Change of the density of electron states caused by the surface of a layered crystal structure

G. Wachutka*
Sektion Physik der Universität München, D-8000 München, Federal Republic of Germany
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Starting from the notion of the "$\mathbf{k}_\parallel$-resolved local density of states," the properties of the "$\mathbf{k}_\parallel$-resolved integrated density of states" are analyzed. While this quantity remains finite when integrated over films or crystal slabs of bounded thickness (leading to the well-known representation of the density of states via Green's functions), it will diverge when the range of integration is extended across a semi-infinite layered structure. It is shown that this divergency can be separated in a suggestive way by introducing the concept of the "change in the density of states," which moreover turns out to be of essential importance in the formulation of a criterion ensuring overall charge neutrality. Explicit expressions for each of the above quantities are derived, which are easy to be evaluated in terms of the dispersion of surface states, the bulk band structure (and the associated Bloch waves) of the substrate material, and the reflection coefficients of the bulk states at the surface.

I. INTRODUCTION

Theoretical understanding and interpretation of experimental data obtained from experiments which affect electron states only in the vicinity of the crystal surface (e.g., scanning tunneling microscopy[1,2]), or which allow discrimination between surface and bulk effects (e.g., angle-resolved photoemission[3,4] or angle-resolved inverse photoemission[5]) require concepts such as the "$\mathbf{k}_\parallel$-resolved local density of states" (KRLDOS), the "$\mathbf{k}_\parallel$-resolved integrated density of states" (KRIDOS), or the "$\mathbf{k}_\parallel$-resolved change in the density of states" (KRCDOS). The latter quantity characterizes the modification of the bulk density of states due to the existence of the crystal boundary; furthermore, it proves to be of central importance for the self-consistent calculation of the electronic structure of a semi-infinite crystal with a (possibly reconstructed and relaxed) real surface, because it enables the formulation of a simple sum rule ensuring overall charge neutrality. In Sec. II the relation between the above notions shall be clarified, and the derivation of a charge neutrality criterion will be given.

As far as consideration is restricted to films or crystal slabs of bounded thickness, the KRCDOS is related to the total density of states in a one-to-one way, and could therefore be calculated from the imaginary part of the Green's operator $G(E)$ of the system; hence, the information contained in the total density of states is only rewritten in a different way. In the case of a semi-infinite layered structure, however, the usual definition of the total density of states (via Green's function) becomes ambiguous, because it can be applied only if the Green's operator $G(E)$ is the resolvent $(H-E)^{-1}$ of a *self-adjoint* operator H, being the Hamiltonian of the system considered. Unfortunately, for a semi-infinite medium, there does not exist a properly defined Hamiltonian H, which could simultaneously describe both the surface adapted bulk states and the surface states, and thus the commonly used notion of a Green's function makes no sense here. The inherent problem in defining the density of states is that the attempt of retaining the surface contributions causes the bulk contributions to diverge; if, on the other hand, one tries to normalize the bulk contributions, a certain arbitrariness is unavoidable (so, for example, in averaging the local density of states along a sequence of periodically repeated bulk monolayers as in the recursive process proposed by Zhang *et al.*[6]), involving doubts whether it has properly been accounted for the surface effects. In this situation, separation of the divergent bulk terms by introducing the difference between the total density of states of a sequence of infinitely repeated ideal bulk monolayers and that of the physical system actually under consideration is suggested. Elaborating this idea leads to the concept of the KRCDOS, which indeed provides a mathematically rigorous way to overcome the above difficulties.

A rather formal approach to KRIDOS and KRCDOS has been suggested by García-Moliner and his coworkers,[7–10] which represent the density of states in terms of surface Green functions. The way they proceed is not very intuitive, and some formal operations seem to lack mathematical rigor: So, for instance, certain abstract scattering-theoretic arguments, which apply to the case of a perturbation localized in space (such as a vacancy, for instance[11]), are likely to fail when extended to a delocalized perturbation (such as a missing half-crystal). Hence, in the course of a concrete calculation (see, e.g., Louis and Vérges[12]), quantities may appear which prove to be not uniquely defined and, therefore, have to be fixed arbitrarily by means of *ad hoc* assumptions.

In this paper, analytical expressions for the KRLDOS, KRIDOS, and KRCDOS of a semi-infinite real crystal are derived, which are based upon a representation of the electron wave functions being characteristic of the "assembly of boundary-controlled monolayers" (ABCM) formalism;[13,14] however, the resulting formulas are easily evaluated in terms of invariant quantities such as the

dispersion of surface states, the bulk band structure and the associated Bloch waves of the substrate material, and the asymptotic form of the wave functions deep inside the bulk. In contrast to the surface Green's-functions approach, where all of the contributions to the KRCDOS are lumped together, the analysis developed here allows a clear distinction between the influence of the bulk substrate and that of the surface. When applied to the special case of simple model systems (jellium, nearly free electrons), the results of García-Moliner and Flores[9] are straightforwardly verified. The detailed considerations of Sec. III deal with the practical calculation of the KRIDOS and KRCDOS; in some respects, they generalize, correct, or give a precise meaning to the analysis which has been presented by Appelbaum and Blount.[15]

II. THE CONCEPTS OF KRLDOS, KRIDOS, AND KRCDOS IN THE CASE OF A SEMI-INFINITE REAL CRYSTAL

A semi-infinite crystal with real surface is mathematically represented by an infinite column $Z\times\mathbb{R}$ together with an electronic potential $w(\mathbf{r}_\parallel,z)$ defined on $Z\times\mathbb{R}$. Here, Z denotes a two-dimensional unit cell being characteristic of the planar translational symmetry of any plane parallel to the crystal surface; the potential $w(\mathbf{r}_\parallel,z)$ is supposed to be asymptotically constant for $z\to-\infty$ (vacuum region), and to exhibit the three-dimensional translational symmetry of the substrate crystal for $z\to\infty$ (bulk region). It is well known that the bound single-electron states ψ of such a half-crystal are completely determined by the following properties:

(i) ψ is a (weak) solution to the single-particle Schrödinger equation within the column $Z\times\mathbb{R}$.

(ii) ψ satisfies a planar Bloch condition characterized by a two-dimensional propagation vector $\mathbf{k}_\parallel$ belonging to $\overline{BZ}_1$, the (planar) first Brillouin zone in a plane parallel to the crystal surface.

(iii) For any $z_0\in\mathbb{R}$, ψ is square integrable within the half-column $Z\times(-\infty,z_0)$ including the vacuum side of the crystal.

(iv) Deep inside the bulk region (i.e., for $z\to\infty$), ψ tends to resemble a finite linear combination of 2σ propagating Bloch waves

$$\psi^{(B)}_{E,\mathbf{k}_\parallel}=\sum_{\mu=1}^{2\sigma}\alpha_\mu(E,\mathbf{k}_\parallel)\psi^{(\mu)}_{E,\mathbf{k}_\parallel}\ . \tag{1}$$

Here, E denotes the energy of the electron, and $\sigma=\sigma(E,\mathbf{k}_\parallel)$ counts how many times, at fixed $\mathbf{k}_\parallel$, the one-dimensional real band structure of the substrate crystal, $k_\perp\mapsto E_n(\mathbf{k}_\parallel,k_\perp)$, is intersected by the line $E=\text{const}$, with the group velocity $(\partial E_n/\partial k_\perp)(\mathbf{k}_\parallel,k_\perp)$ being positive[16] (see Bross[4] and Wachutka[13]). The functions $\psi^{(\mu)}_{E,\mathbf{k}_\parallel}$ are the Bloch waves associated with the points $\mathbf{k}=\mathbf{k}_\parallel+k_\perp^{(\mu)}\mathbf{e}_z$, $E=E_n(\mathbf{k}_\parallel,k_\perp^{(\mu)})$ in $(\mathbf{k},E)$ space.

