



ELSEVIER

Surface Science 340 (1995) 172–178

surface science

Tensor LEED for the approximation of non-spherical atomic scattering

O. Rubner, M. Kottcke, K. Heinz *

Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany

Received 17 March 1995; accepted for publication 29 May 1995

Abstract

We present a new approach to consider non-spherical atomic charge densities for the computation of intensities in low energy electron diffraction (LEED). This might be important for covalently bonded atoms for example in adsorbed molecules, semiconductors or compound materials. In a first step the non-spherical charge distribution of a surface atom is approximated by Hartree–Fock calculations applied to a small atomic cluster surrounding the atom under consideration. Then, starting with a LEED reference calculation for spherical scatterers as usual, the deviation from the spherical charge distribution is taken into account by means of the corresponding change of the atomic scattering matrix which becomes non-diagonal. Eventually, this is made to enter the perturbation scheme tensor LEED. This procedure allows easy access to trial structures with realistic atomic scattering. We applied the method to an example of practical importance, i.e. to the unreconstructed Si(100) surface. A rough estimation neglecting multiple scattering between the non-spherical and spherical part of the atomic potential proves, however, that the influence of non-spherical scattering on intensities in a typical energy range (20–150 eV) is practically negligible.

Keywords: Electron–solid interactions, scattering, diffraction; Low energy electron diffraction (LEED); Silicon

1. Introduction

Today's surface structure determination by low energy electron diffraction (LEED) has reached a remarkable potential and level of accuracy [1]. For not too complex structures atomic positions can be determined with – in favourable cases – a precision of 0.01 Å. Last but not least this is due to the fact that the search for the best structure has been extended to include all relevant structural parameters of

the surface, even of atoms in the fourth or fifth layer. This progress was made possible by the introduction of automated structural search procedures (for a review see Ref. [2]) and the development of the perturbation method tensor LEED [3–5] whereby a combination of both seems to be most powerful. However, the increasing structural precision required also the more careful consideration of non-positional parameters. Concerning the atomic scattering, the layer dependent stoichiometry was taken into account in case of substitutionally disordered compounds by use of the average *t*-matrix approximation. This proved to yield excellent results for disordered alloys (for reviews see Refs. [6,7]). More recently, the influence

* Corresponding author.

of surface dipoles on diffraction was investigated [8] and the consideration of anisotropic thermal vibrations was introduced into practical surface structure determination [9,10].

However, little efforts were made to go beyond the usual approximation of atomic scattering which is based on a muffin-tin potential usually using a spherical charge density distribution inside the muffin-tin spheres and a constant charge density level outside [11]. Probably this is because the non-sphericity of the atomic scattering potentials is very small in the case of metal surfaces as proved by the often excellent agreement between measured and computed spectra. However, for surface atoms with covalent bonding as in the case of semi-conductors or adsorbed molecules this might be an insufficient approximation. This was pointed out quite early by Nagano and Tong [12] and more recently by Joly [13], whereby also computational schemes to consider non-spherical atomic scattering were proposed. Nagano and Tong made a proposal to calculate the correct non-diagonal atomic scattering matrix (t -matrix) to be used in suitably modified but otherwise conventional LEED codes [12]. Yet, the method has not found wide application. On the other hand, Joly used a finite-difference method for the intensity calculation [13] which, however, does not fit into current LEED programs and turned out to be rather time consuming.

Therefore, in the present paper we propose a method which tries to avoid these drawbacks whereby our aim is threefold: First, we want to introduce a method which allows the easy calculation of intensities when the scattering matrix is non-diagonal due to non-spherical atomic scattering. Second, we propose a method to calculate the non-spherical charge distribution and the corresponding atomic scattering matrix. And third, we want to estimate the effect of non-spherical scattering for an example of practical importance. With tensor LEED there is a tool at hand which easily meets the first point: It allows the fast calculation of intensity changes due to the non-spherical part of the scattering potential when the reference calculation is made for spherical scatterers. It simultaneously fits into current LEED programs. We describe the method shortly in the next section. The calculation of non-spherical charge distributions by the Hartree–Fock formalism will be presented in

Section 3. Finally we apply the method to estimate the effect of non-spherical atomic scattering for the Si(100)-(1 × 1) surface.

