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Sum Rule for Crystalline Metal Surfaces

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We have derived a sum rule for the electronic scattering phase shifts in a metal, produced by a planar boundary surface. The sum rule, which states that a weighted Fermi-surface average of the asymptotic phase of the electronic wave function in the presence of a metal surface is equal to $-\pi/4$, is derived for the case where explicit account is taken of the energy bands and crystalline structure of the solid. This extends the sum rule originally stated by Sugiyama for a jellium model of a metal. Modifications of the sum rule in the presence of an applied electric field and for complex band structure are also considered.

I. INTRODUCTION

The requirement that the surface of a bulk metal produces no long-range monotonic potential or charge disturbance deep in the bulk leads to a sum rule for the asymptotic phase of the electron wave functions. This sum rule, analogous to the Friedel sum rule for metallic impurities,[1] was first stated by Sugiyama[2] and recently was proved in detail by Langreth.[3] The sum rule states that a weighted Fermi-surface average of the asymptotic phase of the electronic wave function in the presence of a metal surface is equal to $-\pi/4$. Both these authors discussed this sum rule in the context of the jellium model for a solid surface,[4] which neglects the lattice structure and the concomitant energy bands of the real solid.

It is the purpose of this paper to extend the discussion of the sum rule to include lattice and energy-band effects. To this end we have organized the remainder of the paper into two sections. In Sec. II the phase rule is derived for boundary conditions appropriate to a semi-infinite solid, while in Sec. III the problem in finite-slab geometry is studied and the connection between the sum rule and simple counting arguments is made clear.

II. PHASE RULE FOR SEMI-INFINITE GEOMETRY

We restrict ourselves to metal surfaces parallel to a crystallographic plane in which there has been no change in the two-dimensional periodicity parallel to the surface. The coordinate axes are chosen so that $\hat{z}$ is normal to the metal surface, with positive $\hat{z}$ pointing out of the solid, and its origin is chosen near the last plane of atoms. (The precise position of this origin will be made clear later.)

The metal can be thought of as occupying the entire left half-space or as being terminated near $z=-L$ by another surface. Both cases will be considered; for the present we need not make a choice.

Electron wave functions in the presence of the surface can be labeled by the quantum numbers $\vec{k}_\parallel$ and E, where $\vec{k}_\parallel$ is the Bloch quantum number for periodic translations in the surface plane and E the total energy. Under the assumption that the bulk band structure of the metal admits only two degenerate Bloch waves (this assumption will be relaxed at the end of this section) for a given $\vec{k}_\parallel$ and E, the electron states $\psi_{\vec{k}_\parallel,E}$ can be written in the interior of the crystal as

$$\psi_{\vec{k}_\parallel,E}=a_1\varphi_{\vec{k}_\parallel,k}-a_2e^{-2i\chi}\varphi_{\vec{k}_\parallel,l}\ , \qquad (2.1)$$

where $\varphi_{\vec{k}_\parallel,(k,l)}$ are the two Bloch waves with energy E and wave vectors $\vec{k}_\parallel$ and k or l. a_1 and a_2 are to be chosen so that $\psi_{\vec{k}_\parallel,E}$ has no net current, and χ is the phase between the incident Bloch wave, taken to have wave vector k, and the reflected Bloch wave with wave vector l.

Following Langreth,[3] we proceed by constructing an expression for the total charge per unit area A, in the state $\psi_{\vec{k}_\parallel,\epsilon}$, to the right of a plane $\bar{z}$ parallel to the surface. Denoting this by $N_{\vec{k}_\parallel,\epsilon}(\bar{z})$ we have

$$N_{\vec{k}_\parallel,\epsilon}(\bar{z})=\int_A\int_{\bar{z}}^{\infty}\left|\psi_{\vec{k}_\parallel,\epsilon}(z)\right|^2dz\,dS\ , \qquad (2.2)$$

where a denotes the Wigner–Seitz cell in the surface plane, whose area is A. This can be rewritten in terms of only $\psi_{\vec{k}_\parallel,\epsilon}$ and its energy and z derivatives on the plane $z=\bar{z}$. We have

$$[-\nabla^2/2+V(\vec{x})]\psi^*_{\vec{k}_\parallel,E}=E\psi^*_{\vec{k}_\parallel,E} \qquad (2.3a)$$

and

$$[-\nabla^2/2+V(\vec{x})]\psi_{\vec{k}_\parallel,E'}=E'\psi_{\vec{k}_\parallel,E'}\ , \qquad (2.3b)$$

where $V(\vec{x})$ is assumed real. Atomic units ($e=m=\hbar=1$) will be used throughout this paper. Multiplying (2.3a) by $\psi_{\vec{k}_\parallel,E'}$ and (2.3b) by $\psi^*_{\vec{k}_\parallel,E}$, subtracting the resulting expressions, and integrating over the two-dimensional Wigner–Seitz cell, one finds

$$(E'-E)\int_A dS_1\psi_{\vec{k}_\parallel,E'}\psi^*_{\vec{k}_\parallel,E}$$

$$=\tfrac{1}{2}\int_A dS[\psi^*_{\vec{k}_\parallel,E}\nabla^2\psi_{\vec{k}_\parallel,E'}-\psi_{\vec{k}_\parallel,E'}\nabla^2\psi^*_{\vec{k}_\parallel,E}]$$

$$=\tfrac{1}{2}\int dS\,\nabla\cdot[\psi^{*}_{\vec{k}_{\parallel},E}\nabla\psi_{\vec{k}_{\parallel},E'}-\psi_{\vec{k}_{\parallel},E'}\nabla\psi^{*}_{\vec{k}_{\parallel},E}]\,. \qquad (2.4)$$

Integrating now from $z=\overline{z}$ to $z=\infty$ and using the fact that $\psi_{\vec{k}_{\parallel},E}\rightarrow 0$ as $z\rightarrow\infty$, and then taking the limit that $E'\rightarrow E$, one finds

$$N_{k_{\parallel},E}(\overline{z})=\frac{1}{2}\int_A dS\left[\psi^{*}_{\vec{k}_{\parallel},E}\frac{\partial}{\partial z}\frac{\partial}{\partial E}\psi_{\vec{k}_{\parallel},E}\right.$$

$$\left.-\frac{\partial}{\partial E}\psi_{\vec{k}_{\parallel},E}\frac{\partial}{\partial z}\psi^{*}_{\vec{k}_{\parallel},E}\right]. \qquad (2.5)$$

