General expression for the Coulomb interaction in the presence of a surface

S. Peter Apell
Radiation Physics Division, National Bureau of Standards, Gaithersburg, Maryland 20899
and Institute of Theoretical Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

David R. Penn
Radiation Physics Division, National Bureau of Standards, Gaithersburg, Maryland 20899
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A general expression is presented for the Coulomb interaction between two test charges in the presence of an interface. The cases of planar and spherical geometry are considered. The potential is given for the two test particles outside, inside, or on either side of the interface, and appropriate limits are investigated.

I. INTRODUCTION

The tremendous variety of phenomena occurring in solid-state physics is a consequence of the Pauli principle and the Coulomb interaction. This paper will focus on the influence of the geometry on the effective Coulomb interaction. Initially, solid-state physics was concerned with the interaction between the charged particles of a *bulk* (infinite) medium. However, during the last decade we have witnessed an additional interest in the description of properties in the *surface* region of a material. In most cases we communicate with a sample through its contact with the surroundings, and it is of great importance to know the interaction potential between external test probes, such as light, electrons, atoms, ions, or molecules, and the responding medium. Electron scattering from a target, as is done in spectroscopies such as low-energy electron diffraction (LEED), electron-energy-loss spectroscopy (EELS), etc., has been utilized in recent years to provide a wealth of data. In order to extract as much valuable information as possible, it is essential to know the interaction potential, i.e., the form of the interaction itself as well as the response properties of a medium which is not infinite in extent. The former geometrical considerations have such profound effects that new modes appear in the excitation spectrum which are not present for the infinite solid. An example of this is the surface plasmon excitation at a vacuum-metal interface. This mode exists at the interface irrespective of the microscopic description of the response properties of the metal.

It is thus a general property of all models. However, they do differ in their predictions for the frequency and dispersion of the mode. This is then the detailed, local information. We develop a theory which incorporates the condition for the existence of such a surface localized excitation while at the same time being sufficiently general that the results are valid for more than the particular conditions of a specific approximation scheme for the electronic response of the solid. The present work is thus a theoretical formulation of the screening problem at an interface which, from the start, has the main features of the geometrical situation built in. This geometrical influence generally enters on two levels.

Provided one properly includes the presence of for example, an interface, one can go very far in using a response function as calculated from an infinite solid to explain experimental data. This is the *global* geometrical influence. However the response function itself *also* contains information about the geometry. This *local* geometrical information then enters as a correction in most cases (in some situations it is crucial) to the calculation based on the bulk response function. In order to illustrate this point consider the interaction of two electrons in the presence of a solid surface. For simplicity assume translational invariance parallel to the surface. The solid is in the region $z>0$. The interaction between two electrons in the absence of the solid as illustrated in Fig. 1(a) is

$$v(\mathbf{r}-\mathbf{r}')=\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}=\int\frac{d^2k_{||}}{(2\pi)^2}e^{i\mathbf{k}_{||}\cdot(\boldsymbol{\rho}-\boldsymbol{\rho}')}v(z-z')\,, \quad (1.1)$$

where

$$v(z-z')=\frac{2\pi e^2}{k_{||}}e^{-k_{||}|z-z'|}\equiv v_{k_{||}}e^{-k_{||}|z-z'|} \quad (1.2)$$

and the integration in Eq. (1.1) is parallel to the surface. In the presence of the semi-infinite solid the interaction is modified by the polarizability of the surface as shown in Fig. 1(b). Requiring that the potential and the normal component of the **D** field are continuous across the surface yields the classical results:

$$V_{\rm int}(z,z')=\begin{cases} v_{k_{||}}\left[e^{-k_{||}|z-z'|}-\dfrac{\epsilon-1}{\epsilon+1}e^{k_{||}(z+z')}\right], & z,z'<0 \quad (1.3)\\ v_{k_{||}}\dfrac{2}{1+\epsilon}e^{k_{||}(z-z')}, & z<0<z' \quad (1.4)\\ \dfrac{v_{k_{||}}}{\epsilon}\left[e^{-k_{||}|z-z'|}+\dfrac{\epsilon-1}{\epsilon+1}e^{-k_{||}(z+z')}\right], & z,z'>0 \quad (1.5)\end{cases}$$

where $V_{\rm int}$ is the total interaction between the two particles and $\epsilon=\epsilon(\omega)$ is the classical dielectric function which

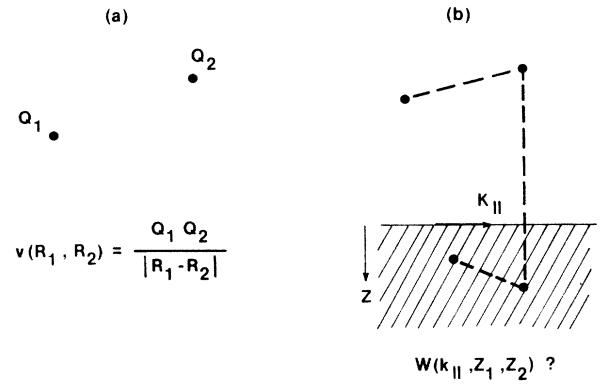

FIG. 1. (a) We can easily write the expression for the interaction of two charges in empty space. (b) In the presence of an interface one can formally write down a very general expression for this interaction, for the two charges outside, inside or on either side of the interface. For simplicity we will assume a translationally invariant surface for the medium, occupying the half-space $z > 0$.

is independent of $k_{||}$. The condition that $1+\epsilon(\omega)=0$ yields the surface plasmon frequency. Quantum-mechanical corrections of the type we are concerned with will modify ϵ and change the analytical form of the z and z dependence of V_{int}. In the classical approximation the dielectric function is not modified by the presence of the surface but the form of the interaction is greatly changed. The classical case will serve as a point of reference in the present work.

Whereas much effort has been devoted to the screened Coulomb interaction for the infinite solid only recently have more careful treatments been made of, e.g., the semi-infinite solid. This is of course directly related to the increased complexity, associated with the symmetry breaking which a surface introduces. One has been forced to use various kinds of models to describe the electronic motion responsible for the screening of external probes, and it is not always clear which results are general or model dependent.

We have therefore developed an approach in which we derive a closed form for the effective dynamical interaction between two electrons in the presence of a planar interface between a solid and vacuum, with as few assumptions as possible. This is achieved by using the wave functions of the solid as a basis set, but in no way specifying them except for the requirement that they should vanish at a certain point that defines the start of the vacuum. Thus all questions of how the wave functions approach zero, as determined by the random-phase approximation (RPA) or some other type of approximation, have no bearing on our final result. Instead this is a task to be dealt with in carrying out numerical calculations, where the required accuracy is set by the experimental demands and available computing power. Naturally our final results are rather complex for an immediate application in a particular situation. However our purpose is to clearly display the structure of the effective interaction, in the presence of an interface, starting from first principles. In doing so it is our firm conviction that this will not only greatly facilitate any numerical undertaking but also make it possible to understand why various model calculations differ or even overlook crucial physical elements.

The resulting potential has a wide variety of applications, particularly in surface science. Together with an appropriate Green's function it can be used to calculate self-energies for various kinds of external probes of the solid. Since small particles have received increasing attention in recent years we also give the potential for a spherical particle in vacuum.

In the next section we derive the effective interaction between two electrons for the solid/vacuum system, which is the main aim of this paper. Then in Sec. III we discuss our result for all possible locations for two test particles interacting via the derived potential. This leads to the definition of a surface dielectric function, and we also make contact with the corresponding classical results. The main mathematical steps in this section are given in Appendix A. In Sec. IV our procedure is repeated for a sphere in vacuum, making contact with the planar interface in the appropriate limit. All mathematical details are given in Appendix B. In Sec. V our scheme is used to calculate the energy loss that an electron experiences in traversing a planar interface. The paper concludes with a short discussion of our findings in Sec. VI. In Appendix C we give the main results obtained from our procedure utilizing the double cosine transform.

II. THEORY: PLANAR INTERFACE

In this section we derive a closed form for the effective interaction between two electrons; $W(\mathbf{x},\mathbf{x}',\omega)$. It is a dynamical interaction because of the time scales involved in the electronic response of the solid. However, retardation effects are neglected. Unlike the bare Coulomb interaction $W(\mathbf{x},\mathbf{x}',\omega)$ is not only a function of the distance between the particles $|\mathbf{x}-\mathbf{x}'|$ but also of their location with respect to the surface $(\mathbf{x}+\mathbf{x}')$. We have chosen to treat a semi-infinite medium extending in the positive z direction in contact with vacuum, defining $z=0$. Furthermore, we assume the solid has translational invariance in the surface plane (x-y plane), leading to a conservation of parallel momentum $\mathbf{k}_{||}$. It is therefore convenient to work with the Fourier transform of $W(\mathbf{x},\mathbf{x}',\omega)$; $W(\mathbf{k}_{||},z,z',\omega)$.

It is a straightforward matter to take into account a real lattice structure by summing over the appropriate reciprocal lattice vectors. An ion interacting with the medium can also be described, substituting the electronic charge with the ionic one. For the sake of clarity in our presentation we comment upon these matters when pertinent. With $v(z-z')$ denoting the bare Coulomb interaction [Eq. (1.2)] and $\chi(\mathbf{k}_{||},z,z',\omega)$ the density-density response function of the solid,[1] the effective interaction can be calculated from[2]

$$W(1,2)=v(1\text{-}2)+\int d3 \int d4\, v(1\text{-}3)\chi(3,4)W(4,2)\,, \tag{2.1}$$

suppressing the $(\mathbf{k}_{||},\omega)$ dependence and 1,2,3,4 stands for the spatial z coordinates.

