ' denotes the tensor product. In order to solve eq. (4.1), we require the two-component spin angular function $\chi_\kappa^\mu(\hat{r})$ defined as

$$\chi_\kappa^\mu(\hat{r}) = \sum_{s=\pm\frac{1}{2}} C(\ell \frac{1}{2} j; \mu-s, s) Y_\ell^{\mu-s}(\hat{r}) \chi(s), \quad (4.2a)$$

where

$$\chi(\pm\frac{1}{2}) = \frac{1}{2} (1 \pm \sigma_3) \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (4.2b)$$

denotes Pauli spinors, and the spherical harmonics $Y_\ell^{\mu-s}(\hat{r})$ and the Clebsch-Gordan coefficients $C(\ell \frac{1}{2} j; \mu-s, s)$ are defined in the usual way. The relation between the quantum numbers κ , ℓ and j is given by

$$\kappa = \begin{cases} -(\ell+1) & \text{for } j = \ell + \frac{1}{2} \text{ (spin up)} \\ \ell & \text{for } j = \ell - \frac{1}{2} \text{ (spin down)} \end{cases} \quad (4.3)$$

We now express the four-spinor $\psi(r, \vartheta, \varphi)$ as

$$\psi = \sum_{\kappa\mu} \left\{ G_\kappa(r) \frac{1}{2} (1 + \beta_3) \otimes \chi_\kappa^\mu(\hat{r}) - i F_\kappa(r) \frac{1}{2} (1 - \beta_3) \otimes \chi_{-\kappa}^\mu(\hat{r}) \right\}, \quad (4.4)$$

where $G_\kappa(r)$ and $F_\kappa(r)$ are unknown radial functions, which are to be determined from the following equations that result from the substitution of eq. (4.4) into eq. (4.1).

*)

We follow Rose (1961) in using the 'standard representation' of the γ -matrices (cf. Appendix C).

$$\left[\partial_r + \frac{1}{r} (1-\kappa) \right] F_\kappa(r) = (\omega - V(r) - 1) G_\kappa(r), \quad (4.5a)$$

$$- \left[\partial_r + \frac{1}{r} (1+\kappa) \right] G_\kappa(r) = (\omega - V(r) + 1) F_\kappa(r). \quad (4.5b)$$

Given an actual ion core potential $V(r)$, numerical integration of the equations allows the determination of scattering phase shifts δ_κ .*) The scattering amplitudes $f(\vartheta)$ and $g(\vartheta)$ are then obtained (cf. e.g. Mott and Massey 1965) as

$$f(\vartheta) = (2ik)^{-1} \sum_{\ell} \left\{ (\ell+1) [\exp(2i\delta_{\ell-1}) - 1] + \ell [\exp(2i\delta_{\ell}) - 1] \right\} P_{\ell}(\cos \vartheta) \quad (4.6)$$

$$g(\vartheta) = (2ik)^{-1} \sum_{\ell} \left\{ -\exp(2i\delta_{\ell-1}) + \exp(2i\delta_{\ell}) \right\} P'_{\ell}(\cos \vartheta),$$

where P_{ℓ} and P'_{ℓ} denote Legendre polynomials and $k = \sqrt{\omega^2 - 1}$. Cross section and spin polarization (for an unpolarized incident beam) are given as

$$I(\vartheta) = |f(\vartheta)|^2 + |g(\vartheta)|^2, \quad P(\vartheta) = -2 \operatorname{Im} [f(\vartheta) g(\vartheta)^*] / I(\vartheta). \quad (4.7)$$

4.2 Pseudopotential in Configuration Space

The information about the actual ion core potential now being available in terms of phase shifts, we proceed to constructing a pseudopotential that reproduces these phase shifts and has good plane-wave convergence properties. Since there is an infinity of possible pseudopotentials, we tried to get some guidance from the literature on nonrelativistic pseudopotentials as to which form to choose. It appeared from a comparative study of the current forms of muffin-tin pseudopotentials and modifications thereof (Pendry and Capart 1969) that the potential derived by Ziman (1965) from the KKR secular equation (Korringa 1947, Kohn and Rostoker 1954) — commonly referred to as the

*) A very practical method for solving eq. (4.5) and obtaining the phase shifts is outlined in Appendix E. It will be used later on in the application of our LEED formalism to tungsten.

KKRZ pseudopotential — should be most suitable for LEED purposes, and was, in fact, used with success (Capart 1969). This evidence, together with the fact that the KKRZ pseudopotential coefficients can readily be expressed as analytic functions of the phase shifts, persuaded us to construct a relativistic pseudopotential which is analogous to the Schrödinger-equation-based KKRZ form.

For the atomic pseudopotential inside a muffin-tin sphere we make the 'ansatz'

$$v_{\alpha} = \sum_{\kappa\mu} B_{\kappa} \delta(r-R_{\kappa}) \frac{1}{2}(1+\beta_3) \otimes \chi_{\kappa}^{\mu}(\hat{r}) \chi_{\kappa}^{\mu}(\hat{r}'), \quad (4.8)$$

where β_3 is a Pauli matrix (cf. Appendix C) and $\chi_{\kappa}^{\mu}(\hat{r})$ is the spin angular function defined in eq.(4.2a). The summation over κ (cf. eq.(4.3)) extends in principle to infinity, in practice over the limited number of values for which $B_{\kappa} \neq 0$. The μ -summation extends from $-j$ to $+j$. We note that v_{α} is local with respect to r , but non-local with respect to ϑ and φ . Assuming basically arbitrary, but definite radii R_{κ}^{*} , the coefficients B_{κ} , which give the strengths of the δ -functions at these radii, have to be determined such that v_{α} produces the same phase shifts as the actual potential. To this end v_{α} from eq.(4.8) is substituted for $V(r)$ into eq.(4.1). Substituting $\psi(r, \vartheta, \varphi)$ from eq.(4.4) one obtains the following equations for the radial functions $F_{\kappa}(r)$ and $G_{\kappa}(r)$:

$$\begin{aligned} \left[\partial_r + \frac{1}{r}(1-\kappa) \right] F_{\kappa}(r) &= [\omega - B_{\kappa} \delta(r-R_{\kappa}) - 1] G_{\kappa}(r) \\ - \left[\partial_r + \frac{1}{r}(1+\kappa) \right] G_{\kappa}(r) &= (\omega+1) F_{\kappa}(r) \end{aligned} \quad (4.9)$$

*) The choice of these radii is arbitrary in pure theory, but rather delicate in actual calculations. The problem is further discussed in Chapter 4.4.

Applying the operator $\lim_{\epsilon \rightarrow 0} \int_{R_\kappa - \epsilon}^{R_\kappa + \epsilon} dr$ to both sides of these equations and making use of the δ -function property

$$\int_{R_\kappa - \epsilon}^{R_\kappa + \epsilon} dr \delta(r - R_\kappa) G_\kappa(r) = \frac{1}{2} (G_\kappa(R_\kappa - 0) + G_\kappa(R_\kappa + 0)) \quad (4.10)$$

we obtain

$$B_\kappa G_\kappa(R_\kappa) = -F_\kappa(R_\kappa + 0) + F_\kappa(R_\kappa - 0), \quad (4.11a)$$

$$G_\kappa(R_\kappa) = G_\kappa(R_\kappa + 0) = G_\kappa(R_\kappa - 0). \quad (4.11b)$$

For $r < R_\kappa$, $G_\kappa(r)$ and $F_\kappa(r)$ are free solutions, which satisfy the boundary condition of regularity at the origin:

$$G_\kappa(r) = j_{\ell'}(kr), \quad F_\kappa(r) = \frac{s}{w+1} k j_{\ell'}(kr), \quad (4.12)$$

where $k = \sqrt{w^2 - 1}$, $s = -\text{sign } \kappa$, $\ell' = \ell + s$, and j_ℓ and n_ℓ are the spherical Bessel and Neumann functions (cf. e.g. Abramovitz and Stegun 1965). The solutions for $r > R$, i.e. after scattering by the δ -potential, are free solutions, which are identical to the asymptotic solutions — characterized by the phase shifts δ_κ — for the actual potential.

$$G_\kappa(r) = C_\kappa [j_\ell(kr) \cos \delta_\kappa - n_\ell(kr) \sin \delta_\kappa], \quad (4.13a)$$

$$F_\kappa(r) = C_\kappa \frac{s k}{w+1} [j_{\ell'}(kr) \cos \delta_\kappa - n_{\ell'}(kr) \sin \delta_\kappa]. \quad (4.13b)$$

The constant C_κ is determined from the continuity condition of $G_\kappa(r)$ at $r = R_\kappa$ (cf. eq. (4.11)) as

$$C_\kappa = j_\ell(kR_\kappa) / [j_\ell(kR_\kappa) \cos \delta_\kappa - n_\ell(kR_\kappa) \sin \delta_\kappa]. \quad (4.14)$$

Substitution of eqs. (4.14), (4.13a) and (4.12) into eq. (4.11) yields the following expression for the pseudopotential coefficients:

$$B_{\kappa} = -\frac{s\kappa}{w+1} \left\{ \frac{j_{\ell'}(\kappa R_{\kappa}) \cos \delta_{\kappa} - n_{\ell'}(\kappa R_{\kappa}) \sin \delta_{\kappa}}{j_{\ell}(\kappa R_{\kappa}) \cos \delta_{\kappa} - n_{\ell}(\kappa R_{\kappa}) \sin \delta_{\kappa}} - \frac{j_{\ell'}(\kappa R_{\kappa})}{j_{\ell}(\kappa R_{\kappa})} \right.$$

$$\left. B_{\kappa} = -\frac{s}{w+1} \frac{-n_{\ell'}(\kappa R_{\kappa}) j_{\ell}(\kappa R_{\kappa}) + n_{\ell}(\kappa R_{\kappa}) j_{\ell'}(\kappa R_{\kappa})}{[j_{\ell}(\kappa R_{\kappa})]^2 [\cot \delta_{\kappa} - n_{\ell}(\kappa R_{\kappa})/j_{\ell}(\kappa R_{\kappa})]} \right.$$

Expressing $n_{\ell'}(\kappa R_{\kappa})$ and $j_{\ell'}(\kappa R_{\kappa})$ by means of the relations

$$f_{\ell+1}(z) = \frac{\ell}{z} f_{\ell}(z) - \frac{d}{dz} f_{\ell}(z), \quad f_{\ell-1}(z) = \frac{\ell+1}{z} f_{\ell}(z) + \frac{d}{dz} f_{\ell}(z),$$

where f stands for j or n , and using

$$(\kappa R_{\kappa})^2 \left(j_{\ell}(z) \frac{d}{dz} n_{\ell}(z) - \frac{d}{dz} j_{\ell}(z) n_{\ell}(z) \right) = 1$$

we obtain

$$B_{\kappa} = \frac{-2}{w+1} \left\{ 2\kappa R_{\kappa}^2 [j_{\ell}(\kappa R_{\kappa})]^2 [\cot \delta_{\kappa} - n_{\ell}(\kappa R_{\kappa})/j_{\ell}(\kappa R_{\kappa})] \right\}^{-1}. \quad (4.15)$$

We notice that — apart from the factor $2/(w+1)$, which goes to unity in the nonrelativistic limit — the coefficients B_{κ} have the same analytic form as the coefficients B_{ℓ} occurring in the nonrelativistic KKRZ potential.

The pseudopotential v_s for the solid is obtained as the superposition of the constituent atomic potentials v_a , (cf. eqs. (4.8) and (4.15)) located at positions $\underline{r}_j$:

$$v_s(\underline{r}, \underline{r}') = \sum_j v_a(\underline{r} - \underline{r}_j, \underline{r}' - \underline{r}_j). \quad (4.16)$$

4.3 Pseudopotential in Mixed Representation

In order to calculate the two-dimensional Fourier coefficients of the ion core pseudopotential as given by eqs. (4.16), (4.8) and (4.15), we find it convenient to derive first the three-dimensional Fourier coefficients

$$v_{\underline{k}\underline{k}'} = \frac{1}{\Omega} \langle \underline{k} | v_s | \underline{k}' \rangle, \quad \text{or}$$

$$v_{\underline{k}\underline{k}'} = \frac{1}{\Omega} \sum_j \exp[i(\underline{k} - \underline{k}') \underline{r}_j] \langle \underline{k} | v_a | \underline{k}' \rangle, \quad (4.17)$$

where Ω is the volume of the unit cell and the j -summation in the structure factor extends over the atomic sites in one unit cell. The plane wave matrix elements of the atomic potential, $\langle \underline{k} | v_a | \underline{k} \rangle$, are calculated as follows. We express the projection operators $\chi_{\kappa}^{\mu}(\hat{r}) \chi_{\kappa}^{\mu\dagger}(\hat{r})$ in v_a (cf. eq.(4.8)) according to eq.(4.2a) as

$$\chi_{\kappa}^{\mu}(\hat{r}) \chi_{\kappa}^{\mu\dagger}(\hat{r}) = \sum_{s, s' = \pm \frac{1}{2}} C(\ell \pm \frac{1}{2} j; \mu-s, s) C^*(\ell \pm \frac{1}{2} j; \mu-s', s') Y_{\ell}^{\mu-s}(\hat{r}) Y_{\ell}^{\mu-s'}(\hat{r}) \chi_s \chi_{s'}^{\dagger}.$$

Using the plane wave expansion

$$| \underline{k} \rangle = 4\pi \sum_{\ell m} i^{\ell} j_{\ell}(kr) Y_{\ell}^{m*}(\hat{k}) Y_{\ell}^m(\hat{r})$$

and the orthogonality relation for the spherical harmonics (cf. e.g. Messiah 1965, vol.1 p.495)

$$\int \sin \vartheta d\vartheta d\varphi Y_{\ell}^{m'}(\vartheta, \varphi) Y_{\ell}^m(\vartheta, \varphi) = \delta_{\ell\ell'} \delta_{mm'}$$

we obtain

$$\begin{aligned} \langle \underline{k} | v_a | \underline{k}' \rangle &= \frac{1}{2}(1+\delta_3) \frac{(4\pi)^2}{\Omega} \sum_{\kappa} B_{\kappa} R_{\kappa}^2 j_{\ell}(kR_{\kappa}) j_{\ell}(k'R_{\kappa}) \sum_{\mu, s, s' = \pm \frac{1}{2}} \sum_{\ell} \left[Y_{\ell}^{\mu-s}(\hat{k}) \right. \\ &\quad \left. \cdot Y_{\ell}^{\mu-s'}(\hat{k}') C(\ell \pm \frac{1}{2} j; \mu-s, s) C^*(\ell \pm \frac{1}{2} j; \mu-s', s') \chi(s) \chi(s')^{\dagger} \right] \end{aligned} \quad (4.18)$$

To make this expression more explicit, we substitute the Clebsch-Gordan coefficients (cf. e.g. Abramovitz and Stegun 1965, p.1007) for the two possible values $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ (which are associated with $\kappa < 0$ and $\kappa > 0$)

$$\begin{aligned} C(\ell \pm \frac{1}{2} \ell \pm \frac{1}{2} j; \mu-s, s) &= \left[(\ell + S_s \mu + \frac{1}{2}) / (2\ell + 1) \right]^{\frac{1}{2}}, \\ C(\ell \pm \frac{1}{2} \ell - \frac{1}{2} j; \mu-s, s) &= -S_s \left[(\ell - S_s \mu + \frac{1}{2}) / (2\ell + 1) \right]^{\frac{1}{2}}, \end{aligned} \quad (4.19)$$

where $S_s = \text{sign } s$, and rewrite, separately for $\kappa = -(\ell+1)$ and $\kappa = \ell$, the μ -summation over the expression in the square bracket of eq. (4.18) for each pair s, s' as a summation over m from $-\ell$ to $+\ell$. After explicitly summing over s and s' one obtains^{*)}

^{*)} We assume $R_{-\ell-1} = R_{\ell}$. For a justification of this choice cf. Ch.4.4

$$\begin{aligned}
 \langle \underline{k} | v_a | \underline{k} \rangle = & \frac{1}{2} (1 + \beta_3) \otimes \left\{ \frac{(4\pi)^2}{\Omega} \sum_{\ell} \frac{R_{\ell}^2}{2\ell+1} \left\{ ((\ell+1) B_{-(\ell+1)} + \ell B_{\ell}) \cdot \right. \right. \\
 & \cdot \sum_m Y_{\ell}^m(\underline{\hat{k}}) Y_{\ell}^{m*}(\underline{\hat{k}}') \left(\chi(\frac{1}{2}) \chi^{\dagger}(\frac{1}{2}) + \chi(-\frac{1}{2}) \chi^{\dagger}(-\frac{1}{2}) \right) + (B_{-(\ell+1)} - B_{\ell}) \cdot \\
 & \cdot \sum_m \left[Y_{\ell}^m(\underline{\hat{k}}) Y_{\ell}^{m*}(\underline{\hat{k}}') \left(\chi(\frac{1}{2}) \chi^{\dagger}(\frac{1}{2}) - \chi(-\frac{1}{2}) \chi^{\dagger}(-\frac{1}{2}) \right) + Y_{\ell}^m(\underline{\hat{k}}) (Y_{\ell}^{m+1*}(\underline{\hat{k}}') \cdot \right. \\
 & \cdot \left. \left. \left. [(\ell+m+1)(\ell-m)]^{\frac{1}{2}} \chi(\frac{1}{2}) \chi^{\dagger}(-\frac{1}{2}) + Y_{\ell}^{m-1*}(\underline{\hat{k}}') [(\ell-m+1)(\ell+m)]^{\frac{1}{2}} \chi(-\frac{1}{2}) \chi^{\dagger}(\frac{1}{2}) \right) \right] \right\} \Big\}.
 \end{aligned}$$

According to eq.(4.2b) the operators $\chi(s) \chi^{\dagger}(s')$ can be expressed as

$$\chi(s) \chi(s') = \begin{cases} \frac{1}{2} (1 + s \beta_3) & \text{for } s=s' \\ \frac{1}{2} (\beta_1 + i s \beta_2) & \text{for } s \neq s' \end{cases}$$

The Pauli matrix products $\beta_3 \otimes \beta_k$ and $1 \otimes \beta_k$, which subsequently occur, are replaced by γ -matrices (cf. Appendix C) in accordance with eqs.(C6). In particular we use

$$1 \otimes \beta_m = -i \gamma^k \gamma^l$$

where $\{k, l, m\}$ is a cyclic permutation of $\{1, 2, 3\}$. We thus obtain the following result for the three-dimensional Fourier coefficients of the relativistic KKRZ pseudopotential

$$\begin{aligned}
 v_{\underline{k}\underline{k}'} = & \frac{1}{\Omega} \sum_j \exp[i(\underline{k}-\underline{k}') \cdot \underline{x}_j] \sum_{\ell} \sum_m v_1^{\ell m}(\underline{k}) v_2^{\ell m}(\underline{k}'), \\
 v_1^{\ell m}(\underline{k}) = & 2\pi R_{\ell} j_{\ell}(k R_{\ell}) Y_{\ell}^m(\underline{\hat{k}}) / (2\ell+1) \\
 v_2^{\ell m}(\underline{k}') = & 4\pi R_{\ell} j_{\ell}(k' R_{\ell}) (1 + i \gamma^0) \left\{ [(\ell+1) B_{-(\ell+1)} + \ell B_{\ell}] Y_{\ell}^{m*}(\underline{\hat{k}}') \right. \\
 & + (B_{-(\ell+1)} - B_{\ell}) [-i \gamma^1 \gamma^2 m Y_{\ell}^{m*}(\underline{\hat{k}}') - \frac{1}{2} (i \gamma^2 - \gamma^1) \gamma^3 [(\ell+m+1)(\ell-m)]^{\frac{1}{2}} Y_{\ell}^{m+1*}(\underline{\hat{k}}') \\
 & \left. - \frac{1}{2} (i \gamma^2 - \gamma^1) \gamma^3 [(\ell-m+1)(\ell+m)]^{\frac{1}{2}} Y_{\ell}^{m-1*}(\underline{\hat{k}}')] \right\}.
 \end{aligned} \tag{4.20}$$

The pseudopotential matrix elements can be seen to consist of essentially two types of additive terms, one with the coefficient combination $(\ell+1) B_{-(\ell+1)} + \ell B_{\ell}$, the other containing $(B_{-(\ell+1)} - B_{\ell})$

and γ -matrix combinations $\gamma^h \gamma^l$, which are essentially spin operators. The second term thus implies an explicit spin dependence of our pseudopotential. For equal 'spin-up' and 'spin-down' atomic phase shifts, i.e. by virtue of eq.(4.15) for $B_{-(l+1)} = B_l$, the second term vanishes and the first one becomes, apart from the matrix $\frac{1}{2}(1+i\gamma^0)$, identical with the nonrelativistic KKRZ pseudopotential matrix element.