Accordingly, the bound states of a semi-infinite crystal, $\psi_{E,\mathbf{k}_\parallel}$, are to be classified as follows: In the case $\sigma(E,\mathbf{k}_\parallel)=0$ (i.e., within an absolute band gap), $\psi_{E,\mathbf{k}_\parallel}$ tends to zero in the bulk region; this is characteristic of an (absolute) surface state. Of course, this situation is allowed to occur only at discrete values of energy, $E=E_j^{ss}(\mathbf{k}_\parallel)$; $j=1,2,3,\ldots$. Consequently, surface states $\psi^{ss}_{j,\mathbf{k}_\parallel}$ can be normalized as

$$\int_{Z\times\mathbb{R}}|\psi^{ss}_{j,\mathbf{k}_\parallel}|^2\,d^2r_\parallel\,dz=1\ , \tag{2}$$

hence yielding the relation of orthonormality

$$\int_{\mathbb{R}^3}\psi^*_{j',\mathbf{k}'_\parallel}\psi_{j,\mathbf{k}_\parallel}\,d^3r=\frac{(2\pi)^2}{A}\delta_{j'j}\delta(\mathbf{k}'_\parallel-\mathbf{k}_\parallel)\ , \tag{3}$$

where $\delta_{j'j}$ and $\delta(\mathbf{k}'_\parallel-\mathbf{k}_\parallel)$ are the Kronecker δ symbol and the Dirac δ function, respectively (A denotes the area of the unit cell Z). In consequence of (3), the $\mathbf{k}_\parallel$-resolved density of surface states (with respect to the column $Z\times\mathbb{R}$) is given by

$$N^{ss}(E,\mathbf{k}_\parallel)=\frac{A}{(2\pi)^2}\sum_j\delta(E-E_j^{ss}(\mathbf{k}_\parallel))\ . \tag{4}$$

It may also happen that, within a relative band gap [i.e., $\sigma(E,\mathbf{k}_\parallel)>0$] and at discrete energies, bound states exist with $\alpha_\mu(E,\mathbf{k}_\parallel)=0$ for all $\mu=1,2,\ldots,2\sigma$. These "relative" surface states also have to be included in the right-hand side of (4).

In the case of positive $\sigma(E,\mathbf{k}_\parallel)$, there exists, in addition, a σ-dimensional space of bound states which do not vanish asymptotically (i.e., $\psi^{(B)}_{E,\mathbf{k}_\parallel}\neq0$). These are known as "surface-adapted bulk states," if their probability density near the surface is not significantly different from that deep inside the bulk, and as "surface resonances," if, compared to the bulk region, the amplitude of the wave function is enhanced in the surface region. Within the framework of the ABCM formalism, it can be shown that both types of bound states are spanned by a set of σ basis functions $\{\psi_{j,E,\mathbf{k}_\parallel};\ j=1,2,\ldots,\sigma(E,\mathbf{k}_\parallel)\}$ which, according to (1), are represented sufficiently deep inside the bulk region as

$$\psi_{j,E,\mathbf{k}_\parallel}=\sum_{\mu=1}^{2\sigma}\alpha_{j\mu}(E,\mathbf{k}_\parallel)\psi^{(\mu)}_{E,\mathbf{k}_\parallel}\quad(j=1,2,\ldots,\sigma)\ , \tag{5}$$

where the $\sigma\times\sigma$ matrix

$$\underline{\alpha}_+(E,\mathbf{k}_\parallel):=[\alpha_{j\mu}(E,\mathbf{k}_\parallel);\quad 1\le j,\mu\le\sigma] \tag{6}$$

may be chosen arbitrarily (if only it is regular), provided the Bloch waves $\psi^{(\mu)}_{E,\mathbf{k}_\parallel}$ are linearly independent and enumerated in such a way that

$$\frac{\partial k_\perp^{(\mu)}}{\partial E}(\mathbf{k}_\parallel,E)\begin{cases}<0 & \text{for } \mu=1,2,\ldots,\sigma\ ,\\ >0 & \text{for } \mu=\sigma+1,\sigma+2,\ldots,2\sigma\ ,\end{cases} \tag{7}$$

holds. The row vectors of the $\sigma\times\sigma$ matrix

$$\underline{\alpha}_-(E,\mathbf{k}_\parallel):=[\alpha_{j\mu}(E,\mathbf{k}_\parallel);\quad 1\le j\le\sigma,\ \sigma+1\le\mu\le2\sigma] \tag{8}$$

depend linearly on the row vectors of $\underline{\alpha}_+(E,\mathbf{k}_\parallel)$ by means of a linear transformation $\underline{L}(E,\mathbf{k}_\parallel)$:

$$\underline{\alpha}_-=\underline{\alpha}_+\underline{L}^T\ . \tag{9}$$

In this context, the following theorem proves to be

useful (first stated by Bross,[4] generalized and rigorously proved by Wachutka[13]):

Let the Hermitean form I be defined as

$$I(\chi,\varphi) := i \int_Z (\chi^* \partial_z \varphi - \partial_z \chi^* \varphi) d^2 r_\parallel \ . \tag{10}$$

Suppose $\sigma(E,\mathbf{k}_\parallel) > 0$ and $(\partial E/\partial k_\perp)(\mathbf{k}_\parallel, k_\perp^{(\mu)}) \neq 0$, there exists a set of linearly independent Bloch waves $\{\psi_{E,\mathbf{k}_\parallel}^{(\mu)}; \mu = 1,2,\ldots,2\sigma\}$ such that

$$I(\psi^{(\mu)},\psi^{(\nu)}) = I_\mu \delta_{\mu\nu} = -N_\mu \left[d \frac{\partial k_\perp^{(\mu)}}{\partial E} \right]^{-1} \delta_{\mu\nu} \tag{11}$$

holds, where I_μ is the probability current of $\psi^{(\mu)}$ passing through the unit cell Z in negative z direction, and N_μ is the normalization factor

$$N_\mu(E,\mathbf{k}_\parallel) := \int_{Z\times(0,d)} | \psi_{E,\mathbf{k}_\parallel}^{(\mu)} |^2 d^3 r \tag{12}$$

(d is the interlayer distance in the bulk). The number of positive currents $I_\mu > 0$ equals that of negative currents $I_\mu < 0$ (and, therefore, is given by the integer number σ).

Hence, we shall suppose in the sequel that all Bloch waves considered satisfy Eqs. (11) and (7).

Now let a coordinate z_B be chosen such that the half-column $Z\times(z_B,\infty)$ only consists of periodically repeated bulk unit cells. Going to the limit

$$Z\times(z_B, z_{\max}) \to Z\times(z_B,\infty) \ ,$$

it can be shown that

$$\int_{\mathbf{R}^3} \psi_{j',E',\mathbf{k}_\parallel'}^* \psi_{j,E,\mathbf{k}_\parallel} d^3 r = \sum_{\mu,\nu=1}^{2\sigma} \alpha_{j'\mu}^*(E',\mathbf{k}_\parallel') \alpha_{j\nu}(E,\mathbf{k}_\parallel) \int_{z_B}^\infty \int_{\mathbf{R}^2} (\psi_{E',\mathbf{k}_\parallel'}^{(\mu)})^* \psi_{E,\mathbf{k}_\parallel}^{(\nu)} d^2 r_\parallel \, dz \ . \tag{13}$$