This equation has previously been solved for the case when z and z' are outside of the solid (≤ 0), using the double cosine transform as an expansion basis for the spatial dependence inherent in $\chi(\mathbf{k}_{||},z,z',\omega)$.[3] However, we find it both unnecessary and unappealing to specify a particular basis set when solving Eq. (2.1) in the presence of a surface. If the true spatial dependence is very far from the cosine description one will be faced with an enormous number of terms. Instead we work with the wave functions of the semi-infinite solid which are also required to calculate $\chi(\mathbf{k}_{||},z,z',\omega)$. $\chi(\mathbf{k}_{||},z,z',\omega)$ can be written in the following way:[1]

$$\chi(\mathbf{k}_{||},z,z',\omega)=\sum_{p,p'}\int\frac{d^2k}{(2\pi)^2}\chi_{pp'}(\mathbf{k},\mathbf{k}+\mathbf{k}_{||},\omega)g_{pp'}(z)g^*_{pp'}(z')\ , \tag{2.2}$$

where the electron-hole pair amplitude

$$g_{pp'}(z)=\psi_p(z)\psi^*_{p'}(z) \tag{2.3}$$

is our basic spatial unit. $\psi_p(z)$ is a ground-state electron wave function for the system. The vanishing of $\psi_p(z)$ and thus $g_{pp'}(z)$ at $z=0$ defines the boundary with the vacuum and in what follows we will write $g_A(z)$ for $g_{pp'}(z)$ where A stands for $\{p,p'\}$. The summation over p and p' in Eq. (2.2) is symbolic for an integration over continuum states and a summation over bound states. It is restricted by the Fermi functions, $f(E_p)$, contained in the polarization bubble $\chi_{pp'}$, which is defined as

$$\chi_{pp'}(\mathbf{k},\mathbf{k}+\mathbf{k}_{||},\omega)=\frac{f(E_p)-f(E_{p'})}{E_p-E_{p'}+\hbar\omega+i\delta}\ , \tag{2.4}$$

where f contains the spin and electron energy level statistics and E_p ($E_{p'}$) is the electronic energy eigenvalue for the motion both parallel

$$\frac{\hbar^2k^2}{2m}\left[\frac{\hbar^2(\mathbf{k}+\mathbf{k}_{||})^2}{2m}\right]$$

and perpendicular to the surface.

In what follows we will make use of the polarization entity

$$R_{pp'}(\mathbf{k}_{||},\omega)=R_A(\mathbf{k}_{||},\omega)\equiv v_{k_{||}}\int\frac{d^2k}{(2\pi)^2}\chi_{pp'}(\mathbf{k},\mathbf{k}+\mathbf{k}_{||},\omega)\ , \tag{2.5}$$

which only depends on the conserved quantities $\mathbf{k}_{||}$ and ω that result from translational invariance in the surface plane and energy conservation, respectively.

In the case of free-electron-like metals which play a crucial role in the development of solid-state physics, and for zero temperature where $f(E_p)=2\Theta(E_F-E_p)$ with 2 for spin and E_F is the Fermi energy, one can evaluate Eq. (2.5) directly. Since we will not be using this explicit form, R_A suffices for our purposes, the interested reader is referred to a paper by Hertel[4] for more details.

However, in the case of an infinite solid we can write down the following form relating R_A in the free-electron case with the Lindhard dielectric function, viz.,

$$\epsilon_L(\mathbf{q},\omega)=1-\frac{4\pi e^2}{k_{||}^2+q^2}\int\frac{d^3p}{(2\pi)^3}\chi_{p,p+q}(\mathbf{k},\mathbf{k}+\mathbf{k}_{||},\omega)$$
$$=1-\frac{2k_{||}}{k_{||}^2+q^2}\int\frac{dp}{2\pi}R_A(\mathbf{k}_{||},\omega)\ , \tag{2.6}$$

where $\mathbf{q}=(\mathbf{k}_{||},q)$ and A denotes $\{p,p+q\}$. The first two terms in the iteration of Eq. (2.1) are now explicitly evaluated because they contain the necessary functions which must be defined and which appear in all higher-order terms. Iterating once leads to the following term

$$vRv=\int_0^\infty dz_1\int_0^\infty dz_2\,e^{-k_{||}|z-z_1|}\chi(\mathbf{k}_{||},z_1,z_2,\omega)\times e^{-k_{||}|z_2-z'|}v^2_{k_{||}}\ . \tag{2.7}$$

Use of Eq. (2.2) and Eq. (2.5) in Eq. (2.7) yields

$$vRv=v_{k_{||}}\sum_A f_A(z)R_Af^*_A(z')\ , \tag{2.8}$$

where $f_A(z)$ is the Coulomb matrix element:

$$f_A(z)=\langle p'|e^{-k_{||}|z-z_1|}|p\rangle=\int_0^\infty dz_1\,e^{-k_{||}|z-z_1|}g_A(z_1)\ . \tag{2.9}$$

It is convenient to rewrite Eq. (2.9) in the following fashion for the case that z is inside the solid ($z>0$):

$$f_A(z)=\int_0^\infty dz_1\{e^{-k_{||}|z-z_1|}+e^{-k_{||}(z+z_1)}\}g_A(z_1)-I_Ae^{-k_{||}z},\quad z>0 \tag{2.10}$$

by adding and subtracting a Coulomb term in the integrand of Eq. (2.9), $e^{-k_{||}|z+z_1|}$, which is the mirror image of z_1 in the dividing plane $z=0$. For $z<0$,

$$f_A(z)=I_Ae^{k_{||}z},\quad I_A=f_A(0)\ . \tag{2.11}$$

The procedure in Eq. (2.10) leads to a separation of $f_A(z)$ into a part which is characteristic of an infinite medium and a part which dies away from the dividing plane. If the potential which is used for calculating $\psi_p(z)$ is extended by mirroring it in the $z=0$ plane we can choose $\psi_p(z)$ even or odd with respect to $z=0$. In this process $g_A(z)$ does not change sign and we can rewrite the first integral in Eq. (2.10) as an integration over *all* space, $\int_{-\infty}^{\infty}dz_1e^{-k_{||}|z-z_1|}g_A(z_1)$, with a kernel which is characteristic of a bulk medium; it depends only on the distance between the points z and z_1. This term will henceforth be designated a bulk term and the other one, $I_Ae^{-k_{||}z}$ in Eq. (2.10) a surface term. With this *global* definition of bulk–surface we have removed the mere *existence* of a dividing line in the bulk term though on a *local* level it still contains the information about the actual surface profile through $g_A(z_1)$. We have therefore taken account of the fact that the dividing plane must be model independent whereas $g_A(z)$ is not. Finally, notice that the kernel in Eq. (2.9) is the Coulomb interaction. From physical considerations it is therefore only the functional form $e^{-k_{||}|z-z'|}$ with appropriate ranges for z and z' which can be used to single out the dividing plane. As we will see later the separation chosen in Eq. (2.10) ensures that

we retrieve the classical result discussed in the Introduction.

The next iteration of Eq. (2.1) yields

$$vRvRv = v_{k_{||}} \sum_{A,B} f_A(z) R_A D_{AB} R_B f_B^*(z') , \tag{2.12}$$

where f_A and R_A are defined above for the first iteration. A,B stands for $\{p,p'\},\{q,q'\}$ and the new entity D_{AB} is given by

$$D_{AB} = \int_0^\infty dz_2 \int_0^\infty dz_3 \, g_A^*(z_2) e^{-k_{||}|z_2 - z_3|} g_B(z_3)$$
$$\equiv \int_0^\infty dz_2 \, g_A^*(z_2) f_B(z_2) . \tag{2.13}$$

D_{AB} is the Coulomb matrix element for two interacting electrons, scattering from (p,q) to (p',q'). Using our division of $f_A(z>0)$ into a bulk and a surface part [Eq. (2.10)] in Eq. (2.13), we obtain

$$D_{AB} = B_{AB} - I_A^* I_B , \tag{2.14}$$

where the bulk term B_{AB} is

$$B_{AB} = \int_0^\infty dz_2 \int_0^\infty dz_3 \{ e^{-k_{||}|z_2 - z_3|} + e^{-k_{||}|z_2 + z_3|} \} \times g_A^*(z_2) g_B(z_3) . \tag{2.15}$$

The surface part is seen to be separable in A and B and is related to I_A (I_B), i.e., f_A (f_B) evaluated at the dividing plane.

Using D_{AB} from Eq. (2.14) the $vRvRv$ term can be written

$$vRvRv = v_{k_{||}} \sum_{A,B} f_A(z) R_A R_{AB} R_B f_B^*(z') - v_{k_{||}} \left[\sum_A I_A^* f_A(z) R_A \right] \left[\sum_B I_B R_B f_B^*(z') \right] . \tag{2.16}$$

The separability of the surface term in Eq. (2.14) results in the separability of the surface part in Eq. (2.16) with respect to z and z'. In analogy with the scattering of electrons by a localized perturbation there is a bound state associated with the separable term[5] and in our case this is a surface plasmon localized at the surface region of the solid.

Comparing Eqs. (2.8) and (2.16) we see that $f_A(z)$ and $f_B(z')$ describe the z and z' dependence. This will be true to all orders in the iteration and, before summing up the series, we give the next-order iteration for completeness:

$$vRvRvRv = v_{k_{||}} \sum_{A,B,C} f_A(z) R_A B_{AB} R_B B_{BC} R_C f_C^*(z') - v_{k_{||}} \sum_{A,B} f_A(z) R_A B_{AB} R_B I_B^* \sum_C I_C R_C f_C^*(z')$$
$$- v_{k_{||}} \sum_A I_A^* f_A(z) R_A \sum_{B,C} I_B R_B B_{BC} R_C f_C^*(z') + v_{k_{||}} \sum_A I_A^* f_A(z) R_A \{ \sum_B I_B R_B I_B^* \} \sum_C I_C R_C f_C^*(z') . \tag{2.17}$$

Figure 2 shows a dictionary to be used in later figures to facilitate an easy inspection of the various orders of iteration. If we first assemble all terms which contain only the inseparable bulk kernel B_{AB}, we obtain

$$F(z,z') \equiv \{ vRv + vRvRv + \cdots \} / v_{k_{||}}$$
$$= \sum_{A,B} f_A(z) \bar{R}_{AB} f_B^*(z') , \tag{2.18}$$

which defines the nonlocal function $F(z,z')$ in terms of $\bar{R}_{AB}$ (see Fig. 3):

$$\bar{R}_{AB} = R_A \delta_{AB} + R_A B_{AB} R_B + \sum_C R_A B_{AC} R_C B_{CB} R_B + \cdots$$
$$= (R\{1 - BR\}^{-1})_{AB} , \tag{2.19}$$

where B_{AB} is given by Eq. (2.15). δ_{AB} is short for $\delta_{pq}\delta_{p'q'}$ when summing over A and B. The series in Eq. (2.19) formally corresponds to an inverse dielectric function ϵ_{AB}^{-1}, and is seen to be a renormalization of the polarization function R_A.