We turn to the task of constructing an explicit form for the bracketed expression in (2.5). For simplicity we suppress the $\vec{k}_{\parallel},E$ subscripts and denote $d\omega/dE$ as ω'. Then

$$\psi'=(a_1'+ik'za_1)\varphi_k-(a_2'-2i\chi'a_2+il'a_2)e^{-i2\chi}\varphi_l$$

$$+a_1e^{ikz}\frac{\partial u_k}{\partial k}k'-a_2e^{-i2\chi+ilz}\frac{\partial u_l}{\partial l}l'\,, \qquad (2.6)$$

where

$$\varphi_k(\vec{x})\equiv e^{ikz}u_k(\vec{x})\,. \qquad (2.7)$$

Taking the z derivatives of ψ and ψ' one finds for

$$\frac{\partial\psi^*}{\partial z}\psi'-\psi^*\frac{\partial}{\partial z}\psi'=\sum_{i=1}^{4}S_i: \qquad (2.8)$$

$$S_1=-a_1(a_2'-2i\chi'a_2+il'za_2)e^{-2i\chi}\left(\frac{\partial\varphi_k^*}{\partial z}\varphi_l-\varphi_k^*\frac{\partial\varphi_l}{\partial z}\right)-a_2(a_1'+ik'za_1)e^{+2i\chi}\left(\frac{\partial\varphi_l^*}{\partial z}\varphi_k-\varphi_l^*\frac{\partial\varphi_k}{\partial z}\right), \qquad (2.9)$$

$$S_2=a_1(a_1'+ik'za_1)\;\frac{\partial\varphi_k^*}{\partial z}\varphi_k-\varphi_k^*\frac{\partial\varphi_k}{\partial z}+a_2(a_2'-2i\chi'a_2+il'za_2)\left(\frac{\partial\varphi_l^*}{\partial z}\varphi_l-\varphi_l^*\frac{\partial\varphi_l}{\partial z}\right), \qquad (2.10)$$

$$S_3=a_1^2k'\left[\frac{\partial\varphi_k^*}{\partial z}e^{ikz}\frac{\partial u_k}{\partial k}-\varphi_k^*\frac{\partial}{\partial z}\left(e^{ikz}\frac{\partial u_k}{\partial k}\right)-i\,|\varphi_k|^2\right]$$

$$+a_2^2l'\left[\frac{\partial\varphi_l^*}{\partial z}e^{ilz}\frac{\partial u_l}{\partial l}-\varphi_l^*\frac{\partial}{\partial z}\left(e^{ilz}\frac{\partial u_l}{\partial l}\right)-i\,|\varphi_l|^2\right], \qquad (2.11)$$

$$S_4=-a_1a_2l'\left[\frac{\partial\varphi_k^*}{\partial z}\frac{\partial u_l}{\partial l}e^{ilz}-\varphi_k^*\frac{\partial}{\partial z}\left(e^{ilz}\frac{\partial u_l}{\partial l}\right)-i\varphi_k^*\varphi_l\right]e^{-2i\chi}$$

$$-a_1a_2k'\left[\frac{\partial\varphi_l^*}{\partial z}\frac{\partial u_k}{\partial k}e^{ikz}-\varphi_l^*\frac{\partial}{\partial z}\left(e^{ikz}\frac{\partial u_k}{\partial k}\right)-i\varphi_l^*\varphi_k\right]e^{2i\chi}\,. \qquad (2.12)$$

Fortunately, enormous simplifications can be effected in these expressions if the required dS integrations on the plane $z=\overline{z}$ are performed and a number of identities valid for the Bloch waves and proved in the Appendix are exploited.

The term $\int_A dS\,S_1$ vanishes because of the identity

$$\int_A dS\left(\frac{\partial\varphi_k^*}{\partial z}\varphi_l-\frac{\partial\psi_l}{\partial z}\varphi_k^*\right)=0\,, \qquad (2.13)$$

proved in the Appendix.

In simplifiying $\int dS\,S_2$ we use

$$\int_A dS\left(\frac{\partial\varphi_k^*}{\partial z}\varphi_k-\varphi_k^*\frac{\partial\varphi_k}{\partial z}\right)=-\frac{2i}{d}\frac{\partial E}{\partial k}\,, \qquad (2.14)$$

where E is the energy and dE/dk the average velocity in the three-dimensional unit cell, and d is the width (in the z direction) of a unit cell. This expression follows from the fact that the left-hand side of (2.14) represents the current through the area A and should therefore be proportional to $\partial E/\partial k$. (See Appendix for complete proof.)

With (2.14) and the analogous expression with k replaced by l one obtains

$$\int_A dS\,S_2=\frac{-i}{d}\left(2a_1a_1'\frac{dE}{dk}+2a_2a_2'\frac{dE}{dl}\right)$$

$$-4a_2^2\chi'/d+2z(a_1^2+a_2^2)/d\,, \qquad (2.15)$$

Turning to $\int dS\,S_3$ we show in the Appendix that the first bracketed expression in (2.11) can be written

$$\frac{2}{d}\frac{dE}{dk}[D_k(z)-Z_k]-\frac{i}{d}\frac{\partial^2E}{\partial k^2}\,, \qquad (2.16)$$

where

$$Z_k=i\int_\Omega u_k^*\frac{\partial}{\partial k}u_k\,dV\,. \qquad (2.17)$$

$D_k(z)$ represents the fluctuation of the integrated charge density of bulk state k and is defined explicitly in the Appendix. Using (2.16) and the analogous expression with k replaced by l one finds

$$\int_A dS\,S_3=\frac{2}{d}\left[|a_1|^2\left(D_k(z)-Z_k-i\frac{\partial^2E}{\partial k^2}\frac{\partial k}{\partial E}\right)\right.$$

$$\left.+|a_2|^2\left(D_l(z)-Z_l-i\frac{\partial^2E}{\partial l^2}\frac{\partial l}{\partial E}\right)\right]. \qquad (2.18)$$

Finally the first bracketed expression in Eq. (2.12) for S_4 is shown in the Appendix to be

$$\frac{ie^{-i(k-l)z}}{\sin[(k-l)d/2]}\,\frac{dE}{dl}\,[1+\Delta_{kl}(z)]\,, \tag{2.19}$$

where $\Delta_{kl}(z)$ is defined in the Appendix. It vanishes as $k-l\to 0$ and is periodic in z with period d; in addition,

$$\Delta_{kl}=\Delta^*_{lk}\,. \tag{2.20}$$

This leads to

$$\int dS\,S_4=\frac{2a_1a_2}{\sin[(k-l)d/2]}\times \operatorname{Im}\{e^{-i(k-l)z}[1+\Delta_{kl}(z)]\}\,. \tag{2.21}$$

