Self-consistent electromagnetic modes at a metal slab

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Abstract. Maxwell's equations are solved in the presence of a metal slab. The response of the electrons in the slab to an electromagnetic wave is a current charge density which appears to be a non-local pseudopotential in the Hemlholtz equation. This pseudopotential comprises Lindhard's longitudinal and transverse dielectric functions internally, the scattering at the surfaces, and the vacuum dielectric function externally. External magnetic modes couple to internal magnetic modes; external electric modes couple to internal electric and longitudinal modes; bound longitudinal modes and bound electric and magnetic modes are shown to arise as well. Explicit secular equations for the frequency of longitudinal and transverse bulk modes are derived which include the scattering at the surfaces. The phase shift of the free transverse modes at the slab is calculated and related to the reflectivity and the surface energy of the slab. The phase shift of the free electric modes is governed by the internal longitudinal dielectric function and that of the free magnetic modes by the internal transverse dielectric function.

1. Introduction

In investigations on the interaction of electromagnetic waves with condensed matter, it is often convenient to use the concept of electric and magnetic permeabilities. The first microscopic calculation into the dynamic response of a jellium ($=$ electron gas $+$ positive background) has been reported by Lindhard (1954). The local current charge density caused by an electromagnetic four-potential is calculated from the Schrödinger equation and the induced four-potential is found from Maxwell's equations. The total electromagnetic potential is composed of the external and the induced four-potential in self-consistent manner. Lindhard obtains explicit expressions for the longitudinal and transverse dielectric functions. The longitudinal dielectric function allows for longitudinal plasmons: the electric field caused by the oscillating charge density is also the driving force for this charge density. The transverse dielectric function exhibits the possibility of diamagnetic currents at zero frequency: the magnetic field caused by the current density at the same time sustains the current density.

The permeability concept has also been applied successfully to a number of surface effects. By assuming that the bulk dielectric function can be used up to the surface, it is possible to calculate the phase shift and reflectivity of external waves and the dispersion function of surface plasmons (Ritchie and Marusak 1966, Fuchs and Kliewer 1971). These investigations hold within the long-wavelength limit, ie the wavelength of the external wave and the normal extension of the surface plasmon must be large compared with the screening length of the electron gas. Even then, it is not *a priori* obvious whether

the longitudinal or the transverse dielectric function is responsible for the main effect. The response of the electrons and ions in condensed matter to an electromagnetic wave is generally non-local, such that each particular wave requires the use of a particular dielectric function. Moreover, the concept of permeabilities fails completely when short distances or wavelengths are considered. In investigations into electron emission from a solid, one has to modify the external electron potential by the image potential. However, the image potential is cut off at short distances, when the external electron sees the individual positions of the internal electrons rather than their average correlation potential. Similar divergences appear in investigations into the surface energy of a solid or on the van der Waals energy between two solids. The total correlation energy diverges if one maintains the concept of permeabilities at close distances. The effective permeability must be cut off either in real or in reciprocal space.

An appropriate cut-off distance in real space is the distance of beginning electronic overlap. Reasonable agreement between experimental data on the energy of physisorption and the theory of van der Waals attraction is obtained if a minimum distance of about 4 Å is used (Krupp 1967). The corresponding cut-off wavenumber in reciprocal space is the Fermi wavenumber of the electrons. Electromagnetic waves with wavelengths shorter than the Fermi wavelength hardly have a chance of being screened by the electrons. Such a cut-off has been used by Schmit and Lucas (1972) in van der Waals-type calculations on the surface energy. However, the problem as to whether it is the missing correlation with the missing electrons in the exterior, or the rearrangement of the electrons within the surface region, which makes the main contribution to the surface energy, has not been resolved. Lang and Kohn (1970) have applied the theory of Hohenberg, Kohn and Sham (Hohenberg and Kohn 1964, Kohn and Sham 1965), which includes all correlation and exchange effects in local pseudopotentials, to an investigation of the surface energy. They calculate the change in electrostatic energy of the electrons due to the change in their ionic surroundings and find reasonable agreement with experimental data too. The difference between the two methods is that the change in correlation energy is calculated explicitly in the former method, whereas it is included in the ionic pseudopotential and forms a part of the electrostatic energy in the latter method.