On the other hand if we only sum to all orders those terms which contain the separable surface parts $I_A^* I_B$ in Eq. (2.14) we find (see Fig. 4)

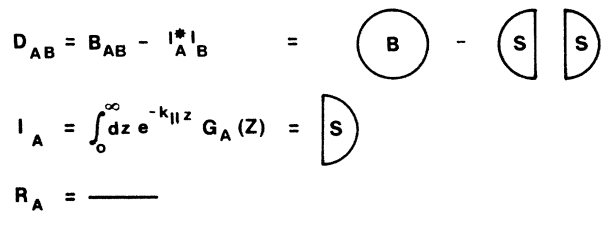

FIG. 2. Dictionary for the diagrammatic representation of the iteration series for the effective interaction $W(\mathbf{k}_{||},z,z',\omega)$. D_{AB} describes the scattering event $p \to p'$ and $q \to q'$ for two interacting electrons. By extending the Coulomb kernel to all space it can be divided in a part characteristic of an infinite medium B_{AB} and a separable part $I_A^* I_B$ which incorporates surface information. R_A is the ordinary polarization bubble [Eq. (2.5)] for a momentum transfer $\mathbf{k}_{||}$ and an energy transfer ω ($g_A = \psi_p \psi_{p'}^*$).

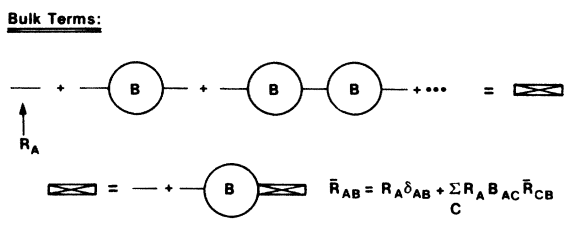

FIG. 3. Summing up only those terms, which include B_{AB}, to infinite order, we can define a renormalized polarization bubble $\bar{R}_{AB}$ to replace the bare R_A.

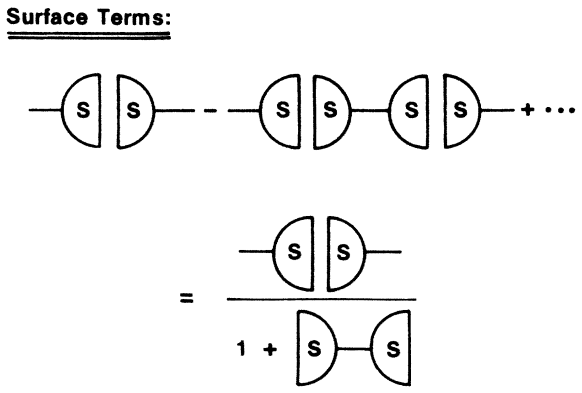

FIG. 4. Separable, so-called surface terms, can also be summed up to infinite order. This yields a renormalization of the lowest order diagram.

$$vRv+vRvRv+\cdots=-\frac{\sum_A I_A^* f_A(z) R_A \sum_A I_A R_A f_A^*(z')}{1+\sum_A I_A R_A I_A^*} v_{k_\parallel} . \tag{2.20}$$

What about the other terms? A careful examination shows, not surprisingly, that they can be incorporated in Eq. (2.20) by replacing the R_A's by $\bar{R}_{AB}$ given in Eq. (2.19); $\sum_A I_A R_A I_A^* \rightarrow \sum_{A,B} I_A \bar{R}_{AB} I_B^*$. This is shown in Fig. 5 in a pictorial way. Clearly, from the definition of $\bar{R}_{AB}$, this amounts to dressing the surface part with the "bulk" screening. As a consequence the surface term can be expressed in terms of $F(z,z')$ of Eq. (2.18). Including the zeroth-order term, the bare Coulomb interaction, we can now write down the following expression for the effective interaction between two electrons at z and z':

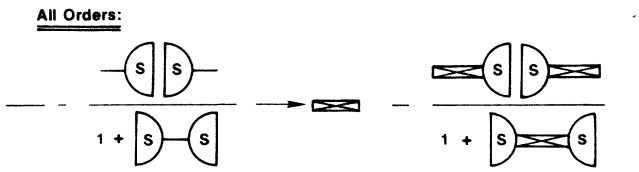

FIG. 5. This figure shows the results of summing all terms, bulk as well as surface, to infinite order. It turns out that it leads very naturally to a replacement of the first term in Figs. 3 and 4, respectively, with their renormalized counterparts, i.e., with $\bar{R}_{AB}$ instead of R_A.

$$W(\mathbf{k}_\parallel,z,z',\omega) = \left[e^{-k_\parallel|z-z'|} + F(z,z') - \frac{F(z,0)F(0,z')}{1+F_0} \right] v_{k_\parallel} , \tag{2.21}$$

which is the main result of our presentation. In Eq. (2.21) we have defined

$$F_0 \equiv F(0,0) = \sum_{A,B} I_A \bar{R}_{AB} I_B^* . \tag{2.22}$$

$W(\mathbf{k}_\parallel,z,z',\omega)$ is symmetric in z and z' and is of the form $W = v_{k_\parallel} e^{-k_\parallel|z-z'|} + W_{\text{ind}}$, with W_{ind} being the induced interaction potential. We note that by making use of the diagrams, it can be shown that

$$W_{\text{ind}}(z,z') = v_{k_\parallel} F(z,z') - F(z,0) W_{\text{ind}}(0,z') , \tag{2.23}$$

from which Eq. (2.21) follows directly.

For the convenience of the reader we repeat the definition of $F(z,z')$

$$F(z,z') = \sum_{A,B} f_A(z) \bar{R}_{AB} f_B^*(z') , \tag{2.18'}$$

$$\bar{R}_{AB} = R_A \delta_{AB} + R_A B_{AB} R_B + \sum_C R_A B_{AC} R_C B_{CB} R_B + \cdots = R_A \delta_{AB} + \sum_C R_A B_{AC} \bar{R}_{CB} , \tag{2.19'}$$

$$f_A(z) = \begin{cases} \int_0^\infty dz_1 \{ e^{-k_\parallel|z-z_1|} + e^{-k_\parallel|z+z_1|} \} g_A(z_1) - I_A e^{-k_\parallel z}, & z>0 \quad (2.10') \\ I_A e^{k_\parallel z}, & z<0 \quad (2.11') \end{cases}$$

$$g_A(z) \equiv g_{pp'}(z) = \psi_p(z) \psi_{p'}^*(z) , \tag{2.3'}$$

$$I_A = f_A(0) = \int_0^\infty dz e^{-k_\parallel z} g_A(z) , \tag{2.11'}$$

$v_{k_\parallel} = 2\pi e^2/k_\parallel$ and R_A is defined in Eq. (2.5).

The vanishing of $1+F_0$ in the denominator of Eq. (2.21) is associated with the excitation of a surface plasmon as will become evident in the following section. We will also discuss in greater detail the features inherent in Eq. (2.21) and make connection with the corresponding classical result, Eqs. (1.3)–(1.5).

Our procedure in this section amounts to an explicit extraction of the presence of a surface in the problem and the consequent evaluation of a "bulk" problem ($\bar{R}_{AB}$). The latter corresponds to the case where all space is filled up by the medium, with a small perturbation located where the "old" surface was. In this respect our scheme is very similar to a calculation for an impurity at the origin of a one-dimensional chain of atoms but in our case the "impurity" is the charge depletion around the surface region of our semi-infinite solid. To see this let $|i\rangle$ represent the electronic wave function on atom i. Furthermore let

$$H=\sum_{i,j} t_{ij}a_i^{\dagger}a_j - I\delta_{i,0}\delta_{j,0}=H_0+V$$

be the Hamiltonian, V denoting the impurity perturbation. With Green's functions $G=(E-H)^{-1}$ and $g=(E-H_0)^{-1}$, we solve the Dyson equation $G=g+gVG$. In the base $|i\rangle$, this becomes $G_{ij}=g_{ij}-g_{i0}IG_{0j}$ having the solution

$$\bar{G}_{ij}=\bar{g}_{ij}-\frac{\bar{g}_{i0}\bar{g}_{0j}}{1+\bar{g}_{00}}\ , \tag{2.24}$$

defining $\bar{G}=IG$ and $\bar{g}=Ig$. This result is clearly the equivalent of our final result in Eq. (2.21). F is the propagator for electromagnetic disturbances in a medium with a surface present and G is the propagator for excitations in a chain having an impurity. The vanishing of $1+\bar{g}_{00}$ in Eq. (2.24) is the condition for an impurity localized mode. With this comparison to the impurity problem we end this section with a few general comments.

The overall form for the interaction in Eq. (2.21) has been achieved without placing any constraints on the wave functions of the system. Its validity and general applicability is directly related to how accurately $\bar{R}_{AB}$, i.e., ultimately $\psi_p(z)$, can be calculated. An interesting scheme for obtaining an inverse dielectric function, and $\bar{R}_{AB}$, in the presence of an interface can be found in Hertel.[4] For two particles with different charges Q_1 and Q_2, Eq. (2.21) remains the same with the replacement $v_{k_{||}}\rightarrow(2\pi Q_1Q_2/k_{||})$. In Appendix C we give a brief summary of the main steps in this section for the case of the double cosine transform expansion of $\chi(\mathbf{k}_{||},z,z',\omega)$.

III. DISCUSSION: PLANAR INTERFACE

The general interaction in Eq. (2.21) can be related to previously defined quantities, such as a surface dielectric function. When both z and z' are outside the solid (<0), the spatial dependence of the f_A's is independent of the summation, Eq. (2.11), and can be taken outside. The resulting expression for the *induced* interaction potential, W_{ind}, is then

$$W_{\text{ind}}(\mathbf{k}_{||},z,z',\omega)\equiv W-v=-v_{k_{||}}e^{k_{||}(z+z')}\rho(\mathbf{k}_{||},\omega)\ , \tag{3.1}$$

where

$$\rho(\mathbf{k}_{||},\omega)=-\frac{F_0}{1+F_0}\ . \tag{3.2}$$

$\rho(\mathbf{k}_{||},\omega)$ can be interpreted as the strength of the reflected "signal" from a solid perturbed by a charge distribution and is the electrostatic analogue of the Fresnel reflection coefficient in optics,[6] see Fig. 6.