Combining (2.15), (2.18), and (2.21),

$$N(z)=-\frac{z}{d}\,(a_1^2+a_2^2)+2\,\frac{a_2^2}{d}\,\chi'\,\frac{\partial E}{\partial l}-\frac{a_1^2}{d}\,[D_k(z)-Z_k]-\frac{a_2^2}{d}\,[D_l(z)-Z_l]+\frac{a_1a_2\sin[(k-l)z+2\chi]}{\sin[(k-l)d/2]}-\frac{a_1a_2}{\sin[(k-l)d/2]}\,\operatorname{Im}[e^{-i[2\chi+(k-l)z]}\,\Delta_{kl}(z)]\,. \tag{2.22}$$

The imaginary terms in $\int dS\,S_n$ cancel upon collection because they sum to $d(a_1^2v_1+a_2v_2)/dE=0$, making $N(z)$ manifestly real. This derivative vanishes because $(a_1^2v_1+a_2^2v_2)$ is the average velocity of the state, which must vanish for all E.

To proceed further, we must determine a_1 and a_2. They are fixed by the relation just mentioned and the normalization. In this section, where we deal with the semi-infinite crystal, we choose to normalize so that

$$\int dV\,\psi^*_{\vec{k}_{\parallel},E}\,\psi_{\vec{k}_{\parallel},E'}=\delta(\vec{k}_{\parallel}-\vec{k}'_{\parallel})\,\delta(E-E')\,. \tag{2.23}$$

This means choosing

$$a_1^2=Ad\,\frac{dk}{dE}\,,\quad a_2^2=-Ad\,\frac{dl}{dE}\,. \tag{2.24}$$

Now, Eq. (2.22) represents the charge to the right of z in a single state $(\vec{k}_{\parallel},E)$. The total electronic charge in this region, due to states within the band at each $\vec{k}_{\parallel}$, is given by

$$N_{\mathrm{TB}}(z)=\frac{1}{(2\pi)^2}\int d^2k_{\parallel}\,dE\;\theta(E_F-E)N_{\vec{k}_{\parallel},E}(z)\,, \tag{2.25}$$

where $\theta(x)=1$ if $x>0$, and $\theta(x)=0$ if $x<0$.

If there are surface states for some $\vec{k}_{\parallel}$, we obtain an additional contribution, independent of z, sufficiently deep in the crystal,

$$N_{\mathrm{TS}}=\frac{1}{(2\pi)^2}\int d^2k_{\parallel}N_{S,\vec{k}_{\parallel}}\,, \tag{2.26}$$

where $N_{S,\vec{k}_{\parallel}}$ is the number of bound states for given $\vec{k}_{\parallel}$. The total electronic charge is then $N_T=N_{\mathrm{TB}}+N_{\mathrm{TS}}$.

The condition that the surface produces no long-range monotonic potential disturbance deep in the bulk is expressed by the equation

$$\lim_{z_0\to-\infty}\int_{z_0}^{z_0+d}[N_T(\bar{z})-N_T^{\mathrm{ion}}(\bar{z})]\,d\bar{z}=0\,, \tag{2.27}$$

where $N_T^{\mathrm{ion}}(\bar{z})$ is the ionic counterpart to $N_T(\bar{z})$.

In evaluating (2.25) using (2.22) and (2.24), we note first that the terms involving $D_k(z)$ and $D_l(z)$ yield zero on integrating over $\bar{z}$, since their spatial average is zero (see Appendix).

The terms containing a_1a_2 in (2.22) require some discussion. As written, they are in a form convenient for the region $k-l<\pi/d$. If $k-l\sim 2\pi/d$, it would be more convenient to replace $k-l$ with $k-l-2\pi/d$ in both terms, with a consequent redefinition of Δ_{kl}. This does not really matter unless the Fermi surface reaches the zone boundary for some $\vec{k}_{\parallel}$. Considering first the case where this does not happen, we can say that the term containing Δ_{kl} contributes only to the Friedel oscillations produced by the surface, which fall off to zero as $z\to-\infty$, and thus do not contribute to (2.27). The other term also contributes to these oscillations, but contains, in addition, a contribution from the neighborhood of $k-l=0$, which is independent of z. In this neighborhood, it is sufficient to set $a_1^2=a_2^2=\frac{1}{2}Ad\,d(k-l)/dE$. Then provided only that $\sin[2\chi(k-l=0)]=0$, we find, on performing the E integration,

$$\frac{A}{(2\pi)^3}\int d^2k_{\parallel}(-\pi/2)$$

as the contribution of the a_1a_2 terms to (2.27). The integral extends over those $\vec{k}_{\parallel}$ within the Fermi surface.

The assumption about $\chi(k-l=0)$ is valid except on the boundaries separating regions of $\vec{k}_{\parallel}$ with bound states from regions without them. The error made in neglecting these regions decreases to zero in the limit $z\to-\infty$.

If the Fermi surface reaches the zone boundary, we must consider the modification just discussed and find that there is an additonal z-independent contribution from the region $k-l\sim 2\pi/d$, which just cancels the contribution already found. The total contribution of the a_1a_2 terms to (2.27) is then just

$$\frac{A}{(2\pi)^3}\int d^2k_{\parallel}(-\pi/2)(n_- - n_+)\,, \tag{2.28}$$

where n_- (n_+) is the number of minima (maxima) in energy, below the Fermi level at $\vec{k}_{\parallel}$.

The contribution of the remaining terms of (2.22)–(2.27) is just

$$-zA\left(\frac{1}{2\pi}\right)^3\int d^2k_{\parallel}(k-l)_F-\frac{2A}{(2\pi)^3}\int d^2k_{\parallel}\times(\chi_F-\chi_0)+\frac{A}{(2\pi)^3}\int d^2k_{\parallel}\int_{l_F}^{k_F}Z_k dk\,, \tag{2.29}$$

where the subscript F means that quantity is to be evaluated at the Fermi surface or the zone boundary, whichever has lower energy, and χ_0 is to be evaluated at the minimum energy for given $\vec{k}_{\parallel}$. The coefficient of $(-z)A$ in this expression is just the electronic density $\bar{\rho}$ of the perfect crystal as it must be.