In order to obtain two-dimensional Fourier components of the potential, for which the mixed representation Dirac equation (eq. (3.3)) is readily soluble, we assume — specifying somewhat further the crystal model assumptions of Chapter 2.3 — the crystal as comprising L monatomic layers of pseudopotentials v_α — the v_α are identical in the substrate, but ^{may} differ for selvedge layers — such that the pseudopotential spheres do not extend beyond the boundaries between adjacent layers. *) We choose — without any loss of generality — the three-dimensional unit cell as primitive such that two basis vectors are identical with the basis vectors of an arbitrary but definite unit cell of the plane parallel to the surface. Denoting the origin of the j^{th} layer by $\mathbf{r}_j = (\mathbf{r}_j^{\parallel}, z_j)$, we then obtain the two-dimensional pseudopotential coefficients $v_{jnn'}(z, z')$ for the j^{th} layer from the three-dimensional ones (eq. (4.20)) as

$$v_{jnn'}(z, z') = \sum_{\ell m} v_{j1n}^{\ell m}(z) v_{j2n'}^{\ell m}(z') \quad (4.21a)$$

where

*) In principle, this additional restriction on the pseudopotential radii should produce no change in LEED results. (cf. discussion of the choice of the pseudopotential radii in section 4.4). In computational practice, however, the validity of the assumption will vary for different materials depending on the actual ion core potential, the crystal structure and the surface under consideration.

$$v_{j1n}^{lm}(z) = \sqrt{A} \left[\exp(-i g_n x_j^{\parallel}) \sum_{g_z} v_1^{lm}(\underline{k}_n, g_z) \exp(i g_z (z - z_j)) \right] \quad (4.21b)$$

$$v_{j2n}^{lm}(z') = \sqrt{A} \left[\exp(i g_n x_j^{\parallel}) \sum_{g_z} v_2^{lm}(\underline{k}_n, g_z) \exp(-i g_z (z' - z_j)) \right]$$

A denotes the area of the surface unit cell, n and n' enumerate the surface reciprocal lattice vectors $\underline{g}_n$ and $\underline{g}_{n'}$; $\underline{k}_n = \underline{g}_n + \underline{k}_0^{\parallel}$

and $g_z = 2\pi h/d$, where d is the layer thickness and $h = 0, 1, 2, \dots$. We note that the above pseudopotential is 'factorized' as a sum of the products of terms that depend only on $\underline{g}_n$ and z or on $\underline{g}_{n'}$ and z'. This property will be seen to be very valuable for actually solving the Dirac equation. Before doing so, however, we have to consider additional contributions to the crystal potential.

4.4 Choice of the Pseudopotential Radii

As indicated in Section 4.2, the choice of the pseudopotential radii R_K requires some further investigation. A natural upper limit of these radii is imposed by the physical condition that neighbouring atomic spheres in the solid must not overlap. When deriving the two-dimensional Fourier coefficients we further specified that the pseudopotential spheres should not extend beyond the boundaries between adjacent atomic layers. *) An obvious mathematical restriction arises from avoiding singularities in the coefficients B_K (cf. eq. (4.15)). The question is now, whether the results of a LEED calculation will depend on the particular values of the R_K chosen in accordance with the above restrictions. Since for any given set of R_K the coefficients B_K are determined such that the pseudopotential yields the same phase shifts as the actual potential, results of a calculation,

*) Whether this condition is more restrictive than the preceding one or not, depends on the crystal structure and the surface under consideration

which could take into account the complete (infinite) set of Fourier coefficients, should be insensitive to the values of the R_{κ} . As in computational practice however, the system of integro-differential equations (eq. 3.3) has to be truncated, the results will require a dependence on the R_{κ} , and one has to aim at optimizing their values.

In Section 4.3 we simplified the problem to some extent by assuming $R_{-(\ell+1)} = R_{\ell}$. This choice is not only convenient, but even imperative, for the following reason. As can be seen from eq.(4.18), the $\underline{k}$ -space convergence of the individual terms in the summation depends on $j_{\ell}(kR_{\kappa})$. A choice $R_{-(\ell+1)} \neq R_{\ell}$ entails therefore different convergence properties for 'spin-up' and 'spin-down' contributions, and a truncation is bound to produce spurious spin polarization effects. To avoid such effects pairs of radii have thus to be chosen as equal. The convergence problem in the relativistic case is then reduced to its nonrelativistic analogue. For the three-dimensional band structure secular equation the problem has been studied by Pendry and Capart (1969), who recommend to choose R_{ℓ} — subject to the condition of non-overlap between atomic spheres — such that $j_{\ell}(kR_{\ell})$ is — where $k = \sqrt{2E}$ — at its first maximum. This criterion is, however, not applicable in the context of our formalism, since in a three-dimensional $\underline{k}$ -space method convergence of the secular problem and thence of the LEED problem (cf. e.g. Capart 1969) is obtained by the convergence of $j_{\ell}(|\underline{k}_0 + \underline{\tilde{g}}| R_{\ell})$ with respect to the three-dimensional reciprocal lattice vectors $\underline{\tilde{g}}$, whereas in our mixed representation method they depend, as can be seen from eqs.(4.21) and (4.20), on the convergence of

$$j_{\ell}(|(\underline{k}_0'' + \underline{g}, g_z)| R_{\ell}) \quad (4.22)$$

with respect to the surface reciprocal lattice vectors $\underline{g}$ and the 'inter-layer' reciprocal coefficients g_z .*) Bearing in mind the behaviour of the spherical Bessel function $j_\ell(z)$ (cf. e.g. Abramovitz and Stegun p. 438), the form of the expression eq.(4.22) suggests, instead, the following criterion as plausible. R_ℓ should be chosen such that for a suitable set of surface reciprocal lattice vectors $\underline{g}$ closest to $\underline{k}_0^\parallel$, $j_\ell(|\underline{k}_0^\parallel + \underline{g}| R_\ell)$ should be in the vicinity of its first maximum. This somewhat vague recommendation becomes clearer and more specific for the case of normal incidence on a square surface lattice ($\underline{k}_0^\parallel = 0$). The above set then consists of the four equivalent reciprocal lattice vectors (which are of equal length $|\underline{g}|$) closest to the origin, and R_ℓ — for $\ell \neq 0$ **) — should be chosen such that $j_\ell(|\underline{g}| R_\ell)$ assumes its first maximum. Whether this condition can be fulfilled without violating the non-overlap restrictions, depends on the value of ℓ as well as on the crystal and the surface specifications. An approximate fulfillment turns out to be feasible for small $\ell \neq 0$ and decreasingly so with increasing ℓ . If, for a given ℓ , the condition is drastically violated, we do not think that the largest permissible R_ℓ -value is necessarily the best, but prefer to consider R_ℓ as an adjustable parameter to be fitted to experimental data.

*) The difference is particularly striking for the case of normal incidence, where $\underline{k}_0^\parallel = 0$

**) For $\ell = 0$ the above criterion does not apply since the first maximum of $j_0(z)$ is assumed at $z = 0$ (and the second would be too far out). In practice, we have found results to be very insensitive to R_0 .

5. Effective Potential Representing the Interaction with the Valence Electrons

In addition to the interaction with the ion cores, a one-electron potential that claims to be realistic for LEED purposes, has to take into account the interaction of the incident electron with the valence electrons in the finite or semi-infinite solid. This interaction is described by means of an effective complex potential, the imaginary part of which is associated with inelastic processes and the real part of which provides an exchange-correlation correction to the inner potential as well as a (real) surface potential barrier. Although the two parts arise, in principle, from the same selfconsistent many-body treatment of the problem, we present them separately in view of applying them to LEED.*) Finally we discuss, whether the inclusion of spin polarization requires the addition of any spin-dependent potential contributions.

5.1 Imaginary Potential Contribution

The inelastic processes, which are of relevance for LEED, consist mainly in the excitation of bulk and surface plasmons and of interband transitions.**)

Energy conservation requires that an

*)

These two types of potential contribution have been extensively dealt with in the literature (cf. references given in the following). We therefore discuss them only briefly in view of selecting models that seem adequate and, at the same time suitable for incorporation in our LEED formalism.

**)

A comprehensive survey of theoretical and experimental aspects of this subject may be found in a 'classical' monograph by Raether (1965).

The interaction with thermal lattice vibrations, i.e. phonon creation and annihilation, belongs, strictly speaking, into the category of inelastic processes. Since, however, the energy losses involved are below the resolution of most currently used LEED equipment (which is of the order of 0.5 eV; cf. the thermal energy at $T = 300^\circ\text{K}$: 0.025 eV), we consider 'thermal scattering' as 'quasi-elastic' and treat it separately in Chapter 7.

electron involved in such processes loses energy and is thus removed from the elastically diffracted beams. The resulting attenuation of these beams can be described by the phenomenological concept of an 'optical potential', which constitutes an imaginary contribution to the crystal potential. First used in quantum mechanical scattering theory by Dirac (1930), this concept was introduced in electron diffraction theory by Slater (1937) and, independently, by Moliere (1939). It plays an important part in current LEED calculations, where it has been found to produce drastic changes in peak heights and peak widths of intensity-energy profiles as compared to purely elastic results. There are basically three kinds of optical potential in use for describing the effect of loss processes in the bulk. The one is an adjustable imaginary parameter, mostly taken as constant over a wide energy range (cf. Hirabayashi 1968, Gafner 1969, Jepsen et al. 1971, Pendry 1973). The second one is an energy-dependent complex self-energy, which is adopted (cf. Strozier and Jones 1969, Duke and Tucker 1969) from the many-body treatment (cf. Pines 1962) of an infinitely extended spatially homogeneous electron gas (in a uniform positive background) (cf. Quinn 1962, Lundquist 1969) of the same average density as the valence electrons in the solid.*) While the first kind of optical potential is of a purely phenomenological nature, the second one can be considered as an approximate first-principles calculation, which appears to be reasonably valid for nearly-free-electron metals. A third — phenomenological — way of taking into account inelastic bulk effects consists in adding imaginary contributions to the real ion core scattering phase shifts (cf. McRae 1966, Jennings and Sim 1972)

*)

The real part of this self-energy provides an energy-dependent contribution to the real inner potential.

The above optical potentials have a basic deficiency in that they disregard the effect of elementary surface excitations, in particular surface plasmons. Such surface effects, have been treated recently by Gersten (1969, 1970), who derived a complex self-energy in the random phase approximation for a semi-infinite homogeneous electron gas. Gersten's optical potential has the form

$$V_{opt} = \alpha(E) \Theta(z) + \beta(E, \vartheta) \delta(z), \quad (5.1)$$

where $\Theta(z)$ is a step function, which is equal to unity inside the solid and vanishes outside; $\delta(z)$ is the Dirac Delta function, and $\alpha(E)$ and $\beta(E, \vartheta)$ are complicated complex functions of the energy E and the angle of incidence (against the surface normal) ϑ , for which numerical values are given in (Gersten 1970). The first term represents the effect of bulk processes and agrees numerically with the infinite jellium results of Quinn (1962). The second term describes surface effects; in particular its imaginary part corresponds to surface plasmon and surface electron-hole excitations. A drastically different form of optical potential for the semi-infinite electron gas has been obtained Feibelman et al. (1972). Whereas in Gersten's potential the surface part is localized, it is highly nonlocal in the potential of Feibelman et al. A non-local RPA potential has also been derived by Inkson (1972).

Assessing the above optical potentials in view of selecting one for our LEED formalism, we firstly consider the use of complex phase shifts as less adequate, since such will not only implement the desired attenuation of the elastic intensities, but will also affect the spin polarizations in a manner, which we consider as unphysical (mainly because of the arbitrariness involved in the choice of the imaginary phase shift contributions). The choice remains then essentially between the Feibelman and the

Gersten form since the first two bulk optical potentials discussed previously can be viewed as contained in either of these two forms. Comparison (cf. Feibelman 1972 p.2454) reveals that — in contrast to the Gersten form — the Feibelman form is derived on the basis of an assumption, the 'high-frequency approximation', which restricts — as Feibelman admits — its validity to a higher energy range ($v \gg v_F$), whereas Gersten (1970) recommends his potential strongly for LEED. Since furthermore, a $\delta(z)$ type potential can be particularly easily treated, we decide to make provision in our formalism for including Gersten's optical potential. In doing so, we must, however, be aware of the fact that the scattering properties of this potential are different for Dirac and for Schrödinger electrons. This follows, on purely theoretical grounds, from the work of Meister and Weiss (1968) who derive as a necessary condition for the equivalence between a relativistic and a nonrelativistic treatment that the potential at any point must be less than the rest energy of the electron. This condition is violated by $\delta(z)$ for $z = 0$. Our conclusion is confirmed by explicit numerical calculations (cf. Appendix F), which show that the relativistic reflection coefficient exceeds the nonrelativistic one by a factor that depends on the strength of the δ -function. A naive substitution of Gersten's potential into our formalism would therefore lead to a discrepancy between relativistic and nonrelativistic intensities, which we consider as spurious, since Gersten obtained the potential in a nonrelativistic context as a convenient, but not unique means of localizing the effect of surface plasmon excitations. Had this localization

*) Theoretical support for incorporating many-body effects by adding a homogeneous electron gas self-energy to an ion core potential -- which may be approximated by a band structure potential -- is provided by the work of Bassani et al. (1962) and of Hedin and Lindqvist (1969).

been effected, for example, by a sufficiently wide Gaussian potential, there would be — since $E \ll mc^2$ — no discrepancy between relativistic and nonrelativistic results. Employing Gersten's potential in our formalism, we, therefore, have to reduce the strength of the δ -function by an appropriate correction factor. As is shown in Appendix F, this correction factor is 0.5, for any energy and beam orientation.

5.2 Real Inner Potential and Surface Potential Barrier.

The ionic and electronic charge distribution in the surface region is such that it gives rise to an electrostatic potential difference ΔV between the vacuum level and the 'inner potential', which for muffin-tin models is conveniently identified with the muffin-tin zero. Since the incident electron energy can be visualized as increased by this 'surface potential barrier', the peak positions in a calculated LEED intensity profile will be translated towards lower energies by ΔV and the non-specular intensity profiles will be truncated by ΔV . It is therefore vital to include the effect of the barrier in LEED calculations. A discussion of various ways, in which an abrupt step model ('square barrier') can be incorporated, and of the resulting effects on LEED intensity profiles was given by Jennings and McRae (1970) and by Jepsen et al. (1972). The abrupt step is, however, a rather crude approximation to the continuous reality, and it has been shown by Jennings (1971a), who employed an image potential, as well as a step barrier that finer details of LEED profiles — McRae's surface state resonances (cf. McRae and Jennings (1969), McRae (1971)), — are sensitive to the position and shape of the surface potential barrier. Earlier work by Cutler and Davis (1964), who calculated reflection coefficients from various one-dimensional surface pot-

ential models, provides some further support for making provision in our LEED formalism for a surface potential $V(z)$, which varies continuously from zero 'far outside the crystal' to the inner potential level inside, the form of which, however, we leave unspecified for the moment.*) As regards possible discrepancies between surface potential reflection coefficients obtained by a relativistic and a nonrelativistic treatment, such do not exist as long as the potential remains well below mc^2 over the entire domain (cf. discussion at the end of the previous section).

5.3 Spin-Dependent Contributions

Since our LEED formalism involves spin, the question arises, whether there might be a spin-dependent contribution to the optical potential. An affirmative answer seems to be suggested by the fact that at energies below 100 eV the exchange interaction — which is spin-dependent — between the incident electron and the electrons inside the solid plays a significant part (cf. de Wames and Vredevoe 1968).**) In order to produce an effective spin-dependence of the optical potential, e.g. in order to remove different numbers of 'spin-up' and 'spin-down' electrons from the elastic beam, however, the average density of 'spin-up' electrons inside the solid has to be different from the density of the 'spin-down' electrons. This is the case only for magnetic materials, e.g. ferromagnets (cf. Appendix B). In the abse-

*) The — to our knowledge — most advanced forms have been obtained by Lang and Kohn (1970) by means of a self-consistent local density approximation method and by Inkson (1972), who generalized the RPA approach of Quinn and Ferrell (1958) to a semi-infinite jellium model.

**) The magnetic dipole-dipole interaction, which could provide a further spin-dependent mechanism, is outweighed by the Coulomb interaction to such an extent that we can safely neglect it.

nance of a long range magnetic order, we can, therefore, adopt a spin-independent imaginary contribution to the optical potential.

A related problem is the possibility of a polarized electron beam becoming depolarized when travelling through an electron gas of equal 'spin-up' and 'spin-down' densities. At first sight, one might argue that spin exchange events between 'beam electrons' and 'solid electrons' would preferentially reverse the majority spins of the beam and thus tend to reduce its degree of polarization. This is, however, not true, as we can see from an argument, which we formulate in the following for the zero temperature case. Reversal of the spin of a 'beam electron' by means of spin exchange requires that a 'solid electron' must reverse its spin. Since all electron states below the Fermi level are occupied, this can, in accordance with the Pauli principle, happen only if the 'solid electron' is simultaneously raised above the Fermi level. This, however, implies, from energy conservation, a loss of energy of the 'beam electron' involved, i.e. its removal from the elastic beam. The latter is thus attenuated, but retains its degree of polarization. For finite temperatures, we arrive at the same conclusion by noting that even for an electron in the vicinity of the Fermi surface spin reversal without a gain of energy would entail a violation of the Pauli principle. The above holds rigorously for a perfectly monochromatic primary beam and a perfectly monochromatic detector. If one allows for an energy spread ΔE_1 of the primary beam and a limited energy resolution ΔE_2 of the detector, 'solid electrons' in an energy range of the order of $\Delta E = \max(\Delta E_1, \Delta E_2)$ from the Fermi surface may produce some depolarization. Since this depolarization effect can, however, in principle be made arbitrarily small, we decided to disregard it in the present work.

6. Solution of the Dirac Equation

In the two previous Chapters we have established a crystal potential model, which consists of a relativistic KKRZ-type ion core potential, a uniform bulk optical potential U_0 , a $\delta(z)$ surface optical potential and a continuous surface potential barrier $V(z)$. We now proceed to determine the solution of the mixed-representation Dirac equation (eq.(3.3)) for this potential model and to derive the propagation matrix M_C (cf. eqs.(3.8) to (3.12)). Since we restrict the diameters of the pseudopotential spheres to the z -axis projections of monatomic layers, the problem can be viewed as consisting of essentially two parts: firstly the determination of the propagation matrices for a single monatomic layer and for the two types of surface potential, and secondly, the combination of the individual propagation matrices to form the propagation matrix of the whole crystal.