Thus an electron outside a surface will experience the potential in Eq. (3.1) due to the induced polarization it sets up in the solid. In analogy with the classical result for the corresponding situation it is illustrative to rewrite $\rho(\mathbf{k}_{||},\omega)$ in the following form:

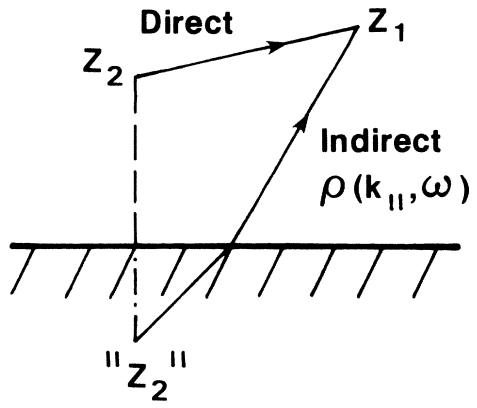

FIG. 6. If we sit in the point z_1, when there is a charge at z_2, we will experience an interaction potential which is composed of two parts, one is the direct Coulomb interaction and the other one is the interaction with the induced effects the charge at z_2 sets up in the metal. The latter is an "effective" image interaction having a strength given by $\rho(\mathbf{k}_{||},\omega)=-F_0/(1+F_0)$, where $F_0=\sum_{A,B}I_A\bar{R}_{AB}I_B$. When $1+F_0=0$, the reflection coefficient diverges and we have the condition for exciting a surface plasmon at the interface.

$$\rho(\mathbf{k}_{||},\omega)=\frac{\epsilon_s(\mathbf{k}_{||},\omega)-1}{\epsilon_s(\mathbf{k}_{||},\omega)+1}\ , \tag{3.3}$$

where

$$\frac{1}{\epsilon_s(\mathbf{k}_{||},\omega)}\equiv 1+2F_0=1+2\sum_{A,B}I_A\bar{R}_{AB}I_B^* \tag{3.4}$$

defines a so-called surface dielectric function.[7] For the situation of a sharp interface between a medium described by a frequency-dependent dielectric function $\epsilon(\omega)$ (e.g., Drude), and vacuum, $\epsilon_s(\mathbf{k}_{||},\omega)=\epsilon(\omega)$, and we immediately recognize the classical image factor $(\epsilon-1)/(\epsilon+1)$ of Eq. (1.3) in the expression for the induced potential in the vacuum region. In Appendix A all the necessary mathematical steps are given for extracting the classical limit of our general result.

In order to make contact with the usual definition of the dielectric function, Eq. (3.10) below, we make use of the set $\{\cos(pz)\}$ which is complete in the half-space $z>0$. Utilizing this basis we can write

$$\begin{aligned}\sum_{A,B} I_A\bar{R}_{AB}I_B^* &= \sum_{A,B} I_A(R_A\delta_{AB}+R_AB_{AB}R_B+\cdots)I_B^* \\ &= \sum_{p,p'} I_p\left[\sum_A 4\langle p\,|\,A\rangle R_A\langle A\,|\,p'\rangle\right]I_{p'}+4\sum_{\substack{p,p'\\q,q'}} I_p\left[\sum_A\langle p\,|\,A\rangle R_A\langle A\,|\,q\rangle\right]4B_{qq'}\left[\sum_B\langle q'\,|\,B\rangle R_B\langle B\,|\,p'\rangle\right]I_{p'}+\cdots \\ &= \sum_{p,p'} I_pR_{pp'}I_{p'}+\sum_{p,p',q} I_pR_{pq}I_qR_{qp'}I_{p'}+\cdots=\sum_{p,p'} I_p[RI(1-RI)^{-1}]_{pp'}=\sum_{p,p'} I_p(\epsilon_{pp'}^{-1}-\delta_{pp'})\end{aligned} \tag{3.5}$$

where use has been made of

$$\delta(z-z')=2\int_0^\infty (dp/\pi)\cos pz\cos pz'$$

and

$$I_p=\int_0^\infty dz\, e^{-k_{||}z}\cos(pz)=k_{||}/(k_{||}^2+p^2)\ , \tag{3.6}$$

$$R_{pp'}=4\sum_A \langle p\mid A\rangle R_A\langle A\mid p'\rangle\ , \tag{3.7}$$

where R_A is given by Eq. (2.5),

$$\langle A\mid p\rangle=\int_0^\infty dz\, g_A^*(z)\cos(pz)\ ,$$

and we have used

$$B_{qq'}=\int_0^\infty dz\int_0^\infty dz'\cos(qz)\times(e^{-k_{||}|z-z'|}+e^{-k_{||}|z+z'|})\cos(q'z')$$

$$\equiv I_q\delta_{qq'}\ . \tag{3.8}$$

From Eqs. (3.4) and (3.5) we have

$$\frac{1}{\epsilon_s(\mathbf{k}_{||},\omega)}=2\sum_{p,p'} I_p\epsilon_{pp'}^{-1}\ . \tag{3.9}$$

The quantity

$$\epsilon_{pp'}=\delta_{pp'}-R_{pp'}I_{p'} \tag{3.10}$$

is the dielectric function that describes the response of a model system to a potential of the form $\cos(p'z)$. The model system consists of the metal plus its reflection in the plane $z=0$. The influence of the surface is such that the wave functions are constrained to be zero at the plane $z=0$ in the model system. The results of the semiclassical infinite barrier model are obtained by the substitution $\epsilon_{pp'}^{-1}\to[\epsilon_L(p)]^{-1}\delta_{pp'}$ in Eq. (3.9), where $\epsilon_L(p)$ is the Lindhard dielectric function. The classical case obtains from $\epsilon_{pp'}^{-1}\to\epsilon^{-1}(\omega)\delta_{pp'}$.

Obviously the classical limit $\rho=(\epsilon-1)/(\epsilon+1)$ is the $k_{||}\to 0$ limit of F_0. The simple form for $k_{||}\to 0$ is a reflection of the fact that in this limit the orthogonality between the wave functions building up I_A and B_{AB} form simple δ functions. We will therefore further manipulate Eq. (3.3) to bring out this feature. When $k_{||}\to 0$, I_A in Eq. (3.4) becomes $\delta_{pp'}$. Defining

$$\frac{1}{\tilde{\epsilon}}=1+2\sum_{A,B}\delta_{pp'}\bar{R}_{AB}I_B^*\ , \tag{3.11}$$

we can rewrite Eq. (3.3) as

$$\rho(\mathbf{k}_{||},\omega)=\frac{(\tilde{\epsilon}-1)[1-k_{||}d_\perp(\mathbf{k}_{||},\omega)]}{\tilde{\epsilon}+1+(\tilde{\epsilon}-1)k_{||}d_\perp(\mathbf{k}_{||},\omega)}\ , \tag{3.12}$$

where the new quantity $d_\perp(\mathbf{k}_{||},\omega)$ is given by

$$d_\perp(\mathbf{k}_{||},\omega)=\sum_{A,B}(\delta_{pp'}-I_A)\bar{R}_{AB}I_B^*\Big/\left[k_{||}\sum_{A,B}\delta_{pp'}\bar{R}_{AB}I_B^*\right]\ . \tag{3.13}$$

With the induced density

$$\delta\rho(z)\propto\sum_{A,B} g_A(z)\bar{R}_{AB}I_B^*$$

we can write this as

$$d_\perp(\mathbf{k}_{||},\omega)=\frac{\int_0^\infty dz(1-e^{-k_{||}z})\delta\rho(\mathbf{k}_{||},z,\omega)}{k_{||}\int_0^\infty dz\,\delta\rho(\mathbf{k}_{||},z,\omega)}\ . \tag{3.14}$$

In the long-wavelength limit it has previously been shown[6] that the first correction to the classical expression for ρ takes the following form:

$$\rho(\mathbf{k}_{||},\omega)=\frac{(\epsilon-1)(1-k_{||}d_\perp)}{\epsilon+1+(\epsilon-1)k_{||}d_\perp} \tag{3.15}$$

to lowest order in $k_{||}d_\perp$, where the length $d_\perp$ is defined as

$$d_\perp=\frac{\int dz\, z\delta\rho(\mathbf{k}_{||}\to 0,\omega)}{\int dz\,\delta\rho(\mathbf{k}_{||}\to 0,\omega)} \tag{3.16}$$

and z is measured from half a lattice distance in front of the outermost lattice plane; the classical surface position.[8] $d_\perp(\omega)$ is seen to be the center of gravity of the induced charge and Eqs. (3.15) and (3.16) are the long wavelength limits of Eqs. (3.12) and (3.14), respectively. This is obvious for $d_\perp$ and in Appendix A we show that $\tilde{\epsilon}(0,\omega)\to\epsilon(\omega)$. In the limit of large $k_{||}$, $d_\perp\propto 1/k_{||}$ and $\rho(\mathbf{k}_{||},\omega)$ vanishes because $\tilde{\epsilon}$ approaches 1 for very large $k_{||}$. The latter fact is connected with the vanishing of $\bar{R}_{AB}$ for very large momentum transfers.

Having established some useful quantities and concepts we now turn to the situation when $z>0$ and $z'<0$; the potential inside when we have a charge outside. In this case the total potential is

$$W(\mathbf{k}_{||},z,z',\omega)=v_{k_{||}}e^{k_{||}z'}\left[e^{-k_{||}z}+\frac{2\epsilon_s}{1+\epsilon_s}\sum_{A,B}f_A(z)\bar{R}_{AB}I_B^*\right]\ , \tag{3.17}$$

where $e^{-k_{||}z}$ is from the direct interaction and the rest is the induced potential. Notice that $W(\mathbf{k}_{||},0,0,\omega)=v_{\mathbf{k}_{||}}[1-\rho(\mathbf{k}_{||},\omega)]$, i.e., it is automatically continuous across the boundary without invoking any boundary conditions. Once the microscopic response is specified there is no need for any macroscopically imposed boundary conditions. Both Eqs. (3.1) and (3.17) contain a factor $1+\epsilon_s$ in the denominator. The vanishing of this denominator indicates an induced potential in the absence of any external perturbation. This is the condition for an eigenmode of the coupled vacuum–solid interface and the vanishing of $1+\epsilon_s(\mathbf{k}_{||},\omega)$ provides a relation between ω and $k_{||}$ which is the dispersion relation for the surface plasmon. This fact then provides additional evidence that our splitting of the surface and bulk terms is the appropriate one since the scheme retrieves the proper surface plasmon dispersion relation for the classical case, yielding $\omega^2=\omega_p^2/2$ when $\epsilon_s(\mathbf{k}_{||},\omega)$ is replaced by its classically derived limit.