The presence of the Z_k in (2.29) is a bit of an inconvenience. This quantity is familiar from band theory (see Ref. 5, p. 313). It has the property that it is sensitive to the choice of over-all phases for the Bloch functions. This is also true of the χ's and the Z_k occur in just such a way as guarantees that (2.29) be invariant if the phases are changed. If the undisturbed crystal has a symmetry under which z changes sign, such as inversion or a mirror plane parallel to the surface, the natural choice of phases will make the integral of the Z_k in Eq. (2.29) vanish. Lacking such a symmetry, the attempt to make the integral vanish would not be worthwhile.

To discuss the contribution of bound states, we suppose at first that for some $\vec{k}_{\parallel}$, there are no bound states. For such $\vec{k}_{\parallel}$, we choose $\chi_0=0$. Then if we move in $\vec{k}_{\parallel}$ to a region where a bound state has split off below the band edge, we lose a state from the band. If χ_F is continuous in this region, this means that χ_0 decreases dicontinuously by π. Thus the number of bound-states split off is given by $-\chi_0/\pi$. Similarly, if the Fermi surface reaches the zone boundary, and a state is split off at the top, χ_F increases dicontinuously by π.

It follows that the surface states below the bottom of the band for $\vec{k}_{\parallel}$ within the Fermi surface can be accounted for by eliminating χ_0 from Eq. (2.29). Surface states below the bottom of the band for other $\vec{k}_{\parallel}$, or above the top of the band for $\vec{k}_{\parallel}$ where all states are occupied, must be included explicitly. This contribution can be designated by $\hat{N}_{\mathrm{TS}}(\vec{k}_{\parallel})$.

We now write the total electronic contribution to (2.27) as

$$-\bar{\rho}A(z-\bar{Z}_k)-\frac{A}{(2\pi)^2}\int d^2k_{\parallel}\frac{\chi_F}{\pi}+\frac{A}{(2\pi)^2}\int d^2k_{\parallel}\hat{N}_{\mathrm{TS}}(\vec{k}_{\parallel})-\frac{A}{4(2\pi)^2}\int d^2k_{\parallel}(n_- - n_+)\,, \tag{2.30}$$

where $\bar{Z}_k$ is the average of Z_k over the Fermi sea.

Now $N_T^{\mathrm{ion}}(\bar{z})$ will have, in the interior of the crystal, the form

$$N_T^{\mathrm{ion}}(\bar{z})=\bar{\rho}^{\,\mathrm{ion}}A(\bar{Z}-Z_{\mathrm{ion}})+\text{oscillating terms.} \tag{2.31}$$

The oscillating terms average to zero. The quantity Z_{ion} is determined by the arrangement of ions in the perfect crystal and by the nature of the surface, that is, by where the cut is made and what ions are removed. Its position with respect to a given plane of atoms in the interior does not depend upon surface rearrangements of the atoms.

For complicated crystal structures or surfaces, z_{ion} must be computed. For an important class of situations, however, it can be determined easily. This class consists of those cases where the metal contains just the ions on one side of a plane, about which the undisturbed average planar density, integrated over x and y, is symmetric. In such cases z_{ion} is simply the value of z on this plane. All such cases are included among the cases where $\bar{z}_k$ can conveniently be made to vanish.

Now the coefficients of z in (2.30) and (2.31) must cancel, since the undisturbed crystal is neutral. Therefore, (2.27) can be put in the form

$$-\int d^2k_{\parallel}\chi_F-\tfrac{1}{4}\pi\int d^2k_{\parallel}(n_- - n_+)+\pi\int d^2k_{\parallel}N_{\mathrm{TS}}+\bar{\rho}(\bar{Z}_k-z_{\mathrm{ion}})=0. \tag{2.32}$$

In accordance with the previous discussion, there will be many cases, probably almost all those of current interest, where the final term can be made to vanish by suitable choice of phases and origin of coordinates. When this is done our expression differs from those of Langreth and Sugiyama only by the presence of n_+ in the second integral, and in the third term. The first of these is a result of band structures which has no analog for jellium. The second represents an oversight in Langreth's footnote 6.

We should note that this derivation has assumed that there is no external field. In the presence of such a field, Equation (2.27) should be modified by a right-hand side proportional to the field, which would then appear also in (2.32).

So far, we have assumed that, for each $\vec{k}_{\parallel}$, only two Bloch states have a given energy. This is not a very desirable restriction, and we would like to sketch briefly the consequences of its removal.

A set of states which satisfy the boundary condition on the right can be written

$$\psi_{i,E}=(\psi_{k_i}-\bar{\psi}_{k_j}u_{ji})\,. \tag{2.33}$$

Here the ψ_k's are Bloch functions whose velocity v_k is positive, while the $\overline{\psi}_l$ have negative velocities. Their normalizations are chosen so that they all have the same current—relative to the φ_k's used so far, they are divided by $|v_k|^{1/2}$. The matrix u_{ij} describes the reflection from the boundary of the states ψ_k. The index $\vec{k}_\parallel$ is suppressed and we have used a summation convention.

An arbitrary function $\Psi_{s,E}$ of energy E can be written, in the interior of the medium, as

$$\Psi_{s,E}=(\psi_{ki}-\overline{\psi}_{lj}u_{ji})\,\alpha_{is}\,. \tag{2.34}$$

Any such function must have a vanishing expectation value of velocity. Imposing this requirement leads to the conclusion that u_{ij} is a unitary matrix—which is why we have chosen this normalization for the ψ_{ki}.

The functions $\psi_{i,E}$ are normalized to $\delta(E-E')$ and we can find the total density by squaring $\psi_{i,E}$, summing over i, and integrating over $\vec{k}_\parallel$ and E.

The result of a calculation paralleling that above is $-2\chi_F$ should be replaced by $(\ln|u|)_F$. This, of course, reduces to $(-2\chi_F)$ when there are only two states at the Fermi surface.

With this modification our results are also applicable in cases of reconstruction, whose principal effect for present purposes is to result in a smaller Brillouin zone, by mapping several $\vec{k}_\parallel$ into one. This necessarily produces more than two states of given energy at a given $\vec{k}_\parallel$.

III. PHASE RULE FOR SLAB GEOMETRY

We have now established the sum rule for the case of a semi-infinite medium. It is of some interest to consider instead the case of a finite slab, where the relation between the sum rule and simple counting arguments is more apparent.