Attempts to calculate the response of a finite electron system to an electromagnetic wave have been reported by Fedders (1967), Feibelman (1968), Gerlach (1969), Newns (1970) and Beck and Celli (1970). The aim of these investigations is to obtain an improved knowledge of the surface potential and of the properties of the surface plasmons. Plane parallel surfaces, ie half-spaces or slabs, are considered and the electrostatic limit is applied. The surfaces imply that the induced potential does not exhibit the same normal wavenumber as the external potential, but takes the form of a Fourier series. The electrostatic limit does not allow a consistent specification of the boundary conditions. The self-consistency condition requires the inversion of the response matrix between the Fourier components of the induced and external potentials or rather the solution of the equivalent integral equation; this is conveniently done by iteration. The zeroth-order response to an external charge distribution yields the potential of the respective image charge. A review of the methods and the applications to electron–solid scattering was given by Feibelman *et al* (1972). Several attempts to include dynamic scattering have been initiated (Sunjić *et al* 1972, Harris and Jones 1973).

In this paper we consider the interaction of an electromagnetic wave with a finite electron system in the electrodynamic limit. This means that we do not restrict ourselves to the longitudinal electromagnetic modes within matter, but deal with longitudinal

and transverse modes internally and with transverse modes externally. Subdividing the transverse modes as usual into electric modes and magnetic modes, we find that the external magnetic modes interact with the internal magnetic modes, whereas the external electric modes interact with the internal electric and the longitudinal modes. No difficulty arises regarding the boundary conditions. Explicit dispersion functions for the bulk and surface modes are given and explicit expressions for the phase shift and the reflectivity of the external electromagnetic modes (photons) are derived.

Considering electromagnetic rather than electrostatic equations not only renders improved dispersion functions, but is particularly important with respect to investigations into correlation effects. It has often been argued that the van der Waals energy between two solids is due to the interaction between their surface plasmons (van Kampen *et al* 1968). However, van der Waals attraction exists also if the surface plasmons are fictitious quantities, which require imaginary frequencies. The interaction via surface plasmons is merely an electrostatic substitute for the electrodynamic interaction via the external electric and magnetic modes (Langbein 1974). In order to obtain the correct van der Waals energy, one has to integrate the total free energy of the external modes relative to the case of infinite separation. Using the state density integration technique introduced by van Kampen *et al* it is possible to express this total free energy in terms of the phase shift of the external modes, ie the surface energy of a slab of matter is obtained by integrating the difference in phase shift between two slabs in contact and at infinite separation. An early transition to the electrostatic limit cannot yield the correct surface energy because it does not give the correct decrease of phase shift with wavenumber.

In § 2 we consider the current charge density induced in a finite electron system by an electromagnetic wave represented by its four-potential. In § 3 we discuss the reaction four-potential resulting from the current charge density of the electrons by means of Maxwell's equations. We obtain four coupled integro-differential equations which can be reduced to a single scalar equation in the case of magnetic modes (§ 4) and to two coupled equations in the case of electric modes (§ 5). In § 6 we transform these integro-differential equations into a linear secular system by means of Green function techniques. In § 7 we simplify the resultant equations by assuming that the metal slab under investigation can be represented by a jellium slab. The secular system for the bulk and surface modes and the phase shift of the external modes are calculated explicitly in §§ 8 and 9. The reflectivity and surface energy of the slab are discussed in § 10.

2. Current charge density

The literature on the response of an electron system to an external perturbation is substantial. If we are interested in the linear response to a monochromatic perturbation, it is sufficient to use time-dependent perturbation theory. Let us consider a system of electrons, whose one-electron states

$$\psi(r, t) = |k> \exp(-iE_k t/\hbar) \tag{1}$$

satisfy the stationary Schrödinger equation

$$[(i\hbar\nabla)^2/2m + U(r) - E_k]|k> = 0. \tag{2}$$

$U(r)$ is a pseudopotential representing the average Coulomb interaction with the

remaining electrons and with the positive ions. In order to obtain the perturbed one-electron states $\psi(r, t)$ in the presence of the monochromatic four-potential

$$(A(r, t), V(r, t)) = (A(r), V(r)) \exp(-i\omega t), \tag{3}$$

we introduce the latter into the time-dependent Schrödinger equation

$$[(i\hbar\nabla + eA(r, t)/c)^2/2m + U(r) + V(r, t) - i\hbar \, \partial/\partial t]\psi(r, t) = 0. \tag{4}$$

In equation (3) and in the following we use the complex representation of the four-potential where we actually mean the real part. Linearizing with respect to the vector potential $A(r, t)$ we obtain

$$[(i\hbar\nabla)^2/2m + U(r) + \delta U(r) \exp(-i\omega t) - i\hbar \, \partial/\partial t]\psi(r, t) = 0 \tag{5}$$

where

$$\delta U(r) = (ie\hbar/2mc)(\nabla \cdot A(r) + A(r) \cdot \nabla) + eV(r). \tag{6}$$