The orthogonality of the Bloch waves [see Bross,[4] Eq. (4.11)]

$$\int_{z_B}^\infty \int_{\mathbf{R}^2} (\psi_{E',\mathbf{k}_\parallel'}^{(\mu)})^* \psi_{E,\mathbf{k}_\parallel}^{(\nu)} d^2 r_\parallel \, dz = N_\mu \frac{(2\pi)^2}{A} \delta(\mathbf{k}_\parallel' - \mathbf{k}_\parallel) \frac{\pi}{d} \delta(k_\perp^{(\mu)}(E',\mathbf{k}_\parallel) - k_\perp^{(\nu)}(E,\mathbf{k}_\parallel)) \delta_{\mu\nu} \tag{14}$$

and the transformation rule for the δ measure

$$\delta(k_\perp^{(\mu)}(E',\mathbf{k}_\parallel) - k_\perp^{(\mu)}(E,\mathbf{k}_\parallel)) = \left| \frac{\partial k_\perp^{(\mu)}}{\partial E}(E,\mathbf{k}_\parallel) \right|^{-1} \times \delta(E'-E) \tag{15}$$

suggest that the most convenient normalization of the Bloch waves is

$$N_\mu(E,\mathbf{k}_\parallel) = \left| \frac{\partial k_\perp^{(\mu)}}{\partial E}(E,\mathbf{k}_\parallel) \right| \ , \tag{16}$$

implying that, apart from the sign, each of the Bloch waves carries the same amount of probability current. With the exception of the maxima and minima of the one-dimensional band structure $k_\perp \mapsto E_n(\mathbf{k}_\parallel, k_\perp)$, which have to be considered separately, the normalization to unit current can be achieved without any further restriction.

Furthermore, since the $\sigma\times\sigma$ matrix $\underline{1} + \underline{L}^\dagger \underline{L}$ is Hermitean and positive definite, it has σ orthonormal eigenvectors $x_j \in \mathbb{C}^\sigma$ with strictly positive eigenvalues λ_j. Choosing $\lambda_j^{-1/2} x_j$ as rows of the matrix $\underline{\alpha}_+$ yields a $\sigma\times 2\sigma$ matrix

$$\underline{\alpha} := (\underline{\alpha}_+, \underline{\alpha}_-) = (\underline{\alpha}_+, \underline{\alpha}_+ \underline{L}^T) \ , \tag{17}$$

the σ rows of which prove to be orthonormal vectors of $\mathbb{C}^{2\sigma}$. Thus, Eq. (13) is reduced to

$$\int_{\mathbf{R}^3} \psi_{j',E',\mathbf{k}_\parallel'}^* \psi_{j,E,\mathbf{k}_\parallel} d^3 r = \frac{(2\pi)^3}{2V} \delta(\mathbf{k}_\parallel' - \mathbf{k}_\parallel) \delta(E'-E) \delta_{j'j} \tag{18}$$

(with V being the volume of a three-dimensional unit cell in the bulk). This relation indicates how to orthonormalize the basis functions $\psi_{j,E,\mathbf{k}_\parallel}$; hence, we arrive at the following representation of the $\mathbf{k}_\parallel$-resolved local density of states (KRLDOS):[17]

$$N^b(E,\mathbf{k}_\parallel,\mathbf{r}) = \frac{2V}{(2\pi)^3} \sum_{j=1}^{\sigma} | \psi_{j,E,\mathbf{k}_\parallel}(\mathbf{r}) |^2 \ . \tag{19}$$

The explicit evaluation of this expression requires some further considerations: For $z \to -\infty$ the value of $I(\psi_{j,E,\mathbf{k}_\parallel}, \psi_{j',E,\mathbf{k}_\parallel})$ tends to zero; as a consequence of the conservation of probability current, this is also true deep inside the bulk. Hence, because of (11) and (16), it can be concluded that

$$\sum_{\mu=1}^{\sigma} \alpha_{j'\mu}^*(E,\mathbf{k}_\parallel) \alpha_{j\mu}(E,\mathbf{k}_\parallel) = \sum_{\mu=\sigma+1}^{2\sigma} \alpha_{j'\mu}^*(E,\mathbf{k}_\parallel) \alpha_{j\mu}(E,\mathbf{k}_\parallel) \ . \tag{20}$$

On the other hand, the row vectors of $\underline{\alpha}$ are orthonormal *per constructionem;* therefore both matrices, $\sqrt{2}\underline{\alpha}_+$ and $\sqrt{2}\underline{\alpha}_-$, must be unitary. Consequently, the $\sigma\times\sigma$ matrix

$$\underline{A}(E,\mathbf{k}_\parallel) := 2[\underline{\alpha}_+(E,\mathbf{k}_\parallel)]^\dagger \underline{\alpha}_-(E,\mathbf{k}_\parallel) \tag{21}$$

is also unitary; this matrix is useful to express the KRLDOS deep inside the crystal only by means of propagating Bloch waves:

$$N^b(E,\mathbf{k}_\parallel,\mathbf{r})=\frac{V}{(2\pi)^3}\left[\sum_{\mu=1}^{2\sigma}|\psi^{(\mu)}_{E,\mathbf{k}_\parallel}(\mathbf{r})|^2+2\,\mathrm{Re}\sum_{\mu,\nu=1}^{\sigma}[\psi^{(\mu)}_{E,\mathbf{k}_\parallel}(\mathbf{r})]^*A_{\mu\nu}\psi^{(\sigma+\nu)}_{E,\mathbf{k}_\parallel}(\mathbf{r})\right]. \tag{22}$$

Note that $\underline{A}$ remains invariant with respect to a unitary transformation of the basis functions $\{\psi_{j,E,\mathbf{k}_\parallel};\ j=1,2,\ldots,\sigma\}$. In particular, by using $\sqrt{2}\underline{\alpha}^{\dagger}_{+}(E,\mathbf{k}_\parallel)$ as transformation matrix, the following asymptotic form of the basis functions is achieved

$$\tilde{\psi}_{j,E,\mathbf{k}_\parallel}=\frac{1}{\sqrt{2}}\left[\psi^{(j)}_{E,\mathbf{k}_\parallel}+\sum_{\mu=1}^{\sigma}A_{j\mu}(E,\mathbf{k}_\parallel)\psi^{(\sigma+\mu)}_{E,\mathbf{k}_\parallel}\right]\quad(j=1,2,\ldots,\sigma)\,, \tag{23}$$

which allows an intuitive interpretation of the matrix elements $A_{j\mu}$ as reflection coefficients of the Bloch wave $\psi^{(j)}_{E,\mathbf{k}_\parallel}$ due to scattering at the surface region of the crystal.[18]

When integrating $N^b(E,\mathbf{k}_\parallel,\mathbf{r})$ along a sufficiently large column of periodically repeated unit cells of the bulk region, the contribution of the second term[19] of the right-hand side of (22) turns out to be zero; so the relation

$$\int_{z_0}^{z_0+ld}\int_Z N^b(E,\mathbf{k}_\parallel,\mathbf{r})\,d^2r_\parallel\,dz=l\frac{V}{(2\pi)^3}\sum_{\mu=1}^{2\sigma}\left|\frac{\partial k_\perp^{(\mu)}}{\partial E}(E,\mathbf{k}_\parallel)\right| \tag{24}$$

is obtained. Since the measure

$$d\Sigma_E=\sum_n\delta(E-E_n(\mathbf{k}))d^3k=\sum_n\left|\frac{\partial E_n}{\partial\mathbf{k}}\right|^{-1}d\sigma_n(\mathbf{k}) \tag{25}$$