The presence of the right-hand boundary has the consequence that, in the interior of the crystal, the wave function $\psi_{\vec{k}_\parallel,E}$ has the form (2.1). Similarly, a boundary on the left results in the requirement that $\psi_{\vec{k}_\parallel,E}$ has the form

$$\psi_{\vec{k}_\parallel,E}=a_1\varphi_{\vec{k}_\parallel,k}-a_2e^{+2i\zeta}\varphi_{\vec{k}_\parallel,l}\,. \tag{3.1}$$

The phase ζ consists of a part δ intrinsic to the left-hand boundary, as well as a term due to the fact that we shall keep our coordinate origin near the right-hand boundary. Suppose we know ζ for a particular slab, and want to determine it for a thicker slab containing n more unit slabs of thickness d, added on at the left. We easily find that the new ζ, called ζ_n, is just $\zeta-\frac{1}{2}(k-l)nd$. In general, then, for a slab containing N unit slabs, we would write $\zeta=-\frac{1}{2}Nd(k-l)+\delta$. (If the slab should happen not to contain exactly an integral number of unit slabs, as might occur for a not too simple crystal structure, we would choose N to be the nearest integer.)

The condition that (2.1) and (3.1) represent the same $\psi_{\vec{k}_\parallel,E}$ is then

$$\eta\equiv-(\zeta+\chi)=\tfrac{1}{2}Nd(k-l)-\delta-\chi=m\pi, \tag{3.2}$$

where η is a function of E. For a thick slab, this condition leads to a set of levels characterized by a nearly uniform difference between successive values of $q\equiv(k-l)/2$.

We may calculate the normalization integral for $\psi_{\vec{k}_\parallel,E}$ in two steps. First we compute the contribution between planes at z and $+\infty$, as in Sec. II. Then we perform the analogous computation using (3.1) for the contribution between planes at $-\infty$ and z. It is readily seen that the condition (3.2) results in the cancellation, upon adding these two parts, of all terms except those involving χ' or ζ'. The total normalization integral then turns out to be

$$\begin{aligned}1&=\int_A dS\int_{-\infty}^{\infty}dz\ \psi^*\psi\\&=-ia_2^2\left(\frac{\partial\varphi_l^*}{\partial z}\,\varphi_l-\varphi_l^*\,\frac{\partial\varphi_l}{\partial z}\right)\frac{d\eta}{dE}\\&=-2a_2^2\,\frac{v_l}{d}\,\frac{d\eta}{dE}\,.\end{aligned} \tag{3.3}$$

In this evaluation we have used Eqs. (2.13) and (2.14) using $v_l\equiv dE/dl$.

Now, the average current density in the interior of the slab is just $(a_1^2v_k+a_2^2v_l)/d$ which must vanish:

$$a_1^2v_k+a_2^2v_l=0.$$

Therefore, we have

$$\begin{aligned}1&=\frac{2a_1^2v_k}{d}\,\frac{d\eta}{dE}=-\frac{2a_2^2v_l}{d}\,\frac{d\eta}{dE}\,,\\a_1^2&=\frac{d}{2}\,\frac{dk}{d\eta}\,,\\a_2^2&=-\frac{d}{2}\,\frac{dl}{d\eta}\,,\\a_1^2+a_2^2&=d\,\frac{dq}{d\eta}\,,\end{aligned} \tag{3.4}$$

where we freely regard k, l, E, q, or η as independent variables.

We now want to construct a sum rule by means of a two-step argument. First, we shall establish that, for a given Fermi level E_F, the average density of electrons deep in the interior of the slab is the same, to order $1/N^2$, as in the unbounded crystal. This means that in order to maintain neutrality deep in the interior, E_F is the same, to order $1/N^2$, as in the unbounded crystal. Second, we shall obtain an expression for the total number of electrons, in an infinite prism of cross section A, in terms of the phases. The requirement that this number be the same as the nuclear charge will then yield the sum rule.

In this argument we shall ignore some points which were covered in Sec. II. These are bound surface states, and cases where the Fermi level reaches the zone boundary. They could be added at the end, but are irrelevant to our basic purpose in this section.

The charge density for the wave function just discussed in the interior of the slab is given by

$$\psi^*\psi = a_1^2|\varphi_k|^2 + a_2^2|\varphi_l|^2 - 2a_1a_2\,\mathrm{Re}(\varphi_k^*\varphi_l e^{i\chi}). \tag{3.5}$$

For the average density $\bar{\rho}(z_0)$ in a unit cell situated between the planes $z_0 - d/2$ and $z_0 + d/2$, we obtain, upon using (A19),

$$\begin{aligned}\Omega\bar{\rho}(z_0) = {} & a_1^2 + a_2^2 - 2a_1a_2\cos(2\chi + 2qz_0) \\ & - 2a_1a_2\,\mathrm{Re}[\Delta_{kl}(z_0 + d/2)e^{-i(2\chi+2qz_0)}].\end{aligned} \tag{3.6}$$

Here, we could replace χ by $-\zeta$. $\bar{\rho}(z_0)$ is, of course, also dependent on $\vec{k}_\parallel$ and E, and Ω is the unit-cell volume.

Since we want to evaluate the density in the interior, we choose to write z_0 as $-Nd/2 + \epsilon$, where $|\epsilon|$ is $< Nd/4$. (There is no difficulty in choosing $|\epsilon| > Nd/4$, but we would then use a slightly different method of evaluation.)

Using Eq. (3.2), we can write

$$-(2\chi + 2qz_0) = \eta + (\delta - \chi) - 2q\epsilon = m\pi - (\chi - \delta + 2q\epsilon).$$

Then, with the aid of Eq. (3.4), Eq. (3.6) takes the form

$$\begin{aligned}\frac{\Omega\bar{\rho}(z_0)}{d} = \frac{dq}{d\eta}\Bigg(1 - & \frac{2(|v_kv_l|)^{1/2}(-1)^m}{|v_k| + |v_l|} \\ & \times\cos(2q\epsilon - \delta + \chi) \\ & \times\frac{-2(|v_kv_l|)^{1/2}(-1)^m}{|v_k| + |v_l|} \\ & \times\mathrm{Re}[\Delta_{kl}(z_0 + d/2)e^{-i(2q\epsilon-\delta+\chi)}]\Bigg).\end{aligned} \tag{3.7}$$