In order to solve equation (5) by time-dependent perturbation theory we put

$$\psi(r, t) = \left(|k\rangle + \sum_l c(l, k)|l\rangle \exp(-i\omega t) \right) \exp(-iE_k t/\hbar) \tag{7}$$

with $|k\rangle, |l\rangle$ representing the unperturbed one-electron states introduced in equation (1). We obtain

$$c(l, k) = \langle l|\delta U(r)|k\rangle/(E_k - E_l + \hbar\omega). \tag{8}$$

The current charge density $(j/c, \rho)$ due to the one-electron state $\psi(r, t)$ in the presence of a magnetic vector potential $A(r, t)$ is given by

$$j(r, t)/c = (e/2mc)[\psi(i\hbar\nabla - eA/c)\psi^* - \psi^*(i\hbar\nabla + eA/c)\psi] \tag{9}$$

$$\rho(r, t) = e\psi^*\psi. \tag{10}$$

Substituting the one-electron states (7) and summing over all occupied states, we obtain

$$\delta j(r)/c = (ie\hbar/2mc)\sum_k \sum_l (f_k - f_l)c(l, k)(|l\rangle\nabla\langle k| - \nabla|l\rangle\langle k|) - (e^2/mc^2)A(r)\sum_k f_k|k\rangle\langle k| \tag{11}$$

$$\delta\rho(r) = e\sum_k \sum_l (f_k - f_l)c(l, k)|l\rangle\langle k| \tag{12}$$

where f_k is the occupation number of state $|k\rangle$:

$$f_k = \begin{cases} 1 \\ 0 \end{cases} \quad \text{for } |k\rangle \text{ being} \begin{cases} \text{occupied} \\ \text{empty} \end{cases} \tag{13}$$

The response $(\delta j/c, \delta\rho)$ of the electron system arises in terms of the stationary one-electron states $|k\rangle, |l\rangle$.

3. Helmholtz equation

The current charge density induced by the four-potential in turn causes a response of the four-potential. Attributing the screening of fields exclusively to the electron system, we

consider Maxwell's equations in a vacuum:

$$\partial B/\partial(ct) + \nabla \times E = 0 \qquad\qquad \nabla \cdot B = 0 \tag{14}$$

$$-\partial E/\partial(ct) + \nabla \times B = 4\pi\, \delta j/c \qquad \nabla \cdot E = 4\pi\, \delta\rho. \tag{15}$$

We introduce the four-potential $(A(r), V(r))$ as usual:

$$B = \nabla \times A \qquad E = -\partial A/\partial(ct) - \nabla V. \tag{16}$$

Then adopting the Lorentz gauge

$$\nabla \cdot A + \partial V/\partial(ct) = 0, \tag{17}$$

we obtain the inhomogeneous Helmholtz equation

$$[\nabla^2 - \partial^2/\partial(ct)^2](A, V) = -4\pi(\delta j/c, \delta\rho). \tag{18}$$

Since the four-potential and the current charge density both oscillate with frequency ω, we have

$$[\nabla^2 + (\omega/c)^2](A, V) = -4\pi(\delta j/c, \delta\rho). \tag{19}$$

Equations (11), (12) describe the current charge density caused by the four-potential and equation (19) describes the four-potential caused by the current charge density. We have now obtained a self-consistent system of equations for the four-potential and the current charge density, or alternatively, an integro-differential equation for the electrodynamic four-potential in the presence of the electron system under investigation.

Non-vanishing contributions to the current charge density (11), (12) arise from each pair consisting of an occupied and an empty electron state; $|k\rangle$ must be occupied and $|l\rangle$ empty, or vice versa. The current charge density vanishes as expected in the region of vanishing electron density of the occupied states. The solutions of the Helmholtz equation (19) in this region are strictly transverse electromagnetic modes. In view of the fact that the current charge density of the electrons arises by applying a linear integral operator to the four-potential, we may alternatively regard the electron system as a pseudopotential acting on the electromagnetic field.