6.1 For a Single Layer of Ion-Core Pseudopotentials Plus a Uniform Optical Potential.

To determine the propagation matrix $M_S(z_2, z_1)$ for a typical monatomic layer that extends from z_1 to z_2 , we substitute the ion core pseudopotential (eq.(4.21a)) together with a uniform complex potential U_0 , which may be energy-dependent, into the mixed-representation Dirac equation (eq.(3.3)) and — dropping the index j in the potential and replacing the pair ℓm by a collective index v — obtain

$$\begin{aligned} \left[\partial_z + i\gamma^0 \gamma^3 (w - U_0) + \gamma^3 (1 + i\gamma^1 k_n^x + i\gamma^2 k_n^y) \right] \psi_n(z) = \\ = i\gamma^0 \gamma^3 \sum_v v_{1n}^v(z) a^v, \end{aligned} \quad (6.1a)$$

$$a^v = \sum_{n'} \int_{z_1}^{z_2} dz' v_{2n'}^v(z) \psi_{n'}(z'). \quad (6.1b)$$

Since we are dealing with a system of N first-order integro-differential equations, there are N linear independent 'fundamental' solutions, for which the particular form of the right-hand-side of eq.(6.1a) together with eq.(6.1b) suggests the following "ansatz"

$$\psi_{nn'}(z) = \psi_n^0(z) \delta_{nn'} + \sum_{\nu} \psi_{nn'}^{\nu}(z), \quad (6.2)$$

where the index $n = 1, \dots, N$ corresponds to the Fourier expansion index of eq.(3.2b), i.e. is associated with the n th LEED beam, and $n' = 1, \dots, N$ denumerates the fundamental solutions. $\psi_n^0(z)$ is the solution of eq.(6.1a) with the right-hand-side — i.e. the ion core potential — set equal to zero which we write as

$$\psi_n^0(z) = \left[\sum_{\epsilon=1}^6 (f_{n\epsilon}^0(z) + g_{n\epsilon}^0(z) \beta_n P_{\epsilon}) \right] \psi_n^0(z_1), \quad (6.3)$$

$$f_{n\epsilon}^0(z) = \cos k_n^z(z-z_1) - i\epsilon k^{-1}(\omega-v_0) \sin k_n^z(z-z_1),$$

$$g_{n\epsilon}^0(z) = - (k_n^z)^{-1} K_n \sin k_n^z(z-z_1),$$

$$k_n^z = [(\omega-v_0)^2 - k_n^{x2} - k_n^{y2} - 1]^{\frac{1}{2}}, \quad K_n = (1 + k_n^{x2} + k_n^{y2})^{\frac{1}{2}},$$

$$\beta_n = K_n^{-1} \gamma^3 (1 + i\gamma^1 k_n^x + i\gamma^2 k_n^y);$$

P_{ϵ} is the projection operator defined in eq.(3.11a). The function $\psi_{nn'}^{\nu}(z)$ in eq.(6.2) is defined as a solution of the equation

$$\begin{aligned} [\partial_z + i\gamma^0 \gamma^3 (\omega-v_0) + \gamma^3 (1 + i\gamma^1 k_{n'}^x + i\gamma^2 k_{n'}^y)] \psi_{nn'}^{\nu}(z) = \\ = i\gamma^0 \gamma^3 v_{1n}^{\nu}(z) a_n^{\nu}, \end{aligned} \quad (6.4a)$$

$$a_n^{\nu} = \sum_{\ell} \int_{z_1}^{z_2} dz' v_{2\ell}^{\nu}(z') \psi_{\ell n}(z'). \quad (6.4b)$$

Eq.(6.4a) can be regarded as an inhomogeneous differential equa-

tion, which we solve by means of the method of 'variation of the constant'. Knowing the homogeneous solution as given in eq.(6.3), we make the 'ansatz'

$$\psi_{mn}^{\nu}(z) = \left[\sum_{\epsilon} (f_{n\epsilon}^0(z) + g_{n\epsilon}^0(z) \beta_n) P_{\epsilon} \right] c_{mn}^{\nu}(z) \quad (6.5)$$

where $c_{mn}^{\nu}(z)$ is an unknown four-spinor. Substitution of the above expression into eq.(6.4a) yields

$$\left[\sum_{\epsilon} (f_{n\epsilon}^0(z) + g_{n\epsilon}^0(z) \beta_n) P_{\epsilon} \right] \partial_z c_{mn}^{\nu}(z) = i \gamma^0 \gamma^3 v_{1m}^{\nu}(z) a_m^{\nu}. \quad (6.6)$$

The square bracket is re-written with the aid of eq.(6.3) as

$$[\dots] = \cos k_n^z(z-z_1) - (\beta_n K_n + i \gamma^0 \gamma^3 (\omega - v_0)) (\sin k_n^z(z-z_1)) / k_n^z.$$

Noting that its inverse is

$$\cos k_n^z(z-z_1) + (\beta_n K_n + i \gamma^0 \gamma^3 (\omega - v_0)) (\sin k_n^z(z-z_1)) / k_n^z,$$

we obtain from eq.(6.6)

$$c_{mn}^{\nu}(z) = \int_{z_1}^z dz' \left\{ \left[\cos k_n^z(z'-z_1) + (\beta_n K_n + i \gamma^0 \gamma^3 (\omega - v_0)) (\sin k_n^z(z'-z_1)) / k_n^z \right] \cdot i \gamma^0 \gamma^3 v_{1m}^{\nu}(z') a_m^{\nu} \right\}.$$

Substituting this into eq.(6.5), we arrive at the following explicit expression for the solution of eq.(6.4a)

$$\psi_{mn}^{\nu}(z) = [f_{n+}^{\nu}(z) + f_{n-}^{\nu}(z) i (k_n^z)^{-1} (K_n \beta_n + i \gamma^0 \gamma^3 (\omega - v_0))] i \gamma^0 \gamma^3 a_m^{\nu}, \quad (6.7a)$$

$$f_{n\pm}^{\nu}(z) = \frac{1}{2} \left[\omega_{n-}^{\nu}(z) e^{i k_n^z(z-z_1)} \pm \omega_{n+}^{\nu}(z) e^{-i k_n^z(z-z_1)} \right], \quad (6.7b)$$

$$\omega_{n\pm}^{\nu}(z) = \int_{z_1}^z dz' v_{1n}^{\nu}(z') e^{\pm i k_n^z(z'-z_1)}. \quad (6.7c)$$

This solution still involves the unknown coefficients a_m^{ν} . In order to determine them, we insert eq.(6.7a) into eq.(6.2) and the resulting expression into eq.(6.4b), which yields the following system of algebraic equations:

$$a_m^v = \sum_{\tilde{v}=1}^{v_{\max}} \sum_n \int_{z_1}^{z_2} dz' v_{2n}^v(z') [f_{n+}^{\tilde{v}}(z') + f_{n-}^{\tilde{v}}(z') i(k_n^2)^{-1} (K_n \beta_n + i\gamma^0 \gamma^3 (w - v_0))] + i\gamma^0 \gamma^3 a_m^{\tilde{v}} = \int_{z_1}^{z_2} dz' v_{2m}^v(z') \psi_m^0(z'). \quad (6.8)$$

This system can be simplified with the aid of the projection operators

$$\tilde{P}_{\epsilon} = \frac{1}{2} (1 + \epsilon i\gamma^0), \quad \epsilon = \pm \quad (6.9a)$$

which have the properties

$$(\tilde{P}_{\epsilon})^2 = \tilde{P}_{\epsilon}, \quad \tilde{P}_{\epsilon} \tilde{P}_{\epsilon'} = 0, \quad \tilde{P}_{\epsilon} i\gamma^0 = \epsilon \tilde{P}_{\epsilon}, \quad (6.9b)$$

$$\tilde{P}_{\epsilon} \gamma^k = \gamma^k \tilde{P}_{\epsilon'}, \quad k = 1, 2, 3, \quad \epsilon' = -\epsilon.$$

Since the matrix elements $v_{2n}^v(z')$ as given by eqs. (4.21b) and (4.2o) contain $\tilde{P}_+$, multiplication of eq. (6.8) by $\tilde{P}_-$ yields

$$\tilde{P}_- a_m^v = 0, \quad (6.10)$$

Multiplying eq. (6.8) by $\tilde{P}_+$ and making use of eqs. (6.9b) and (6.10) we obtain

$$a_m^v + \sum_{\tilde{v}=1}^{v_{\max}} \sum_n \int_{z_1}^{z_2} dz' v_{2n}^v(z') f_{n-}^{\tilde{v}}(z') i(k_n^2)^{-1} (1+w) a_m^{\tilde{v}} = \int_{z_1}^{z_2} dz' v_{2m}^v(z') \psi_m^0(z'). \quad (6.11)$$

In deriving eq. (6.11) we have also taken into account $\tilde{P}_+ a_m^v = a_m^v$, which follows from eq. (6.10) and $\tilde{P}_+ + \tilde{P}_- = 1$. We note that the 'factorized' form of the ion core pseudopotential (eq. (4.21a)) has enabled us to reduce the original system of integro-differential equations to an inhomogeneous system of algebraic equations. The number of equations, $v_{\max}$, is determined by the number of non-zero phase shift pairs $\delta_{-(l+1)}$ and δ_l as $v_{\max} = \sum_l (2l+1)$.

The system eq.(6.8) has to be solved for each value $m = 1, \dots, N$. The integrations over z' required in eqs.(6.7c) and (6.8) can be readily reduced to simple summations by substituting the potential functions $v_{1m}^v(z)$ and $v_{2m}^v(z)$ according to eq.(4.21b) and explicitly carrying out the integrals over the resulting exponential functions of z' .

Eq.(6.11) is now solved as follows. Substitution of $v_{2m}^v(z)$ according to eqs.(4.21b) and (4.20) leads to the form

$$\left(\sum_{\mu=1}^4 \tilde{F}_{\mu} F_{\mu} \right) \hat{a}_m = \left(\sum_{\mu=1}^4 \tilde{F}_{\mu} \hat{h}_{\mu m} \right) \tilde{P}_+ \psi_m^0(z_1), \quad (6.12a)$$

$$\{\tilde{F}_{\mu}\} = \{1, \gamma^1 \gamma^2, \gamma^2 \gamma^3, \gamma^3 \gamma^1\}, \quad \hat{a}_m = (a_m^1, \dots, a_m^{v_{\max}})^T, \quad (6.12b)$$

The definition of the $(v_{\max} \times v_{\max})$ -matrices F_{μ} and the $v_{\max}$ -column-vectors $\hat{h}_{\mu m}$ becomes obvious from comparison of eq.(6.12) with the equation produced by the above-mentioned substitution. Since the set $\{\tilde{F}_{\mu}\}$ is a closed sub-algebra, the inverse of $\sum_{\mu=1}^4 \tilde{F}_{\mu} F_{\mu}$ has the form $\sum_{\mu} \tilde{F}_{\mu} X_{\mu}$, where the $(v_{\max} \times v_{\max})$ -matrices X_{μ} are obtained from the four equations arising from

$$\left(\sum_{\mu=1}^4 \tilde{F}_{\mu} X_{\mu} \right) \left(\sum_{\mu=1}^4 \tilde{F}_{\mu} F_{\mu} \right) = 1.$$

Multiplying eq.(6.12a) by $\sum_{\mu=1}^4 \tilde{F}_{\mu} X_{\mu}$ we obtain the result

$$\hat{a}_m = \left(\sum_{\mu=1}^4 \tilde{F}_{\mu} \hat{s}_{\mu m} \right) P_+ \psi_m^0(z_1), \quad (6.13)$$

where the $\hat{s}_{\mu m}$ are $v_{\max}$ -column-vectors. Substitution of the components a_m^v from eq.(6.13) into eq.(6.7a) and of the resulting expressions into eq.(6.2) yields the fundamental system of solutions ψ_{nn} , which we now write in the matrix form

$$\hat{M}(z_2, z_1) = \sum_{G=\pm} \sum_{\mu=1}^8 (\Gamma_{\mu} D_G^{\mu}) P_G \quad (6.14)$$

where the sub-algebra $\{\Gamma_{\mu}\}$ is defined according to eq.(3.10) and

the D_{ϵ}^{μ} are (NxN)-matrices obtained in a straight-forward manner by the above substitutions. By virtue of its construction, $\hat{M}(z_2, z_1)$ is the propagation matrix for a monatomic layer between z_1 and z_2 , i.e.

$$\hat{\psi}(z_2) = \hat{M}(z_2, z_1) \hat{\psi}(z_1). \quad (6.15)$$

6.2 For a δ -Function Optical Potential

As discussed in Chapter 5.2, elementary excitations in the surface region can be described by an optical potential $u_s \delta(z-z_1)$ (cf. eq.(5.1)) — we now denote Gersten's $\beta(E, \nu)$ by v_s —, which we locate at z_1 , on top of the outmost layer of the crystal. Since this potential is constant in planes parallel to the surface, the off-diagonal Fourier expansion eq.(3.2a) vanishes and ^{the} mixed-representation Dirac equation eq.(3.3) becomes decoupled and reads

$$[\partial_z + i\gamma^0 \gamma^3 (\omega - v_s \delta(z-z_1)) + \gamma^3 (1 + i\gamma^1 k_n^* + i\gamma^2 k_n^y)] \psi_n(z) = 0. \quad (6.16)$$

Applying the operator $\lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} dz$ and making use of the δ -function property

$$\int dz f(z) \delta(z-z_1) = \frac{1}{2} (f(z_1+0) + f(z_1-0)), \quad (6.17)$$

where $f(z)$ may have a finite discontinuity at $z = z_1$, we obtain

$$\psi_n(z_1+0) - \psi_n(z_1-0) - i\gamma^0 \gamma^3 v_s (\psi_n(z_1+0) + \psi_n(z_1-0)) = 0$$

or

$$(1 - i\gamma^0 \gamma^3 v_s) \psi_n(z_1+0) = (1 + i\gamma^0 \gamma^3 v_s) \psi_n(z_1-0).$$

Multiplication by $(1 + i\gamma^0 \gamma^3 v_s)$ yields — since $(1 + i\gamma^0 \gamma^3 v_s)(1 - i\gamma^0 \gamma^3 v_s) = 1 + \beta^2$ —

$$\psi_n(z_1+0) = (\hat{M}_\delta)_{nn} \psi_n(z_1-0), \quad (6.18a)$$

$$(\hat{M}_\delta)_{nn} = (1 - v_s^2 + 2i\gamma^0\gamma^3 v_s) / (1 + v_s^2). \quad (6.18b)$$

The propagation matrix $\hat{M}_\delta$ across a δ -potential is thus a diagonal matrix with elements — each of which is a 4x4 matrix — as given by eq.(6.18b).

6.3 For a Continuous Surface Potential Barrier

Since the surface potential barrier is assumed to be of the form $v(z)$, the mixed representation Dirac equation (eq.3.3) is decoupled:

$$[\partial_z + i\gamma^0\gamma^3(\omega - v(z)) + K_n\beta_n] \psi_n(z) = 0, \quad (6.19)$$

where K_n and β_n are defined as in eq.(6.3). A method for solving the above type of one-dimensional Dirac equation has been given by Feder and Meister (1969). According to loc.cit. eq.(7), the result can be written in the form

$$\psi_n(z) = \sum_{\epsilon=\pm} (f_{n\epsilon}(z) + g_{n\epsilon}(z)\beta_n) P_\epsilon \psi_n(z_0), \quad *) \quad (6.20)$$

where the complex functions $f_{n\epsilon}(z)$ and $g_{n\epsilon}(z)$ are defined as the solutions of the two coupled differential equations

$$\partial_z f_\pm(z) \pm i(\omega - v(z)) f_\pm(z) + K_n g_{n\pm}(z) = 0 \quad (6.21)$$

$$\partial_z g_\pm(z) \mp i(\omega - v(z)) g_\pm(z) + K_n f_{n\pm}(z) = 0$$

with the initial conditions

$$f_{n\pm}(z_0) = 1, \quad g_{n\pm}(z_0) = 0. \quad (6.22)$$

*) Since — in contrast to loc.cit.eq.(3) — eq.(6.19) involves N one-dimensional Dirac equations, we have to characterize the solutions and consequently the functions $f_{n\epsilon}(z)$ and $g_{n\epsilon}(z)$ by the 'beam index' n .

The projection operator P_{σ} is defined in eq.(3.11a) and z_0 is chosen far enough outside the crystal for $v(z)$ to vanish. Assuming the surface barrier to terminate at z_1 , we see from eqs.(6.22) and (6.20) that the propagation matrix M_S for the surface potential barrier is diagonal with elements

$$(\hat{M}_S)_{nn} = \sum_{\sigma=\pm} (f_{n\sigma}(z_1) + g_{n\sigma}(z_1)\beta_n) P_{\sigma} \quad (6.23)$$

We note that for real $v(z)$ we have to solve only the '+' option of eq.(6.18), since

$$f_-(z) = f_+^*(z), \quad g_-(z) = g_+^*(z). \quad (6.24)$$

This is no longer valid for complex $v(z)$, i.e. if the bulk imaginary potential is assumed to tail off continuously into the vacuum, in which case both options of eq.(6.18) have to be solved. As for the actual method of solution, we give preference to a numerical procedure over an analytical one, because it permits the use of arbitrary potential functions.

6.4 For the Whole Crystal

The propagation matrix $\hat{M}_C$ for the whole crystal, is obtained from the propagation matrices $\hat{M}_1$ and $\hat{M}_2$ of selvedge and substrate as

$$M_C = \hat{M}_2 \hat{M}_1. \quad (6.25)$$

Assuming that the surface potential terminates at the boundary of the topmost layers and that the δ -potential is located at the same position, the selvedge matrix $\hat{M}_1$ is

$$\hat{M}_1 = \left(\prod_{\ell=1}^{L_1} \hat{M}_1^{(\ell)} \right) \hat{M}_{\delta} \hat{M}_S \quad (6.26)$$

where $\hat{M}_1^{(\ell)}$ denotes the propagation matrix of the ℓ th selvedge

layer and is of the form given in eq.(6.18b) and eq.(6.23), respectively. The substrate propagation matrix is basically obtained as the product of the substrate layer matrices $\hat{M}_2^{(\ell)}$ which are of the form given in eq.(6.14):

$$\hat{M}_2 = \prod_{\ell=1}^{L_2} \hat{M}_2^{(\ell)} \quad (6.27a)$$

If the surface projections of all bulk layers coincide, this simplifies to

$$\hat{M}_2 = (\hat{M}_2^{(1)})^{L_2}, \quad (6.27b)$$

i.e. one has to calculate only one single-layer propagation matrix $\hat{M}_2^{(1)}$. For $\tilde{L}_2 \neq 1$ (cf. Chapter 2.3), but $m\tilde{L}_2 = L_2$ with m integer, one has

$$\hat{M}_2 = \left(\prod_{\ell=1}^{\tilde{L}_2} \hat{M}_2^{(\ell)} \right)^m, \quad (6.27c)$$

i.e. one has to calculate $\tilde{L}_2$ single-layer propagation matrices. Although $\hat{M}_C$ is in general an involved product of individual propagation matrices, it can always be expressed in the form specified in eq.(3.12), because the γ -matrix combinations occurring in the individual matrices are the same and form a closed algebra.

The propagation matrix M_C , which is determined as described in this chapter, is substituted into eq.(3.12), and intensities and spin polarizations are subsequently calculated according to the method given in Chapter 3.

7. Thermal Lattice Motion

The theory as developed in the above contains the assumption of a rigid ion core lattice, i.e. thermal lattice motion is not taken into account. Experimental work (Reid 1971) has shown, however, that certain features of LEED spectra are strongly affected by variations in temperature. LEED theories for a rigid lattice can easily be extended to incorporate lattice vibrations, if one treats the atomic motions as independent, i.e. neglects correlations in the vibrations of neighbouring atoms^{*)}. As has been derived in (Duke and Laramore 1970) and (Holland 1971), this approximation amounts to averaging the scattering amplitudes from each atomic potential over the motion of that particular atom. This gives an effective scattering amplitude from each atom at its mean position. A LEED theory incorporating lattice motion is then obtained from a rigid lattice theory by replacing the actual atomic scattering amplitude by this effective scattering amplitude.^{**)} Since the scattering amplitude can be expressed in terms of phase shifts, effective phase shifts for the scattering averaged over the atomic motion can be introduced in terms of the actual phase shifts. (Jepsen et al. 1971).

In the following we incorporate thermal effects into our LEED theory by extending the Schrödinger-equation treatment given in (Jepsen et al. 1971b) to the relativistic case. The scattering of a spin $\frac{1}{2}$ particle by a central potential is com-

*) Inclusion of these correlations entails a substantial complication of the LEED theory, which seems not justified in view of the experimental data currently available for comparison with the theoretical results obtained in this work.