2. Tensor LEED

The basic idea of tensor LEED is mirrored by the fact that diffraction intensities change smoothly when any kind of parameter influencing the intensities changes smoothly as well. Suppose, the total electron wave field within the surface has been calculated for a certain structure (reference structure). Then, if a parameter change leads to a change δt of the scattering matrix of a certain atom, the corresponding change δA of the wave field in kinematic approximation can be written as [3–5]

$$\delta A = T \delta t, \quad (1)$$

whereby T in angular representation is a tensor explaining the name tensor LEED. It depends only on the reference structure and describes any modification of the structure as long as the kinematic calculation of the changes involved holds. So, the quantity δt can be due to geometrical displacements δr of the atom and this is tensor LEED was originally designed for (geometrical tensor LEED [3–5]). Dependent on the actual scattering conditions the displacements can be as large as 0.4 Å. The change δt can also be caused by isotropic and anisotropic vibrations of the atom (thermal tensor LEED [10,14]) or by the chemical substitution of an atom (chemical tensor LEED [15,16]). In geometrical and thermal tensor LEED (the latter for anisotropic vibrations) the δt are non-diagonal. In chemical tensor LEED it remains diagonal when a spherical scatterer is substituted by another spherical one. However, there is no need for that: We can easily generalize chemical tensor LEED to describe the non-spherical scattering of a scatterer by allowing δt to simulate the non-spherical part by non-diagonal elements. The reference structure calculation just needs to describe the total diffraction for spherical scattering as usual.

The general atomic scattering matrix t and atomic potential v are related by

$$t = (1 - G_0 v)^{-1} v, \quad (2)$$

which, by separating them into spherical (t_s, v_s) and non-spherical ($\delta t, \delta v$) parts, yields

$$t_s + \delta t = [1 - G_0(v_s + \delta v)]^{-1}(v_s + \delta v), \quad (3)$$

which in first order approximation gives

$$\delta t = (1 + t_s G_0) \delta v (1 + G_0 t_s). \quad (4)$$

This is supposed to hold as long as $\delta v \ll v$. There are obviously four terms linear in δv . For an estimation of the order of magnitude of the influence of non-spherical scattering it is sufficient to use only the kinematic part, i.e.

$$\delta t \approx \delta v. \quad (5)$$

3. Calculation of the non-spherical atomic potential

A convenient method to calculate the atomic potential for an atom embedded in a surface is the Hartree–Fock method which we apply in the following (see e.g. Ref. [17]). For the sake of simplicity we use closed shell molecular orbitals, i.e. we restrict ourselves to systems with an even number of electrons (restricted Hartree–Fock approximation RHF). The potential operator V of this system then is identical to the Fock operator F :

$$F = O(1) + \sum_j^N 2J_j - K_j, \quad (6)$$

with $O(1)$ the one-electron part of the operator, i.e. the kinetic energy and the interaction with the nuclei. The quantities J_j and K_j are the Coulomb and exchange operators, respectively, and N denotes the number of occupied molecular orbitals. As we are only interested in differences between potentials, the one-electron part cancels out and we get

$$\delta v = \delta F = F^{\text{asym}} - F^{\text{sym}} = \sum_j^N 2 \delta J_j - \delta K_j. \quad (7)$$

As we need δv in the basis of spherical wave functions, i.e.

$$\langle L | \delta v | L' \rangle = \sum_j^N (2 \langle L | \delta J_j | L' \rangle - \langle L | \delta K_j | L' \rangle), \quad (8)$$

with

$$\langle r | L \rangle = L(r) = j_1(kr) Y_{1m}(\Omega_r), \quad (9)$$

the Coulomb part writes as

$$\begin{aligned} & 2 \sum_j^N \langle L | J_j | L' \rangle \\ &= 2 \sum_j^N \int d^3 r_1 \int_{\text{MT}} d^3 r_2 L(r_1) \Psi_j'(r_2) \\ & \quad \times \frac{1}{r_{12}} \Psi_j(r_2) L'(r_1) \end{aligned} \quad (10)$$

and equivalently the exchange part

$$\begin{aligned} \sum_j^N \langle L | K_j | L' \rangle &= \sum_j^N \int d^3 r_1 \int_{\text{MT}} d^3 r_2 L(r_1) \Psi_j'(r_2) \\ & \quad \times \frac{1}{r_{12}} L'(r_2) \Psi_j(r_1), \end{aligned} \quad (11)$$

with Ψ the one-electron wave function. Note that the integral over the potential part (i.e. r_2) needs only to be calculated within the muffin-tin sphere (MT) around the atom under consideration.