The vector Helmholtz equation (19) appears to consist of four scalar equations. However, only three of them are independent. By applying the four-divergence $[\nabla, \partial/\partial(ct)]$ to both sides of equation (19) we find that the left-hand side vanishes according to the Lorentz gauge (17) and that the right-hand side vanishes according to the continuity equation, which is guaranteed by the definition (9), (10) of the current charge density. If the dependence of the fourth equation (19) on the first three equations is not obvious from the beginning, we may change the gauge of the four-potential. It is well known that when $\delta V(r)$ satisfies the homogeneous Helmholtz equation, we can change the four-potential by $[\nabla\, \delta V(r), (i\omega/c)\, \delta V(r)]$ without causing an additional magnetic or electric field or an additional current charge density.

By applying equations (11), (12) and (19) to an infinite jellium and using the translational invariance (Bloch's theorem), we readily recover Lindhard's longitudinal and transverse dielectric functions. Their zeros yield the dispersion relations of the bulk plasmons. In real lattices we find a coupling of electromagnetic waves with wavevectors q and $q+g$, where g is a reciprocal lattice vector, and a corresponding splitting of the dispersion curves into bands confined by Brillouin zones (Pandey *et al* 1974).

4. Magnetic modes

As we are interested in the effect of surfaces, let us now consider the inhomogeneous Helmholtz equation (19) in the presence of a metal slab. We put the x axis of a rectangular coordinate system normal to the slab and the y axis along the surface of the slab in the plane of incidence of the external wave. The slab is assumed to have thickness L_x in the x direction and to extend infinitely in the y and z directions ($L_y, L_z \rightarrow \infty$).

Assuming that the lattice potential in the slab under investigation varies only smoothly in the tangential directions y and z, we represent the one-electron states $|k\rangle$ by plane waves tangential and an arbitrary function $|k_x\rangle$ normal to the surfaces, ie

$$|k\rangle = |k_x\rangle \exp(ik_y y + ik_z z)/(L_y L_z)^{1/2}. \tag{20}$$

The solutions of the vector Helmholtz equation (19) in the exterior are well known to be electric or magnetic modes. They result by applying the curl operator to any vector solution of the scalar Helmholtz equation (Morse and Feshbach 1953). In rectangular coordinates it is convenient to use

$$(A(r), V(r)) = ((\nabla \times)^s a \exp(iqr), 0) \tag{21}$$

with $s = 1$ for magnetic modes and $s = 2$ for electric modes; a is an arbitrary constant vector.

Looking for the magnetic modes in the presence of a slab, we use the Bloch theorem tangential to the surfaces but allow for an arbitrary variation of $A(r)$ in the x direction, ie we put

$$(A(r), V(r)) = (\nabla \times a(x) \exp(iq_y y), 0) \tag{22}$$

where $a(x)$ is a vector normal to the surfaces, exhibits the periodicity of the lattice internally and is a plane wave externally; q_z equals zero according to our choice of coordinates. Substituting the electron states (20) and the four-potential (22) into the matrix element (8) we obtain

$$\langle l|\delta U(r)|k\rangle = \delta_{l_y k_y + q_y} \delta_{l_z k_z}(ieh/2mc)2q_y k_z \langle l_x|a(x)|k_x\rangle. \tag{23}$$

The wavenumber tangential to the surfaces is conserved, ie

$$l_y = k_y + q_y, \qquad l_z = k_z \tag{24}$$

and matrix element (23) is an odd function of k_z.

Substituting equation (23) into the current charge density given by equations (11) and (12), we make use of the fact that E_k and E_l are even functions of k_z. We find that the current density in the plane of incidence and the charge density both vanish and we are left with a current density in the z direction. The induced current density is parallel to the four-potential and we obtain the scalar equation

$$(\nabla_x^2 + q_x^2)a(x) = 2 \sum_{k_x} \sum_{l_x} Q(k_x, l_x)\langle l_x|a(x)|k_x\rangle|l_x\rangle\langle k_x| \tag{25}$$

where

$$Q(k_x, l_x) = \frac{1}{2\pi} \iint dk_y \, dk_z \, f_k \left[\left(\frac{eh}{mc}\right)^2 \sum_{\pm \omega} \frac{k_z^2}{E_k - E_l + \hbar\omega} + \frac{e^2}{mc^2} \right] \tag{26}$$

and

$$q_x^2 + q_y^2 = (\omega/c)^2. \tag{27}$$

We are left with an ordinary integro-differential equation for the scalar factor $a(x)$ in the vector potential (22). Outside the metal slab we again obtain plane waves. The response of the slab is represented in terms of the electron states $|k_x\rangle$, $|l_x\rangle$. The explicit form of $|k_x\rangle$, $|l_x\rangle$ has not been used so far. Equation (25) is valid in the presence of arbitrary one-electron potentials $U(x)$.