[with $d\sigma_n$ denoting the Lebesgue surface measure on the manifold $\{\mathbf{k};\ E_n(\mathbf{k})=E\}$] concentrated on the equienergy surface in $\mathbf{k}$ space

$$\Sigma(E)=\{\mathbf{k}=(\mathbf{k}_\parallel,k_\perp^{(\mu)}(E,\mathbf{k}_\parallel))\mid\mathbf{k}_\parallel\in\overline{\mathrm{BZ}}_1;\ \mu=1,2,\ldots,2\sigma(E,\mathbf{k}_\parallel)\}=\bigcup_{n\in\mathbb{N}}\{\mathbf{k};\ E_n(\mathbf{k})=E\} \tag{26}$$

may also be expressed as

$$d\Sigma_E=\sum_{\mu=1}^{2\sigma}\left|\frac{\partial k_\perp^{(\mu)}}{\partial E}\right|d^2k_\parallel \tag{27}$$

by the use of the parametrization $\mathbf{k}_\parallel\mapsto k_\perp^{(\mu)}(E,\mathbf{k}_\parallel)$, it becomes obvious that the "total density of states," within the column $Z\times(z_0,z_0+ld)$, is just given by the number of involved bulk unit cells, l, multiplied by the total density of states (per unit cell) of an infinitely extended three-dimensional crystal

$$N^{\mathrm{vol}}(E)=\frac{V}{(2\pi)^3}\int d\Sigma_E\,, \tag{28}$$

which, of course, is expected by physical intuition:

$$\int_{\overline{\mathrm{BZ}}_1}\int_{z_0}^{z_0+ld}\int_Z N^b(E,\mathbf{k}_\parallel,\mathbf{r})\,d^2r_\parallel\,dz\,d^2k_\parallel=lN^{\mathrm{vol}}(E)\,. \tag{29}$$

Although there is no direct way to compare the density of surface states (being proportional to the area A of the two-dimensional unit cell Z) with that of surface-adapted bulk states or resonances (being proportional to $lAd=lV$, with $l\to\infty$), the following concept proves to be useful: Let the "$\mathbf{k}_\parallel$-resolved integrated density of states" (KRIDOS)[20] be defined as

$$N^b_{\mathrm{int}}(E,\mathbf{k}_\parallel,z_0,l):=\int_{-\infty}^{z_0+ld}\int_Z N^b(E,\mathbf{k}_\parallel,\mathbf{r})\,d^2r_\parallel\,dz\,. \tag{30}$$

By separating the asymptotic part being proportional to the bulk density of states

$$\Delta N^b_{\mathrm{int}}(E,\mathbf{k}_\parallel,z_0,l):=N^b_{\mathrm{int}}(E,\mathbf{k}_\parallel,z_0,l)-l\frac{V}{(2\pi)^3}\sum_{\mu=1}^{2\sigma}\left|\frac{\partial k_\perp^{(\mu)}}{\partial E}(E,\mathbf{k}_\parallel)\right|, \tag{31}$$

it makes sense to define the limit

$$\Delta N(E,\mathbf{k}_\parallel,z_0):=\lim_{l\to\infty}\Delta N^b_{\mathrm{int}}(E,\mathbf{k}_\parallel,z_0,l)+N^{\mathrm{ss}}(E,\mathbf{k}_\parallel) \tag{32}$$

as "$\mathbf{k}_\parallel$-resolved change in the density of states" (KRCDOS). Here, the plane of reference, $z=z_0$, may be situated anywhere, if only within the bulk region; however, it proves to be convenient to put it in the vicinity of the surface region. Then, the KRCDOS describes the

modification of the density of states of an infinitely extended crystal due to cutting it along the plane $z=z_0$ and replacing the "left" half by the vacuum and surface regions. Moreover, the plane $z=z_0$ serves as a reference surface in order to adjust the arbitrary phase factors of the individual Bloch waves involved in the practical calculation of the KRCDOS (see Sec. III).

The arbitrariness in the choice of z_0 manifests in the fact that a change of z_0 by an amount of Δz_0 corresponds to an additional term on the right-hand side of (32) being just $\Delta z_0/d$ multiplied by the bulk density of states. This property is useful for the formulation of a "charge neutrality condition" expressing that the electronic charge contained in the column $Z\times(-\infty,z_0+ld)$ (including charge relaxation resulting from the surface states and the adaption of the bulk states to the boundary conditions at the crystal surface) and the fixed charge of the ion cores (including excess or deficit charges near the surface) must compensate each other in the limit $l\to\infty$: The charge of the surface states amounts to

$$Q_{\rm el}^{\rm ss}=2e\int_{-\infty}^{E_F}\int_{\overline{\rm BZ}_1}N^{\rm ss}(E,\mathbf{k}_\parallel)d^2k_\parallel dE \tag{33}$$

(E_F denotes the Fermi level) and, according to (28)–(31), the charge of the surface-adapted bulk states is given by

$$Q_{\rm el}^{b}=2e\left[\int_{-\infty}^{E_F}\int_{\overline{\rm BZ}_1}\Delta N_{\rm int}^{b}(E,\mathbf{k}_\parallel,z_0,l)\,d^2k_\parallel\,dE+l\int_{-\infty}^{E_F}N^{\rm vol}(E)dE\right]. \tag{34}$$

It is reasonable to suppose that, for $z\geq z_0$, the charge density of the ion cores, when integrated across Z, may be partitioned into three terms

$$\rho_{\rm ion}(z)=\bar{\rho}_{\rm ion}+\rho_{\rm ion}^{\rm osc}(z)+\rho_{\rm ion}^{ev}(z) \tag{35}$$

in such a way that $\bar{\rho}_{\rm ion}$ is the mean value of $\rho_{\rm ion}(z)$, taken along the interval $(\hat{z},\hat{z}+d)$ in the limit $\hat{z}\to\infty$, and that the contribution of $\rho_{\rm ion}^{\rm osc}$ is vanishing, when integrated along any interval of length d, and that, for any $\hat{z}$, the integral value of $\rho_{\rm ion}^{ev}(z)$ over the interval $(\hat{z},\infty)$ remains finite. Because of the charge neutrality of the three-dimensional perfect crystal, it can be concluded that

$$\bar{\rho}_{\rm ion}=\frac{2e}{d}\int_{-\infty}^{E_F}N^{\rm vol}(E)dE\ . \tag{36}$$

Thus, by requiring the difference between the ionic charge contained in $Z\times(-\infty,z_0+ld)$,

$$Q_{\rm ion}=\int_{-\infty}^{z_0}\rho_{\rm ion}(z)dz+l\bar{\rho}_{\rm ion}d+\int_{z_0}^{z_0+ld}\rho_{\rm ion}^{ev}(z)dz\ , \tag{37}$$

and the respective electronic charge $Q_{\rm el}^{b}+Q_{\rm el}^{\rm ss}$ tending to zero in the limit $l\to\infty$, the condition

$$2e\int_{-\infty}^{E_F}\int_{\overline{\rm BZ}_1}\Delta N(E,\mathbf{k}_\parallel,z_0)d^2k_\parallel\,dE=\int_{-\infty}^{z_0}\rho_{\rm ion}(z)dz+\int_{z_0}^{\infty}\rho_{\rm ion}^{ev}(z)dz \tag{38}$$

is implied. However, apart from simple models (e.g., the jellium model with infinite potential barrier at the vacuum side[20]), one cannot expect this (strong) criterion to be exactly satisfied for any choice of the plane $z=z_0$. Therefore it seems favorable to assure for "charge neutrality in the (microscopic) mean," which means that Eq. (38) holds only after having been averaged with respect to z_0 (along one or some layers of the bulk region).

In the case of a self-consistent calculation of the electronic and ionic charge density, the condition of charge neutrality must be satisfied by itself in the end; but in the course of a non-self-consistent calculation, condition (38) may serve as a useful criterion for adjusting the ionic part to the electronic part of the total charge density.