To sum the first term of (3.7) over allowed E's for fixed $\vec{k}_\parallel$, we write

$$\sum_{\substack{m \\ E<E_F}}\frac{dq}{d\eta} = \int\frac{dq}{d\eta}\left(\frac{1}{\pi} + \frac{ds}{d\eta}\right)d\eta, \tag{3.8}$$

where s is a sawtooth function, equal to $\frac{1}{2}$ at 0, decreasing linearly to $-\frac{1}{2}$ at π, jumping to $\frac{1}{2}$, and so on. Thus, we have

$$\sum_m\frac{dq}{d\eta} = \frac{1}{\pi}\int_0^{q_F}dq + s\frac{dq}{d\eta}\bigg|_0^{q_F} - \int s\frac{d^2q}{d\eta^2}\,d\eta, \tag{3.9}$$

where q_F is the value of q for $E = E_F$ at the given $\vec{k}_\parallel$. The contribution of the last term is of order $1/N^2$ and we shall neglect it. Thus we have

$$\sum\frac{dq}{d\eta} = \frac{q_F}{\pi} - \frac{1}{2}\frac{dq}{d\eta}\bigg|_0 + s\frac{dq}{d\eta}\bigg|_{q_F}. \tag{3.10}$$

The final term fluctuates with mean value zero, as a function of η. It is of order $1/N$ and, on integrating over $\vec{k}_\parallel$, becomes of order $1/N^2$, so that we shall neglect it also.

The remaining terms of (3.7) can be written

$$\sum_{\substack{m \\ E<E_F}}(-1)^m\frac{dq}{d\eta}f(\eta), \tag{3.11}$$

where $f(q)$ is a slowly varying function of η for $\epsilon \ll L$. This sum can be written

$$\int d\eta\frac{d\sigma}{d\eta}\frac{dq}{d\eta}f(\eta), \tag{3.12}$$

where $\sigma(\eta)$ is a square wave function equal to $\frac{1}{2}$ for $2m\pi < \eta < (2m+1)\pi$ and equal to $-\frac{1}{2}$ for $(2m-1)\pi < \eta < 2m\pi$. Integrating by parts we obtain

$$-\frac{1}{2}\frac{dq}{d\eta}f\bigg|_0 + \sigma\frac{dq}{d\eta}f\bigg|_{q_F} - \int\sigma\frac{d}{d\eta}\left(\frac{dq}{d\eta}f\right). \tag{3.13}$$

The last two terms are negligible in the same way as the corresponding terms of (3.9), and we are left with

$$\frac{\Omega}{d}\bar{\rho}_{\vec{k}_\parallel}(z_0) = \frac{q_F}{\pi} + \frac{1}{2}\frac{dq}{d\eta}(1 + f)\bigg|_0. \tag{3.14}$$

Now, as $q \to 0$ $(k \to l)$, $1 + f$ vanishes provided that $\delta_0(0) = \chi(0) = 0$, and the final result, on integrating over $\vec{k}_\parallel$, is that

$$\bar{\rho}_{\mathrm{tot}}(z_0) = \frac{V_F}{(2\pi)^3} + O\left(\frac{1}{N^2}\right), \tag{3.15}$$

where V_F is the volume of the Fermi surface. This is, of course, the same density as that of the infinite crystal for the same Fermi level. In accordance with our previous remarks, then, we see that the requirement of neutrality in the interior of the slab implies that E_F is unchanged, at least to order $(1/N^2)$.

Finally, we evaluate the total number N_t of electrons in an infinite prism of cross section A:

$$\begin{aligned}N_t &= \frac{A}{(2\pi)^2}\int d^2k_\parallel\, n_{\vec{k}_\parallel}, \\ n_{\vec{k}_\parallel} &= \sum_{E<E_F} 1.\end{aligned} \tag{3.16}$$

We carry out the first sum, over E at fixed $\vec{k}_\parallel$, exactly as in (3.8), replacing $dq/d\eta$ by 1, obtaining

$$n_{\vec{k}_\parallel} = \frac{\eta_F}{\pi} - \tfrac{1}{2} + s(\eta_F). \tag{3.17}$$

The first term is of order N, while the last two are of order 1. The final term, however, fluctuates with mean zero and, on integrating over $\vec{k}_\parallel$, becomes of order $1/N$, or of order $1/N^2$ relative to the first term, and we shall neglect it. Using our previous definitions, we write

$$n_{\vec{k}_\parallel} = q_F Nd/\pi - (1/\pi)(\delta_F + \chi_F + \pi/2). \tag{3.18}$$

On integrating over $\vec{k}_{\parallel}$, we have

$$N_l = NdA\bar{\rho}_{\text{tot}} - \frac{1}{2\pi^3}\int d^2k_{\parallel}\,[(\delta_F + \chi_F)/2] + \pi/4. \tag{3.19}$$

Now, if the slab contains N unit slabs of atoms and is neutral, we find

$$\langle \chi_F + \delta_F \rangle/2 = -\pi/4, \tag{3.20}$$

where $\langle\,\rangle$ is the average over $\vec{k}_{\parallel}$.

We note that the Z_k simply do not enter in this discussion. They are not needed to preserve phase invariance, because changes in phase cancel between δ and χ. Likewise, z_{ion} does not enter, since we have used only the total amount of ionic charge, not its location.

It is easy to see that the term $-\pi/4$ is directly related to the fact that there is no state for $q = 0$. In the slab geometry, we have states at $\eta = m\pi$ for $m > 0$. In periodic boundary conditions, with box size Nd, we have states for $kNd = 2m\pi$, m not restricted. If the energy is an even function of k, this is equivalent to having a state for $q = 0$ and two states for each q such that $qL = 2m\pi$, $m > 0$. If we take the sum over these states as in Eq. (3.16), we find that $n_{\vec{k}_{\parallel}}$ is just qL, not $qL - \frac{1}{2}$, plus negligible oscillating terms. Stated otherwise, $1 + 2[\eta/2\pi]$ is always greater than $[\eta/\pi]$, where $[\,]$ means integral part, and the average difference is $\frac{1}{2}$. This is the same $\frac{1}{2}$ that occurs in Eq. (3.17).

The corresponding effect in the calculation of the density can be seen in Eq. (3.13), but this is compensated by the contribution from the terms with $(-1)^m$. This reflects the fact that the wave functions $\psi_{\vec{k}_{\parallel},E}$ have their density concentrated in the interior. This is particularly noticeable for the lowest state which has one large peak at the center of the slab and falls like $\cos(\pi\delta/L)$ towards the ends. In the idealized case of a slab with infinite barriers at the ends, the density vanishes at the ends and is piled up a bit in the interior, for any Fermi level.

If the slab contains extra material beyond N unit slabs (or less), or has a periodic adsorbed layer, obvious adjustments can be made in (3.20).