From Eq. (3.17) we see that we can conveniently introduce a generalized surface dielectric function $\epsilon_s(z)$ according to

$$1/\epsilon_s(z)=e^{-k_{||}z}+\sum_{A,B}f_A^b(z)\bar{R}_{AB}I_B^*\ , \tag{3.18}$$

dividing $f_A(z)$, Eq. (2.10), in the following way:

$$f_A(z)=f_A^b(z)-I_A e^{-k_{||}z}, \tag{3.19}$$

when $z>0$, where f_A^b represents the bulk part

$$f_A^b(z)=\int_0^\infty dz g_A(z)\{e^{-k_{||}|z-z'|}+e^{-k_{||}|z+z'|}\}\ ; \tag{3.20}$$

Eq. (3.17) can thus be rewritten as

$$1/\epsilon_s(z)=2\sum_p I_p\cos(pz)+\sum_{p,p'}4I_p\cos(pz)\sum_{A,B}\{\langle p\,|\,A\rangle R_A\langle A\,|\,p'\rangle\delta_{AB}+\cdots\}2I_{p'}$$
$$=2\sum_p I_p\cos(pz)+2\sum_{p,p'}I_p\cos(pz)(\epsilon_{pp'}^{-1}-\delta_{pp'})=2\sum_{p,p'}I_p\cos(pz)\epsilon_{pp'}^{-1}, \tag{3.22}$$

using Eqs. (3.6) and (3.7). The potential at z in the model system due to a unit charge at z' is

$$\phi(z,z')=4\sum_{p,p'}I_p\cos(pz)\epsilon_{pp'}^{-1}\cos(p'z')v_{k_{||}},$$

thus $2v_{k_{||}}/\epsilon_s(z)$ is the potential at z due to a charge at the surface, $z=0$.

Finally we have the case when both z and z' are inside the system. This and the other cases given above have been presented earlier by Flores and García-Moliner using the semi-classical infinite barrier model when calculating $\bar{R}_{AB}$.[9] Ortuno and Inkson[10] have made an inversion of the dielectric function for an *infinite* semiconductor also using a real-space inversion scheme as we employ here. However this is the first time, to the best of our knowledge, that the more general results have been given.

In terms of $\epsilon_s(z)$ the rather complex expression for W when both z and z' are inside can be written in the alternative form

$$W(\mathbf{k}_{||},z,z',\omega)=v_{k_{||}}\left[\epsilon_s^{-1}(z,z')-\frac{2\epsilon_s}{1+\epsilon_s}\frac{1}{\epsilon_s(z)}\frac{1}{\tilde{\epsilon}_s(z')}\right] \tag{3.23}$$

with

$$\epsilon_s^{-1}(z,z')=e^{-k_{||}|z-z'|}+e^{-k_{||}(z+z')}+\sum_{A,B}f_A^b(z)\bar{R}_{AB}f_B^{b*}(z') \tag{3.24}$$

and

$$1/\tilde{\epsilon}_s(z')=e^{-k_{||}z'}+\sum_{A,B}I_A\bar{R}_{AB}f_B^{b*}(z'). \tag{3.25}$$

Notice that $\epsilon_s^{-1}(z,0)=2\epsilon_s^{-1}(z)$, $\epsilon_s^{-1}(0,z')=2\tilde{\epsilon}_s^{-1}(z')$, and $\epsilon_s^{-1}(0)=\tilde{\epsilon}_s^{-1}(0)=1/\epsilon_s$ [$1/\tilde{\epsilon}_s(z')$ can also be expressed as $1/\epsilon_s^*(z',-\omega)$].

In the basis set $\{\cos(pz)\}$, we find

$$\epsilon_s^{-1}(z,z')=4\sum_{p,p'}I_p\cos(pz)\epsilon_{pp'}^{-1}\cos(p'z'). \tag{3.26}$$

The surface term in Eq. (3.23) which is proportional to $(1+\epsilon_s)^{-1}$ is very similar to Eq. (3.21), the only difference is that $e^{k_{||}z'}$ is replaced by $1/\epsilon_s(z')$ which represents the potential at z' due to a unit charge at $z=0$. In the classical limit $\epsilon_{pp'}^{-1}=\epsilon^{-1}(\omega)\delta_{pp'}$, $\epsilon_s^{-1}(z)=\epsilon^{-1}(\omega)e^{-k_{||}z}$, and $\epsilon_s^{-1}(z,z')=e^{-k_{||}(z+z')}\epsilon^{-1}(\omega)$.

$$W(\mathbf{k}_{||},z>0,z'<0,\omega)=v_{k_{||}}e^{k_{||}z'}\frac{2\epsilon_s}{1+\epsilon_s}1/\epsilon_s(z), \tag{3.21}$$

which is convenient to use in, e.g., golden rule expressions for matrix elements. Equation (3.4) shows that $\epsilon_s\equiv\epsilon_s(0)$, since $f_A^b(0)=2I_A$.

It is again helpful to use the complete set $\{\cos(pz)\}$ to reexpress $\epsilon_s(z)$, from (3.18) and (3.8):

This concludes our formal manipulations and discussions for the planar interface. In the following section we will repeat our scheme for the spherical interface, giving the main steps.

IV. THEORY: SPHERICAL INTERFACE

The derivation for a spherical geometry is in many ways similar to our treatment in Sec. III for the planar surface. We will therefore be very brief and only state the main steps. In Appendix B we make contact with the corresponding classical result as well as results based on the semiclassical infinite barrier model. It is again convenient to define a "reflection coefficient" and express this in terms of a surface dielectric function. Having those ingredients, a number of physical properties pertinent to the interaction between charged particles and a small solid particulate can be calculated.

There are two features which make the results in this section fundamentally different from the ones for the planar case. The sphere is overall neutral and therefore has no excitations with monopole character, i.e., there is no response for $l=0$. Instead the dipolar ($l=1$) symmetry is the important one; when calculating the planar response the surface screening charge could come from the "other" side of the metal or from the outside if the metal is grounded. The other main difference between the sphere and the semi-infinite medium is the size of the system. Whereas for the solid occupying the half space it is reasonable to talk about a bulk limit which is not always a valid description of a small particle, especially as it gets smaller and smaller. This will have some bearing on the way in which we construct the division into bulk and surface terms. However, for large radii the sphere response must resemble that of a planar interface and we are therefore guided by the planar result in making this separation.

We write the Coulomb interaction in spherical coordinates in the following manner:

$$v=\frac{e^2}{|\mathbf{r}_0-\mathbf{r}_1|}\equiv\frac{e^2}{R}\sum_l W_l^0 P_l(\cos\Omega_{01}) \tag{4.1}$$

where

$$P_l(\cos\Omega_{01})=\frac{4\pi}{2l+1}\sum_m Y_{lm}(\Omega_{r_0})Y^*_{lm}(\Omega_{r_1})$$

and

$$W_l^0=R\frac{r_<^l}{r_>^{l+1}}\bigg|_{r_<=\min\{r_0,r_1\},\ r_>=\max\{r_0,r_1\}} \tag{4.2}$$

R being the radius of the sphere. As in Sec. II we make use of the wave functions used in the density-density response function and we have:[11]

$$\chi(\mathbf{r},\mathbf{r}')=\sum_{l,m,A}\chi_{Al}g_A(r)g_A(r')Y_{lm}(\Omega_r)Y^*_{lm}(\Omega_{r'})\ , \tag{4.3}$$

where

$$g_A(r)=\Psi_{n_il_i}\Psi^*_{n_jl_j}\ , \tag{4.4}$$

Ψ being the radial solution to the Schrödinger equation and χ_{Al} corresponds to the polarization bubble χ_A in the planar case, Eq. (2.5). The subscript A is now short for $\{i,j\}$ corresponding to p,p' before, and l plays the role of $k_{||}$. The first-order iteration of Eq. (2.1) in the spherical case gives

$$vRv=\frac{e^2}{r}\sum_l W_l^{(1)}P_l(\cos\Omega_{01})\ ; \tag{4.5}$$

using $R_{Al}\equiv v_l\chi_{Al}$, we have

$$W_l^{(1)}=\sum_A f_A(r_0)R_{Al}f_A(r_1)\ . \tag{4.6}$$

$v_l=4\pi e^2R/2l+1$ and approaches $v_{k_{||}}$ in Eq. (1.2) as R and $l\to\infty$, in such a way that their ratio is equal to $k_{||}$. This defines the limiting procedure for approaching the planar case. The spatial function $f_A(r)$ in Eq. (4.6) is given by

$$f_A(r_0)=\int_0^\infty dr\,r^2\frac{r_<^l}{r_>^{l+1}}\bigg|_{r_<=\min\{r_0,r\},\ r_>=\max\{r_0,r\}}g_A(r) \tag{4.7}$$

and can be written as follows [$I_A=f_A(R)$]:

$$f_A(r_0)=I_A\times\begin{cases}(R/r_0)^{l+1}, & r_0>R \qquad (4.8)\\ \int_0^R dr\,r^2G(r_0,r)g_A(r)/I_A & \\ \quad -\dfrac{l+1}{l}(r_0/R)^l, & r_0<R \qquad (4.9)\end{cases}$$

splitting up the "inside" part in a bulk and a surface term. $I_A=f_A(R)$ and the division is achieved by defining the function $G(r_0,r)$ as

$$G(r_0,r)=\frac{r_<^l}{r_>^{l+1}}\bigg|_{r_<=\min\{r_0,r\},\ r_>=\max\{r_0,r\}}+\frac{l+1}{l}\frac{(r_0r)^l}{R^{2l+1}}\ . \tag{4.10}$$

It has the same purpose as the addition of the mirror image of the Coulomb interaction in Eq. (2.10). For the planar case this meant that we formed a kernel which gave the potential from charges placed symmetrically with respect to the surface. Thus, for a classical charge distribution, $g_A(z)\propto\delta(z-d)$, the resulting part of $f_A(z)$ is even around the surface with zero derivative. The same arguments lead to Eq. (4.10), which has the following properties. It reduces to the planar case when R and $l\to\infty$, the factor $l+1/l$ ensures the vanishing of the derivative demanded by the symmetric placing of the charges and finally Eq. (4.10) guarantees that our treatment will produce the classical result in the appropriate limit. See Appendix B for further details about the last point.

The next order in the iteration yields the amplitude

$$W_l^{(2)}=\sum_{A,B}f_A(r_0)R_{Al}D^l_{AB}R_{Bl}f_B(r_1)\ , \tag{4.11}$$

where D^l_{AB} is the scattering matrix element

$$D^l_{AB}=\frac{1}{R}\int_0^R dr\,r^2\times\int_0^R dr'(r')^2\frac{r_<^l}{r_>^{l+1}}\bigg|_{r_<=\min\{r,r'\},\ r_>=\max\{r,r'\}}\times g_A(r)g_B(r')\ . \tag{4.12}$$

Using the division into bulk and surface parts we write

$$D^l_{AB}=B^l_{AB}-\frac{l+1}{l}I_AI_B\ , \tag{4.13}$$

where $I_A=f_A(R)$ [Eq. (4.7)] and

$$B^l_{AB}\equiv\frac{1}{R}\int_0^R dr\,r^2\int_0^R dr'(r')^2G(r,r')g_A(r)g_B(r')\ . \tag{4.14}$$

Summing up the inseparable "bulk" terms to all orders, we get the result

$$F_l(r_0,r_1)=(W_l^{(1)}+W_l^{(2)}+\cdots)_{\text{bulk}}\equiv\sum_{A,B}f_A(r_0)\bar{R}_{ABl}f_B(r_1)\ , \tag{4.15}$$

where

$$\bar{R}_{ABl}=R_{Al}\delta_{AB}+R_{Al}B^l_{AB}R_{Bl}+\cdots=R_{Al}\delta_{AB}+\sum_C R_{Al}B^l_{AC}\bar{R}_{CBl}\ , \tag{4.16}$$

the series corresponding to Eq. (2.19) for the planar case. Summing all separable terms we again find that they become dressed by the "bulk" screening in Eq. (4.16) and we can finally write for the induced potential W_l^{ind}:

$$W_l^{\text{ind}}=F_l(r_0,r_1)-\frac{F_l(r_0,R)F_l(R,r_1)}{l/(l+1)+F_{0l}}\ . \tag{4.17}$$

In Eq. (4.17)

$$F_{0l}\equiv F_l(R,R)=\sum_{A,B}I_A\bar{R}_{ABl}I_B\ , \tag{4.18}$$

which is the crucial quantity for the dispersion of surface modes.