Expansion of the one-electron functions Ψ_j in a basis set of M functions Φ_p with weights c_{pj} , i.e.

$$\Psi_j(r) = \sum_p^M c_{pj} \Phi_p(r), \quad (12)$$

yields

$$\begin{aligned} & 2 \sum_j^N \langle L | J_j | L' \rangle \\ &= 2 \sum_j^N \sum_{pq}^M \int d^3 r_1 \int_{\text{MT}} d^3 r_2 L(r_1) c_{pj}^* \Phi_p^*(r_2) \\ & \quad \times \frac{1}{r_{12}} c_{qj} \Phi_q(r_2) L'(r_1) \end{aligned} \quad (13)$$

and

$$\begin{aligned} & \sum_j^N \langle L | K_j | L' \rangle \\ &= 2 \sum_j^N \sum_{pq}^M \int d^3 r_1 \int_{\text{MT}} d^3 r_2 L(r_1) c_{pj}^* \Phi_p^*(r_2) \\ & \quad \times \frac{1}{r_{12}} c_{qj} L'(r_2) \Phi_q(r_1). \end{aligned} \quad (14)$$

Using the so-called “charge-density-bond-order” matrix

$$P_{pq} = 2 \sum_j^N c_{pj}^* c_{qj} \quad (15)$$

and the abbreviations

$$\begin{aligned} \langle Lp | Lq \rangle &= \int d^3r_1 \int_{\text{MT}} d^3r_2 L(r_1) \Phi_p^*(r_2) \\ &\quad \times \frac{1}{r_{12}} L(r_1) \Phi_q(r_2) \end{aligned} \quad (16)$$

and

$$\begin{aligned} \langle Lp | qL' \rangle &= \int d^3r_1 \int_{\text{MT}} d^3r_2 L(r_1) \Phi_p^*(r_2) \\ &\quad \times \frac{1}{r_{12}} \Phi_q(r_1) L'(r_2), \end{aligned} \quad (17)$$

Eqs. (11) and (12) transform to

$$2 \sum_j^N \langle L | J_j | L' \rangle = \sum_{pq}^M P_{pq} \langle Lp | Lq \rangle \quad (18)$$

and

$$\sum_j^N \langle L | K_j | L' \rangle = \frac{1}{2} \sum_{pq}^M P_{pq} \langle Lp | qL' \rangle. \quad (19)$$

Eventually this leads to

$$\langle L | \delta v | L' \rangle = \sum_{pq}^M \delta P_{pq} (\langle Lp | Lq \rangle - \frac{1}{2} \langle Lp | qL' \rangle). \quad (20)$$

The quantities δP_{pq} denote the difference of the charge-density-bond-order matrix of the non-spherical and the spherical system. As the spherical system consists only of one single atom while the non-spherical system is determined also by the surrounding cluster of atoms, the number of basis functions necessary to describe both is different. Therefore, one has to extend the dimension for the spherical P -matrix artificially setting the unnecessary coefficients to zero.

Eq. (20) is the final expression for δv and via Eq. (4) also for δt . It suits us perfectly well because the time consuming part of the calculation, i.e. the evaluation of the one-electron integrals (16, 17) needs to be carried out only once for the various values of l , m and k (note that the integrals consist merely of known functions). They can be used for any surface geometry because the latter enters the formalism only via the coefficients of the P -matrix. These coefficients can be calculated by common quantum chemistry programs which solve the Roothaan equa-