The kernel $Q(k_x, l_x)$ arises by integration over the wavenumbers k_y, k_z tangential to the surfaces. $Q(k_x, l_x)$ is an even function of frequency; the summation in equation (26) extends over both signs of ω. This summation results from interchanging the labelling of states $|k\rangle$ and $|l\rangle$ in the term containing f_l in equations (11) and (12).

5. Electric modes

Turning to electric modes, equation (21) for $s = 2$, we learn that it is no longer possible simply to replace $\mathbf{a}$ by a vector $\mathbf{a}(x)$ normal to the surfaces. The substitution of the resultant four-potential into matrix element (8) and subsequently into the current charge density, equations (11) and (12), shows that the induced current charge density is not parallel to the four-potential, even after changing the gauge of the latter. In order to separate the Helmholtz equation (19) we must add an internal longitudinal mode. It turns out convenient to put

$$(A(\mathbf{r}), V(\mathbf{r})) = ((\nabla \times)^2 \mathbf{a}_1(x) + (\mathrm{i}\omega/c)^2 \mathbf{a}_2(x), (\mathrm{i}\omega/c)\nabla \cdot \mathbf{a}_2(x)) \exp(\mathrm{i}q_y y) \tag{28}$$

where $\mathbf{a}_1(x)$ and $\mathbf{a}_2(x)$ are both vectors normal to the surfaces; $\mathbf{a}_1(x)$ describes a purely electric mode, whereas $\mathbf{a}_2(x)$ allows for a longitudinal mode internally.

Insertion of the four-potential (28) into the matrix element (8) yields

$$\langle l|\delta U(\mathbf{r})|k\rangle = \delta_{l_y k_y + q_y}\delta_{l_z k_z}(\mathrm{i}e\hbar/2mc)\sum_{j=1,2}(C_{1j}\langle\nabla_x l_x|a_j(x)|k_x\rangle + C_{2j}\langle l_x|a_j(x)|\nabla_x k_x\rangle) \tag{29}$$

where for convenience we write $\nabla_x|k_x\rangle \equiv |\nabla_x k_x\rangle$, and where

$$
\begin{aligned}
C_{11} &= 2q_y k_y & C_{21} &= 2q_y l_y \\
C_{12} &= -2m\omega/\hbar + (\omega/c)^2 & C_{22} &= -2m\omega/\hbar - (\omega/c)^2.
\end{aligned}
\tag{30}
$$

The wavenumber tangential to the surfaces is again conserved, ie equation (24) is valid.

By substituting the matrix element (29) into the current charge density and using the fact that matrix element (29) and E_k and E_l are even functions of k_z, we find that the z component of the current density and the respective component of the four-potential (28) vanish. We are left with three scalar Helmholtz equations (19), which are interrelated by the Lorentz gauge and the continuity equation. The Helmholtz equation relating to the tangential components of the four-potential and the current density can be written as

$$(\nabla_x^2 + q_x^2)\nabla_x a_1(x)$$
$$= 2\sum_{k_x}\sum_{l_x}(\langle\nabla_x l_x|Q_{11}a_1(x) + Q_{12}a_2(x)|k_x\rangle + \langle l_x|Q_{21}a_1(x) + Q_{22}a_2(x)|\nabla_x k_x\rangle)|l_x\rangle\langle k_x| \tag{31}$$

where

$$Q_{ij}(k_x, l_x) = -\frac{1}{2\pi}\iint \mathrm{d}k_y\,\mathrm{d}k_z\,f_k\left[\left(\frac{e\hbar}{2mc}\right)^2\sum_{\pm\omega}C_{ij}\frac{(k_y + l_y)/q_y}{E_k - E_l + \hbar\omega} + \delta_{1j}\frac{e^2}{mc^2}\right] \tag{32}$$

and $i, j = 1, 2$. The second term in the square brackets of equation (32) is the contribution of the charge density (12).

The corresponding Helmholtz equation relating to the electric potential and the charge density reads

$$(\nabla_x^2 + q_x^2)\nabla_x a_2(x)$$
$$= 2 \sum_{k_x} \sum_{l_x} (\langle \nabla_x l_x | R_{11} a_1(x) + R_{12} a_2(x) | k_x \rangle + \langle l_x | R_{21} a_1(x) + R_{22} a_2(x) | \nabla_x k_x \rangle) | l_x \rangle \langle k_x | \tag{33}$$

where

$$R_{ij}(k_x, l_x) = -\frac{e^2}{2\pi} \iint dk_y \, dk_z \, f_k \sum_{\pm \omega} C_{ij} \frac{\hbar/2m\omega}{E_k - E_l + \hbar\omega}. \tag{34}$$

The longitudinal amplitude $a_2(x)$ is considerably more affected by the response of the electrons than the transverse amplitude $a_1(x)$. The ratio between the respective kernels equals $2mc^2/\hbar\omega$.