In analogy with the planar case a surface dielectric function is defined by considering the potential when both

r_0 and r_1 are outside of the sphere. In that instance the spatial dependence of $f_A(r)$ is independent of A and can be taken outside of the summation, yielding

$$W_l^{\text{ind}}(r_0,r_1>R)=\frac{lF_{0l}}{l+(l+1)F_{0l}}\left[\frac{R^2}{r_0r_1}\right]^{l+1}$$
$$\equiv-\frac{\epsilon_s^l-1}{\epsilon_s^l+(l+1)/l}\left[\frac{R^2}{r_0r_1}\right]^{l+1} \quad (4.19)$$

and a surface dielectric function ϵ_s^l is defined by

$$\epsilon_s^l=\left[1+\frac{2l+1}{l}F_{0l}\right]^{-1} . \quad (4.20)$$

The classical result for F_{0l} is (see Appendix B)

$$F_{0l}^{\text{cl}}=\frac{l}{2l+1}\frac{1-\epsilon}{\epsilon} , \quad (4.21)$$

leading to what we would expect; $\epsilon_s^{l,\text{cl}}=\epsilon(\omega)$. Notice that as $l\to\infty$, F_{0l}^{cl} approaches the planar surface result cf. Appendix A, Eq. (A9). In Appendix B we give a detailed derivation of the steps we have gone through in this section, using a particular basis set in making contact with the classical result as well as some recent work. Finally, we make the remark that for $l=0$ one can show the correspondence between Eq. (4.18) and the integral over the $l=0$ component of the induced density. Since the latter has to vanish for an isolated sphere this assures F_{00} and thus W_0^{ind} are zero.

V. ELECTRON ENERGY LOSS

In this section we give a derivation of the transition probability, per unit time, that a particle decays from a state b to d exciting an electron from a to c in a semi-infinite solid, transferring an energy ω and momentum $k_{||}$, as shown in Fig. 7. The golden rule gives

$$P_{bd}=\frac{2\pi}{\hbar}\sum_{a,c}f_a(1-f_c)\,|\langle c,d\,|\,W\,|\,a,b\rangle|^2$$
$$\times\delta(E_c-E_a-\hbar\omega) , \quad (5.1)$$

f_a and f_c being occupation factors, W our general interaction, Eq. (2.21), and the energy transfer $\hbar\omega=E_b-E_d$.

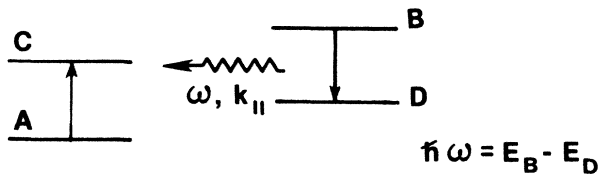

FIG. 7. Schematic picture for calculating the deexcitation of a charged particle from B to D while exciting an electron from A to C. The latter is in the semi-infinite solid while the transition from B to D can be for a penetrating particle as well as for one that remains outside the solid. This particle can be an atom, molecule, ion or an electron. ω is the energy transfer and $\mathbf{k}_{||}$ the momentum transfer.

Rewriting $\delta(E_c-E_a-\hbar\omega)$ as $\text{Im}(E_c-E_a-\hbar\omega-i\delta)^{-1}$ and adding $\text{Im}(E_c-E_a+\hbar\omega+i\delta)^{-1}$, which does not contribute for positive ω, we can write P_{bd} in the more symmetric form:

$$P_{bd}=\frac{2}{\hbar}\text{Im}\left[-\sum_{a,c}\frac{f_c-f_a}{E_c-E_a-\hbar\omega-i\delta}\,|\langle c,d\,|\,W\,|\,a,b\rangle|^2\right] . \quad (5.2)$$

Because of translational invariance along the surface

$$\Psi_{a,c}=\frac{1}{2\pi}e^{i\mathbf{k}_{a,c}\cdot\boldsymbol{\rho}}\psi_{p,p'}(z) \quad (5.3)$$

and the matrix element can be written as

$$\langle c,d\,|\,W\,|\,a,b\rangle\equiv\int\frac{d^2k_{||}}{(2\pi)^2}\delta(\mathbf{k}_a-\mathbf{k}_c+\mathbf{k}_{||})P_A(k_{||})v_{k_{||}} , \quad (5.4)$$

with

$$P_A(\mathbf{k}_{||})\equiv\int d^3x\,\psi_d^*(\mathbf{x})\psi_b(\mathbf{x})e^{-i\mathbf{k}_{||}\cdot\boldsymbol{\rho}}$$
$$\times\int dz'\,g_A(z')W(\mathbf{k}_{||},z,z',\omega)/v_{k_{||}} . \quad (5.5)$$

Introducing the general form for W from Eq. (2.21), and defining

$$f_A\equiv\int d^3x\,\psi_d^*(\mathbf{x})\psi_b(\mathbf{x})e^{-i\mathbf{k}_{||}\cdot\boldsymbol{\rho}}f_A(z) , \quad (5.6)$$

we can rewrite P_A as

$$P_A(\mathbf{k}_{||})=f_A+\sum_{B,C}f_B\bar{R}_{BC}D_{CA}$$
$$-\frac{1}{1+F_0}\left[\sum_{B,C}f_B\bar{R}_{BC}I_C^*\right]\left[\sum_{B,C}I_B\bar{R}_{BC}D_{CA}\right] \quad (5.7)$$

We manipulate this expression further by splitting D_{AB} into B_{AB} and $I_A^*I_B$, according to Eq. (2.14), yielding

$$P_A=f_A+\sum_{B,C}f_B\bar{R}_{BC}B_{CA}$$
$$-\frac{1}{1+F_0}\left[I_A+\sum_{B,C}I_B\bar{R}_{BC}B_{CA}\right]\left[\sum_{B,C}f_B\bar{R}_{BC}I_C^*\right] . \quad (5.8)$$

Now

$$\sum_{a,c}=\int\frac{d^2k_a}{(2\pi)^2}\int\frac{d^2k_c}{(2\pi)^2}\sum_A ,$$

where A is short for a summation over p,p' and spin. Equations (5.2) and (5.4) then give the following compact expression for the transition probability:

$$P_{bd}=\frac{2}{\hbar}\int\frac{d^2k_{||}}{(2\pi)^2}v_{k_{||}}\text{Im}\left[-\sum_A R_A\,|\,P_A\,|^2\right] , \quad (5.9)$$

with P_A given by Eq. (5.8).

Using the equation of motion for $\bar{R}_{AB}$, Eq. (2.19), the product R_AP_A immediately simplifies:

$$R_A P_A = \sum_B f_B \bar{R}_{BA} - \frac{1}{1+F_0}\left[\sum_B I_B \bar{R}_{BA}\right]\left[\sum_{B,C} f_B \bar{R}_{BC} I_C^*\right] . \quad (5.10)$$

Multiplying this with P_A^*, summing over A and taking the imaginary part, according to Eq. (5.9), many of the terms drop out since they are real (for details see Appendix D). In the following, a much more transparent result is obtained:

$$P_{bd} = -\frac{2}{\hbar}\int \frac{d^2k_{||}}{(2\pi)^2} v_{k_{||}} \mathrm{Im}\left[\sum_{A,B} f_A \bar{R}_{AB} f_B^* - \frac{1}{1+F_0}\left[\sum_{A,B} f_A \bar{R}_{AB} I_B^*\right]\left[\sum_{A,B} I_A \bar{R}_{AB} f_B^*\right]\right] . \quad (5.11)$$

Use of Eq. (5.6) in Eq. (5.11) results in the simple and beautiful form:

$$P_{bd} = \mathrm{Im}\left[-\frac{2}{\hbar}\int d^3x \int d^3x' \, \psi_d^*(\mathbf{x}) \psi_b(\mathbf{x}) W_{\mathrm{ind}}(\boldsymbol{\rho}-\boldsymbol{\rho}', z, z', \omega) \psi_d(\mathbf{x}') \psi_b^*(\mathbf{x}')\right] , \quad (5.12)$$

where $W_{\mathrm{ind}} \equiv W - v$, v being the bare Coulomb interaction. Comparing with the general *bulk* treatment in Ref. 2 we see that W_{ind} plays the role of a position-dependent self-energy. Another observation is that even though Eq. (5.1) is quadratic in W, Eq. (5.12) above shows a linear relationship. In fact we immediately obtain Eq. (5.12) if in Eq. (5.9) one of the P_A's is replaced with its "bare" form f_A; cf., Eq. (5.8).