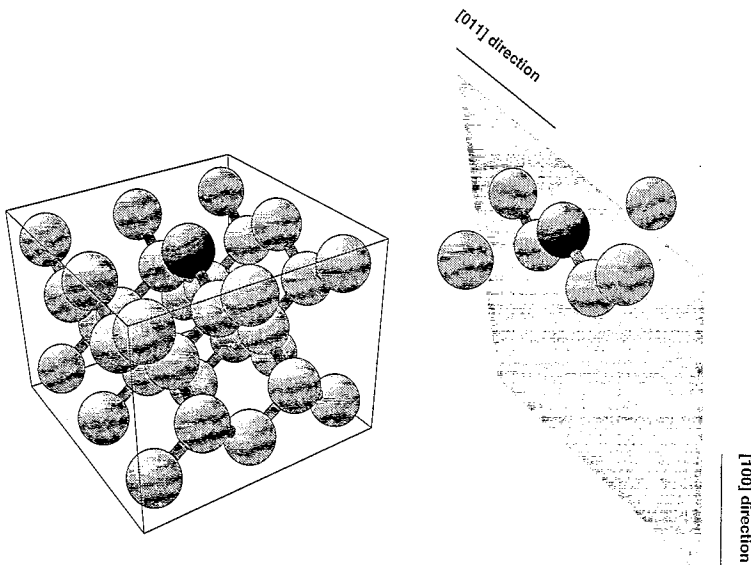


Fig. 1. Left: Silicon structure with the top face being (100). Right: Cluster used to calculate the charge density for a surface Si atom (dark atom).

tions. In our case we used the program package GAMESS [18].

4. Application

In the following we apply the formalism introduced above to the unreconstructed Si(100)-(1 × 1) surface. We aim only to estimate the order of magnitude of the influence of non-sphericity and therefore use the crude approximation $\delta t \approx \delta v$ (Eq. (5)). LEED intensity spectra were calculated for surfaces with spherically symmetric silicon atoms as a reference. Subsequently, intensity data for the same beams were obtained via tensor LEED using non-spherical atomic potentials. Quantitative comparison of the spectra is made by application of the Pendry R -factor R [19], whereby $R = 0$ results for ideal agreement, $R = 1$ for uncorrelated and $R = 2$ for anticorrelated data.

The non-sphericity of the scattering potential of a certain silicon atom is due to its bonding to the surrounding atoms. Consequently, surface atoms have to be described by potentials different from that for bulk atoms. The atomic cluster used for the Hartree–Fock calculation consists of seven atoms for

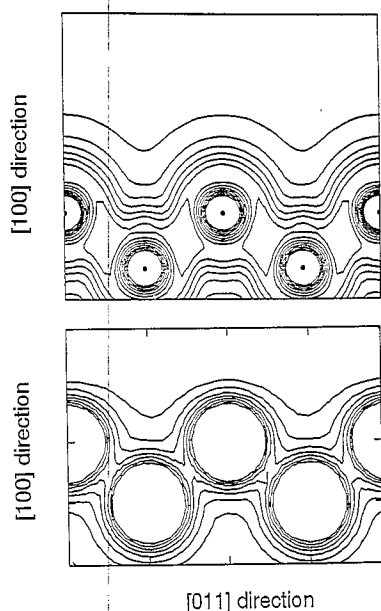


Fig. 2. Surface potential of Si(100) as calculated in the present paper (top) and by Appelbaum et al. [20] (bottom), whereby the plane displayed corresponds to the shaded area displayed in Fig. 1.

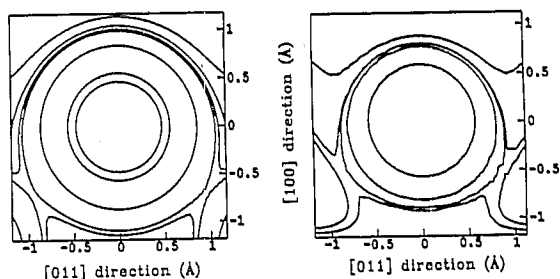


Fig. 3. Charge density contour lines around a surface silicon atom represented by orbitals of all cluster atoms (left) and the same after approximative representation using only orbitals of the atom under consideration (right).

first layer atoms (Fig. 1) whereby silicon bonds to atoms outside the cluster were saturated by hydrogen. Bulk atoms were simulated by the silyl-analog of neopentane. The shape of the resulting surface potential compares very well to results by Appelbaum et al. [20] as demonstrated in Fig. 2. In order to give the reader an idea about the relative change