The third relevant Helmholtz equation, that relating to the normal component of the vector potential and the current density, is implicitly included in equations (31) and (33). By applying the ∇_x operator to the Helmholtz equation for the normal component, we obtain a linear combination of the former equations. This reduces the meaning of the third Helmholtz equation to the condition that the normal current density must vanish at the surfaces, that is

$$\{(\nabla_x^2 + q_x^2)[q_y^2 a_1(x) - (\omega/c)^2 a_2(x)]\}_{\text{surface}} = 0. \tag{35}$$

We are left with two coupled integro-differential equations, rather than with the single equations obtained in the case of magnetic modes. The statements made in the two final paragraphs of § 4 concerning the properties of the kernels and the form of the electrostatic potential $U(x)$ and the electron states $|k_x\rangle, |l_x\rangle$ hold in the case of the electric modes as well. The obvious reason for the coupling of the external electric modes to the internal longitudinal modes is the fact that the electric modes exhibit a non-vanishing electric field normal to the surfaces. The induced normal current density must be cancelled by a coupling to an internal longitudinal mode before the boundary conditions between external and internal electric modes can be satisfied.

In the electrostatic limit, ie when $c = \infty$ is assumed, we find that the response of the electrons to a magnetic mode vanishes. In the case of external electric modes we may cancel the Helmholtz equation for the internal transverse amplitude $a_1(x)$ and are left with the internal variation of the longitudinal amplitude $a_2(x)$. Using the fact that $R_{12}(k_x, l_x)$ and $R_{22}(k_x, l_x)$ become equal in the electrostatic limit we obtain

$$(\nabla_x^2 + q_x^2)V(x) = -2 \sum_{k_x} \sum_{l_x} R_{12}(k_x, l_x) \langle l_x | V(x) | k_x \rangle | l_x \rangle \langle k_x |. \tag{36}$$

Equation (36) describes the screening of external electrostatic fields by the electrons and has been used by Feibelman (1968), Gerlach (1969) and Newns (1970) for investigations into surface plasmon dispersion.

6. Secular system

We have now reduced the vector Helmholtz equation (19) to a single scalar integral equation describing magnetic modes and two coupled integral equations describing

electric and longitudinal modes. The response of the electrons to the driving electromagnetic wave gives rise to the pseudopotential given on the right-hand sides of equations (25) and (31), (33). This pseudopotential is not only confined to the region of non-vanishing electron density, but also depends on the frequency and the wavenumber of the wave under investigation. It comprises Lindhard's longitudinal and transverse dielectric functions internally, the scattering at the surfaces, and the vacuum dielectric function externally.

The solutions of second-order differential equations containing a confined potential are well known to be either plane waves or to decrease exponentially in the exterior. We obtain free electromagnetic modes, whose wavenumber is increased internally and whose eigenvalue spectrum is continuous. Since the outgoing and ingoing waves q_x and $-q_x$ are degenerate, we have

$$(a(x))_{ext} = a \cos q_x(x - x_0) \tag{37}$$

in the case of magnetic modes, whereas the case of electric modes is covered by adding the subscript $j = 1, 2$. We shall discuss the phase x_0 of the external modes in § 9.

Secondly, there are bulk modes which oscillate internally and decrease exponentially externally and whose eigenvalue spectrum is discrete. We denote the external damping parameter by π_x, ie we put

$$(a(x))_{ext} = a \exp(-\pi_x|x|) \tag{38}$$

where

$$\pi_x^2 = -q_x^2 = q_y^2 - (\omega/c)^2. \tag{39}$$

Thirdly, depending on the properties of the pseudopotential, it is possible that surface modes exist. They are localized at the surface and decrease exponentially internally and externally. Like the bulk modes, they satisfy equation (38) and contribute to the discrete eigenvalue spectrum.