In the situation that both ψ_d and ψ_b represent electronic states which are outside of the solid, we can use Eq. (3.1) for W_{ind} and P_{bd} splits very nicely into a part describing the solid's response and a matrix element containing the Coulombic coupling, viz.,

$$P_{bd} = \frac{2}{\hbar}\int \frac{d^2k_{||}}{(2\pi)^2} v_{k_{||}} [\mathrm{Im}\rho(\mathbf{k}_{||}, \omega)] \, |M_{bd}|^2 , \quad (5.13)$$

defining

$$M_{bd} = \int d^3x \, \psi_d^*(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}} \psi_b(\mathbf{x}) , \quad (5.14)$$

with $\mathbf{q} = (\mathbf{k}_{||}, ik_{||})$. Equation (5.13) clearly shows the role of the imaginary part of the reflection coefficient in describing loss phenomena. Since we have not specified the states b and d other than that they are outside of the solid, they can represent an electron attached to an atom, an ion a molecule or, for that matter, a single electron. In the latter case the transition probability, Eq. (5.13), determines the decay rate for say a scattering electron or an electron bound to an excited image state, thus giving a width to these so-called Rydberg states.[12]

VI. SUMMARY AND CONCLUSIONS

In the previous sections we have developed a formalism from which we derive a general expression for the interaction between two test charges in the presence of an interface. The main results are given in Eqs. (2.21) and (4.17), respectively, for the planar and the spherical surfaces. They can be used in conjunction with appropriate propagators to calculate a number of important quantities characterizing the interaction between charged particles and a solid medium of semi-infinite and finite extent. The final result is basically two series summed to infinite order. One series yields the bulk screening and the other, when summed, has a pole which determines the dispersion of the surface modes. This is most clearly seen by comparing Eq. (3.2) for the reflection coefficient $\rho = (-F_0)/(1+F_0)$ and its classical limit $\rho_{\mathrm{cl}} = (\epsilon-1)/(\epsilon+1)$, in the planar case. Both can be written as $\rho = \gamma + \gamma^2 + \gamma^3 + \cdots = \gamma + \gamma\rho$, with $\gamma = -F_0$ and $\gamma_{\mathrm{cl}} = \frac{1}{2}(1 - 1/\epsilon)$. The series in γ is the "surface" series, Fig. 4, leading to a Dyson equation for ρ. The lowest-order approximation is $\rho \cong \gamma$ having a pole when $\epsilon = 0$ ($F_0 \to \infty$), i.e., the condition for the collective excitation in an infinite medium, the bulk plasmon. However, summing up to infinite order, the pole in ρ occurs for $\gamma = 1$, i.e., for $\epsilon = -1$ ($F_0 = -1$), which we recognize as the surface-plasmon dispersion relation for a semi-infinite medium in contact with vacuum. The second series is contained in $\gamma(F_0)$ itself and is a bulk series. See Fig. 3 and the definition of F_0 in Eq. (2.2).

Looking at the classical result it is seen to be an expansion in $\zeta \equiv 1 - \epsilon$, since $\gamma_{\mathrm{cl}} = -\frac{1}{2}[\zeta/(1-\zeta)]$, and it is therefore an expansion in the deviation from vacuum ($\epsilon = 1$). Notice as pointed out before, that F_0 is related to $\epsilon^{-1} - 1$, the 1 coming from the dielectric function for vacuum. This series then corresponds to building up the medium from vacuum, the deviation being proportional to $\epsilon - 1$. Starting out from the first term which has a pole for $\epsilon = \infty$, we end up with the infinite order result, a pole at $\epsilon = 0$, which determines the plasma frequency of the bulk medium. This is then the starting point for building up the semi-infinite medium through the "surface" series.

Our general results are only a more sophisticated way of expressing the same ideas, but allowing for (i) a dependence on wave number (since we include the full spatial nonlocality in our treatment) and (ii) the "ϵ" going into the "bulk" series contains surface information through the wave functions of the system [cf. $\bar{R}_{AB}$, Eq. (2.19)]. Notice that the classical calculation takes ϵ for a bulk medium and couples it to vacuum yielding $\rho_{\mathrm{cl}} = (\epsilon-1)/(\epsilon+1)$. Such an approach works very well for the optical properties of solids. This latter aspect suggests an interesting approximation scheme, which is illustrated for the spherical case in Appendix C; it may be sufficient to calculate $\bar{R}_{AB}$ within a bulk scheme since we have taken care of the main surface structure in the problem through the I_A's. For the spherical case this corresponds to approximating $\bar{R}_{AB}$ which, for a sphere that is sufficiently large that the

curvature does not affect the screening, should yield a first insight into the behavior of the response of the small particle.

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APPENDIX A

It is important to establish the classical limit of our quantum-mechanical scheme, to see that our formulation has the appropriate limits. There is a well-defined way starting out with the quantum mechanical expression for the microscopic response function and obtaining the classical contribution.[13] It is based on isolating terms which are characteristic of a bulk (infinite) medium; starting with the infinite barrier model proceeding via the semiclassical infinite barrier model and its long-wavelength limit yielding the classical response.

With the infinite barrier model as a basis we start out having a $\psi_p(z)$:

$$\psi_p(z)=(\sqrt{2/\pi})\sin(pz),\quad z\geq 0\ . \tag{A1}$$

Inserting this into the definition of I_A, Eq. (2.11), we can write

$$I_A=\frac{1}{\pi}\int_0^\infty dz\, e^{-k_{||}z}[\cos(p-p')z-\cos(p+p')z]\ . \tag{A2}$$

The second term in the bracket has to be dropped since it is not a bulk term and we get for I_A

$$I_A=\frac{k_{||}}{\pi(k_{||}^2+s^2)}\quad \text{with } s=p'-p\ , \tag{A3}$$

which is a representation of a δ function in p and p' when $k_{||}\to 0$.

The next quantity to evaluate is B_{AB}, Eq. (2.15). Proceeding in the same manner, only keeping terms going as $p-p'$ and $q-q'$, we get

$$B_{AB}=I_s\delta_{st}\quad \text{with } t=q'-q\ , \tag{A4}$$

i.e., it is diagonal in s and t. Similarly we get for $f_A(z)$, Eqs. (2.10) and (2.11)

$$f_A(z)=I_A\times\begin{cases}2\cos(sz)-e^{-k_{||}z}, & z>0\\ e^{k_{||}z}, & z<0\ .\end{cases} \tag{A5}$$

It is only a function of $p-p'(s)$. The summation over p and q for $\bar{R}_{AB}$, in the definition of $F(z,z')$, Eq. (2.19), can then be performed, yielding

$$\sum_{p,q}\bar{R}_{pp'qq'}=\delta_{st}\left[\sum_p R_{p,p+s}\right]\times\left[1+\sum_q R_{q,q+s}I_s+(\cdots)^2(\cdots)\right], \tag{A6}$$

using the simple form for B_{AB} in Eq. (A4) and $\delta_{AB}=\delta_{pq}\delta_{st}$.

From the definition of the Lindhard dielectric function in Eq. (2.6), Eq. (A6) is seen to be an expansion in $1-\epsilon_L$ with the result that

$$\sum_{pq}\bar{R}_{pp'qq'}=\delta_{st}\frac{1-\epsilon_L(\mathbf{k}_{||},s,\omega)}{\epsilon_L(\mathbf{k}_{||},s,\omega)I_s}\ . \tag{A7}$$

The expression for $F(z,z')$ is then considerably simplified leading to the semiclassical infinite barrier model result for $F(z,z')$:[9]

$$F(z,z')=\sum_s f_s(z)\left[\frac{1-\epsilon_L}{\epsilon_L}\right]f_s(z')/I_s\ . \tag{A8}$$

To arrive at the classical result where we describe the response of the semi-infinite medium with a frequency-dependent dielectric function $\epsilon(\omega)$, $\epsilon_L(\mathbf{k}_{||},s,\omega)$ in Eq. (A8) is replaced by its long-wavelength limit $\equiv\epsilon(\omega)$. The summation over s can then be performed explicitly ($\sum_s I_s=\frac{1}{2}$) and we get

$$F(z,z')=\frac{1-\epsilon}{2\epsilon}\begin{cases}e^{k_{||}(z+z')}, & z,z'<0\\ e^{k_{||}(z-z')}, & z<0<z'\\ 2e^{-k_{||}|z-z'|}-e^{-k_{||}(z+z')}, & z,z'>0\end{cases} \tag{A9}$$

leading to the classical expression for the total effective interaction between two electrons in Eqs. (1.3)–(1.5).

Finally, in Sec. III we defined an effective dielectric function

$$1/\tilde{\epsilon}=1+2\sum_{A,B}\delta_{pp'}\bar{R}_{AB}I_B^*\ .$$

Clearly in the limit when $k_{||}\to 0$, and since $\bar{R}_{AB}$ is evaluated for $p=p'$, it is the long-wavelength limit of Eq. (A7) which is pertinent. This then gives $1/\tilde{\epsilon}=1+2\times\frac{1}{2}(1/\epsilon-1)=1/\epsilon(\omega)$, i.e., $\tilde{\epsilon}$ is the frequency-dependent bulk dielectric function of the material in this limit, as we stated.

APPENDIX B

In this appendix we give the main mathematical steps for deriving the classical interaction in a spherical geometry. It is equivalent to the main derivation in the text provided $g_A(r)=j_l(q_{lp}r)$ and the summation over A and B is for p and p'. We choose to work with the set of j_l's which are such that $j_l'(\eta_{lp})=0$, where $\eta_{lp}=q_{lp}R$, R being the sphere radius. This choice allows $\chi(\mathbf{r},\mathbf{r}')$ to have a finite amplitude on the surface which is a characteristic feature of the classical response.

Having made the choice for $g_A(r)$ we can perform the various integrations introduced in Sec. IV and we summarize here the results. We obtain

$$f_p(r_0)=I_p\times\begin{cases}(R/r_0)^{l+1}, & r_0>R\\ \dfrac{2l+1}{l}\dfrac{j_l(q_{lp}r_0)}{j_l(\eta_{lp})}-\dfrac{l+1}{l}(r_0/R)^l, & r_0>R\end{cases} \tag{B1}$$

where clearly $G(r_0,r)$ acting on j_l gives back j_l; our bulk expansion set. I_p is nothing but $f_p(R)$ and is given by

$$I_p=\frac{lR^2}{\eta_{lp}^2}j_l(\eta_{lp})\ . \tag{B2}$$

Furthermore, we introduced the scattering matrix element $D^l_{pp'}$ having the bulk part $B^l_{pp'}$, which turns out to be diagonal and we can write

$$B^l_{pp'}=B^l_p\delta_{pp'}\ , \tag{B3}$$

with

$$\begin{aligned}B^l_p&=(l+\tfrac{1}{2})I_p^2[\eta_{lp}^2-l(l+1)]/l^2\\ &\equiv(l+\tfrac{1}{2})I_p^2\tilde{\eta}_{lp}^{\,2}\ .\end{aligned} \tag{B4}$$

Before proceeding we have to relate the polarization bubble $\chi_{pp'l}$, Eq. (4.3), and the dielectric function. Using

$$\delta(\mathbf{x}-\mathbf{x}')-\epsilon(\mathbf{x},\mathbf{x}',\omega)=\int d^3x^{\parallel}\frac{e^2}{|\mathbf{x}-\mathbf{x}^{\parallel}|}\chi(\mathbf{x}^{\parallel},\mathbf{x}',\omega)\ , \tag{B5}$$

relating χ to ϵ we will find the χ corresponding to the classical situation, $\chi^{\rm cl}$, from the condition that it should yield $\delta(\mathbf{x}-\mathbf{x}')[1-\epsilon(\omega)]$ on the left-hand side of Eq. (B5) when inserted on the right-hand side. Expanding χ according to Eq. (4.3) and expressing the δ function in our basis set as (for the radial part)

$$\delta(r-r')/r^2=\sum_p A_p j_l(q_{lp}r)j_l(q_{lp}r') \tag{B6}$$

and

$$\epsilon(r,r',\omega)=\sum_p A_p\epsilon^B_{pp'}j_l(q_{lp}r)j_l(q_{lp'}r')\ , \tag{B7}$$

with

$$A_p=2\eta_{lp}^2/\{R^3j_l^2(\eta_{lp})[\eta_{lp}^2-l(l+1)]\}\ , \tag{B8}$$

we get ($R_{pp'}=v_l\chi_{pp'l}$),

$$\delta_{pp'}-\epsilon^B_{pp'}=B_pR_{pp'}\ . \tag{B9}$$

We have then kept only the "bulk" part of the integration in Eq. (B5) in accordance with the classical model being a bulk model with no information about where the surface is. The classical result for $\epsilon(r,r',\omega)=\epsilon(\omega)\delta(r-r')/r^2$ is obtained for with $\epsilon^B_{pp'}=\delta_{pp'}\epsilon(\omega)$.