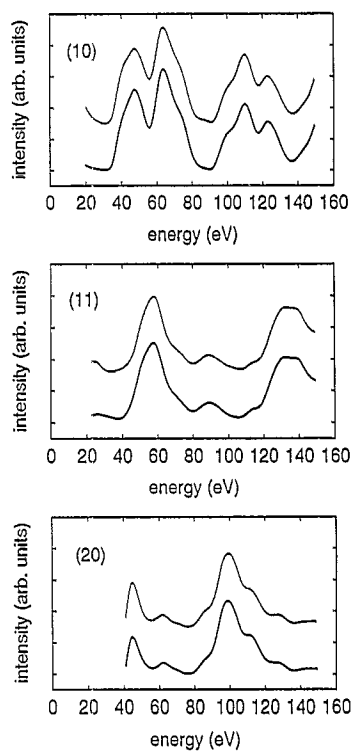


Fig. 4. Comparison of intensity spectra for some selected beams of Si(100)-(1 × 1) for silicon atoms assumed to scatter spherically (solid lines) and non-spherically (broken lines). The Pendry R -factor between both sets of spectra averaged over eight beams is $R = 0.03$.

of the potential we should mention that at the edge of the muffin-tin sphere of a surface atom the charge density changes on average by a factor of 1.15 compared to the spherically symmetric charge distribution, being at a maximum value of 2.8 in the midth between two neighbouring atoms.

In order to use only basis functions centred at the atom under consideration for the calculation of δv , which makes the evaluation of the above integrals much easier, the influence of the neighbour atoms was considered by expanding their basis functions into basis functions of the centre atom. As this basis is not complete this introduces some deviations as demonstrated by the charge density maps shown in Fig. 3. Though the symmetry of the charge distribution is approximately reproduced, the absolute level of the non-spherical charge density level is overemphasized. However, as we aim only to estimate the order of magnitude of the effect of non-sphericity on the diffraction intensities the approximation is still useful.

The $I(E)$ spectra calculated for the spherical and non-spherical potentials are compared in Fig. 4 for some selected beams in the energy range 20–150 eV. Only at the very low energy end near 20 eV there are some small discrepancies. Otherwise the curves are extremely close to each other as quantitatively confirmed by the Pendry R -factor, whose eight beam average is only $R = 0.03$.

5. Discussion

In this paper we introduced a new approach to take into account non-spherical atomic scattering potentials in LEED intensity calculations. Our proposal is twofold: First, we suggest to use tensor LEED for the perturbative treatment of the non-diagonal atomic scattering matrix whereby the reference calculation is for the diagonal matrix based on the spherical approximation of scatterers. Second, the non-spherical scattering potential due to the crystalline surrounding of an atom and the corresponding non-diagonal atomic scattering matrix is proposed to be computed by a Hartree–Fock program using atomic orbitals as a set of basis functions. This procedure allows the fast calculation of the t -matrix for different surface structures, i.e. different bonding configurations of the atoms.

As demonstrated, a first application to Si(100)-(1 \times 1) with, however, only the order of magnitude of the influence of non-sphericity estimated, shows that for this case the non-sphericity of the atomic potentials is of practically negligible influence on the intensity spectra. We believe that this result is representative though we have used certain approximations, i.e.

- The Hartree–Fock calculation does not take into account correlation effects.
- The uncomplete basis set of atomic orbitals of only the atom under consideration was used to describe the non-spherical charge distribution.
- Only kinematic scattering from the non-sphericity was considered ($\delta t \approx \delta v$), i.e. scattering between the spherical and non-spherical part was neglected.
- The perturbation method tensor LEED was applied to calculate the influence of δt on the intensities.