**) It should be noted that this procedure is not equivalent to scattering from an averaged potential.

pletely described by the two scattering amplitudes $f(\vartheta)$ and $g(\vartheta)$ given in eq. (4.6). Averaging over the motion of the scattering centre yields effective scattering amplitudes $\langle f(\vartheta) \rangle_{av}$ and $\langle g(\vartheta) \rangle_{av}$ given by

$$\langle f(\vartheta) \rangle_{av} = \langle e^{i(\underline{k}-\underline{k}') \cdot \underline{r}} \rangle_{av} f(\vartheta) , \quad (7.1)$$

$$\langle g(\vartheta) \rangle_{av} = \langle e^{i(\underline{k}-\underline{k}') \cdot \underline{r}} \rangle_{av} g(\vartheta) ,$$

where $\underline{k}, \underline{k}'$ are the plane wave vectors between which the scattering amplitude $f(\vartheta)$ has been taken and $\underline{r}$ is the displacement of the scattering centre from its equilibrium position (i.e. from its rigid lattice site). Assuming a Debye spectrum of lattice modes, the factor $\langle e^{i(\underline{k}-\underline{k}') \cdot \underline{r}} \rangle_{av}$ is the Debye-Waller factor (cf. Maradudin et al. 1963):

$$\langle e^{i(\underline{k}-\underline{k}') \cdot \underline{r}} \rangle_{av} = e^{-A(\underline{k}-\underline{k}')^2} \quad (7.2a)$$

$$A = [3/(2M k_B \Theta_D)] \left[\frac{1}{4} + \left(\frac{T}{\Theta_D} \right)^2 \int_0^{\Theta_D/T} \frac{x dx}{e^x - 1} \right] , \quad (7.2b)$$

where M is the atomic mass, k_B Boltzmann's constant and Θ_D the Debye temperature. Applying the familiar plane wave expansion (cf. Messiah 1965)

$$e^{i \underline{k} \cdot \underline{r}} = \sum_{\ell=0}^{\infty} (2\ell+1) j_{\ell}(kr) P_{\ell}(\cos \vartheta_{kr}) \quad (7.3)$$

to eq. (7.2a) we obtain

$$\langle e^{i(\underline{k}-\underline{k}') \cdot \underline{r}} \rangle_{av} = e^{-2Ak^2} \sum_{\ell=0}^{\infty} (2\ell+1) i^{\ell} j_{\ell}(-2iAk^{\ell}) P_{\ell}(\cos \vartheta_{kk'}). \quad (7.4)$$

The averaged scattering amplitudes are now evaluated by substituting eq. (7.4) and eq. (4.6) into eqs. (7.1) and using (cf. Edmonds 1957)

$$P_{\ell_1}(\cos \vartheta) P_{\ell_2}(\cos \vartheta) = \sum_{\ell} (\ell_1 \ell_2 \ell, 000)^2 (2\ell+1) P_{\ell}(\cos \vartheta) \quad (7.5a)$$

$$P_{\ell_1}(\cos \vartheta) P_{\ell_2}'(\cos \vartheta) = [(\ell_2+1)!]^{-\frac{1}{2}} [(\ell_2-1)!]^{-\frac{1}{2}} \sum_{\ell} (\ell_1 \ell_2 \ell, 000) \cdot \\ \cdot (\ell_1 \ell_2 \ell, 011) [(\ell-1)!]^{-\frac{1}{2}} [(\ell+1)!]^{-\frac{1}{2}} (2\ell+1) P_{\ell}'(\cos \vartheta) \quad (7.5b)$$

where $(\ell_1 \ell_2 \ell, 000)$ and $(\ell_1 \ell_2 \ell, 011)$ are Wigner 3-j coefficients (cf. Edmonds 1957). We thus obtain

$$\langle f(\vartheta) \rangle_{av} = (2ik)^{-1} \sum_{\ell_1 \ell_2 \ell} B_{\ell_1 \ell_2 \ell} [(\ell_2+1)(e^{2i\bar{\delta}_{\ell_2-1}} - 1) + \ell_2(e^{2i\bar{\delta}_{\ell_2}} - 1)] P_{\ell}(\cos \vartheta), \quad (7a)$$

$$B_{\ell_1 \ell_2 \ell} = e^{-2Ak^2} (2\ell+1)(2\ell_1+1) i^{\ell_1} j_{\ell_1}(-2iAk^2) (\ell_1 \ell_2 \ell, 000)^2, \\ \langle g(\vartheta) \rangle_{av} = (2ik)^{-1} \sum_{\ell_1 \ell_2 \ell} C_{\ell_1 \ell_2 \ell} (-e^{2i\bar{\delta}_{\ell_2-1}} + e^{2i\bar{\delta}_{\ell_2}}) P_{\ell}'(\cos \vartheta) \quad (7b)$$

$$C_{\ell_1 \ell_2 \ell} = e^{-2Ak^2} (2\ell+1)(2\ell_1+1) i^{\ell_1} j_{\ell_1}(-2iAk^2) \sqrt{\frac{(\ell_2+1)! (\ell-1)!}{(\ell_2-1)! (\ell+1)!}} (\ell_1 \ell_2 \ell, 000) (\ell_1 \ell_2 \ell, 011).$$

Comparing these expressions for the averaged scattering amplitudes with those for the actual ones (cf. eq.(4.6), we note that they have the same formal structure. We can therefore introduce effective phase shifts $\bar{\delta}_{\ell-1}$ and $\bar{\delta}_{\ell}$ which are determined by the following equations:

$$(\ell+1)(e^{2i\bar{\delta}_{\ell}} - 1) + \ell(e^{2i\bar{\delta}_{\ell-1}} - 1) = \\ = \exp(-2Ak^2) \sum_{\ell_1 \ell_2} B_{\ell_1 \ell_2 \ell} [(\ell_2+1)(e^{2i\bar{\delta}_{\ell_2-1}} - 1) + \ell_2(e^{2i\bar{\delta}_{\ell_2}} - 1)], \quad (7.7a)$$

$$-e^{2i\bar{\delta}_{\ell}} + e^{2i\bar{\delta}_{\ell-1}} = \exp(-2Ak^2) \sum_{\ell_1 \ell_2} C_{\ell_1 \ell_2 \ell} (-e^{2i\bar{\delta}_{\ell_2-1}} + e^{2i\bar{\delta}_{\ell_2}}). \quad (7.7b)$$

From eqs. (7.7a,b) $\exp(2i\bar{\delta}_{\ell-1})$ and $\exp(2i\bar{\delta}_{\ell})$ are easily obtained individually in terms of the actual phase shifts $\delta_{\ell-1}$ and δ_{ℓ} . We note that the effective phase shifts $\bar{\delta}_{\ell-1}$ and $\bar{\delta}_{\ell}$ will in general be complex in accordance with the interpretation of the excitation of thermal lattice motions as inelastic processes.

8. Comparison between the Present Theory and Jennings'

Spin-Polarized LEED Formalism

While the present work was in progress, an alternative LEED formalism incorporating spin polarization and further relativistic effects has come forth (Jennings 1970, 1971b), which is essentially a two-component generalization of a combination of Kambe's (1967, 1968) KKR approach and of McRae's (1968) transfer matrix method. It seems appropriate to compare Jennings' work with ours and to try to establish the relative merits and shortcomings, firstly from a point of view of theory and secondly from that of numerical results. Relegating the second aspect to Chapter 10, we now proceed to the theoretical aspect, where we find it convenient to distinguish between 'general features', by which we mean features already present in the Schrödinger-equation-based analogues of the two formalisms (cf. Jennings and McRae 1970, Appendix A of the present work, respectively), and specifically 'relativistic features'. (For brevity, we refer to Jennings' theory as TJ and to ours as TF.)

8.1 General Features

Both TJ and TF separate the LEED problem into two parts: (1) the inter-layer multiple scattering problem and the boundary value problem, (2) the multiple scattering problem by atoms within a single layer, which is infinite and perfectly periodic.

Part (1) is approached in TJ by means of the transfer matrix method of McRae (1968), in TF by means of the propagation matrix method (cf. Marcus and Jepsen 1968). Since the two matrices are connected by a simple transformation, the two approaches are so far equivalent. A difference exists, however, with respect to the crystal model, which is semi-infinite in TJ and slab-like

in TF. For a discussion of these two assumptions we refer to Chapter 2.3.

As regards part (2), the treatment of the intra-layer multiple scattering, we first note as a common feature that both TJ and TF assume the actual crystal potential, for which they adopt the muffin-tin approximation, as known and process the information about the scattering centres in terms of phase shifts. TJ then follows Kambe's (1967, 1968) KKR approach, which essentially involves a spherical wave representation, whereas TF uses the phase shifts to construct a pseudopotential, which is separable in the mixed representation, and solves the problem in the mixed representation. If the pseudopotential in TF is chosen of the KKRZ-type, the two approaches are theoretically equivalent, the spherical wave representation, however, offering the practical advantage of being able to obviate possible convergence problems by the use of an Ewald summation technique. In TF, the remedy to convergence difficulties would consist in adopting a 'better' pseudopotential*).

A further difference between the two methods lies in the manner, in which they take into account the effect of inelastic bulk processes. While TF does this by means of an energy-dependent spatially uniform imaginary potential, TJ (Jennings 1972) uses imaginary phase shift contributions. As discussed in Chapter 5.1, we feel that imaginary phase shifts are a less realistic approximation than a constant imaginary potential, in particular in view of their influence on spin polarization.

*) In Chapter 5, the KKRZ-form was selected as being the 'best' out of a certain family of known pseudopotentials. We expect a pseudopotential, which is continuous in r -space, e.g. a sum of Gaussian wells—(instead of the δ -function spheres in KKRZ) — to converge better, but did not yet adopt such a form because of the more complicated nature of its mixed representation coefficients.

8.2 Relativistic Features

We now consider the manner, in which TJ and TF take into account spin polarization and further relativistic effects. Firstly we note that they both employ the full four-component Dirac equation to obtain the scattering phase shifts of a single muffin-tin sphere.*) TF then continues using the Dirac equation for treating the multiple scattering between the muffin-tin spheres, whereas TJ applies the (two-component) Pauli equation to this problem. Since the relativistic effects originate at the ion core sites and are thence already contained in the phase shifts, the Pauli approximation appears to be acceptable at this stage. The choice between the two equations then becomes a matter of practicality, and one might, from this point of view, intuitively favour the latter. Closer inspection shows, however, that the amounts of computational labour required by the two alternatives are similar: The main computational effort is concentrated in two processes: (1) the construction of the propagation or transfer matrix, (2) the diagonalization or multiplication (by itself or related ones) of the respective matrix. Process (1) consists both in TJ and in TF to a large extent in solving an algebraic system of equations (eq.(21) in (Jennings 1970) and eq.(6.11) in the present work). The number of these equations in TJ is clearly $2 \sum_{\ell} (2\ell+1)$, where the angular momentum quantum number ℓ corresponds to all non-zero phase shift pairs δ_{ℓ} and $\delta_{-(\ell+1)}$. In TF it can be seen from eq.(6.12) — from the fact that only 4 matrices $\tilde{\Gamma}_{\mu}$ occur (instead of the 16 of the full Dirac algebra) — that the number is also $2 \sum_{\ell} (2\ell+1)$ (and not

*)

TJ originally (Jennings 1970) proposed to use for this purpose a two-component approximation to the Dirac equation, but subsequently revised (Jennings 1971b) this opinion on the grounds of the results of Meister and Weiss (1968) (cf. Chapter 2.2).

$4 \sum_{\ell} (2\ell+1)$, as the first impression of eq.(6.11) might suggest). As regards process (2), the labour required depends on the size of the propagation matrix. Since the Dirac equation involves four first order equations and the Pauli equation two second order equations, the propagation matrix is in either case of the size $(4N \times 4N)$. The criterion of computational practicality thus seems to provide no discrimination between using the Pauli or the Dirac equation. *Ceteris paribus*, we feel that the Dirac equation provides more flexibility to our formalism as regards the possible use of pseudopotentials, which are not expressed by means of phase shifts.

In conclusion of the comparison between TJ and TF, we find that the two methods are fairly equivalent and should yield, if adequately applied, comparable results. As far as we know, TJ does not yet provide for continuous and δ -function surface potentials and for the effect of thermal lattice vibrations. It seems, however, that these features can be added to TJ in a similar manner as they have been added to TF. The same applies to a constant imaginary potential, which has so far been absent in Jennings' work.

9. Assumptions Specific to Our Present Calculations for Tungsten

In the following two chapters, we are concerned with applying our relativistic LEED formalism to tungsten and obtaining numerical results for intensities and spin polarizations. Tungsten has been selected for the following two reasons: firstly, its large atomic number ($Z=74$) suggests (cf. Chapter 1.2) that spin polarization and further relativistic effects should be of importance, and secondly, its behaviour under ultra-high-vacuum conditions has been extensively investigated and a fair amount of experimental LEED intensity data is available, in particular for the (001) and the (110) surface. In order to perform numerical calculations for these two tungsten surfaces, we require — in addition to the general model assumptions (cf. Chapter 2) that underly our formalism — several further assumptions, which are specific to this application.

9.1 Energy Range

We choose the energy range below about 40 eV, for the following four reasons. Firstly, we expect the discrepancy between relativistic and nonrelativistic LEED intensity results to become increasingly important with decreasing energy, since the discrepancy between relativistic and nonrelativistic phase shifts is the larger the smaller l is (cf. Chapter 2.2) and small- l phase shifts, in particular the s-wave phase shift, become predominant at very low energies. Secondly, multiple scattering effects, which we expect to be of great interest in connection with spin polarization, are most pronounced at energies below the excitations thresholds of bulk and surface plasmons. In particular, we can thus hope to find appreciable spin polarization effects in association with surface state resonances (cf. McRae 1971). Thirdly, a number of

of experimental results, against which calculated intensities can be compared, is available in this energy range. And last, not least, very low energies offer computational advantages, since there are fewer phase shifts and propagating beams that have to be taken into account.

9.2 Phase Shifts

The relativistic pseudopotential derived in Chapter 4 requires as input information the relativistic phase shifts describing the scattering of an electron by the actual potential inside a single muffin-tin sphere. Since potentials derived for band structure calculations turned out to be applicable for LEED purposes (cf. e.g. Jepsen et al. 1972), we have decided to use such a potential obtained by Mattheiss (1965) from nonrelativistic atomic wave functions in the Hartree-Fock-Slater approximation.*) We are aware of the fact that this potential has basically two deficiencies, namely its descent from nonrelativistic atomic wave functions instead of relativistic ones and the neglect of exchange between the incident electron and the atomic electrons. Since the introduction of exchange has been found to alter the potential by a larger amount than relativity does, (Walker 1971), the main improvement would have to consist in properly taking into account the above exchange. This would require, however, a theoretical effort that seems unwarranted at the present stage of a 'pilot study'.

relativistic Following Jennings (1971b), we have obtained the relativistic phase shifts from Mattheiss' potential by means of the Bunyan-Schönfelder (1965) method (cf. Appendix E) and the Numerov method (cf. e.g. Loucks 1967), respectively. The results, which are consequ-

*) This potential has also been used by Jennings (1971b)

Fig. 9.1 Relativistic phase shifts δ_{l-1} (—), δ_l (---) and nonrelativistic phase shifts δ_p (.....) as functions of energy (relative to the muffin-tin zero) for Mattheiss' (1965) muffin-tin potential for tungsten.

ently identical to Jennings', are reproduced (up to $l=3$ and $E = 50$ eV (relative to the muffin-tin zero)) in Fig. 9.1. We note the significant difference between the relativistic and the nonrelativistic set for $l=0,1$ over the entire range and for $l=2$ mainly below about 20 eV, the relativistic phase shifts being consistently larger than their nonrelativistic counterparts. In order to get some more guidance as to how many ^{phase} shifts have to be taken into account in our computations, we have calculated the atomic differential cross section and degree of spin-polarization (as functions of the scattering angle) according to eq.(4.7).

From these results it appears that the set up to $\ell = 2$ is adequate below about 25 eV and that an accurate calculation above that energy should include the $\ell = 3$ phase shifts. Since we are mainly interested in very low energies, we have taken into account only the five phase shifts up to $\ell = 2$.

It might seem the logically next step to complete the ion core pseudopotential requirements by specifying the radii R_ℓ . Since the choice of these is, however, as discussed in Chapter 4.4, linked to a knowledge of lattice parameters, in particular the reciprocal surface lattice vectors, we have to introduce these first.

9.3 Lattice Specifications and Number of Beams

The crystal structure of tungsten is body-centred cubic with a lattice constant of $3.16 \text{ \AA}$. The direct and the reciprocal surface lattices for the (001)- and the (110)-face are shown in figures 9.2 and 9.3, where we have also indicated the primitive unit

Fig. 9.2 (001) surface of tungsten

- (a) direct lattice; full circles denote the topmost layer and empty circles the one beneath
- (b) reciprocal lattice; full circles denote the reciprocal lattice vectors taken into account in most of our numerical work.

Fig. 9.3 (110) surface of tungsten ((a) and (b) as in fig. 9.2)

cells chosen for our calculations. In the direct lattice diagrams the full circles indicate the top layer and the empty circles the second layer, which is displaced with respect to the first one by $\underline{d} = (1.58, 1.58, 1.58)[\text{\AA}]$ for W(001) and $\underline{d} = (0, 1.58, 2.24)[\text{\AA}]$ for W(110). The reciprocal lattice vectors are designated in the manner recommended by Wood (1964). Full circles indicate the vectors taken into account in most of our numerical work. The number of beams included is thus 9 for W(001) and 7 for W(110). To indicate the propagating or evanescent character of these beams, we have added two circles of radii $k = \sqrt{2E}$ around the origin, the inner circle for $E = 10$ eV, the outer one for $E = 50$ eV. We thus see in particular that, at energies below 50 eV for normal incidence, the set of beams included in the calculations always comprises all propagating and, with decreasing energy, an increasing number of evanescent waves. For computations at non-normal incidence, we displaced the 'Ewald circle' corresponding to the mean energy $\bar{E}$ of the

range under consideration by $k^{\parallel}(\bar{E}, \vartheta)$ from the origin of the reciprocal lattice and took into account the vectors inside the circle plus those closest to its circumference — up to a maximum number of nine.

9.4 Pseudopotential Radii

The criteria laid down in Chapter 4.4 for specifying the pseudopotential radii, are now applied to $W(001)$ and $W(110)$. From the lattice dimensions given in the preceeding Section, we find as upper limits dictated by the non-overlap condition:

$$R_{\max}^{001} = 0.79 \text{ \AA}, \quad R_{\max}^{110} = 1.12 \text{ \AA}. \quad (9.1)$$

We choose R_0 equal to the respective $R_{\max}$. As regards R_1 and R_2 , we note (cf. Abramovitz and Stegun 1965 p.457) that the first maxima of $j_1(z)$ and $j_2(z)$ occur at $z_1 = 2.1$ and $z_2 = 3.3$, respectively. Choosing as the 'closest' reciprocal lattice vectors the sets $\{10, 01, \bar{1}0, 0\bar{1}\}$ for $W(001)$ and $\{11, 01, \bar{1}\bar{1}, 0\bar{1}\}$ for $W(110)$, with $|q| = 1.95 \text{ \AA}^{-1}$ and $2.38 \text{ \AA}^{-1}$, respectively, we find the following radii

$$R_1^{001} = 1.06, \quad R_2^{001} = 1.66, \quad R_1^{110} = 0.88, \quad R_2^{110} = 1.38. \quad (9.2)$$

Comparing the values given in eq.(9.2) with those in eq.(9.1), we notice that R_1^{110} is smaller than $R_{\max}^{110}$, whereas the other radii would exceed the respective $R_{\max}$ if chosen according to our criterion, the excess being worst (more than a factor 2) for R_2^{001} . We therefore adopt in our numerical work the value from eq.(9.2) for R_1^{110} and treat R_2^{110} , R_1^{001} and in particular R_2^{001} as adjustable parameters.

9.5 Imaginary Potential Contribution

In Chapter 5.1 we decided to represent the effect of inelastic processes by means of an optical potential of the form eq.(5.1) (Gersten 1969, 1970)

$$V_{opt} = -iv_i(E) \Theta(z) - iv_s(E, \vartheta) \delta(z).$$

The problem remains, how to choose the functions $v_i(E)$ and $v_s(E, \vartheta)$ in view of calculations for tungsten.

The values given by Gersten (1970, figs. 5 and 6) have been obtained for a semi-infinite jellium model. This provides a reasonable approximation for the electron gas in a simple metal, but is invalid for a complicated transition metal like tungsten. In the absence of a first principles many-body treatment of the electron gas in tungsten, we therefore have to consider v_i and v_s as adjustable parameters, which must be fitted to experimental LEED curves. Some guidance with respect to the energy dependence of these parameters may, however, be obtained from energy loss

Fig. 9.4 Energy loss profile from W(001) for a 100 eV beam of normal incidence. (cf. from Burkstrand et al. 1972).

measurements. To illustrate this point, we reproduce in fig. 9.4 an experimental energy loss profile for W(001) (Burkstrand et al. 1972). The loss peaks can be associated with specific inelastic processes as follows. The peak near 4.5 eV. as well as a 1.5 eV loss — (not shown in fig. 9.4, reported by Edwards and Propst (1971)) — are ascribed to interband transitions, presumably involving surface states, as is suggested by their sensitivity to surface contamination and

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by the fact that peaks of a similar behaviour occur at slightly different energies on W(110) (Avery 1972). The loss near 10 eV, which was previously (Scheibner and Tharp 1967) associated with surface plasmon excitations, has been found by Burkstrand et al. (1972) to increase in loss energy and intensity as oxygen is added to the surface. Although this behaviour contradicts the surface plasmon hypothesis, the sensitivity to contamination indicates that a surface loss process is involved. The 16.5 eV loss has not been observed in previous work. It is found to be very sensitive to the energy and the scattering angle, for which the loss profile is measured, and its interpretation seems still ambiguous. The peak near 31 eV can be regarded as a combination of the loss mechanisms near 10 eV and 22 eV.

Trying to deduce some information on the behaviour of the two inelastic parameters, we first note that the threshold energy, E_{th} at which an incident electron can produce a loss of energy E_L , is given as

$$E_{th} = E_L - \phi ,$$

where ϕ is the work function for the surface under consideration. Since for all low index faces of tungsten $\phi > 4.5$ eV and since surface states are not as extremely localized as $\delta(z)$, we assume both v_i and v_s as small constants ($\approx + 0.5$ eV) in the energy range from 0 to the threshold $E_{th}(10)$ of the 10 eV loss peak. In the vicinity of $E_{th}(10)$ we assume a steep rise in v_s and possibly some rise in v_i ^{*)}. We ignore the 16.5 eV peak because of its above-mentioned properties, and finally assume a rise in v_i near $E_{th}(22)$ and $E_{th}(31)$. For the work function we

*) Since the origin of the 10 eV peak is still doubtful, we have no information about the degree of localization of the underlying inelastic process.

adopt the values 4.65 ± 0.12 eV for W(001) (Fehrs and Stickney 1971) and 5.3 ± 0.1 eV for W(110) (Todd and Rhodin 1973).

Since the above assumptions about the behaviour of v_i and v_s entail a substantial number of parameters, we simplify them, however, in our numerical applications — on a case to case basis — as much as the aim of the respective calculations permits.

9.6 Real Inner Potential and Surface Potential Barrier

The real inner potential v_r comprises the real part of an exchange-correlation contribution that depends on the energy of the incident electron (cf. e.g. Sham and Kohn 1966). Since free-electron gas results are inadequate for tungsten and a proper first principles calculation is not available at present, we prefer to determine v_r by performing a LEED calculation at normal incidence without an inner potential and subsequently shifting the calculated intensity-energy profile such that it matches to the corresponding experimental one. The value of v_r thus obtained is then used in further calculations, in particular at non-normal incidence.