In order to transform the above integro-differential equations (25) and (31), (33) into a linear secular system with discrete eigenvalues, we must try to reproduce on the left-hand side the matrix elements $\langle l_x|a(x)|k_x \rangle$ appearing on the right-hand side. This may be achieved by applying Green function techniques. The Green function of the differential operator $\nabla_x^2 + q_x^2$, which guarantees an exponential decrease externally for $q_x = i\pi_x$, can be written

$$G(x - \xi) = (2iq_x)^{-1} \exp(iq_x|x - \xi|), \tag{40}$$

yielding in the case of magnetic modes

$$a(x) = 2 \sum_{k_x} \sum_{l_x} Q(k_x, l_x) \langle l_x|a(x)|k_x \rangle \int_{x_1}^{x_2} d\xi \langle k_x|G(x - \xi)|l_x \rangle. \tag{41}$$

The lower and upper integration limits x_1 and x_2 are conveniently chosen to coincide with the slab surfaces. By multiplying equation (41) with a second pair $|m_x\rangle \langle n_x|$ of electron states and integrating over the slab we obtain the secular system

$$\langle n_x|a(x)|m_x \rangle = 2 \sum_{k_x} \sum_{l_x} Q(k_x, l_x) \langle l_x|a(x)|k_x \rangle \langle n_x|\langle k_x|G(x - \xi)|l_x \rangle|m_x \rangle. \tag{42}$$

The inner integration in the last term on the right-hand side refers to ξ, and the outer integration refers to x. Interchanging the arguments x and ξ leaves the Green function $G(x - \xi)$ unchanged, so that the pairs $|l_x\rangle \langle k_x|$ and $|m_x\rangle \langle n_x|$ may also be interchanged.

The secular system (42) contains more equations than we need. The electron states $|k_x\rangle$ represent a complete set of functions in the slab, whereas the considered set of products $|l_x\rangle\langle k_x|$ is overcomplete. We are free to select a complete set of products $|m_x\rangle\langle n_x|$ and to expand the matrix elements $\langle l_x|a(x)|k_x\rangle$ accordingly. We may, in particular, choose $\langle n_x|$ to be a fixed electron state and run through the set of states $|m_x\rangle$ only. Another appropriate expansion is that with respect to the electron density $|m_x\rangle\langle m_x|$ in the individual states $|m_x\rangle$. The inversion of the reduced secular system (42) is the central task in order to find the possible eigenfrequencies of magnetic modes in the presence of a metal slab. The corresponding eigenfrequencies of electric modes arise by applying an equivalent Green function and integration technique to equations (31) and (33).

7. Jellium slab

In order to simplify the above secular system, let us assume that we may represent the one-electron potential of the metal slab under investigation by a rectangular potential well with depth ΔU. We are then dealing with free electrons moving in the rectangular potential of a positive background, ie with a jellium. We find bound electron states, which are plane waves internally and drop off exponentially externally, and free electron states, which are plane waves internally and externally. We are mainly interested in the bound states. Assuming the surfaces of the potential well to be at ξ_1 and ξ_2 (see figure 1), we put

$$|k_x\rangle = \begin{cases} c_1 \exp(+\varkappa_x x) & \text{on the left} \\ c_2 \sin k_x(x-x_1) & \text{internally} \\ c_3 \exp(-\varkappa_x x) & \text{on the right} \end{cases} \tag{43}$$

with the internal wavenumber k_x and the external exponent $\varkappa_x$ being related by the depth ΔU of the potential well according to

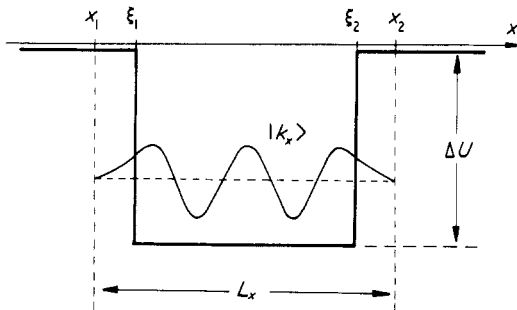$$(\hbar^2/2m)(k_x^2 + \varkappa_x^2) = \Delta U. \tag{44}$$

Figure 1. Jellium slab.