III. THE PRACTICAL CALCULATION OF KRIDOS AND KRCDOS

Suppose the matrix of reflection coefficients, $\underline{A}(E,\mathbf{k}_\parallel)$, has been made available by means of an appropriate method,[21] the explicit calculation of the integrated density of states may be performed in the following way: Starting from the relation

$$\int_{-\infty}^{z_l}\int_{Z}|\psi_{j,E,\mathbf{k}_\parallel}|^2d^2r_\parallel\,dz=\int_{Z\times\{z_l\}}(\partial_E\psi_{j,E,\mathbf{k}_\parallel}^{*}\partial_z\psi_{j,E,\mathbf{k}_\parallel}-\partial_E\partial_z\psi_{j,E,\mathbf{k}_\parallel}^{*}\psi_{j,E,\mathbf{k}_\parallel})d^2r_\parallel \tag{39}$$

(with $z_l=z_0+ld$; $l\in\mathbb{N}$), which is based upon Schrödinger's equation and the continuity of probability current, it can straightforwardly be shown that

$$\frac{(2\pi)^3}{V}N_{\rm int}^{b}(E,\mathbf{k}_\parallel,z_0,l)=\sum_{\mu=1}^{2\sigma}D_{\mu\mu}(E,\mathbf{k}_\parallel,z_l)+2\,{\rm Re}\left[\sum_{\mu,\nu=1}^{\sigma}A_{\mu\nu}(E,\mathbf{k}_\parallel)D_{\mu,\sigma+\nu}(E,\mathbf{k}_\parallel,z_l)\right]-\frac{i}{d}{\rm tr}[\underline{A}(E,\mathbf{k}_\parallel)^{\dagger}\partial_E\underline{A}(E,\mathbf{k}_\parallel)]\ , \tag{40}$$

where

$$D_{\mu\nu}(E,\mathbf{k}_\parallel,z):=\int_{Z\times\{z\}}[\partial_E(\psi_{E,\mathbf{k}_\parallel}^{(\mu)})^{*}\partial_z\psi_{E,\mathbf{k}_\parallel}^{(\nu)}-\partial_E\partial_z(\psi_{E,\mathbf{k}_\parallel}^{(\mu)})^{*}\psi_{E,\mathbf{k}_\parallel}^{(\nu)}]d^2r_\parallel\ . \tag{41}$$

Because the Bloch waves $\psi_{E,\mathbf{k}_\parallel}^{(\mu)}$ are subject to Bloch's boundary condition (characterized by the wave vector $\mathbf{k}=\mathbf{k}_\parallel+k_\perp^{(\mu)}\mathbf{e}_z$), it is possible to refer $D_{\mu\nu}(E,\mathbf{k}_\parallel,z_l)$ to $D_{\mu\nu}(E,\mathbf{k}_\parallel,z_0)$ by

$$D_{\mu\nu}(E,\mathbf{k}_\parallel,z_l)=D_{\mu\nu}(E,\mathbf{k}_\parallel,z_0)e^{i(k_\perp^{(\nu)}-k_\perp^{(\mu)})ld}+\delta_{\mu\nu}l\left|\frac{\partial k_\perp^{(\mu)}}{\partial E}\right| . \tag{42}$$

This formula indicates explicitly that, indeed, the bulk density of states (24) can be separated from the KRIDOS in the way postulated above. Furthermore, as a consequence of the unitariness of $\underline{A}(E,\mathbf{k}_\parallel)$,

$$\mathrm{tr}[\underline{A}(E,\mathbf{k}_\parallel)^\dagger\partial_E\underline{A}(E,\mathbf{k}_\parallel)]=i\frac{\partial}{\partial E}\arg\{\det[\underline{A}(E,\mathbf{k}_\parallel)]\} \tag{43}$$

holds; hence, the KRIDOS may be written in the form

$$\Delta N_{\mathrm{int}}^{b}(E,\mathbf{k}_\parallel,z_0,l)=\Delta N_{\mathrm{int}}^{(1)}(E,\mathbf{k}_\parallel,z_0)+\Delta N_{\mathrm{int}}^{(2)}(E,\mathbf{k}_\parallel,z_0,l) \tag{44}$$

with

$$\Delta N_{\mathrm{int}}^{(1)}(E,\mathbf{k}_\parallel,z_0):=\frac{A}{(2\pi)^2}\left[\frac{1}{2\pi}\frac{\partial}{\partial E}\arg\{\det[\underline{A}(E,\mathbf{k}_\parallel)]\}+\frac{d}{2\pi}\sum_{\mu=1}^{2\sigma}D_{\mu\mu}(E,\mathbf{k}_\parallel,z_0)\right] \tag{45}$$

and

$$\Delta N_{\mathrm{int}}^{(2)}(E,\mathbf{k}_\parallel,z_0,l):=\frac{V}{(2\pi)^3}2\,\mathrm{Re}\left[\sum_{\mu,\nu=1}^{\sigma}A_{\mu\nu}(E,\mathbf{k}_\parallel)D_{\mu,\sigma+\nu}(E,\mathbf{k}_\parallel,z_l)\right] . \tag{46}$$

Note that $\Delta N_{\mathrm{int}}^{(1)}$ does not depend on the length of integration z_l. An interpretation of this quantity is easily obtained in the case that only two propagating Bloch waves exist in the bulk region: Then, by necessity, the directions of probability current are opposite [i.e., $\sigma(E,\mathbf{k}_\parallel)=1$], and the unitary matrix $\underline{A}(E,\mathbf{k}_\parallel)$ degenerates into a phase factor $\exp[i2\eta(E,\mathbf{k}_\parallel)]$, with $\eta(E,\mathbf{k}_\parallel)$ being the phase shift between the two Bloch waves involved [see Eq. (23)]. Therefore we arrive at the well-known result that the "continuous part" of the KRCDOS is given by the energy derivative of the phase shift, provided the gauge of the phase factors of the individual Bloch waves has been chosen such that $D_{11}+D_{22}$ vanishes at $z=z_0$.[15,20] For an arbitrary gauge, the second term of the right-hand side of (45) just compensates the resulting change in the energy dependence of the phase shift; thus, $\Delta N_{\mathrm{int}}^{(1)}$ proves to be invariant under gauge transformations.

The generalization of this is to the case $\sigma(E,\mathbf{k}_\parallel)>1$ is expressed by Eq. (45): Transforming the Bloch waves according to

$$\hat{\psi}_{E,\mathbf{k}_\parallel}^{(\mu)}=e^{i\beta^{(\mu)}(E,\mathbf{k}_\parallel)}\psi_{E,\mathbf{k}_\parallel}^{(\mu)} \tag{47}$$

[where the real phases $\beta^{(\mu)}(E,\mathbf{k}_\parallel)$ are supposed to be smooth functions of E] induces the transformation rule for $\underline{A}(E,\mathbf{k}_\parallel)$

$$\hat{\underline{A}}(E,\mathbf{k}_\parallel)=\underline{U}_+(E,\mathbf{k}_\parallel)\underline{A}(E,\mathbf{k}_\parallel)[\underline{U}_-(E,\mathbf{k}_\parallel)]^\dagger \tag{48}$$

with

$$\begin{aligned}\underline{U}_+ &:= \mathrm{diag}(e^{i\beta^{(1)}},e^{i\beta^{(2)}}\ldots,e^{i\beta^{(\sigma)}}) ,\\ \underline{U}_- &:= \mathrm{diag}(e^{i\beta^{(\sigma+1)}},e^{i\beta^{(\sigma+2)}}\ldots,e^{i\beta^{(2\sigma)}}) .\end{aligned} \tag{49}$$

Consequently, we have

$$\frac{\partial}{\partial E}\arg[\det(\hat{\underline{A}})]=\frac{\partial}{\partial E}\arg[\det(\underline{A})]+\sum_{\nu=1}^{\sigma}\left[\frac{\partial\beta^{(\nu)}}{\partial E}-\frac{\partial\beta^{(\sigma+\nu)}}{\partial E}\right] . \tag{50}$$

On the other hand, normalizing the Bloch waves to unit current [see Eq. (16)] ensures the relation

$$\hat{D}_{\mu\mu}(E,\mathbf{k}_\parallel,z)=D_{\mu\mu}(E,\mathbf{k}_\parallel,z)-\frac{1}{d}\mathrm{sgn}(I_\mu)\frac{\partial\beta^{(\mu)}}{\partial E}(E,\mathbf{k}_\parallel) \tag{51}$$

and, therefore, $\Delta N_{\mathrm{int}}^{(1)}$ does not change under gauge transformations also in the general case $\sigma>1$.