As regards the specific form of the surface potential barrier, we will use two models, firstly an abrupt step of height v_r , and secondly an exponential barrier

$$- v_r / (1 + \exp(-z/a)) , \quad a = 0.25 \text{ \AA} , \quad (9.3)$$

where the choice of the scale, at which the variation takes place, has been guided by the theoretical results of Lang and Kohn (1971).*)

9.7 Thermal Lattice Vibrations

Although our theory makes provision for incorporating the effect

*) This type of barrier has also been used by Andersson and Pendry (1973).

of thermal lattice vibrations on LEED results, we have decided not to take it into account in our present computations. This approximation may find some theoretical justification on the grounds that temperature effects are less important at lower energies (cf. e.g. Jepsen et al. 1972) and our main results will be in the range below about 25 eV. A more pragmatic support for initially neglecting temperature effects is provided by the experimental results of Loth (1967), who obtained appreciable degrees of spin polarization at energies of several hundred eV and at a temperature of about 2000°K.

9.8 Spin Polarization of the Primary Beam

Our formalism permits the calculation of intensity and spin polarization of the diffracted beams for an arbitrary mixed state of polarization of the primary beam. Considering the two extreme cases (a) of an unpolarized primary beam and (b) of a completely polarized one with a spatial polarization vector $\underline{\epsilon} \underline{t}$ ($\epsilon = +$ or $-$), we can show from our formalism (cf. also e.g. Rose 1961) that there is a close relation between the respective results. Denoting by I_n and P_n the intensity and spin polarization of the n^{th} diffracted beam in case (a) and by I_n^ϵ and P_n^ϵ the intensity and spin polarization of the n^{th} beam in case (b) with $\underline{t}$ normal to the plane spanned by the wave vectors of the primary beam and the n^{th} diffracted beam, we have

$$P_n^\epsilon = \epsilon, \quad I_n = \frac{1}{2} (I_n^+ + I_n^-), \quad P_n = \frac{I_n^+ - I_n^-}{I_n^+ + I_n^-}. \quad (9.4)$$

This result implies that the knowledge of the results of case (a) is equivalent to the knowledge of the results of case (b) (with the spin direction chosen as stated), i.e. spin polarization and further relativistic effects that manifest themselves in the one case, do so in the other as well by virtue of eq.(9.4). As regards the inter-

mediate case of a partially polarized primary beam, we can consider such a beam as a statistical mixture of completely polarized beams and thus easily extend the argument to this case.

We can therefore without loss in generality, restrict our numerical work to one of the two extreme cases. We decide to choose the case of an unpolarized primary beam, since this allows a more illustrative presentation of the effects we want to investigate.

10. Numerical Results for W(001) and W(110)

In view of predicting quantitative intensity and spin polarization results, our LEED formalism has been translated into a FORTRAN V computer programme, details of which may be found in Appendix G. Numerical computations have been performed for the (001) and the (110) surfaces of tungsten, which were chosen for the reasons stated in the introduction to Chapter 9. In the following, intensities and spin polarizations, that we have calculated for the case of an unpolarized primary beam as functions of the primary beam energy for a variety of polar angles in the ($\bar{1}0$) azimuth, will be presented and discussed. *)

10.1 Comparison with Experimental Results

Our theory predicts — for each LEED beam — the behaviour of two observable quantities, intensity and spin polarization, as functions of the energy of the primary beam and of its orientation with respect to the crystal surface. Since so far no successful measurement of spin polarization in LEED has come to our attention, we can check the validity of our predictions against experiment only as regards intensity. More specifically, the experimental data currently available for tungsten at energies below about 50 eV require this check to be carried out on intensity-energy profiles for fixed primary

*) The number of monatomic layers that was found adequate, is 6 for an imaginary bulk potential $v_i = 0.5$ eV and 4 for $v_i \geq 2$ eV.

Intensities are given — unless specifically stated otherwise — in fractions of the intensity of the primary beam (which is assumed to be unity), and spin polarizations range from -1 to +1, the two limits corresponding to complete polarization with 'spin down' and 'spin up' (with respect to the normal to the plane spanned by the wave vector of the primary beam and that of the diffracted beam under consideration), respectively. (The plane that we have just referred to is obviously not defined for the specular beam in the case of normal incidence. There is, however, no need for it, since, given an unpolarized primary beam, the specular beam will be unpolarized in this special case, as one can already anticipate from the symmetry of the problem.)

beam orientations. "Agreement" between theory and experiment would then ideally mean, that the calculated and the measured intensity-energy profiles should be completely identical. It is, however, implicit in our model assumptions that this ideal goal is unattainable. In particular, the assumption of an ideal surface of perfect two-dimensional periodicity, i.e. disregard of surface steps and surface roughness (cf. e.g. Houston and Park 1971), is bound to make the theoretical absolute intensities excessively large. If one neglects the effect of thermal lattice vibrations, this excess will even be further enhanced (cf. Jepsen et al. 1972). Since, moreover, many experimental data do not give absolute intensities, it appears as an obvious second best choice to focus attention on the heights of peaks relative to each other. As regards the positions of peaks with respect to the energy axis, arbitrariness enters on the theoretical side with the choice of the real part of the inner potential and is usually corrected for, together with experimental errors in the origin of the energy scale, by an a posteriori energy shift such as to achieve alignment of the most prominent features of the profile. Significance can, however, still be attributed to peak widths and to positions of peaks relative to each other. One thus arrives at a pragmatic definition of "agreement" between theory and experiment, which involves the following three criteria: relative peak positions, peak widths and relative peak heights.

It is with these three criteria in mind that we proceed now to comparing, for the (001)- and (110)-surfaces of tungsten, our calculated intensity-energy profiles with experimental ones. The experimental data against which we check our results comprise, in addition to proper LEED data, 'reflection coefficient'

measurements by means of the retarding potential technique (Khan et al. 1963, Zollweg 1964), since the 'reflection coefficient' is equivalent to the (oo)-beam intensity below the threshold of emergence of nonspecular beams.

10.1.1 For W(001)

Fig. 10.1 Comparison of calculated (oo)-intensity (for normal incidence) (—) and experimental reflection coefficient (---) from W(001).

In fig. 10.1 we compare our calculated (oo)-intensity profile for $\vartheta = 0$ with the reflection coefficient measured by Khan et al. (1963). The calculation was performed with a step potential barrier of 11.5 eV, an imaginary bulk potential of 1 eV for $E \leq 16$ eV and 2 eV for $E > 16$ eV and an imaginary surface potential $-iv_s \delta(z)$ with $v_s = 2$ eV. The pseudopotential radii were chosen as $R_0 = R_1 = R_{max}^{001}$ (cf. eq.(9.1)) and $R_2 = 0.5 R_{max}^{001}$. We see from fig. 10.1 that our theory reproduces the three peaks of the experimental curve. The relative heights and widths agree reasonably well. As regards the peak positions, they are correct for the main peak at 8 eV and the peak at 4 eV, whereas there is a discrepancy of about 3 eV for the peak near 16 eV. We wish to draw particular attention to the fact that the appearance of the peak at 4 eV, which is absent in the profile obtained by Jennings and McRae (1970), is a consequence of

the imaginary $\delta(z)$ potential. (The peak vanishes for $v_s = 0$) This seems to suggest that the 4 eV peak is associated with inelastic processes in the surface region. *)

Fig. 10.2 Comparison of calculated (—) and experimental (---) oo-intensity from W(ool) for $\vartheta = 53^\circ$ (The experimental intensity is plotted in arbitrary units). Arrows indicate beam emergence thresholds.

In fig. 10.2 we present a comparison between theory and experiment (Propst and Edwards, unpublished; the experimental curve may be found in (Estrup and McRae 1971, fig. 14)) for the oo-profile for $\vartheta = 53^\circ$. In our calculation we used in particular a real step potential of -10 eV and

$$v_1 = \begin{cases} 0.5 \text{ eV} & \text{for } E \leq 5 \text{ eV} \\ 2.0 \text{ eV} & \text{for } 6 \text{ eV} \leq E \leq 16 \text{ eV} \\ 4.0 \text{ eV} & \text{for } E > 17 \text{ eV} \end{cases}$$

(with linear interpolation of v_1 in the 'gaps'), but no imaginary surface potential. We notice that there is again good agreement as regards relative peak heights and widths and the positions of the features near 4 eV and 20 eV, whereas there is a discrepancy with respect to the position of the peak occurring at 16 eV in the experiment. Details of the feature near 4 eV which is associated with a surface state resonance (McRae 1971),

*) For an extensive discussion of the nature of this peak cf. McRae and Wheatley (1972).

Fig. 10.3 Comparison of calculated (—) and experimental (---) (oo)-intensity from W(001) for $\vartheta = 53^\circ$. (The experimental intensity is plotted in arbitrary units, which are smaller than those used in fig. 10.2)

are shown in fig. 10.3, which reveals good agreement between our calculated result and the experiment.

We have also calculated intensity profiles for a sequence of angles of incidence similar to the one for which McRae and Wheatley (1972) recently reported measurements. For the larger angles, results calculated with a step potential and no imaginary surface potential (cf. fig. 10.12) were found to be in good qualitative agreement with the corresponding experimental results. At intermediate angles, the shape of the surface potential barrier and the strength of the imaginary (z) potential appear to be of crucial importance and further detailed calculations are required.

10.1.2 For W(110)

Experimental intensity-energy profiles for the (110) surface of tungsten are available in the literature for the (oo)-, the (ol)- and the (lo)-beam for the case of normal and slightly off-normal incidence of the primary beam. In fig. 10.4 we

Fig. 10.4 Intensity-energy profiles for the (oo)-beam from W(110):
 ---- experiment (Taylor 1966), energy-origin marked by "↑", intensity in arbitrary units
 ---- experiment (Fedorus 1971), energy-origin marked by "↑", intensity x5 in fractions of the primary beam intensity
 — relativistic theory, intensity in fractions of the primary beam intensity.

compare (00)-intensity profiles measured by Taylor (1966) and Fedorus (1971) with one calculated by means of our relativistic formalism for a step potential of -10 eV a bulk imaginary potential of 2 eV, and pseudopotential radii $R_0 = R_1 = 0.9 R_{\max}^{110}$, $R_2 = 0.7 R_{\max}^{110}$. The experimental curves have been shifted towards higher energies by 3 eV and 11 eV, respectively, in order to achieve alignment of corresponding peak positions. We note that a relative shift of 8 eV is required to align the peak positions of the two experimental curves and ascribe this partly to the fact that in the experiment of Fedorus (1971) no correction was made for the contact potential between cathode and crystal. *) Comparing the three curves of fig. 10.4 with respect to relative peak positions, peak widths and relative peak heights **) we find that satisfactory agreement has been achieved between theory and experiment. In particular, we notice that the agreement between our theoretical curve and the experimental curve of Fedorus is significantly better than the agreement between the two experimental curves. The slight discrepancy in the position of the 60 eV peak could be explained by the fact that we have assumed the inner potential as constant over the entire energy range. Since, in reality, the exchange-correlation contribution to the inner potential decreases with increasing energy (cf. Jepsen et al. 1972), a real inner potential, which is reduced by

(at $\vartheta = 30^\circ$)

*) The fact that Fedorus worked slightly off normal incidence, can be ignored in the present context. An intensity profile that we have calculated at $\vartheta = 30^\circ$, differs only marginally from the one at $\vartheta = 0^\circ$.

**) As regards the curve by Taylor (1966), we have to take into consideration that it is not normalized with respect to the primary beam intensity. Since the latter increases with increasing energy, the double peak around 40 eV should be reduced relative to the one around 25 eV. The agreement with the other two curves will thus improve.

a few eV, would be theoretically more appropriate in the vicinity of 60 eV. It can be seen from fig. 10.4 that an improvement of the agreement of the 60 eV peak position would result. On the other hand, we have to bear in mind that the assumptions underlying the present computation do not entitle us to expect correct predictions at energies above about 50 eV. As for reflection coefficient data (Khan et al. 1963), agreement has so far been at best qualitative, possibly for the following reason. Since the reciprocal lattice for the (110) face is more widely spaced than that for the (001) face (cf, figs. 9.2 and 9.3), the set of reciprocal lattice vectors closest to the origin might — at very low energies — give rise to evanescent waves that are so strongly exponentially increasing or decreasing that the finite-layer assumption underlying our formalism leads to numerical difficulties (cf. footnote p.18).

Fig. 10.5 Intensity-energy profiles for the (01)-beam from W(110); ---experiment (Farnsworth and Bellina 1968), arbitrary intensity units; — present theory, intensity in fractions of primary beam intensity.

In fig. 10.5 we compare our calculated (01)-beam intensity profile with the one measured by Farnsworth and Bellina (1968) for a clean-annealed surface. Alignment of the positions of the peaks at 25 eV and at 33 eV was achieved by shifting the experimental curve by 3 eV towards the low energy side. Since we used an inner potential $V_r = -10$ eV, this would correspond

to a shift of roughly 7 eV between the experimental curve and a theoretical one obtained without an inner potential. From fig. 10.5 we see that the relative peak heights agree reasonably well. The slight misalignment in the positions of the main peak can be at least partly remedied by invoking the above-mentioned reduction of the real part of the inner potential with increasing energy. We have also computed an intensity-energy profile for the (10)-beam, which emerges 10 eV above the (01) threshold, i.e. at 31 eV, and compared it to experimental results by Farnsworth and Bellina (1968) and by Fedorus (1971). The most prominent feature of these data, a large peak of about 10 eV half-width, which is centered about 6 eV above the emergence threshold of the beam, is well reproduced by our calculation. As regards further features which appear above 50 eV, we find considerable discrepancies between our result and each of the experimental profiles. This is little surprising, since, as already mentioned, the approximations underlying our computation become very poor at energies above 50 eV. On the other hand, it should also be borne in mind that in the experiments of Farnsworth and Bellina the cleanliness of the surface was not monitored by Auger analysis and appears therefore doubtful (Gafner 1973).

It is interesting to note that our calculated (01)- and (10)-profiles agree with the 'clean-annealed' data of Farnsworth and Bellina and not with those measured after bombarding the surface with ions. This finding is at variance with the results of calculations by Gafner (1970), who obtained agreement with the bombarded-surface data. The apparent contradiction has recently been resolved (Gafner 1973) by noting that Gafner's LEED method (Gafner 1969), although it includes inter-layer multiple scattering, shows kinematical features due to the neglect of intra-layer multiple

scattering. It is therefore plausible that it should reproduce the data for the bombarded surface; since these are of a more kinematical nature, whereas our method, which includes intra-layer multiple scattering should be valid for the annealed surface.

In conclusion, we feel that generally good agreement with experimental data has been achieved for a fair number of calculated intensity-energy profiles.

10.2 Comparison of Relativistic and Nonrelativistic Intensity Profiles

In order to assess the nature of relativistic effects in LEED intensity profiles, we have performed calculations with the Schrödinger-equation-based analogue (cf. Appendix A) of our relativistic LEED formalism, using the nonrelativistic phase shifts $\tilde{\delta}_l$ (cf. fig. 9.1). The difference between corresponding relativistically and nonrelativistically calculated results is typically illustrated by figs. 10.6, 10.7 and 10.8, where we compare oo-intensities for normal incidence $W(o o l)$ and $W(l l o)$ and for off-normal incidence ($\vartheta = 40^\circ$) $W(o o l)$. We notice that the nonrelativistic intensities are consistently smaller than the relativistic ones. The changes are minor for normal incidence and become more pronounced for larger angles of inci-

Fig. 10.6 Relativistic (—) and nonrelativistic (---) oo-intensity from $W(o o l)$ for $\vartheta = 0$, $v_r = -11.5$ eV and $v_i = 1$ eV (2 eV) for $E \leq (>) 16$ eV.

Fig. 10.7 Relativistic (—) and nonrelativistic (---) oo-intensity from $W(ool)$ for $\vartheta=40^\circ$, $v_r = -10$ eV and $v_i = 0.5$ eV.

Fig. 10.8 Relativistic (—) and nonrelativistic (---) oo-intensity from $W(110)$, for $\vartheta = 0$, $v_r = -10$ eV and $v_i = 2$ eV.

dence. We have also studied the effect on nonspecular beams, where the difference is found to be somewhat larger than for the specular beam.

We thus conclude that relativistic effects are noticeable in LEED ^{intensity}~~energy~~ profiles for tungsten. We realize, however, that their incorporation in a LEED intensity calculation becomes meaningful only if one ensures at the same time that the phase shifts are taken from a relativistically derived ion core potential and that exchange between the incident electron and the electrons in the ion core is adequately taken into account.

10.3 Spin Polarization

Having shown the agreement of our intensity results with experimental data and the differences between relativistically and nonrelativistically calculated intensity energy profiles,

we now proceed to presenting and evaluating spin polarization results that are predicted by our relativistic LEED formalism. Some further intensity results that are related to spin polarization features will be noted in passing.

10.3.1 General features

For normal incidence, we find that the specular beam, as was to be expected from symmetry considerations, remains unpolarized, whereas appreciable polarization values appear for the nonspecular beams Fig. 10.9 and 10.10 show typical results of

Fig. 10.9 Spin polarization (—) and intensity (---) of the (10)-beam from W(001) for $\vartheta = 0$, $v_r = 0$ and $v_i = 2$ eV.

Fig. 10.10 Spin polarization (—) and intensity (---) of the (01) beam from W(110) for $\vartheta = 0$, $v_r = -10$ eV, $v_i = 2$ eV.

the (10)-beam from W(001) and the (01)-beam from W(110), respectively. We notice very pronounced polarization features, in particular for W (001), with peak values of 35% and 25%. (However, in fig. 10.9 no inner potential correction has been applied, so that the main polarization peak would lie below the emergence

threshold of the observable (10) beam.) Comparing the polarization and the intensity profile, it appears from both figures that polarization maxima occur at energies for which the intensity is minimal. This is a feature, which is well known from atomic scattering (cf. e.g. Kessler 1969). A discussion, whether it is as 'compulsory' in LEED as it is for atomic scattering, will be given later, after further results have been presented.

Since the intensities of the nonspecular beams are substantially smaller than that of the specular beam, it seems desirable in view of actual spin polarization measurements to investigate polarization features of the specular beam. To this end we have carried out calculations off normal incidence for a variety of angles of incidence in the (10) azimuth for both $W(001)$ and $W(110)$. For $W(001)$, we have selected those angles of incidence and energy ranges, for which experimental intensity data were available and specified the parameters entering in our model calculation — the pseudopotential radii, the real and imaginary bulk and surface potential — such that agreement between calculated and experimental intensity profiles was achieved (cf. Chapter 10.1, figs. 2 and 3). In figs. 10.11 and 10.12

Fig. 10.11 Spin polarization (—) and intensity (---) of the (00) beam from $W(001)$ for $\varphi = 53^\circ$. $V_T = -10$ eV.

$$V_i = \begin{cases} 0.5 \text{ eV for } E \leq 5 \text{ eV} \\ 2.0 \text{ eV for } 6 \text{ eV} \leq E \leq 16 \text{ eV} \\ 4.0 \text{ eV for } E \geq 17 \text{ eV} \\ \text{linear interpolation in 'gaps' } \end{cases}$$

Fig. 10.12 Spin polarization (—) and intensity (---) of the (oo)-beam from W(ool) for angles of incidence as indicated in the top left corner of each diagram. A step potential $v_r = -10$ eV was used and $v_l = 0.5$ eV. Arrows $\uparrow$ indicate the threshold energy for the $(\bar{1}0)$ -beam.

spin polarization and intensity profiles of the specular beam are shown for angles of incidence between 40° and 60° — (These are the actual angles between the primary beam and the surface normal.) — and for potential parameters v_r and v_l as given in the figure caption. A step surface potential of -10 eV has been used and no imaginary $\delta(z)$ -potential. The separation between the energy points used in the calculations is $\Delta E = 0.2$ eV for $E \leq 6.4$ eV and $\Delta E = 1$ eV for $E \geq 7$ eV. Both figures reveal very pronounced polarization features of the specular beam. In particular we notice that, although the polarization maxima are again correlated with the intensity minima, very appreciable polarization values occur in conjunction with intensities, which can still be considered as large. We wish to draw special attention to the results given in fig. 10.12. As has been discussed in detail by McRae and Wheatley (1972), the dip-

peak feature slightly to the left of the emergence threshold for the the (10)-beam can be associated with a surface state resonance (cf. McRae 1971). Our results indicate that a strong spin polarization peak of about 1 eV half-width is associated with this surface state resonance.*) The sensitivity of the polarization peak and the intensity feature to details of the surface potential barrier and to the addition of a surface imaginary potential deserves further investigation. Preliminary results obtained from similar calculations including an exponential surface barrier (cf. Chapter 9.5) or an imaginary surface potential of the strength $v_s = 1$ eV indicate that the polarization peak is noticeably reduced by an imaginary potential (e.g. from 34% to 24% for $\vartheta = 53^\circ$) and only slightly so by an exponential surface barrier (that replaces the step barrier). For the above very low energies we do not, however consider an imaginary $\delta(z)$ -potential of appreciable strength as realistic, since they are below the inelastic threshold indicated by the 10 eV loss peak in fig. 9.2.