Inverting Eq. (B9) we get the inverse dielectric function

$$\epsilon^{-1}_{pp'}=\delta_{pp'}+B_p\bar{R}_{pp'}\ , \tag{B10}$$

where

$$\bar{R}_{pp'}=R_{pp'}+\sum_q R_{pq}B_q\bar{R}_{pp'} \tag{B11}$$

is the dressed propagator. Combining Eqs. (B4) and (B9) for the classical case where all terms are diagonal, we get for the full polarization propagator:

$$\bar{R}_{pp'l}=\delta_{pp'}R_p/\epsilon(\omega)\ , \tag{B12}$$

i.e., the screened propagator R_p ($R_p=[1-\epsilon(\omega)]/B_p$). Finally this now gives for F_{0l}

$$F_{0l}=\sum_{p,p'}I_p\bar{R}_{pp'}I_{p'}=\frac{2}{2l+1}\frac{1-\epsilon}{\epsilon}\sum_p\frac{1}{\tilde{\eta}_{lp}^{\,2}}\ . \tag{B13}$$

If we multiply Eq. (B6) with $(r')^{l+2}$ and integrate over r' and then let $r=R$, the sum over the inverse zeros can be shown to be equal to $l/2$. This then yields the classical expression for F_{0l}, in Eq. (4.21), viz.,

$$F^{\rm cl}_{0l}=\frac{l}{2l+1}\frac{1-\epsilon}{\epsilon}\ . \tag{B14}$$

We now proceed to go one step beyond the classical result. Instead of using the classical dielectric function in Eqs. (B12) and (B13) we use the semiclassical infinite barrier model result from Eq. (A7). In other words our form factors I_A, f_A, etc., reflect the spherical symmetry giving the form of the effective interaction but when taking the bulk screening, as represented by the series for $\bar{R}_{ABl}$, instead of using the classical result with a frequency-dependent dielectric function which has no information whatsoever about the spherical aspects of the problem we use a somewhat better screening based on the Lindhard dielectric function, as in Eq. (A7). Equation (B13) is then changed in such a way that $(1/\epsilon-1)$ is inside of the summation, since the Lindhard dielectric function depends also on the momentum transfer η_{lp}/R. Then adding and subtracting the classical part considered above we get the following result:

$$F_{0l}=-\frac{l(\epsilon-1)}{\epsilon(2l+1)}(1-ld_r/R)\ , \tag{B15}$$

where we have introduced a length d_r (corresponding to $d_\perp$ in the planar case) defined as

$$\begin{aligned}d_r(\omega)/R=\frac{2\epsilon}{\epsilon-1}\sum_p\frac{1}{\eta_{lp}^2-l(l+1)}\\ \times\left[\frac{1}{\epsilon_L(\eta_{lp}/R,\omega)}-\frac{1}{\epsilon(\omega)}\right]\end{aligned} \tag{B16}$$

where ϵ_L is the Lindhard dielectric function. With the definitions made in Eq. (B15) we ensure that the reflection coefficient [Eq. (4.19)] coincides with the general form it must have according to the theory of Apell and Ljungbert.[14] Furthermore, we notice that Eq. (B16) coincides directly with the expression given in Ref. 15, and our treatment therefore provides an understanding of what approximations have to be made to achieve this result.

APPENDIX C

For completeness we give the main steps and results for the effective potential using the double cosine transform for comparison with the approach in Sec. II. In this scheme, the density-density correlation function is expanded as

$$\chi(\mathbf{k}_{||},z,z',\omega)=\sum_{p,p'}\chi_{pp'}\cos(pz)\cos(p'z') \tag{C1}$$

where p and p' now stands for external variables in contrast to our expansion using the g_A's in Eq. (2.2). Calculating the first iteration term vRv it can be written exactly in the same form as Eq. (2.8), viz.,

$$vRv = v_{k_{||}} \sum_{p,p'} f_p(z) R_{pp'} f_{p'}(z') , \tag{C2}$$

however, with different expressions for f_p and $I_p = f_p(0)$,

$$f_p(z) = I_p \begin{cases} 2\cos(pz) - e^{-k_{||}z}, & z > 0 \\ e^{k_{||}z}, & z < 0 \end{cases} \tag{C3}$$

and

$$I_p = \frac{k_{||}}{k_{||}^2 + p^2} , \tag{C4}$$

which are very close to the classical limit of our treatment as a comparison with Appendix A gives at hand ($R_{pp'} = v_{k_{||}} \chi_{pp'}$).

The next iteration order generates $D_{pp'}$ corresponding to our D_{AB} in Eq. (2.13), which is found to be

$$D_{pp'} = I_p \delta_{pp'} - I_p I_{p'} \tag{C5}$$

i.e., diagonal for the bulk part and separable for the surface part. Defining $F(z,z')$,

$$F(z,z') = \sum_{pp'} f_p(z) \bar{R}_{pp'} f_{p'}(z') , \tag{C6}$$

where

$$\bar{R}_{pp'} = R_{pp'} + \sum_q R_{pq} B_q R_{qp'} + \cdots = [R(1 - BR)^{-1}]_{pp'} \tag{C7}$$

and $B_q \equiv I_q$, we can again write the total effective interaction as

$$W(\mathbf{k}_{||}, z, z', \omega) = v_{k_{||}} \left[e^{-k_{||}|z - z'|} + F(z,z') - \frac{F(z,0)F(0,z')}{1 + F_0} \right] \tag{C8}$$

if we sum up the series $v + vRv + vRvRv \cdots$ to infinite order.

The expression for the surface dielectric function $\epsilon_s(\mathbf{k}_{||}, \omega)$ is ($\sum_p I_p = \frac{1}{2}$):

$$\epsilon_s^{-1}(\mathbf{k}_{||}, \omega) = 2 \sum_{pp'} I_p \epsilon_{pp'}^{-1} , \tag{C9}$$

where $\epsilon_{pp'}^{-1} \equiv \delta_{pp'} + \bar{R}_{pp'} I_{p'}$ defines an inverse dielectric function. The semiclassical limit is $\epsilon_{pp'}^{-1} = \delta_{pp'} / \epsilon_L(\mathbf{k}_{||}, p, \omega)$, which gives the semiclassical infinite barrier model result for $\epsilon_s(\mathbf{k}_{||}, \omega)$:

$$\epsilon_s^{-1}(\mathbf{k}_{||}, \omega) = 2 \sum_p I_p \epsilon_L^{-1} = \int_{-\infty}^{\infty} \frac{dp}{\pi} \frac{k_{||}}{k_{||}^2 + p^2} \frac{1}{\epsilon_L(\mathbf{k}_{||}, p, \omega)} , \tag{C10}$$

ϵ_L being the Lindhard dielectric function. Finally for the double cosine transform we have a sum rule[7] which results from the vanishing of the induced density at $z = 0$:

$$\delta\rho(z = 0) = 0 \rightarrow \sum_{p'} \epsilon_{pp'}^{-1} = \tfrac{1}{2} , \tag{C11}$$

which is automatically satisfied in our scheme since $g_A(z = 0) \equiv 0$, because this condition defines $z = 0$.

APPENDIX D

We demonstrate here the steps required in going from Eq. (5.9) to Eq. (5.11). We introduce

$$H_A = \sum_B f_B \bar{R}_{BA} , \tag{D1}$$

$$G_A = \sum_B I_B \bar{R}_{BA} , \tag{D2}$$

and

$$R = \sum_A H_A I_A^* , \quad S = \sum_A G_A f_A^* , \tag{D3}$$

from before $F_0 = \sum_A G_A I_A^*$ [Eq. (2.22)]. We can then write

$$R_A |P_A|^2 = \left[H_A - \frac{1}{1 + F_0} G_A R \right] \left[f_A^* + \sum_B H_B^* B_{BA}^* - \frac{1}{1 + F_0^*} (I_A^* + \sum_B G_B^* B_{BA}^*) R^* \right] . \tag{D4}$$

Taking the imaginary part and summing over A we obtain the following:

$$\mathrm{Im} \sum_A R_A |P_A|^2 = \mathrm{Im} \left[\sum_A H_A f_A^* + \sum_{A,B} H_A B_{AB} H_B^* - \left[\frac{R^*}{1 + F_0^*} \right] \left[R + \sum_{A,B} H_A B_{AB} G_B^* \right] - \frac{R}{1 + F_0} \left[S + \sum_{A,B} G_A B_{AB} H_B^* \right] + \left| \frac{R}{1 + F_0} \right|^2 \left[F_0 + \sum_{A,B} G_A B_{AB} G_B^* \right] \right] . \tag{D5}$$

Obviously, since B_{AB} contains the product of g_A^* and g_B [Eq. (2.15)], the second and last terms are real and do not contribute.

When writing down Eq. (D5), we have furthermore used that $B_{BA}^* = B_{AB}$. Moreover the fourth and sixth terms are each others' complex conjugate and they can also be deleted. Forming a common denominator for the third term, part of it is found to cancel the seventh one and the remaining part is real. This leaves us with the following terms:

$$\mathrm{Im}\sum_A R_A \mid P_A \mid^2 = \mathrm{Im}\left[\sum_A H_A f_A^* - \frac{RS}{1+F_0}\right], \tag{D6}$$

which is nothing but the integrand in Eq. (5.11) as we set out to demonstrate.

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