Differentiating Eq. (11) with respect to energy shows that, because of the normalization (16), $D_{\mu\mu}(E,\mathbf{k}_\parallel,z)$ is real valued. Hence, it is possible to choose the real phases $\beta^{(\mu)}(E,\mathbf{k}_\parallel)$ in such a way that

$$\frac{\partial\beta^{(\mu)}}{\partial E}(E,\mathbf{k}_\parallel)=d\ \mathrm{sgn}(I_\mu)D_{\mu\mu}(E,\mathbf{k}_\parallel,z_0) \tag{52}$$

is satisfied, with the result that $\hat{D}_{\mu\mu}(E,\mathbf{k}_\parallel,z_0)$ vanishes, and that $\Delta N_{\mathrm{int}}^{(1)}$ can be determined only by the energy derivative of $\arg\{\det[\underline{A}(E,\mathbf{k}_\parallel)]\}$.

By arguments similar to those above, it can also be concluded that the products $A_{\mu\nu}D_{\mu,\sigma+\nu}$ do not depend on the choice of the phases $\beta^{(\mu)}(E,\mathbf{k}_\parallel)$, so $\Delta N_{\mathrm{int}}^{(2)}$ proves to be gauge invariant also. With respect to the variable z_l, this quantity shows a rapidly oscillating behavior [see Eq. (42)]. Since, for $\mu\neq\nu$, the equality

$$D_{\mu\nu}(E,\mathbf{k}_\parallel,z_0)=(e^{i(k_\perp^{(\nu)}-k_\perp^{(\mu)})d}-1)^{-1}\times\int_{z_0}^{z_0+d}\int_Z(\psi_{E,\mathbf{k}_\parallel}^{(\mu)})^*\psi_{E,\mathbf{k}_\parallel}^{(\nu)}\,d^2r_\parallel\,dz \tag{53}$$

holds, it is obvious that the amplitudes of the oscillations are more enhanced the closer E approaches one of those

energy values $E_\nu^\mu(\mathbf{k}_\parallel)$ where two branches, $k_\perp^{(\mu)}(E,\mathbf{k}_\parallel)$ and $k_\perp^{(\sigma+\nu)}(E,\mathbf{k}_\parallel)$, of the (one-dimensional) band structure $k_\perp \mapsto [E_n(\mathbf{k}_\parallel,k_\perp)]_{n\in\mathbb{N}}$ join each other:

$$k_\perp^{(\sigma+\nu)}(E_\nu^\mu(\mathbf{k}_\parallel),\mathbf{k}_\parallel)=k_\perp^{(\mu)}(E_\nu^\mu(\mathbf{k}_\parallel),\mathbf{k}_\parallel) := k_\nu^\mu(\mathbf{k}_\parallel) \mod(2\pi/d) . \tag{54}$$

Note that intersections of energy bands with different symmetry are not to be included here, because in this case the overlap integral in Eq. (53) is known to be zero; therefore, in the regular case,[22] the points $(k_\nu^\mu(\mathbf{k}_\parallel),E_\nu^\mu(\mathbf{k}_\parallel))$ are to be regarded as the local maxima and minima of the (one-dimensional) band structure $k_\perp \mapsto [E_n(\mathbf{k}_\parallel,k_\perp)]_{n\in\mathbb{N}}$ (see Fig. 1).

The integration of $\Delta N_{\rm int}^{(2)}$ over $(E,\mathbf{k}_\parallel)$ space required for determining the electronic charge $Q_{\rm el}^b(z_l)$ [see Eq. (34)] yields two terms, the one which oscillates with z_l and is proportional to z_l^{-1} (Friedel oscillations) and, hereby, tends to zero in the limit $z_l\to\infty$, while the other arises from those regions in $(E,\mathbf{k}_\parallel)$ space where $E\approx E_\nu^\mu(\mathbf{k}_\parallel)$, and approaches a finite nonzero value for $z_l\to\infty$. In what follows, the latter shall be discussed in detail.

For the investigation of the asymptotic behavior of the KRIDOS in the vicinity of one of the critical energies $E_\nu^\mu(\mathbf{k}_\parallel)$, it proves convenient to consider the difference function

$$\kappa_\nu^\mu(E,\mathbf{k}_\parallel) := k_\perp^{(\sigma+\nu)}(E,\mathbf{k}_\parallel)-k_\perp^{(\mu)}(E,\mathbf{k}_\parallel) \tag{55}$$

[being defined, with respect to E, within a one-sided neighborhood of $E_\nu^\mu(\mathbf{k}_\parallel)$], and to factorize the quantities $D_{\mu,\sigma+\nu}$ according to

$$D_{\mu,\sigma+\nu}(E,\mathbf{k}_\parallel,z)=\frac{\exp[i\kappa_\nu^\mu(E,\mathbf{k}_\parallel)z]}{2i\sin[\kappa_\nu^\mu(E,\mathbf{k}_\parallel)d/2]}\Pi_{\mu\nu}(E,\mathbf{k}_\parallel,z) , \tag{56}$$

where the function

$$\Pi_{\mu\nu}(E,\mathbf{k}_\parallel,z):=\int_z^{z+d}\int_Z(\psi_{E,\mathbf{k}_\parallel}^{(\mu)})^*\psi_{E,\mathbf{k}_\parallel}^{(\sigma+\nu)}d^2r_\parallel\,d\xi e^{-i\kappa_\nu^\mu(E,\mathbf{k}_\parallel)(z+d/2)} \tag{57}$$

is periodic with respect to z, with the period being the interlayer distance d. Provided both of the branches, $k_\perp^{(\mu)}(E,\mathbf{k}_\parallel)$ and $k_\perp^{(\sigma+\nu)}(E,\mathbf{k}_\parallel)$, are smoothly connected at $E=E_\nu^\mu(\mathbf{k}_\parallel)$ [forming a locally parabolic (one-dimensional) energy band], κ_ν^μ may be represented within a one-sided neighborhood of $E_\nu^\mu(\mathbf{k}_\parallel)$ as

$$\kappa_\nu^\mu(E,\mathbf{k}_\parallel)=2\frac{\partial\kappa_\nu^\mu}{\partial E}(E,\mathbf{k}_\parallel)[E-E_\nu^\mu(\mathbf{k}_\parallel)] \times[1+O((E-E_\nu^\mu)^{1/2})] \tag{58}$$

from which it is easy to conclude[23] that

$$\lim_{E\to E_{\nu(-)}^\mu+0}\left|\frac{\partial\kappa_\nu^\mu}{\partial E}\right|^{-1}\left|\frac{\partial k_\perp^{(\mu)}}{\partial E}\right|^{1/2}\left|\frac{\partial k_\perp^{(\sigma+\nu)}}{\partial E}\right|^{1/2}=\frac{1}{2} \tag{59}$$

("+" in the case of an energy minimum, and "−" in the case of a maximum). Because of the normalization to unit current (16), the limit

$$C_{\mu\nu}(\mathbf{k}_\parallel,z):=\lim_{E\to E_{\nu(-)}^\mu+0}2\left|\frac{\partial\kappa_\nu^\mu}{\partial E}\right|^{-1}\Pi_{\mu\nu}(E,\mathbf{k}_\parallel,z) \tag{60}$$

exists; thus, $\Pi_{\mu\nu}$ can be written in the form

$$\Pi_{\mu\nu}(E,\mathbf{k}_\parallel,z)=[\tfrac{1}{2}C_{\mu\nu}(\mathbf{k}_\parallel,z)+\Delta_{\mu\nu}(E,\mathbf{k}_\parallel,z)]\left|\frac{\partial\kappa_\nu^\mu}{\partial E}\right| \tag{61}$$

with $\Delta_{\mu\nu}$ tending to zero as E is approaching $E_{\nu(-)}^\mu+0$.