As regards the case of off-normal incidence for W(110), we have found specular beam polarizations of an order of magnitude and of a behaviour similar to that of the polarization in the specular beam for W(001) above about 6 eV. In particular, we have again found polarization maxima clearly correlated with intensity minima of a still appreciable magnitude. We have so far not investigated surface state resonance features on W(110), since the (lowest) nonspecular beam emergence thresholds are considerably higher in energy than those for W(001) and we therefore expect more inelastic damping, which would in particular have the effect of substantially reducing spin polarization peaks.

*)

A spin polarization feature in conjunction with a surface state resonance has been reported by Jennings (1971c) for the specular beam from Cu(001).

10.3.2 Influence of Inelastic Processes

We have already mentioned in the preceding section that inelastic processes in the surface region as described by an imaginary $\delta(z)$ potential were — if present — prone to reduce the degree of spin polarization expected in connection with a surface state resonance. The result of a further investigation is shown in fig. 10.13.

Fig. 10.13 Intensity and spin polarization of the (00)- and the (10) beam from W(001) for $\vartheta = 10^\circ$, $v_r = 0$, $v_i = 0.5$ eV, and $v_s = 0$ (—) and $v_s = 2$ eV (---).

Spin polarization and intensity of the (00)-beam and the (10)-beam from W(001) for an angle of incidence 10° have been calculated using no real inner potential, a weak imaginary bulk potential $v_i = -0.5$ eV and an imaginary $\delta(z)$ potential of strength either 0 or -2 eV. We notice that the $\delta(z)$ potential has the effect of reducing intensity and polarization peaks. This reduction is most pronounced for the spin polarization peak of

the specular beam near 13 eV and negligible for the polarization peaks of the (10) beam above 20 eV. The decrease of the effect of the $\delta(z)$ potential with increasing energy appears plausible from the scattering properties of this potential as shown in Appendix F fig. F.1. The particularly strong reduction of the (00) polarization peaks as compared to that of the (10) polarization peaks may find a heuristic explanation as follows. The $\delta(z)$ potential reflects part of the primary beam in a spin-independent manner into the specular beam. Since polarizations maxima of a beam correspond to a predominant population of 'spin-up' or 'spin-down' electrons the addition of an equal number of 'spin-up' and 'spin-down' electrons to the beam reduces its degree of polarization. We therefore expect a reduction of the polarization peaks of the specular beam. As for non-specular beams, there is no direct contribution due to the barrier, so that their polarization should remain entirely unaffected if it were not for multiple scattering effects between barrier and substrate.

The effect of bulk inelastic processes on intensities and spin polarizations is illustrated in 10.14, which shows spin-

Fig. 10.14 Intensity and spin polarization of the (10)-beam from W(001) for normal incidence and a surface potential step of 10 eV. The bulk imaginary potential v_i is in (a) and (c) — $v_i = 0.5$ eV, --- $v_i = 3$ eV, in (b) and (d) — $v_i = 0.5$ eV, --- $v_i = 3$ eV.

polarization and intensity profiles of the (10)-beam from W(001) for the case of normal incidence for several values of the bulk imaginary potential v_i . For increasing v_i we notice firstly a drastic reduction in intensity, as was to be expected, and secondly a very interesting behaviour of the spin polarization. The polarization feature near 25 eV, which is associated with an intensity minimum, is most pronounced for small v_i and virtually no existent for large v_i . The polarization maximum near 16 eV (i.e. near the emergence threshold), on the other hand, is still very appreciable over an even wider energy range for large v_i . We attempt to interpret this different behaviour by associating the polarization feature near 25 eV with multiple scattering processes. For weak inelastic damping it is thus to be expected to be very pronounced, whereas it should vanish in the strong inelastic limit. Since the strong inelastic limit will yield the polarization values characteristic of a single muffin-tin sphere (cf. Feder 1972b, 1973; Jennings and Sim 1972), the feature near 16 eV could be regarded as being of an atomic origin.

10.4 Comparison with Results Predicted by Jennings' Spin-Polarized LEED Formalism

It would seem very interesting to make a detailed comparison between our results and their counterparts predicted from Jennings' spin-polarized LEED formalism, discussed in Chapter 8. Unfortunately, the possibilities for such a comparison are very limited at present, for the following reasons: Firstly, only a small number of data on tungsten obtained by Jennings have come to our attention. (These data are for normal and 10° off-normal incidence on W(001) (Jennings and Sim 1971b, 1972)). Secondly, about half of these data relate to the purely elastic case, — i.e. inelastic effects have not been taken into account — to

which our method is not applicable^{*)}. Thirdly, absorption is taken into account by Jennings and Sim (1972) in terms of imaginary phase shift contributions, whereas we have used a constant potential.

Although this state of affairs obviates a quantitative comparison we find that certain qualitative features of the predictions from the two formalisms can be compared with each other.

Firstly and mainly, we note that there is a basic agreement in so far as Jennings also reports very pronounced spin polarization features and rates them highly as possible sources of additional information about the surface region.

As we already mentioned, Jennings (1971c) has also reported spin polarization in connection with surface state resonances, however for a different material and of far narrower width in energy.

Secondly we also find a partial agreement as regards the assessment of the influence of inelastic processes (cf. Jennings and Sim 1972): absorption, by suppressing multiple scattering, brings LEED spin polarization features closer to those in electron-atom scattering. We wish to add — cf. our results in the previous section — that the degree of polarization of the specular beam is substantially reduced in the presence of an imaginary potential (either uniform or of the $\delta(z)$ -type) due to reflection at the imaginary potential.

A further point of interest is the problem, whether one can expect the correlation between spin polarization maxima

*) Considering inelastic effects as indispensable in LEED we have adopted the finite-layer assumption (cf. Chapter 2.3), which rests — both as regards theoretical validity and computational viability — on the presence of absorptive processes.

and intensity minima that is known from atomic scattering. Jennings denies the existence of this correlation in LEED, whereas our results seem to support the assumption of such a correlation. A further and more fundamental investigation seems, however, still required.

11. Conclusion

In part I of the present work we have developed a relativistic theory of LEED that permits in particular the investigation of spin polarization effects. The computational application of this theory — in Part II — to the (001) and the (110) surface of tungsten has been found to yield generally good agreement with experimental intensity-energy profiles and to predict very pronounced spin polarization features.*)

From these predictions, which are supplemented by preliminary results that indicate large spin polarization effects in LEED from ferromagnetic iron (cf. Appendix B), we conclude that spin polarization in LEED should be of great relevance in the following respects:

- (1) The measurement of spin polarization in conjunction with theoretical model calculations can be expected to provide surface structural information, which is not or not as readily obtainable by intensity measurements only. In particular, one can thus expect to obtain information about:
 - (a) the detailed shape of the real and imaginary surface potential, since surface state resonance polarization features are very sensitive to these potential contributions;
 - (b) the exchange interaction between the incident electron and the electrons in the ion cores, as is suggested by the sensitivity of very low energy electron-atom-scattering phase shifts to this exchange;
 - (c) the inequivalence of the scattering properties of sur-

*) The spin polarization results of our calculations cannot be compared with experimental data, since such are not available at present.

face atoms as compared with bulk atoms (cf. Duke and Tucker 1969);

(d) magnetic surface properties of ordered magnetic structures.

- (2) The occurrence of appreciable degrees of polarization in conjunction with fairly high intensities — which has been found in the specular beam from W(001) for large angles of incidence at very low energies, and, in a more pronounced way, in the specular beam from ferromagnetic Fe(001) for normal incidence over a fairly wide energy range — suggests that spin-polarized LEED could provide a strong source of highly polarized electrons as well as a mechanism for measuring the degree of polarization of a given beam of low energy electrons without having to accelerate to the high energies (about 100 keV) required by the conventional Mott detector.

In conclusion, we therefore wish to emphasize the importance of spin polarization effects in LEED and to express the hope that experimental investigations may materialize in a near future.

Appendix A

Schrödinger-Equation-Based Analogue of Relativistic LEED Formalism

In view of comparing the LEED intensities predicted by our relativistic theory with non-relativistic intensities, we have developed the Schrödinger-equation-based analogue of our theory. This analogue also can be considered as a LEED formalism in its own right, which is applicable to materials, for which spin-orbit and further relativistic effects are negligible (i.e. low Z materials). In the following, we give a brief outline of this non-relativistic LEED theory.

The basic assumptions are the same as in the relativistic theory (cf. Feder 1972, p. 700), except that the dynamical basis is now Schrödinger's equation

$$\left(\frac{1}{2} \Delta + E \right) \psi(\underline{x}) = \int d^3 \underline{x}' V(\underline{x}, \underline{x}') \psi(\underline{x}') \quad , \quad (\text{A.1})$$

where E is the energy of the incident electron and $V(\underline{x}, \underline{x}')$ is a complex potential operator describing the effective electron-solid interaction. The integration is over the volume occupied by the solid, i.e. over a slab of infinite extension in the (x, y) plane and confined between z_1 and z_2 .^{†)} Potential and wave function are expanded in Fourier series with respect to the

^{†)} Given a certain number of atomic layers, the choice of z_1 and z_2 with respect to the centres of the top layers is somewhat arbitrary, depending on the surface potential approximation adopted for the particular calculation.

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^{†)} Given a certain number of atomic layers, the choice of z_1 and z_2 with respect to the centres of the top layers is somewhat arbitrary, depending on the surface potential approximation adopted for the particular calculation.

surface reciprocal lattice (cf. Laue 1931):

$$V(\underline{x}, \underline{x}') = \sum_{mn} v_{mn}(z, z') \exp[-i \underline{g}_m \cdot \underline{x}' + i \underline{g}_n \cdot \underline{x}] , \quad (\text{A.2a})$$

$$\psi(\underline{x}) = \sum_m \psi_m(z) \exp[i \underline{k}_m \cdot \underline{x}] , \quad (\text{A.2b})$$

where m and n enumerate the surface reciprocal lattice vectors $\underline{g}_m$, of which a finite number N is taken into account in numerical calculations; $\underline{k}_m = \underline{k}_0 + \underline{g}_m$, where $\underline{k}_0$ is the wave vector of the incident beam. Substitution of eqs. (A.2) into eq. (A.1) yields

$$(\partial_z^2 + k_m^2) \psi_m(z) = 2 \sum_n \int dz' v_{mn}(z, z') \psi_n(z') , \quad (\text{A.3})$$

where $k_m^2 = 2E - (\underline{k}_0 + \underline{g}_m)^2$. The calculation of LEED intensities now proceeds in two steps: firstly the determination of the solution of the above system of N ordinary linear integro-differential equations inside the crystal, secondly the matching of this solution to the solutions in the vacuum.

The method applicable for the first step depends strongly on the type of crystal potential chosen for the calculation. For local potentials (i.e. $v_{mn}(z, z') = v_{mn}(z) \delta(z - z')$), eq. (A.3) is solved by numerical integration (cf. Marcus and Jepsen 1968). For non-local pseudopotentials, which are separable in $\underline{k}$ -space, i.e. can be written in the form

$$v_{mn}(z, z') = \sum_v v_{1m}^v(z) v_{2n}^v(z') , \quad (\text{A.4})$$

we propose the following procedure^{†)}. Eq. (A.4) is substituted into eq. (A.3) to yield

$$(\partial_z^2 + k_m^2) \psi_m(z) = 2 \sum_v v_{1m}^v a^v, \quad a^v = \sum_n \int_{z_1}^{z_2} dz' v_{2n}^v(z') \psi_n(z'). \quad (A.5)$$

Since this is a system of N second-order equations, there are 2N linear independent solutions, which we write in the form

$$\psi_{mn\sigma}(z) = \exp[i\sigma k_n(z-z_1)] \delta_{mn} + \sum_v \psi_{mn\sigma}^v(z), \quad (A.6)$$

where the index $m = 1, \dots, N$ corresponds to the Fourier expansion (i.e. beam -) index (cf. eq. (A.2b)), and the indices $n = 1, \dots, N$ and $\sigma = +1$ and -1 denumerate the "fundamental" solutions. $\psi_{mn\sigma}^v(z)$ satisfies the inhomogeneous differential equation

$$(\partial_z^2 + k_n^2) \psi_{mn\sigma}^v(z) = 2 v_{1m}^v(z) a_{n\sigma}^v, \quad (A.7a)$$

$$a_{n\sigma}^v = \sum_k \int_{z_1}^{z_2} dz' v_{2k}^v(z') \psi_{kn\sigma}(z'). \quad (A.7b)$$

^{†)} The KKRZ pseudopotential (cf. Ziman 1965), which has been recommended for LEED purposes by Pendry and Capart (1969), is of this form, where v is a collective index denoting the angular momentum representation indices ℓ and m . As for the procedures of obtaining the $v_{lm}^v(z)$ from the atomic pseudopotential in configuration space and of evaluating the z' -integrals in the following, we refer to the relativistic treatment, since there is a complete analogy.

Eq. (A.7a) is solved by means of the standard method of "variation of the constant". One obtains

$$\psi_{mns}^v(z) = a_{ns}^v f_m^v(z), \quad f_m^v(z) = \frac{i}{k_m} \sum_{l=1}^{\infty} \left(\int_{z_1}^{z_2} dz' v_{lm}^v(z') e^{i\tau k_m(z'-z_1)} \right) e^{-i\tau k_m(z-z_1)}. \quad (A.8)$$

From eqs. (A.8), (A.6) and (A.7b) one obtains an algebraic system of equations for determining the constants a_{ns}^v

$$\sum_{\tilde{s}} \left[\delta_{s\tilde{s}} - \sum_k \int_{z_1}^{z_2} dz' v_{2k}^v(z') f_k^v(z') \right] a_{ns}^v = \int_{z_1}^{z_2} dz' v_{2n}^v(z') e^{i\delta k_n(z'-z_1)}. \quad (A.9)$$

We have thus reduced the original system of integrodifferential equations (eq. (A.3)) to a system of inhomogeneous algebraic equations, which can be easily solved by standard methods.

Instead of now using the fundamental solutions given by eq. (A.6), it is more convenient to transform to an equivalent set of fundamental solutions

$$\varphi_{mn}(z) = \frac{1}{2} (\psi_{mn+}(z) + \psi_{mn-}(z)), \quad (A.10)$$

$$\varphi_{m,n+N}(z) = (2ik_m)^{-1} (\psi_{mn+}(z) - \psi_{mn-}(z)); \quad m, n = 1, \dots, N;$$

which satisfy the initial conditions

$$\varphi_{mn}(z_1) = \delta_{mn}, \quad \partial_z \varphi_{mn}(z_1) = 0, \quad (A.11)$$

$$\varphi_{m,n+N}(z_1) = 0, \quad \partial_z \varphi_{m,n+N}(z_1) = \delta_{mn}.$$

The $2N$ vectors

$$\hat{\varphi}_n(z) = \left(\varphi_{1n}(z), \dots, \varphi_{Nn}(z), \partial_z \varphi_{1n}(z), \dots, \partial_z \varphi_{Nn}(z) \right)^T \quad (\text{A.12})$$

define a $2N \times 2N$ "propagation matrix" $M(z, z_1)$ (cf. Marcus and Jepsen 1968, Feder and Meister 1969) with the properties

$$M(z_1, z_1) = I_{2N} \quad , \quad (\text{A.13})$$

$$\hat{\psi}(z) = M(z, z_1) \hat{\psi}(z_1) \quad , \quad (\text{A.14})$$

where $\hat{\psi}(z)$ is the general solution vector, which is a linear combination of fundamental solution vectors $\hat{\varphi}_n(z)$ (eq. A.12) with the components of the initial condition vector $\hat{\psi}(z_1)$ as coefficients. If the crystal is assumed to consist of monatomic layers of muffin tin spheres, the propagation matrix of each layer can be found independently (z_1 and z_2 then delimit the z -axis projection of the respective layer), and the propagation matrix of the entire crystal is simply the product of the single-layer propagation matrices. This entails a particularly valuable reduction of computational labour, if all the constituent single layers are assumed to be equivalent. The effect of inelastic processes, if described by a phenomenological spatially uniform and energy-dependent imaginary potential v_i and the effect of a real inner potential v_r can easily be incorporated in the above by replacing E in eq. (A.1) and thence in eq. (A.3) by $E - v_r - v_i$.

The second part of the LEED intensity calculation consists in equating the solutions inside the crystal and their derivatives to their counterparts in the vacuum at the boundaries z_1 and z_2 .

Assuming the electron beam as a plane wave incident from $z = -\infty$, the vacuum solutions comprise the (normalized) incident beam $\exp(ik_1 z)$ and the reflected beams $u_{rn} \exp(-ik_n z)$ on the one side of the crystal slab and the transmitted beams $u_{tn} \exp(ik_n z)$ on the other side. If we write - in analogy to eq. (A.12) - the 3 types of vacuum wave functions and their derivatives as $2N$ -component vectors $\hat{u}_i$, $\hat{u}_r$ and $\hat{u}_t$, eq. (A.14) allows to write the matching conditions in the compact form

$$\hat{u}_t = M(z_2, z_1) (\hat{u}_i + \hat{u}_r). \quad (A.15)$$

This is an inhomogeneous system of $2N$ algebraic equations, from which the $2N$ unknowns u_{rn} and u_{tn} can be obtained by standard methods. The particular structure of the vectors $\hat{u}_\ell$ - $\ell = i, r, t$ - allows, however, a computational simplification through reduction to an $N \times N$ system. To this end we write

$$\hat{u}_\ell = \begin{pmatrix} \hat{u}_\ell^{(1)} \\ \hat{u}_\ell^{(2)} \end{pmatrix}, \quad M^{-1}(z_2, z_1) = \begin{pmatrix} M_1 & M_2 \\ M_3 & M_4 \end{pmatrix}. \quad \dagger) \quad (A.16)$$

Defining K as an $N \times N$ diagonal matrix with elements k_n and noting that $\hat{u}_\ell^{(2)} = i K u_\ell^{(1)}$ for $\ell = i, t$ and $\hat{u}_r^{(2)} = -i K \hat{u}_r^{(1)}$, eq. (A.15) leads to

$$\hat{u}_i^{(1)} + \hat{u}_r^{(1)} = (M_1 + M_2 K) \hat{u}_t^{(1)}, \quad (A.17a)$$

$$i K (\hat{u}_i^{(1)} - \hat{u}_r^{(1)}) = (M_3 + M_4 K) \hat{u}_t^{(1)}. \quad (A.17b)$$

[†]) In the actual computation, $M^{-1}(z_2, z_1)$ is not determined by inverting $M(z_2, z_1)$ but by simply interchanging z_1 and z_2 in the procedure for obtaining $M(z_2, z_1)$.

Substitution of $\hat{u}_r^{(1)}$ from eq. (A.17a) into (A.17b) gives

$$[iK(M_1 + M_2 K) + M_3 + M_4 K] \hat{u}_t^{(1)} = 2iK \hat{u}_i^{(1)}, \quad (A.18)$$

which is an $N \times N$ system for determining the N transmission amplitudes u_{tn} . The reflection amplitudes u_{rn} are then obtained from eq. (A.17a). The intensities I_{rn} and I_{tn} of the reflected and transmitted propagating beams (i.e. those with real k_n) are given as

$$I_{rn} = \frac{k_n}{k_1} |u_{rn}|^2, \quad I_{tn} = \frac{k_n}{k_1} |u_{tn}|^2. \quad (A.19)$$

It should be noted that as a consequence of the current conservation theorem of quantum mechanics we have the relation

$$\sum_{n=1}^{N_0} (I_{rn} + I_{tn}) \leq 1, \quad (A.20)$$

where N_0 is the number of propagating beams. The "=" sign holds in the absence of inelastic processes (i.e. for real crystal potential) (cf. McRae 1968 and Marcus and Jepsen 1968).

In view of the practical importance of the case of normal incidence ($k_0^{\parallel} = 0$)[†], we wish to emphasize the drastic reduction of computational effort that we have achieved in this case by making use of the κ -fold rotational symmetry of the problem with respect to the surface normal. The basic idea is to add those equations in the system eq. (A.3) with m relating to rotationally equivalent beams and to replace κ -tuples of wave functions $\psi_m(z)$ by a single

[†]) A large fraction of the currently available experimental data

function $\psi_m(z)$. If the pseudopotential (eq. (A.4)) is of the "angular momentum type", i.e. $v_{ik}^v(z) = v_{ik}^{\ell m}(z) \propto Y_{\ell}^m$, where Y_{ℓ}^m denotes the spherical harmonics,^{†)} the resulting change in the above construction of the propagation matrix consists in replacing each κ -tuple of corresponding equations in eq. (A.3) and following by a single equation and in multiplying the potential factor $v_{ik}^v(z) = v_{ik}^{\ell m}(z)$ in eqs. (A.7a) and (A.8) by a factor

$$s_v = s_{\ell m} = \begin{cases} \kappa & \text{for } m = 0, \kappa, 2\kappa, \dots \\ 0 & \text{otherwise} \end{cases} \quad (\text{A.21})$$

The size of the propagation matrix is thus considerably reduced, e.g. for a 9 beam calculation on a bcc (001) surface ($\kappa=4$) from 18×18 to 6×6 . Since a large proportion of computer time is spent on calculating and processing this matrix, the gain in time is very appreciable. The validity of this reduced method has been tested by comparing results with those of an unreduced calculation.