If the slab possesses a symmetry relating the left and right surfaces, so that $\langle\chi_F\rangle$ must equal $\langle\delta_F\rangle$, we recover individual sum rules

$$\langle\chi_F\rangle = \langle\delta_F\rangle = -\pi/4. \tag{3.20$'$}$$

This result, of course, agrees with the results of Sec. II when those results are specialized to agree with the suppositions of this discussion.

In the absence of a symmetry which forces the result (3.20′), we would have to use an additional argument to obtain sum rules on the $\langle\chi_F\rangle$, $\langle\delta_F\rangle$, or $\langle\chi_F - \delta_F\rangle$. These arguments would be based on the requirement, not yet used in this section, that the average value of the field in the slab is zero for a material with a free Fermi surface, and would essentially duplicate the derivation of Sec. II, with the complication arising from the finiteness of the slab.

APPENDIX

In this appendix we shall derive some identities useful in the simplification of Eq. (2.8).

The first two results are trivial consequences of the equation of continuity. If ψ and φ are two solutions of the Schrödinger equation with the same energy, it follows immediately that

$$\nabla\cdot(\varphi\nabla\psi^* - \psi^*\nabla\varphi) = 0. \tag{A1}$$

We are particularly concerned with Bloch functions, which we shall write in the form

$$\varphi_k = e^{ikz}u_k, \tag{A2}$$

where u_k contains the factor $e^{i\vec{k}_{\parallel}\cdot\vec{x}_{\parallel}}$ as well as the usual periodic part. We are suppressing the subscript $\vec{k}_{\parallel}$, since in any given equation, only functions with the same $\vec{k}_{\parallel}$ will occur. Then, from Eq. (A1), we see that the integral

$$I_{kl}(z) = i\int_{A(z)} dS\left(\varphi_l\,\frac{\partial\varphi_k^*}{\partial z} - \varphi_k^*\,\frac{\partial\varphi_l}{\partial z}\right) \tag{A3}$$

is independent of z. The integral is to be understood as taken over a unit cell $A(z)$ in the plane $z = \text{const}$. On the other hand, if we take the integral on the plane $z + d$, where d is the distance between lattice planes in the z direction, we have

$$I_{kl}(z+d) = e^{i(l-k)d}I_{kl}(z).$$

Therefore, if $l \neq k$, $I_{kl}(z) = 0$. This establishes Eq. (2.13).

If $k = l$ and ψ is normalized to unity over a unit cell, we find on integrating over a unit cell and, using the constancy of $I_{kk}(z)$, that

$$i\int_{A(z)} dS\left(\varphi_k\,\frac{\partial\varphi_k^*}{\partial z} - \varphi_k^*\,\frac{\partial\varphi_k}{\partial z}\right) = \frac{2v_k}{d}, \tag{A4}$$

where $v_k = dE/dk$ is the z component of the expectation value of the velocity for state ψ_k. This establishes Eq. (2.14).

In exact analogy to the derivation of Eq. (4), we can write

$$\begin{aligned}2v_k\int_{A(z)} dS\,\varphi_k^*\varphi_k &= \frac{d}{dz}\left(\int_{A(z)} dS\left[\frac{\partial\varphi_k^*}{\partial z}\,\frac{\partial\varphi_k}{\partial k} - \varphi_k^*\,\frac{\partial^2\varphi_k}{\partial z\,\partial k}\right]\right)\\ &= \frac{d}{dz}\,P_k + \frac{2v_k}{d},\end{aligned} \tag{A5}$$

where

$$P_k(z) \equiv \int_{A(z)} dS\left(\frac{\partial\varphi_k^*}{\partial z} e^{ikz} \frac{\partial u_k}{\partial k} - \varphi_k^* \frac{\partial}{\partial z} e^{ikz} \frac{\partial u_k}{\partial k} - i\varphi_k^* \varphi_k\right) . \tag{A6}$$

$P_k(z)$ will be recognized as the expression occurring twice in Eq. (2.11). To obtain this form we used Eq. (A4).

Now we multiply this equation by $(z - z_0 - d/2)$ and integrate from z_0 to $z_0 + d$, obtaining

$$2v_k \int_{z_0}^{z_0+d} dz (z - z_0 - d/2)\left[\int_{A(z)} dS\, \psi_k^* \psi_k - 1/d\right] = \int_{z_0}^{z_0+d} dz\left(z - z_0 - \frac{d}{2}\right)\frac{dP_k}{dz} . \tag{A7}$$

This can be rewritten as

$$2v_k \int_{z_0}^{z_0+d} dz \int_{A(z)} dS\, \psi_k^* \psi_k (z - z_0 - d/2) = d[P_k(z_0) - \overline{P}_k], \tag{A8}$$

where we have used the manifest periodic character of $P_k(z)$, and $\overline{P}_k$ is the average value of $P_k(z)$. We define the quantity $D_k(z)$ as the dipole moment, about the plane $z_0 + d/2$, of the charge density for state ψ_k in the unit cell bounded by z_0 and $z_0 + d$:

$$D_k(z_0) = \int_{z_0}^{z_0+d} dz \int_{A(z)} dS\, \psi_k^* \psi_k (z - z_0 - d/2). \tag{A9}$$

It is obvious that $D_k(z)$ has periodicity d and Eq. (A8) shows that its average value is zero.

We must now investigate $\overline{P}$. From (A6) we can write

$$d\overline{P}_k = \int_\Omega dV\left(\frac{\partial\varphi_k^*}{\partial z} e^{ikz} \frac{\partial u_k}{\partial k} - \varphi_k^* \frac{\partial}{\partial z} e^{ikz} \frac{\partial u_k}{\partial k} - i\varphi^*\varphi\right), \tag{A10}$$

when the integration is over a unit cell. Now we can write

$$\frac{\partial u_k}{\partial k} = - i \sum_\mu u_{nk} Z_{n0} - i u_k Z_k . \tag{A11}$$

Here the u_{nk}'s are functions defined as in (A2), for the other bands. It is easily seen, using the orthonormality properties of the u_{nk} over a unit cell, that

$$Z_{n0} = i \int_\Omega u_{nk}^* \frac{\partial u_k}{\partial k} , \qquad Z_k = i \int_\Omega u_k^* \frac{\partial u_k}{\partial k} . \tag{A12}$$

Then we have

$$d\overline{P}_k = - 2v_k Z_k - 2\sum V_{0n} Z_{n0} - i , \tag{A13}$$

where

$$V_{0n} = \tfrac{1}{2} i \int_\Omega \left(\frac{\partial\psi_k^*}{\partial z} \psi_{nk} - \psi_k^* \frac{\partial\psi_{nk}}{\partial z}\right) dV. \tag{A14}$$

The V_{0n} are the matrix elements of velocity between the bands in question. It is one of the basic theorems of band theory[5] that the sum of the last two terms on the right is just $(- i dv_k/dk)$. Finally, then

$$\overline{P}_k = \frac{-i}{d} \frac{dv_k}{dk} - \frac{2v_k Z_k}{d} \tag{A15}$$

and

$$P_k(z) = \frac{2v_k}{d} [D_k(z) - Z_k] - \frac{i}{d} \frac{dv_k}{dk} . \tag{A16}$$

This result is quoted in (A16).