As it is shown in the Appendix, the quantities $C_{\mu\nu}$ do not depend on the variable z, so we can summarize the results obtained hitherto as

$$\mathrm{Re}[A_{\mu\nu}(E,\mathbf{k}_\parallel)D_{\mu,\sigma+\nu}(E,\mathbf{k}_\parallel,z_l)]=\frac{\sin[\kappa_\nu^\mu(z_0+ld)]}{2\sin(\kappa_\nu^\mu d/2)}\mathrm{Re}\{A_{\mu\nu}[\tfrac{1}{2}C_{\mu\nu}+\Delta_{\mu\nu}(z_0)]\}\left|\frac{\partial\kappa_\nu^\mu}{\partial E}\right| +\frac{\cos[\kappa_\nu^\mu(z_0+ld)]}{2\sin(\kappa_\nu^\mu d/2)}\mathrm{Im}\{A_{\mu\nu}[\tfrac{1}{2}C_{\mu\nu}+\Delta_{\mu\nu}(z_0)]\}\left|\frac{\partial\kappa_\nu^\mu}{\partial E}\right| . \tag{62}$$

Now, the limit $l\to\infty$ can be performed without difficulty. The limit of the first term behaves, with respect to integration over the energy E, like a δ function:

$$\frac{\sin[\kappa_\nu^\mu(E,\mathbf{k}_\parallel)(z_0+ld)]}{2\sin[\kappa_\nu^\mu(E,\mathbf{k}_\parallel)d/2]}\left|\frac{\partial\kappa_\nu^\mu}{\partial E}\right|\to\frac{\pi}{2d}\delta(E-E_\nu^\mu(\mathbf{k}_\parallel)) \text{ as } l\to\infty . \tag{63}$$

The second term is approximated by the expression

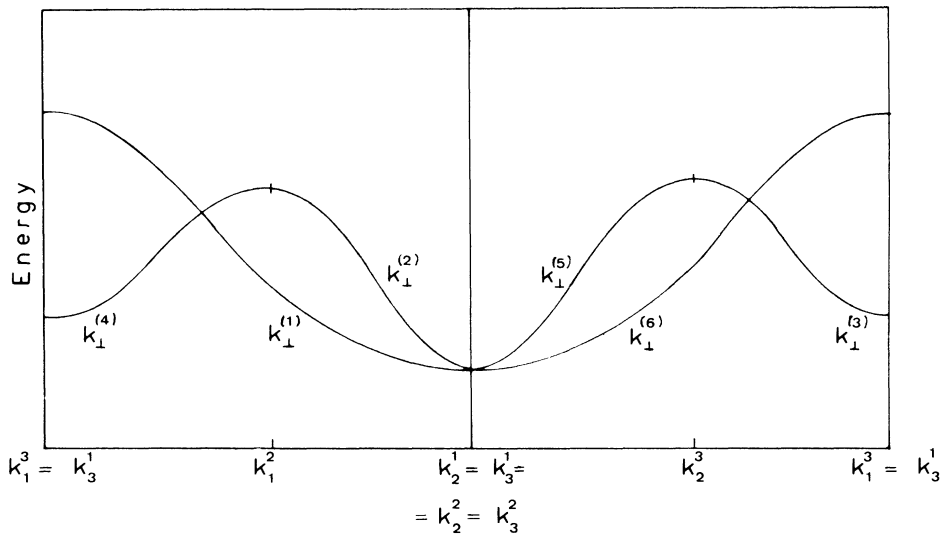

FIG. 1. Schematic one-dimensional band structure showing the labeling of the maxima and minima where the individual branches $k_\perp^{(\mu)}(E,\mathbf{k}_\parallel)$ are smoothly connected.

$$\{2d[E-E_\nu^\mu(\mathbf{k}_\parallel)]\}^{-1}\,\mathrm{Im}[\tfrac{1}{2}A_{\mu\nu}(E,\mathbf{k}_\parallel)C_{\mu\nu}(\mathbf{k}_\parallel)] \tag{64}$$

if only E is sufficiently close to $E_\nu^\mu(\mathbf{k}_\parallel)$ (within a one-sided neighborhood). Allowing for an interpretation as density in $\mathbf{k}$ space necessitates this expression being integrable with respect to energy; hence, for $E\to E_\nu^\mu$, the numerator $\mathrm{Im}(A_{\mu\nu}C_{\mu\nu})$ must tend to zero sufficiently fast. Using the model of free electrons as guidelines, the assumption that this quantity behaves like $|E-E_\nu^\mu|^\lambda$, with the exponent λ being positive, seems reasonable. Then it can be shown that in the limit $l\to\infty$ the contribution of the second term in Eq. (62) to the $\mathbf{k}$-space integral must vanish.

So, finally, the following explicit formula for the KRCDOS results:

$$\Delta N(E,\mathbf{k}_\parallel,z_0)=\frac{A}{(2\pi)^2}\left[\sum_j\delta(E-E_j^{\mathrm{ss}}(\mathbf{k}_\parallel))+\frac{1}{2\pi}\frac{\partial}{\partial E}\arg\{\det[\underline{A}(E,\mathbf{k}_\parallel)]\}+\frac{d}{2\pi}\sum_{\mu=1}^{2\sigma}D_{\mu\mu}(E,\mathbf{k}_\parallel,z_0)\right.$$
$$\left.+\tfrac{1}{4}\sum_{\mu,\nu=1}^{\sigma}\mathrm{Re}[A_{\mu\nu}(E_\nu^\mu(\mathbf{k}_\parallel),\mathbf{k}_\parallel)C_{\mu\nu}(\mathbf{k}_\parallel)]\delta(E-E_\nu^\mu(\mathbf{k}_\parallel))\right] \tag{65}$$

[here, $C_{\mu\nu}(\mathbf{k}_\parallel)$ must be set to zero if $k_\perp^{(\mu)}(E,\mathbf{k}_\parallel)$ and $k_\perp^{(\sigma+\nu)}(E,\mathbf{k}_\parallel)$ do not intersect or exhibit different symmetry; $A_{\mu\nu}(E_\nu^\mu(\mathbf{k}_\parallel),\mathbf{k}_\parallel)$ has to be regarded as limit $E\to E_\nu^\mu(\mathbf{k}_\parallel)+0$ from the right or from the left, respectively].

The last term in formula (65) originating from $\Delta N_{\mathrm{int}}^{(2)}$ may be explained as follows. It is at energies $E=E_\nu^\mu(\mathbf{k}_\parallel)$ where the dimension of the space of propagating Bloch waves, $2\sigma(E,\mathbf{k}_\parallel)$, and, hereby, the number of linearly independent surface-adapted bulk states, $\sigma(E,\mathbf{k}_\parallel)$, is (discontinuously) changing by an integer amount: In the case of a local minimum of the band structure $k_\perp\mapsto E_n(\mathbf{k}_\parallel,k_\perp)$, for instance, the number $\sigma(E,\mathbf{k}_\parallel)$ jumps from σ_0 to σ_0+1,[24] while increasing the energy from $E<E_\nu^\mu(\mathbf{k}_\parallel)$ to $E>E_\nu^\mu(\mathbf{k}_\parallel)$. The value of $\sigma(E,\mathbf{k}_\parallel)$ at $E_\nu^\mu(E,\mathbf{k}_\parallel)$ is determined by the number of (linearly independent) linear combinations of Bloch waves matching the boundary conditions at the surface; this is a delicate problem[25] whose solution is implicitly given by the expression developed above.