^{†)} the KKRZ-pseudopotential falls into this category.

Appendix B

Spin Polarization in Low Energy Electron Diffraction from Ferromagnetic Fe (001)

For a spin-polarized beam of low energy electrons incident on a ferromagnet, the exchange interaction between the incoming electrons and the unpaired electrons in the solid, and, therefore, the intensities of the diffracted beams, depend on the alignment of the polarization vector of the initial beam with respect to the magnetic axis of the crystal. This implies that for an unpolarized incident beam, which can be regarded as an incoherent superposition of an equal number of 'spin up' and 'spin down' electrons, the diffracted beams will be partially polarized. For the case of Fe and energies below 50 eV, spin polarization values up to 86% have been estimated on the grounds of a kinematical treatment (Vredevoe and De Wames 1968). However, kinematical theory is inadequate for quantitative LEED calculations. In the following, we therefore outline a dynamical treatment and then present intensity and spin polarization results for normal incidence on ferromagnetic Fe(001).

The electron-solid interaction is approximated by a one-electron potential of the muffin tin form, which we have obtained by means of the 'renormalized atom approach' (Segall 1962). The local electron charge densities $\rho_{\uparrow}$ and $\rho_{\downarrow}$ for spin antiparallel and parallel to the magnetic axis have been determined from atomic Hartree-Fock wave functions (Clementi et al. 1967), assuming the conduction electron configurations as $3d^{4.65} 4s^{0.45}$ and $3d^{2.45} 4s^{0.45}$ for 'spin up' and 'spin down', respectively (Wakoh and Yamashita 1966). The Coulomb contribution to the potential is then easily obtained from $(\rho_{\uparrow} + \rho_{\downarrow})$.

As for the exchange term, we have adopted an energy-dependent local approximation (Slater et al. 1969). Since the incident electron experiences exchange only with solid electrons of parallel spin and since $\uparrow \neq \downarrow$, we have different exchange potentials for the 'spin up' and the 'spin down' case:

$$V_{\uparrow,\downarrow}^{ex} = -8 F(k/k_F) (3/4\pi \uparrow,\downarrow)^{1/3}, \quad (B.1)$$

where the function $F(k/k_F)$ is determined as suggested by Slater et al. (1969). Two separate LEED intensity calculations have been performed for the 'spin up' and 'spin down' crystal potentials using a mixed-representation matching formalism, which is the Schrödinger-equation-based analogue (cf. Appendix A) of our relativistic LEED formalism. Since spin flip is associated with magnon excitation or annihilation and therefore inelastic, the spin state of the incident electron is not changed during elastic diffraction, i.e. for a 'spin up' ('spin down') incident beam all diffracted beams are 'spin up' ('spin down') with intensities $I_{n\uparrow}$ ($I_{n\downarrow}$), where n enumerates the surface reciprocal lattice vectors. Hence, for an unpolarized incident beam, the diffracted beams are partially polarized with intensities I_n and polarizations P_n given as

$$I_n = (I_{n\uparrow} + I_{n\downarrow})/2, \quad P_n = (I_{n\uparrow} - I_{n\downarrow})/(I_{n\uparrow} + I_{n\downarrow}). \quad (B.2)$$

Numerical results of an elastic calculation without inner potential correction for normal incidence on Fe(001) are shown in figures 1 and 2. In particular, we wish to point out that the two polarization peaks at 13 and 19 eV, which are close to unity, are associated with intensity maxima. To obtain more realistic predictions, the effect of inelastic processes has to be taken into account, in particular the

Fig.1 Intensity of the oo-beam for 'spin up' (—) and 'spin down' (----) without absorption

Fig.2 Spin polarization of the oo-beam without absorption

excitation of magnons. Since the latter is associated with the reversal of a spin originally aligned antiparallel with the magnetic axis (i.e. a 'spin up'), it follows from the conservation of angular momentum that the excitation can be created only by 'spin down' electrons in the original beam, which flip their spin in the process and are removed from the elastic beam. We hence anticipate an imaginary optical potential, which is stronger for 'spin down' electrons than for 'spin up' ones. This has been confirmed in a quantitative

Fig.3 Imaginary self-energy for 'spin up' (----) and 'spin down' (—) electrons.

manner by a model calculation of Babanov et al. (1973), whose imaginary self-energy contribution we reproduce in figure 3. The results of a calculation, which we carried out with constant imaginary potentials $V_i = -0.5$ eV and $V_i = -4$ eV chosen to approximate the result of figure 3, are presented in figures 4 and 5. We note a drastic difference in the

Fig.4 Intensity of the oo-beam for 'spin up' (—) and 'spin down' (---) obtained with an imaginary potential of -0.5 eV and -4.0 eV, respectively.

Fig.5 Spin polarization of the oo-beam obtained with an imaginary potential of -0.5 eV for 'spin up' and -4.0 eV for 'spin down'.

'spin up' and 'spin down' intensity profiles and consequently a large spin polarization, which is in the vicinity of 80% over a wide energy range. Assuming that an inner potential correction between 15 and 20 eV is appropriate, we expect the main peak of 90% spin polarization between 5 and 15 eV primary electron energy.

Although further work is required, in particular as regards a thorough check of the applicability of the model assumptions underlying the calculation of Babanov et al. (1973) to Fe, our results substantiate the hope that LEED from ferromagnets should provide a strong source of polarized electrons and a mechanism for measuring the polarization of low energy electrons.

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Appendix C

The Dirac γ -Matrices

Since a full treatment of the γ -matrices may be found in standard text books on quantum mechanics (e.g. Messiah 1965, vol.2 p. 896) we only state some basic relations and conventions, which are particularly relevant for our formalism.

The γ -matrices satisfy the algebraic relation

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2g^{\mu\nu}, \quad \mu, \nu = 0, 1, 2, 3, \quad (C.1)$$

where $g^{\mu\nu}$ is the metric tensor $\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$.

We define

$$\gamma^5 = -\gamma_5 \equiv \gamma^0 \gamma^1 \gamma^2 \gamma^3, \quad \gamma^5 \gamma^5 = -1. \quad (C.2)$$

The four γ -matrices generate the Dirac algebra that consists of the following 16 (4x4)-matrices $\Gamma^\mu - \mu=1, \dots, 16$ —

$$\{1, \gamma^0, \gamma^k, \gamma^k \gamma^0, \gamma^1 \gamma^2, \gamma^2 \gamma^3, \gamma^3 \gamma^1, \gamma^1 \gamma^2 \gamma^3, \gamma^k \gamma^5, \gamma^5\}, \quad (C.3)$$

where $k=1, 2, 3$. We recall that the trace

$$\text{tr } \Gamma^\mu = 4 \delta_{1\mu}, \quad (C.4)$$

and that any (4x4)-matrix can be represented as a linear combination of the above matrices.

As for specific representations of the γ -matrices, we allow all those in which

$$(i\gamma^0)^+ = i\gamma^0; \quad \gamma^{k+} = \gamma^k, \quad k=1, 2, 3; \quad (i\gamma^5)^+ = i\gamma^5, \quad (C.5)$$

where $\gamma^{\mu+}$ denotes the adjoint matrix to γ^μ . In particular, we make use of the "standard representation", in which the γ -matrices are expressed by means of tensor products of

(2x2) Pauli matrices ρ_k and σ_k as follows

$$i\gamma^0 = \rho_3 \otimes 1_2, \quad \gamma^k = \rho_2 \otimes \sigma_k, \quad k = 1, 2, 3; \quad (C.6)$$

$$1_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \rho_k = \sigma_k. \quad (C.7)$$

Appendix D

Calculation of Intensities and Spin Polarization Vectors of the LEED Beams from the Statistical Operators

In the following, we give details of the derivation of the intensity R_ℓ (eq.(3.29)) and the polarization vector ξ_ℓ^μ (eq.(3.31)) of the ℓ th reflected beam from the statistical operator $\rho_{r\ell}$ (eq.(3.28)).

D.1 Intensity

The intensity R_ℓ is calculated as the trace of the statistical operator $\rho_{r\ell}$:

$$R_\ell = \text{tr}[\rho_{r\ell}] . \quad (\text{D.1})$$

In evaluating this expression, we first make use of the algebraic properties of the operators P_+ and P_- (eq.(3.11)) and then substitute the matrices Γ_μ (cf.eq.(3.10)) and the coefficients $\tilde{a}_\ell^\mu$ (cf.eq.(3.25)). We thus obtain

$$\begin{aligned} R_\ell &= \text{tr} \left\{ \left[\left(\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_\ell^\mu \right) \left(\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_\ell^{\mu+4} \right) \gamma^3 + \right. \right. \\ &\quad \left. \left. + \left(\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_\ell^{\mu+4} \right) \gamma^3 \left(\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_\ell^\mu \right) \right] P_- \rho_i \right\} \\ &= \text{tr} \left\{ \left[(a_\ell^{1*} - \gamma^1 a_\ell^{2*} - \gamma^2 a_\ell^{3*} - \gamma^1 \gamma^2 a_\ell^{4*}) (a_\ell^5 + \gamma^1 a_\ell^6 + \gamma^2 a_\ell^7 + \gamma^1 \gamma^2 a_\ell^8) - \right. \right. \\ &\quad \left. \left. - (a_\ell^{5*} + \gamma^1 a_\ell^{6*} + \gamma^2 a_\ell^{7*} - \gamma^1 \gamma^2 a_\ell^{8*}) (a_\ell^1 - \gamma^1 a_\ell^2 - \gamma^2 a_\ell^3 + \gamma^1 \gamma^2 a_\ell^4) \right] \gamma^3 P_- \rho_i \right\} \end{aligned}$$

Since the matrices $\{\Gamma_\mu\}$ form a closed subset of the Dirac algebra, multiplication of two linear combinations of these matrices gives another linear combination, and we can write

$$\begin{aligned} R_\ell &= \text{tr} \left[2 \left(\sum_{\mu=1}^4 \Gamma_\mu d_{\ell\mu} \right) \gamma^3 P_- \rho_i \right] , \text{ or} \\ R_\ell &= \sum_{\mu=1}^4 d_{\ell\mu} \text{tr} [\Gamma_\mu (\gamma^0 + \gamma^3) \rho_i] , \end{aligned} \quad (\text{D.2})$$

where the coefficients $d_{\ell\mu}$ are given as

$$\begin{aligned}
 d_{\ell 1} &= i \operatorname{Im} [a_{\ell}^{1*} a_{\ell}^5 - a_{\ell}^{2*} a_{\ell}^6 - a_{\ell}^{3*} a_{\ell}^7 + a_{\ell}^{4*} a_{\ell}^8] \\
 d_{\ell 2} &= i \operatorname{Im} [a_{\ell}^{1*} a_{\ell}^6 - a_{\ell}^{2*} a_{\ell}^5 + a_{\ell}^{3*} a_{\ell}^8 - a_{\ell}^{4*} a_{\ell}^7] \\
 d_{\ell 3} &= i \operatorname{Im} [a_{\ell}^{1*} a_{\ell}^7 - a_{\ell}^{2*} a_{\ell}^8 - a_{\ell}^{3*} a_{\ell}^5 + a_{\ell}^{4*} a_{\ell}^6] \\
 d_{\ell 4} &= \operatorname{Re} [a_{\ell}^{1*} a_{\ell}^8 - a_{\ell}^{2*} a_{\ell}^7 + a_{\ell}^{3*} a_{\ell}^6 - a_{\ell}^{4*} a_{\ell}^5]
 \end{aligned} \tag{D.3}$$

Eq.(D.2) involves traces of basically three types of expressions, which are evaluated by inserting ρ_i from eq.(3.24) and making use of the anticommutation relations eq.(C.1) and of $\operatorname{tr} [\gamma^{\mu}] = 0$.

One obtains

$$\operatorname{tr} [\gamma^{\mu} \rho_i] = -i p_i^{\mu}, \quad \operatorname{tr} [\gamma^{\mu} \gamma^{\nu} \rho_i] = \varepsilon^{\mu\nu\sigma\tau} \xi_{i\sigma} p_{i\tau}, \tag{D.4}$$

$$\operatorname{tr} [\gamma^{\mu} \gamma^{\nu} \gamma^{\sigma} \rho_i] = \varepsilon^{\mu\nu\sigma\tau} \xi_{i\tau},$$

where $p_{i\sigma} = g_{\sigma\tau} p_i^{\tau}$, $\xi_{i\sigma} = g_{\sigma\tau} \xi_i^{\tau}$,

$$\varepsilon^{\mu\nu\sigma\tau} = \begin{cases} +1 & (-1) \text{ if } \mu\nu\sigma\tau \text{ is an even (odd) permutation of } 0123 \\ 0 & \text{otherwise.} \end{cases}$$

With the aid of eqs.(D.4) we obtain from eq.(D.2) — we now replace the four-vectors p_i and ξ_i by our previous notations (w, k_0^x, k_0^y, k_0^z) and $(\xi_i^0, \xi_i^x, \xi_i^y, \xi_i^z)$ —

$$\begin{aligned}
 R_{\ell} &= -i d_{\ell 1} (w + k_0^z) + i d_{\ell 2} [-\xi_i^y (w + k_0^z) + k_0^y (\xi_i^0 + \xi_i^z)] + \\
 &\quad + i d_{\ell 3} [\xi_i^x (w + k_0^z) - k_0^x (\xi_i^0 + \xi_i^z)] + d_{\ell 4} (\xi_i^0 + \xi_i^z)
 \end{aligned}$$

Substitution of the $d_{\ell\mu}$ from eqs.(D.3) and replacement of the a_{ℓ}^{μ} for $\mu=5, \dots, 8$ according to eqs.(3.21b) and (3.16b) yields

$$\begin{aligned}
 R_{\ell} &= \left\{ (w + k_0^z) \sum_{\mu=1}^4 |a_{\ell}^{\mu}|^2 + 2[(w + k_0^z) \xi_i^x - k_0^x (\xi_i^0 + \xi_i^z)] \operatorname{Re} [a_{\ell}^1 a_{\ell}^{3*} + \right. \\
 &\quad \left. + a_{\ell}^2 a_{\ell}^{4*}] + 2[(w + k_0^z) \xi_i^y - k_0^y (\xi_i^0 + \xi_i^z)] \operatorname{Re} [-a_{\ell}^1 a_{\ell}^{2*} + a_{\ell}^3 a_{\ell}^{4*}] + \right. \\
 &\quad \left. + 2(\xi_i^0 + \xi_i^z) \operatorname{Im} [a_{\ell}^1 a_{\ell}^{4*} + a_{\ell}^2 a_{\ell}^{3*}] \right\} / (w - k_0^z). \tag{D.5}
 \end{aligned}$$

D.2 Spin Polarization Vector

The covariant polarization vector ξ_l^μ of the l th LEED beam is obtained from the statistical operator ρ_{rl} as the expectation value of the covariant spin operator (cf. Meister 1962 eq.(3.5)).

$$\xi_l^\mu = \text{tr} [\gamma^5 \gamma^\mu \rho_{rl}] / \text{tr} [\rho_{rl}]. \quad (\text{D.6})$$

According to eq.(D.1), the denominator is equal to the reflection coefficient R_l and has been calculated in the previous section.

The numerator, which we denote by ξ_l^μ , is evaluated as follows.

We first substitute ρ_{rl} according to eq.(3.28), which gives

$$\xi_l^\mu = \text{tr} [P_+ (\sum_{\mu=1}^8 \Gamma_\mu \tilde{a}_l^\mu) \gamma^5 \gamma^\mu (\sum_{\mu=1}^8 \Gamma_\mu a_l^\mu) P_- \rho_i]$$

Substituting the matrices Γ_μ (cf.eq.(3.10)) and using the algebraic properties of the operators $P_\pm$ given in eq.(3.11) together with

$$P_6 \gamma^0 = \gamma^0 P_{-6} \quad \text{and} \quad P_6 \gamma^5 = \gamma^5 P_6,$$

which follows easily from eq.(3.11), we obtain

$$\begin{aligned} \xi_l^{\tilde{\mu}} = \text{tr} \{ & [(\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_l^\mu) \gamma^5 \gamma^{\tilde{\mu}} (\sum_{\mu=1}^4 \Gamma_\mu a_l^\mu) + (\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_l^{\mu+4}) \gamma^3 \gamma^5 \gamma^{\tilde{\mu}} \\ & \cdot (\sum_{\mu=1}^4 \Gamma_\mu a_l^{\mu+4}) \gamma^3] P_- \rho_i \} \quad \text{for } \tilde{\mu}=0,3 \end{aligned} \quad (\text{D.7a})$$

$$\begin{aligned} \xi_l^{\tilde{\mu}} = \text{tr} \{ & [(\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_l^\mu) \gamma^5 \gamma^{\tilde{\mu}} (\sum_{\mu=1}^4 \Gamma_\mu a_l^{\mu+4}) \gamma^3 + (\sum_{\mu=1}^4 \Gamma_\mu \tilde{a}_l^{\mu+4}) \gamma^5 \gamma^{\tilde{\mu}} \\ & \cdot (\sum_{\mu=1}^4 \Gamma_\mu a_l^\mu)] P_- \rho_i \} \quad \text{for } \tilde{\mu}=1,2 \end{aligned} \quad (\text{D.7b})$$

We now substitute $\gamma^5 = \gamma^0 \gamma^1 \gamma^2 \gamma^3$ and $P_- = \frac{1}{2}(1 - \gamma^0 \gamma^3)$ into eqs. (D.7a) and (D.7b) and — making use of the algebraic properties of the Dirac matrices (cf.eq.(C.1)) — shift all matrices γ^0 and γ^3 to the right to combine them with P_- with the aid of the relation

$$\gamma^\mu P_- = \frac{1}{2} (\gamma^0 + \gamma^3) \quad \text{for } \mu = 0,3.$$

This leaves us, for each component $\tilde{f}_\ell^\mu$, with a sum of products of linear combinations of the matrices Γ_ν -- $\nu=1, \dots, 4$ -- inside the square brackets of eqs. (D.7a) and (D.7b). Since the Γ_ν form a closed sub-algebra of the Dirac algebra, this sum can be written as a linear combination of the Γ_ν . Denoting the coefficients of the linear combinations thus obtained by $f_\ell^{\mu\nu}$, where μ relates to the component $\tilde{f}_\ell^\mu$ and ν to the matrix Γ_ν , eqs. (D.7a) and (D.7b) can be written in the form

$$\begin{aligned}\tilde{f}_\ell^\mu &= \frac{1}{2} \text{tr} \left[\left(\sum_{\nu=1}^4 \Gamma_\nu f_\ell^{\mu\nu} \right) (\gamma^0 + \gamma^3) \right] \eta_i, \text{ or} \\ \tilde{f}_\ell^\mu &= \frac{1}{2} \sum_{\nu=1}^4 f_\ell^{\mu\nu} \text{tr} \left[\Gamma_\nu (\gamma^0 + \gamma^3) \right] \eta_i.\end{aligned}$$

The expressions inside the traces are seen to be the same as in eq. (D.2) and are evaluated in the same manner. One obtains

$$\begin{aligned}\tilde{f}_\ell^\mu &= -\frac{i}{2} f_\ell^{\mu 1} (w + k_0^z) + \frac{i}{2} f_\ell^{\mu 2} [-(w + k_0^z) \xi_i^y - k_0^y (\xi_i^0 + \xi_i^z)] + \\ &+ \frac{i}{2} f_\ell^{\mu 3} [(w + k_0^z) \xi_i^x - k_0^x (\xi_i^0 + \xi_i^z)] + \frac{1}{2} f_\ell^{\mu 4} (\xi_i^0 + \xi_i^z).\end{aligned}\quad (\text{D.8})$$

The 16 coefficients $f_\ell^{\mu\nu}$ are elementary algebraic functions of the original coefficients a_ℓ^μ (cf. eq. (3.21)). Since they are, however, in general rather lengthy, we content ourselves with stating here only those which are relevant for the important special case of an unpolarized incident beam.

$$\begin{aligned}f_\ell^{01} &= 2i k_\ell^z c_\ell, \quad f_\ell^{11} = 4i \left\{ \text{Re} [a_\ell^1 a_\ell^{3*} - a_\ell^2 a_\ell^{4*}] / (w - k_\ell^z) + k_\ell^x c_\ell \right\}, \\ f_\ell^{21} &= 4i \left\{ \text{Re} [a_\ell^1 a_\ell^{2*} + a_\ell^3 a_\ell^{4*}] / (w - k_\ell^z) + k_\ell^y c_\ell \right\}, \quad f_\ell^{31} = -2i w c_\ell,\end{aligned}$$

where

$$c_\ell = \text{Im} [a_\ell^1 a_\ell^{4*} - a_\ell^2 a_\ell^{3*}] / (w - k_\ell^z).$$

Appendix E

Calculation of Relativistic Phase Shifts for a Central Potential

Since the relativistic pseudopotential (cf. Chapter 4) used in our LEED formalism contains as information input the phase shifts due to the actual ion core potential, we require a procedure for obtaining these phase shifts. We adopt —because of its computational speed — a method due to Bunyan and Schonfelder (1965) ^{*)}, of which we give an outline in the present Appendix.