As we only aim to estimate the effect of non-sphericity, neglectation of correlation, which is only a correction anyway, is allowed. Also and as demonstrated in Fig. 3, the use of a basis centred on the atom under consideration introduces no drastic errors with respect to the symmetry of the charge distribution, i.e. a more precise calculation using two-centre two-electro integrals unlikely would produce totally different results. However, the absolute level of non-spherical charges results to be too high. Fortunately, this is at least partly balanced by the second approximation with only the kinematic term of $\delta t \approx \delta v$ considered and the other three terms of Eq. (4) neglected. Moreover, as these terms are at most of the same weight as δv – and possibly weaker, as they describe the scattering between the non-spherical and spherical part of the atomic charge – again no change by an order of magnitude is expected by inclusion of these terms. Concerning the tensor LEED approximation, this has proved to work with high accuracy when, as in the present case, no propagators are involved in the calculation of δt [15,16]. So, there are good arguments that for surfaces of solids like silicon or similarly bonded atoms, the use of spherical scatterers is a safe approximation. Even if the correct R -factor between intensity spectra calculated for spherical and non-spherical scatterers would increase as much as by a factor of three, i.e. to

$R \approx 0.1$, this would be considerably below R -factors usually obtained in a complex surface structure determination using experimental data. We admit, however, that the smallness of the effect detected may be due to the tetragonal bonding of silicon which produces an only very limited non-sphericity. The effect might be larger for other compounds or for adsorbed molecules exhibiting linear, i.e. strong non-spherical covalent bonding. Also, the charge transfer between atoms which frequently accompanies their mutual bonding, might have an effect which exceeds that caused by non-sphericity. However, it requires the application of methods of atom potential calculation beyond those described and was not subject of the present paper.

Acknowledgement

This work was supported by Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungsbereich 292.

References

- [1] K. Heinz, Rep. Progr. Phys. 58 (1995) 637.
- [2] M.A. Van Hove, W. Moritz, H. Over, P.J. Rous, A. Wander, A. Barbieri, N. Máterer, U. Starke and G.A. Somorjai, Surf. Sci. Rep. 19 (1993) 191.
- [3] P.J. Rous, J.B. Pendry, D.K. Saldin, K. Heinz, K. Müller and N. Bickel, Phys. Rev. Lett. 57 (1986) 2951.
- [4] P.J. Rous and J.B. Pendry, Surf. Sci. 219 (1989) 355, 373.
- [5] P.J. Rous, Progr. Surf. Sci. 39 (1992) 3.
- [6] Y. Gauthier and R. Baudoing, Surface Segregation and Related Phenomena, Eds. P.A. Dowben and A. Miller (CRC, Boca Raton, FL, 1990) 169.
- [7] U. Bardi, Rep. Progr. Phys. 57 (1994) 939.
- [8] V. Fritzsche, J.B. Pendry, U. Löffler, H. Wedler, M.A. Mendez and K. Heinz, Surf. Sci. 289 (1993) 389.
- [9] H. Over, W. Moritz and G. Ertl, Phys. Rev. Lett. 70 (1993) 315.
- [10] U. Löffler, U. Muschiol, P. Bayer, K. Heinz, V. Fritzsche and J.B. Pendry, Surf. Sci. 331–333 (1995) 1435.
- [11] J.B. Pendry, Low Energy Electron Diffraction (Academic Press, London, 1974).
- [12] S. Nagano and S.Y. Tong, Phys. Rev. B 32 (1985) 6562.
- [13] Y. Joly, Phys. Rev. Lett. 68 (1992) 950.
- [14] U. Löffler, R. Döll, K. Heinz and J.B. Pendry, Surf. Sci. 301 (1994) 346.
- [15] R. Döll, M. Kottcke and K. Heinz, Phys. Rev. B 48 (1993) 1973.
- [16] R. Döll, M. Kottcke, K. Heinz, L. Hammer, K. Müller and D.M. Zehner, Surf. Sci. 307–309 (1994) 434.
- [17] A. Szabo and N.S. Ostlund, Modern Quantum Chemistry (McGraw-Hill, New York, 1989).
- [18] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, J.H. Jensen, S. Koseki, M.S. Gordon, K.A. Nguyen, T.L. Windus and S.T. Elbert, QCPE Bull. 10 (1990) 52.
- [19] J.B. Pendry, J. Phys. C 13 (1980) 937.
- [20] J.A. Appelbaum, G.A. Baraff and D.R. Hamman, Phys. Rev. B 12 (1975) 5749.