In conclusion, it is illustrative to rewrite the charge neutrality condition (38) by integrating the expression (65) over the set of $\mathbf{k}$ vectors enclosed by the Fermi surface; this yields the following sum rule for the reflection coefficients $A_{\mu\nu}$:

$$N_F^{\mathrm{ss}}+\frac{A}{(2\pi)^2}\left[\int_{\overline{\mathrm{BZ}}_1}\frac{1}{\pi}\eta_F(\mathbf{k}_\parallel)+\tfrac{1}{4}g_F(\mathbf{k}_\parallel)d^2k_\parallel+\frac{1}{2\pi}\Delta\beta_F(z_0)\right]=\frac{1}{2e}\left[\int_{-\infty}^{z_0}\rho_{\mathrm{ion}}(z)dz+\int_{z_0}^{\infty}\rho_{\mathrm{ion}}^{ev}(z)dz\right], \tag{66}$$

where the individual terms have been defined as

$$N_F^{\mathrm{ss}}:=\int_{-\infty}^{E_F}\int_{\overline{\mathrm{BZ}}_1}N^{\mathrm{ss}}(E,\mathbf{k}_\parallel)d^2k_\parallel dE \tag{67}$$

(equal to the number of surface states below the Fermi level, E_F),

$$\eta_F(\mathbf{k}_\parallel):=\tfrac{1}{2}\arg\{\det[\underline{A}(E_F,\mathbf{k}_\parallel)]\} \tag{68}$$

(equal to the "collective scattering phase shift" at E_F)

$$g_F(\mathbf{k}_\parallel):=\sum_{E_\nu^\mu(\mathbf{k}_\parallel)\le E_F}\mathrm{Re}[A_{\mu\nu}(E_\nu^\mu(\mathbf{k}_\parallel),\mathbf{k}_\parallel)C_{\mu\nu}(\mathbf{k}_\parallel)] \tag{69}$$

(equal to the weight by which the maxima and minima of the one-dimensional band structure $k_\perp \mapsto E_n(\mathbf{k}_\parallel, k_\perp)$ contribute to the number of surface-adapted bulk states), and

$$\Delta\beta_F(z_0) := d \int_{-\infty}^{E_F} \int_{\overline{BZ}_1} \sum_{\mu=1}^{2\sigma} D_{\mu\mu}(E, \mathbf{k}_\parallel, z_0) d^2k_\parallel dE \tag{70}$$

("total phase shift correction" for all Bloch waves below E_F). Thus, the sum rule presented by Appelbaum and Blount[15] is confirmed and completed by giving a precise meaning to each of the terms appearing in their formula, especially, if more than two Bloch waves are involved in the calculation.

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APPENDIX

It is to be shown that the quantities $C_{\mu\nu}$ [see definition (60)] do not depend on the variable z. The proof of this is based on the identity

$$\Pi_{\mu\nu}(E, \mathbf{k}_\parallel, z) - \Pi_{\mu\nu}(E, \mathbf{k}_\parallel, \hat{z}) = \int_0^d e^{i\kappa_\nu^\mu(\zeta - d/2)} [U_{\mu\nu}(z+\zeta) - U_{\mu\nu}(\hat{z}+\zeta)] d\zeta \tag{A1}$$

with $U_{\mu\nu}(z)$ being defined as an overlap integral

$$U_{\mu\nu}(z) := \int_z u^{(\mu)}(\mathbf{r}_\parallel, z)^* u^{(\sigma+\nu)}(\mathbf{r}_\parallel, z) d^2r_\parallel , \tag{A2}$$

where the function $u^{(\mu)}(\mathbf{r}) := \exp(-i\mathbf{k}^{(\mu)}\mathbf{r})\psi^{(\mu)}(\mathbf{r})$ denotes that part of the propagating Bloch wave $\psi^{(\mu)}$ which exhibits the three-dimensional translational symmetry of the bulk crystal. By definition, $U_{\mu\nu}$ is a periodic function of z (with the period being the interlayer distance d) and, therefore, the mean value of the shifted function $\zeta \mapsto U_{\mu\nu}(z+\zeta)$ along the interval $[0,d]$ equals that of the function $\zeta \mapsto U_{\mu\nu}(\hat{z}+\zeta)$. By expanding the exponential under the integral sign in Eq. (A1), it becomes evident that, due to normalization to unit current [Eq. (16)], the right-hand side behaves like

$$\Pi_{\mu\nu}(E, \mathbf{k}_\parallel, z) - \Pi_{\mu\nu}(E, \mathbf{k}_\parallel, \hat{z}) = i\kappa_\nu^\mu(E) \left| \frac{\partial k_\perp^{(\mu)}}{\partial E} \right|^{1/2} \left| \frac{\partial k_\perp^{(\sigma+\nu)}}{\partial E} \right|^{1/2} F(z, \hat{z}, E) , \tag{A3}$$

where $F(z,\hat{z},E)$ is a bound function. Multiplying this equation by $|\partial\kappa_\nu^\mu/\partial E|^{-1}$, going to the limit $E \to E_{\nu(-)}^\mu + 0$, and using Eq. (59) yields

$$C_{\mu\nu}(\mathbf{k}_\parallel, z) = C_{\mu\nu}(\mathbf{k}_\parallel, \hat{z}) , \tag{A4}$$

because κ_ν^μ tends to zero as E approaches E_ν^μ [from a right-sided neighborhood in the case of a minimum, and from a left-sided neighborhood in the case of a maximum of the (one-dimensional) band structure].

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*Present address: Research Laboratories, Siemens A.G., Otto-Hahn-Ring 6, D-8000 Munich 83, Federal Republic of Germany.

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[16] Note that degenerate energy bands have to be counted individually according to their multiplicity.
[17] Note that this formula also indicates how to correctly evaluate the formal sum $\sum_\nu |\psi_\nu(\mathbf{r})|^2 \delta(E_\nu - E)$ (the formal representation of the local density of states) in the vicinity of the crystal surface, which, for instance, is important in the theory of the scanning tunneling microscope (Refs. 1 and 2): From Eq. (18), it becomes evident that the formal summation with respect to ν has to be replaced by integration over the variables E and $\mathbf{k}_\parallel$, thus yielding the $\mathbf{k}_\parallel$ integral in Eq. (19) as a result.
[18] This provides a rigorous justification of the assumed asymptotic behavior of electronic states deep inside the bulk, as proposed, e.g., by Appelbaum and Blount (Ref. 15); J. A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. **48**, 479, (1976); and Bross (Ref. 4).
[19] This term causes the well-known "Friedel oscillations" of the electronic charge density (see also, Ref. 20).
[20] See *Introduction to the Theory of Solid Surfaces,* Ref. 9, Sec. 3.1.
[21] This may be efficiently achieved by the ABCM method, for instance (see Refs. 13 and 14).
[22] Exceptions of the regular case are at most allowed to occur at isolated points in $\mathbf{k}$ space, or along so-called contact curves, otherwise only with "vanishing probability" in the sense of C. Herring, Phys. Rev. **52**, 365 (1937).
[23] For a more compact notation, the explicit $\mathbf{k}_\parallel$ dependence will often be suppressed in the sequel.
[24] Provided there is no degeneracy of energy bands at $E = E_\nu^\mu(\mathbf{k}_\parallel)$.
[25] An intuitive presentation of this, within the framework of the free-electron model, has been given by García-Moliner and Flores, *Introduction to the Theory of Solid Surfaces,* Ref. 9, Sec. 3.1.