Instead of directly solving the two coupled first order linear differential equations (eqs.(4.5)) for the radial functions $F_{\kappa}(r)$ and $G_{\kappa}(r)$, new radial functions $A_{\kappa}(r)$ and $\phi_{\kappa}(r)$ are introduced by means of the transformation

$$F_{\kappa}(r) = A_{\kappa}(r) \frac{\sin \phi_{\kappa}(r)}{r}, \quad G_{\kappa}(r) = A_{\kappa}(r) \frac{\cos \phi_{\kappa}(r)}{r} \quad (\text{E.1})$$

Substitution of eqs.(E.1) into eqs.(4.5) yields two nonlinear first order differential equations, which are partially decoupled:

$$\partial_r \phi_{\kappa}(r) = \frac{\kappa}{r} \sin 2\phi_{\kappa}(r) + w - U(r) - \cos 2\phi_{\kappa}(r) \quad (\text{E.2a})$$

$$A_{\kappa}^{-1}(r) \partial_r A_{\kappa}(r) = -\frac{\kappa}{r} \cos 2\phi_{\kappa}(r) - \sin 2\phi_{\kappa}(r) \quad (\text{E.2b})$$

The phase shifts δ_{κ} are obtained, as usual, by matching the free solution

$$G_{\kappa}^0(r) = j_{\ell}(kr) \cos \delta_{\kappa} - n_{\ell}(kr) \sin \delta_{\kappa}, \quad (\text{E.3})$$

where j_{ℓ} and n_{ℓ} denote the spherical Bessel and Neumann functions (cf. e.g. Abramovitz and Stegun 1965), and its slope to $G_{\kappa}(r)$

^{*)}

This method is also used by Jennings (1971) in his spin-polarized LEED formalism.

and $G'_\kappa(r)$ at the muffin-tin radius R :

$$\tan \delta_\kappa = \frac{[G'_\kappa(R)/G_\kappa(R)] j_\ell(kR) - k j'_\ell(kR)}{[G'_\kappa(R)/G_\kappa(R)] n_\ell(kR) - k n'_\ell(kR)} \quad (E.4)$$

The ratio $G'_\kappa(R)/G_\kappa(R)$ can now be expressed, with the aid of eq.(4.5b) and eqs.(E.1), in terms of the function $\phi_\kappa(R)$:

$$\frac{G'_\kappa(R)}{G_\kappa(R)} = -(\omega+1) \frac{F_\kappa(R)}{G_\kappa(R)} - \frac{1+\kappa}{R} = -(\omega+1) \tan \phi_\kappa(R) - \frac{1+\kappa}{R} \quad (E.5)$$

Substitution of eq.(E.5) into eq.(E.4) finally yields

$$\tan \delta_\kappa = \frac{k j_{\ell+1}(kR) - j_\ell(kR) \{(\omega+1) \tan \phi_\kappa(R) + (1+\ell+\kappa)/R\}}{k n_{\ell+1}(kR) - n_\ell(kR) \{(\omega+1) \tan \phi_\kappa(R) + (1+\ell+\kappa)/R\}} \quad (E.6)$$

We notice that this result depends only on $\phi_\kappa(R)$, i.e. the determination of phase shifts by the method of Bunyan and Schonfelder requires only the solution of a single first order differential equation (eq.(E.2a)).

Appendix F

Relativistic and Nonrelativistic Scattering by a One-Dimensional Dirac Delta-Function Potential

In discussing — in Chapter 5.1 — the description of inelastic effects in the surface region by means of an imaginary Dirac δ -function potential, we stated that the scattering by this type of potential would be different for a relativistic and a nonrelativistic electron. We confirm this in the present Appendix by explicitly calculating the reflection and transmission coefficients for the potential

$$V_z = -i \tilde{V}_z \delta(z), \quad \tilde{V}_z \text{ real} \quad (\text{F.1})$$

for both the Dirac and the Schrödinger case.

In the nonrelativistic case we have the following solutions of Schrödinger's equation

$$\psi(\underline{\rho}, z) = \begin{cases} e^{i \underline{k}^{\parallel} \cdot \underline{\rho}} (e^{ik^z z} + r e^{-ik^z z}) & \text{for } z < 0 \\ e^{i \underline{k}^{\parallel} \cdot \underline{\rho}} t e^{ik^z z} & \text{for } z > 0 \end{cases} \quad (\text{F.2})$$

where $\underline{\rho}$ is the two-dimensional vector (x,y) in the surface plane, $\underline{k}^{\parallel}$ is the projection of the momentum $\underline{k}$ on to the surface plane, and $k^z = \sqrt{2E - \underline{k}^{\parallel 2}}$; r and t denote the reflection and transmission amplitudes. The boundary conditions of continuity of the wave function and discontinuity of the slope at $z=0$ require then

$$1+r=t \quad \text{and} \quad k^z(r-1) = -(k^z - 2\tilde{V}_z) t \quad (\text{F.3})$$

From these two equations we obtain the reflection and transmission amplitudes as

$$r = - \frac{\tilde{v}_3}{k^2 + \tilde{v}_3} , \quad t = \frac{k^2}{k^2 + \tilde{v}_3}$$

and thence the reflection coefficient R and the transmission coefficient T as

$$R = \frac{\tilde{v}_3^2}{(k^2 + \tilde{v}_3)^2} , \quad T = \frac{k^2}{(k^2 + \tilde{v}_3)^2} . \quad (F.4)$$

An absorption coefficient A can be introduced as

$$A = 1 - (R+T) = 2k^2 \tilde{v}_3 (k^2 + \tilde{v}_3)^{-2} . \quad (F.5)$$

In the relativistic case ^{*)} we have the following free solutions of the Dirac equation

$$\psi(\underline{q}, z) = \begin{cases} e^{i \underline{k} \cdot \underline{q}} (u_i e^{ik^z z} + u_r e^{-ik^z z}) & \text{for } z < 0 \\ e^{i \underline{k} \cdot \underline{q}} u_t e^{ik^z z} & \text{for } z > 0 , \end{cases} \quad (F.6)$$

where u_i , u_r , and u_t are the four-spinor amplitudes of the incident, the reflected and the transmitted beam, respectively, and the other quantities are defined as in eq.(F.2). With the aid of the propagation matrix given in eq.(6.18b), we can write the boundary condition at $z=0$ as

$$u_t = (a + b \gamma^0 \gamma^3) (u_i + u_r) \quad (F.7a)$$

$$a = \frac{1 - v_3^2}{1 + v_3^2} = \frac{1 + \tilde{v}_3^2}{1 - \tilde{v}_3^2} , \quad b = \frac{2i v_3}{1 + v_3^2} = \frac{2 \tilde{v}_3}{1 - \tilde{v}_3^2} . \quad (F.7b)$$

Multiplication by $P_{\pm} = \frac{1}{2}(1 \pm \gamma^0 \gamma^3)$ —cf.eq.(3.11)— gives

^{*)}

The problem could, of course, be solved numerically by means of the general method given in Chapter 3. In view of its simplicity we prefer, however, to obtain results in an analytical form.

$$u_t^+ = (a+b) (u_i^+ + u_r^+) , \quad u_t^- = (a-b) (u_i^- + u_r^-) , \quad (F.8)$$

where $u_s^\pm = P_\pm u_s$, $s=i,r,t$. From eq.(3.16) we have the following connection between u_s^+ and u_s^- :

$$u_s^+ = (\omega + k_s^z)^{-1} iK\beta u_s^- , \quad k_i^z = k_t^z = k^z, \quad k_r^z = -k^z , \quad (F.9)$$

$$\beta = K^{-1} (1 + ik^x \gamma^1 + ik^y \gamma^2) , \quad K = \sqrt{(1 + k^{x2} + k^{y2})} .$$

Substituting this into the first equation of eqs.(F.8), we obtain, after an elementary calculation, the result

$$u_r^- = f u_i^- , \quad f = (\omega - k^z) b / (\omega b + k^z a) . \quad (F.10)$$

This leads, with the aid of eq.(F.9), to

$$u_r = u_r^+ + u_r^- = f \left(1 + \frac{iK}{\omega - k^z} \beta \right) u_i^- = f \left(P_- + P_+ \frac{iK}{\omega - k^z} \beta \right) u_i ,$$

which we can — using the one-dimensional version of eq.(3.13) — write as

$$u_r = \frac{f}{\omega - k^z} (\omega + k^z \gamma^0 \gamma^3) u_i . \quad (F.11)$$

The reflection coefficient R is now obtained as the trace of the statistical operator

$$\rho_r = \frac{|f|^2}{(\omega - k^z)^2} (\omega + k^z \gamma^0 \gamma^3) \rho_i (\omega - k^z \gamma^0 \gamma^3)$$

using eq.(D.4) of Appendix D.1 :

$$R = |f|^2 (\omega + k^z) / (\omega - k^z)$$

Substitution of f according to eq.(F.10) and subsequently of a and b according to eq.(F.7b) yields

$$R = 4 \tilde{v}_3^2 (\omega^2 - k^{z2}) [2\omega \tilde{v}_3 + k^z (1 + \tilde{v}_3^2)]^{-2} . \quad (F.12)$$

To calculate the transmission coefficient T , we substitute eq.(F.11) into eq.(F.7a) and hence obtain eventually

$$T = k^2 (1 - \tilde{v}_s^2) [2\omega \tilde{v}_s + k^2 (1 + \tilde{v}_s^2)]^{-2} \quad (F.13)$$

The absorption coefficient is again obtained as $A=1-(R+T)$. Since we are interested in low energy electrons, we take the nonrelativistic limits of eqs.(F.13) and (F.13), remembering that in the natural units, which we are using, $mc^2 = 1$ and therefore $\omega \rightarrow 1$ for small energies, and $v_s^2 \ll 1$.

$$R = 4 \tilde{v}_s^2 / D, \quad T = k^2 / D, \quad D = (2\tilde{v}_s + k^2)^2. \quad (F.14)$$

Comparing these results with their nonrelativistic analogues as given in eqs.(F.4), we notice that the relativistic reflection is stronger and the transmission weaker. More precisely, we see that the two sets of results become identical, if we replace $\tilde{v}_s$ in eq.(F.14) by $\frac{1}{2}\tilde{v}_s$. (This relation has also been explicitly confirmed by numerical computations according to eqs(F.4) and eqs.(F.12) and (F.13)). Magnitude and energy dependence below 50 eV of R, T and A — as calculated from eqs.(F.4) and (F.5) — are illustrated in fig.F.1 for the typical value $\tilde{v}_s = 4$ eV ^{*)} for the case of normal incidence. We

Fig.F.1

Reflection (----), transmission (.....) and absorption (—) coefficients R, T and A for normal incidence on an imaginary δ -potential of constant strength 4 eV, computed nonrelativistically. (The intensity units on the ordinate are relative to the incident intensity).

^{*)}

We disregard in this simple model illustration the energy dependence of $\tilde{v}_s$, in particular the steep increase in the vicinity of the surface plasmon threshold, which is essential for a realistic model.

notice that the three quantities vary rapidly in the energy range below about 10 eV, but only very slowly above about 20 eV, the reflection being only of about 1% as compared to about 15% absorption. As for the angular dependence for constant energy and potential strength, we can see from eqs.(F.4) and (F.5) — remembering that $k^z = |\underline{k}| \cos \vartheta$, where ϑ is the angle of incidence against the surface normal — that the reflection coefficient increases with increasing ϑ until it reaches unity for grazing incidence, whereas the transmission and the absorption coefficient decrease. The ratio between absorption and reflection, $A/R = 2k^z/\tilde{v}_s$, decreases with increasing angle of incidence.

As regards the use of a δ -function-type optical potential in our relativistic LEED formalism, we conclude from the above correspondence between relativistic and nonrelativistic results that this is legitimate provided we reduce the strength of the δ -function by a factor 0.5 with respect to the value found suitable in a nonrelativistic context.

Appendix G

Computer Programmes

The numerical results presented in Chapter 10 and in Appendix B have been obtained on a Univac 1106 Computing System by means of FORTRAN V programmes, which we have developed in accordance with our relativistic LEED formalism and its nonrelativistic analogue. As was to be expected, the relativistic programme version turned out to be fairly complicated, comprising about 2000 FORTRAN statements. Since our primary aim was to obtain physical predictions from our theory before spending an additional substantial amount of time on increasing the elegance and computational efficiency of the programmes, we consider them rather as prototypes, which could still be refined, and, therefore, do not present full listings, but content ourselves with giving a description of their general structure, and in particular their input and output information, and indicating the proportions of computing time spent on the various stages of the computational procedure in the relativistic and the nonrelativistic cases. In the following, details are given — unless otherwise stated — for the relativistic programmes only, since the nonrelativistic ones are built in essentially the same manner.

G. 1 Input Information

The programme input consists of the following information:

- (1) the basis vectors of the surface unit cell, a three-dimensional vector indicating the relative displacement of adjacent monatomic layers, and the total number of layers

constituting the model crystal;

- (2) a set of beams — specified in the form (00), (01), etc — together with a switch parameter that allows to take into account either the full set, a specified number of beams, or only the set of propagating beams (which are then automatically determined for each energy value);
- (3) the range of energies, angular and azimuthal angles, of the incident beam, given in the (self-explanatory) form:
 $X_{\min}$, $X_{\max}$, X_{step} ;
- (4) the ion-core phase shifts — which have been computed once and for all according to the method described in Appendix E — over an energy range that comprises the beam energy range;
- (5) the pseudopotential radii R_l , expressed in fractions of the maximal value (cf. eq.(9.1)), which is determined automatically from the lattice geometry input;
- (6) the strength parameters of the real inner potential and of the bulk and surface imaginary potential for an arbitrarily dense set of energy points;
- (7) parameters specifying the surface potential barrier, and a switch parameter that determines whether a barrier should be included or not.
- (8) switch parameters that determine the output mode (line-printout only or addition of line-printer-plot and/or card output) and, in the nonrelativistic case, whether and if so which rotational symmetry with respect to the surface normal is to be used.

G.2 Output Information

The basic programme output appears on the line printer and contains the following information:

- (1) part of the input information in order to permit an easy identification of the computed results;
- (2) the computed intensities and degrees of spin polarization of the propagating beams as functions of energy and primary beam orientation.

Provision has been made to obtain this output also in forms of line-printer plots and cards that can be used as input for a CALCOMP plotting programme.

G.3 General Programme Structure

In view of the complexity of the relativistic programme, we found it convenient — in order to facilitate the development as well as to avoid running into core size problems — to divide it, in accordance with the structure of the theory, into three separate programmes — called FUN, PROP and MATCH — that run sequentially, intermediate information being stored on disk file. We give in the following a brief characterization of these three programmes.

Programme FUN receives the information input as specified in Section G.1 and stores it on disk to preserve it for the following two programmes and the output. FUN then determines the reciprocal lattice vectors corresponding to the surface unit cell and thence, for each energy value — augmented by the real and imaginary inner potential —, the wave vectors of the beams taken into account. After interpolation of the phase

shift input to suit the specified energies, the pseudo-potential coefficients B_{κ} are computed according to eq.(4.15) and stored on disk. FUN then computes the γ -matrix-free terms in the Fourier coefficient functions $v_{1n}(z)$ and $v_{2n}(z)$ according to eq.(4.20) and subsequently carries out the three types of z' -integrations required in eqs.(6.7c) and eq.(6.8) in the form of summations over the layer-spacing reciprocal constants g^z (cf. remarks following eq.(6.11)). These results are also stored on disk.

As an additional option, FUN can calculate the propagation matrix of a z -dependent continuous surface potential barrier (cf. Chapter 6.3) by means of a step-wise numerical procedure (either Runge-Kutta or a fifth order predictor-corrector method).

The results stored by FUN are used as input to PROP, which calculates the single-layer propagation matrix (cf. Chapter 6.1) in essentially three steps. Firstly, the matrix and the inhomogeneous part of eq. (6.1), which both involve γ -matrices, are established in the form indicated by eq.(6.12), i.e. the four $(V_{max} - v_{max})$ -matrices F_{μ} and the four v_{max} -vectors h_{μ} are determined (the latter for each beam). Secondly, the matrix in eq.(6.12) is inverted by means of a subroutine designed for matrices of the type $\sum_{\mu=1}^4 \Gamma_{\mu} F_{\mu}$ (without explicitly representing the matrices Γ_{μ}) and the constants $\hat{a}_m$ are obtained by multiplying the right-hand-side of eq.(6.12) by the inverse matrix (cf. eq. (6.13)). Thirdly the single-layer propagation matrix (cf. eq. 6.14) is obtained in terms of the $(N \times N)$ -matrices D_6^{μ} , which are stored on disk.

Programme MATCH retrieves this information and first calculates the propagation matrix for the whole crystal. In the case of a model consisting of identical layers with identical surface

projections, this is done by taking the single-layer propagation matrix to the power corresponding to the number of layers. In the case of a model with inequivalent layers, PROP will have provided the propagation matrix for each of the inequivalent layers, and MATCH multiplies these matrices in a manner suitable to yield the propagation matrix for the whole crystal. If a surface potential barrier is to be included, MATCH also retrieves the barrier propagation matrix as provided by FUN and multiplies it on to the crystal propagation matrix. Since all these matrix multiplications are of the type (cf. eq.(6.14))

$$\left[\sum_{\sigma=\pm} \left(\sum_{\mu=1}^8 \Gamma_{\mu} \otimes D_{\sigma}^{\mu} \right) P_{\sigma} \right] \times \left[\sum_{\sigma=\pm} \left(\sum_{\mu=1}^8 \Gamma_{\mu} \otimes F_{\sigma}^{\mu} \right) P_{\sigma} \right] = \\ = \sum_{\sigma=\pm} \left(\sum_{\mu=1}^8 \Gamma_{\mu} G_{\sigma}^{\mu} \right) P_{\sigma} ,$$

we have designed a subroutine that takes as input the 32 (NxN)-matrices D_{σ}^{μ} and F_{σ}^{μ} and calculates the 16 (NxN)-matrices G_{σ}^{μ} in an algebraic way without requiring a specific representation of the matrices. The (diagonal) propagation matrix of the $\delta(z)$ imaginary surface potential (cf. eq.(6.18)) is easily multiplied on to the crystal propagation matrix by using the properties of the operators $P_{\pm}$ (cf. eq.(3.11)). Intensities and spin polarizations are then computed in a straightforward manner according to the relevant expressions in Chapter 3, again using subroutines designed for handling linear combinations of γ -matrices with (NxN) matrices as "coefficients".

The nonrelativistic programme version has been built in an analogous manner except that the above parts FUN and PROP have been merged into one.

G.4 Computing Time

The computing time required depends obviously very strongly on the number of phase shifts and of beams that are taken into account. We typically used in our computations five phase shifts (i.e. up to $\ell=2$), nine beams and five layer-spacing reciprocal constants. The computing time distribution over the constituent programmes is illustrated for these values in Table G.1.

	<u>relativistic</u>		<u>nonrelativistic</u>	
	(no symmetry used)		4-fold symmetry	no symmetry
FUN	24.4	} 34.9	9	29
PROP	10.5			
MATCH	31 for 4 layers		1.7	 9
	46 for 6 layers		2.5	 13
Total	65.9 for 4 layers		10.7	 38
	80.9 for 6 layers		11.5	 42

Table G.1 Computing time in seconds per 'point' (E, ϑ, φ).

We notice a substantial increase (of about a factor 2) in total computing time for the relativistic version as compared to the nonrelativistic one. This increase stems from two clearly distinct sources. Firstly, there is a contribution from FUN and PROP, which is small, because most time in FUN is spent on calculating γ -matrix-free potential Fourier coefficients — which are essentially the same in both cases —, and because PROP, which involves γ -matrices, uses only a fairly small fraction of the

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Relativistic Theory of Low Energy Electron Diffraction

R. Feder

Ph.D. Thesis

Misprints in Chapters 9 and 10:

- p.67 4th line from bottom: relativistic and nonrelativistic phase shifts (instead of: relativistic phase shifts)
- p.68 4th line from bottom: how many phase shifts (instead of: how many shifts)
- p.73 3rd line from top: Scheibner (instead of: Scheibne)
6th line from bottom: 0.5 eV (instead of: -0.5 eV)
- p.74 eq.(9.3): $(1+\exp(-z/a))$ (instead of: $(1+\exp(-z/a))$)
- || p.83 Fig. 10.5: from W(110) (instead of: from W(001))
- p. 85 4th line from bottom: incidence on W(001)
(instead of: incidence W(001))
5th line from bottom: on W(001) (instead of: from W(001))
- p.86 10th line from bottom: LEED intensity profiles
(instead of: LEED energy profiles)