In analogy with Eq. (A5), we write

$$2v_l \int_{z_0}^{z_0+d} dz \int_{A(z)} dS\, \psi_k^* \psi_l = \int_{A(z)} dS\left(\frac{\partial\psi_k^*}{\partial z} \frac{\partial\psi_l}{\partial l} - \psi_k^* \frac{\partial^2\psi_l}{\partial z \partial l}\right)\Bigg|_{z_0}^{z_0+d} = S_{kl}(z_0 + d) - S_{kl}(z_0), \tag{A17}$$

where

$$S_{kl}(z_0) = \int_{A(z)} dS\left[\frac{\partial\psi_k^*}{\partial z} e^{ilz} \frac{\partial u_l}{\partial l} - \psi_k^* \frac{\partial}{\partial z}\left(e^{ikz} \frac{\partial u_l}{\partial l}\right) - i\psi_k^* \psi_l\right] . \tag{A18}$$

S_{kl} is just the expression occurring in Eq. (2.12). Evidently $S_{kl}(z_0 + d) = e^{i(l-k)d} S_{kl}(z_0)$, and we find

$$S_{kl}(z_0) = \frac{v_l e^{i(l-k)z_0}}{i \sin[(l-k)d/2]} \int_{z_0}^{z_0+d} dz \times \int_{A(z)} dS\, \psi_k^* \psi_l e^{-i(l-k)(z_0+d/2)} = \frac{v_l e^{i(l-k)z_0}}{i \sin[(l-k)d/2]} [1 + \Delta_{kl}(z_0)] . \tag{A19}$$

Here, $\Delta_{kl}(z)$ is defined as a periodic function of z and it vanishes as $k \to l$. Its behavior for small $k - l$ is readily obtained:

$$\int_{z_0}^{z_0+d} dz \int_{A(z)} dS\, \psi_k^* \psi_l e^{i(l-k)(z_0+d/2)} = \int_\Omega u_k^* u_l dv + i(l-k) \int_{z_0}^{z_0+d} dz \times \int dS\, u_k^* u_l (z - z_0 - d/2) + \cdots . \tag{A20}$$

As l approaches k we have

$$\Delta_{kl}(z_0)=(l-k)\int_\Omega u_k^*\,\frac{\partial u_l}{\partial k}\,dV+i(l-k)D_k(z_0)=i(l-k)[D_k(z_0)-Z_k]\,. \tag{A21}$$

Equation (A19) is quoted in Eq. (2.20) of the text.

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Inelastic Low-Energy-Electron Diffraction for Surface-Plasmon Studies: Extended Measurements on Epitaxial Al(111)*†

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Inelastic low-energy-electron diffraction measurements on a clean Al(111) surface have been greatly extended and improved. This provides the experimental basis for a much more accurate determination of the high-momentum surface-plasmon dispersion and lifetime. The surface is prepared *in situ* in an ultrahigh-vacuum scanning diffractometer by epitaxial deposition on a Si(111) single-crystal wafer. Specular beam inelastic intensity profiles are measured in the $\langle 11\bar{2}\rangle$ and $\langle 1\bar{1}0\rangle$ directions at 15° and 25° incidence. The primary beam energy is chosen to correspond closely to both diffraction-before-loss and loss-before-diffraction processes involving different vestigial Bragg peaks at roughly 50 and 100 eV. Present emphasis is on loss profiles, which have recently been shown to be essentially free of complicating dynamical effects. The use of a 100-meV data grid and a more efficient computer differentiation technique permits determination of loss peak positions to 50 meV under favorable conditions. Internal consistency of the data is demonstrated here and in a more comprehensive analysis by Duke and Landman, published separately. The analysis leads to a substantially different evaluation of the surface-plasmon dispersion than previously obtained. There is evidence that the visibly smoother substrate used in the present work does not affect this result significantly. Experimental procedures and results are discussed in detail.

I. INTRODUCTION

The role of surfaces is critical in many solid-state electronic and optical applications. Device performance often depends on the physical, chemical, and geometrical features which determine the electron-density distribution at the surface. Measurable characteristics of this distribution are therefore of considerable practical interest. Surface plasmons[1] offer such a characteristic in the form of parameters defining the surface-plasmon dispersion and lifetime (SPDL). When the plasmon wave vector $p_\parallel$ is small compared to the dimensions of the Brillouin zone[2] the SPDL may be evaluated from optical measurements. The spatial resolution for electron-density variations normal to the surface is quite limited, however, being of the order of $2\pi/p_\parallel$. The SPD at larger values of $p_\parallel$ has been obtained from the distribution of 34-keV electrons scattered in a Mg foil,[3] but the surface was not well characterized. The surface-plasmon signal using this method is often too weak for precise results.

A more promising method, which is compatible with elastic low-energy-electron diffraction (ELEED),[4,5] Auger-electron spectroscopy,[6] and other surface analytic tools,[7] is based on inelastic low-energy-electron diffraction (ILEED).[5,8–15] Here electrons having ~10 – 100-eV energy are involved in an inversive two-step process: (a) An electron loses energy and a related momentum in exciting a surface plasmon; (b) the electron is elastically diffracted backward by the lattice. As a result, each vestigial Bragg peak in the *elastic* intensity vs energy curve (elastic energy profile) of an ELEED beam is accompanied by an *inelastic* intensity distribution which provides information on the surface plasmon. Sections of the inelastic distribution lying in the azimuth of the ELEED beam are called energy, angular, or loss profiles,[9,11] depending on whether the primary energy E, exit (polar) angle θ', or energy loss w, respectively, is chosen as the scanned variable; other variables, including the azimuth ψ and the incidence angle θ, remain fixed. The loss profile is now known to be the most useful data form for determination of the SPDL.[13,14]