If we require continuity of $|k_x\rangle$ and $\nabla_x|k_x\rangle$ across the surfaces at ξ_1 and ξ_2 we obtain the boundary conditions

$$\varkappa_x = k_x \cot k_x(\xi_1 - x_1) = -k_x \cot k_x(\xi_2 - x_1). \tag{45}$$

Hence,

$$k_x = \pi N/L_x, \qquad N \text{ integer} \tag{46}$$

$$L_x = (\xi_2 - \xi_1) + 2(\xi_1 - x_1) \tag{47}$$

$$\xi_1 - x_1 = k_x^{-1} \sin^{-1}[\hbar k_x/(2m\,\Delta U)^{1/2}]. \tag{48}$$

Provided that the kinetic energy of all states under consideration is small enough to prevent the electrons from leaving the jellium, $\hbar^2 k_x^2/2m < \Delta U$, we find that the phase $\xi_1 - x_1$ of the electron states $|k_x\rangle$ at the surfaces depends only smoothly on the wavenumber k_x, so that the set of possible wavenumbers according to equation (46) is approximately equidistant. The jellium appears to be broadened by twice the width $\xi_1 - x_1$. The effective thickness L_x of the slab according to equation (47) is given by the width $\xi_2 - \xi_1$ of the potential well plus twice the extension $\xi_1 - x_1$ of the electron states to the exterior. Normalizing states (43) within $-\infty \leqslant x \leqslant +\infty$ yields

$$c_2 = (2/L_x)^{1/2}. \tag{49}$$

A more rigorous treatment of the electron states in the vicinity of surfaces has to account for the fact that the electrons themselves disturb the rectangular potential attributed to the positive background. The electron density and the effective potential approach their bulk value via Friedel oscillations having twice the Fermi wavenumber (Bardeen 1936). However, accounting for these oscillations and for the external variation of the correlation and exchange potential would considerably exceed the scope of the present investigations.

8. Bulk and surface modes

Since the one-electron states $|k_x\rangle$ are plane waves internally, we find that the matrix elements arising in the secular system (42) are actually Fourier cosine transforms of $a(x)$ in the slab. Defining

$$a(p_x) = \int_{\text{slab}} dx\, a(x) \cos p_x(x - x_1) \tag{50}$$

where $p_x = \pi N/L_x$, N integer, we obtain

$$\langle l_x|a(x)|k_x\rangle = L_x^{-1}(a(k_x - l_x) - a(k_x + l_x)). \tag{51}$$

The Fourier cosine transformation of equation (41) yields

$$\left(p_x^2 + \pi_x^2 + L_x^{-1} \sum_{\pm k_x} Q(k_x, p_x + k_x)\right) a(p_x)$$

$$= L_x^{-1} \sum_{\pm k_x} \{Q(k_x, p_x + k_x) + \pi_x[1 - \exp(ip_x L_x - \pi_x L_x)]S(p_x + 2k_x, \pi_x)\} a(p_x + 2k_x) \tag{52}$$

where

$$S(p_x, \pi_x) = L_x^{-1} \sum_{\pm k_x} Q(k_x, p_x + k_x)\{(p_x^2 + \pi_x^2)^{-1} - [(p_x + 2k_x)^2 + \pi_x^2]^{-1}\}. \tag{53}$$

Equation (52) represents an explicit secular system for magnetic bulk and surface modes. The factor $1 - \exp(ip_x L_x - \pi_x L_x)$ in front of the second term on the right-hand side of equation (52) characteristically depends on the question of whether the wave under investigation fits into the slab. If the thickness of the slab is small compared to the external extension of the wave, $\pi_x L_x \ll 1$, this factor oscillates as $\sin \frac{1}{2} p_x L_x$, ie the wavelength is compared with the slab thickness. In the opposite case, when the external extension of the wave can be neglected, this factor approaches one.

Attempting to represent the amplitude $a(x)$ in the slab in terms of the Fourier components (50), we note that equation (52) provides Fourier cosine components with respect to twice the slab thickness, $2L_x$, but no Fourier sine components. Putting

$$(a(x))_{\text{slab}} = L_x^{-1} \sum_{\pm p_x} a(p_x) \cos p_x(x - x_1), \tag{54}$$

we actually obtain that function which arises by continuing $a(x)$ symmetrically across the surfaces x_1 and x_2. We can use equation (54) for finding $(a(x))_{\text{surface}}$, but may not differentiate with respect to x at the surface: the derivative is discontinuous.

Let us now consider electric bulk and surface modes. Rather than the single differential equation (25), we have to solve the coupled differential equations (31) and (33). Using the jellium states (43) we find that the matrix elements of $a_j(x)$, $j = 1, 2$, arising in equations (31) and (33) are actually Fourier sine transforms of $a_j(x)$ in the slab. Now defining

$$a_j(p_x) = \int_{\text{slab}} \mathrm{d}x \, a_j(x) \sin p_x(x - x_1) \tag{55}$$

we obtain

$$\langle \nabla_x l_x | a_j(x) | k_x \rangle = l_x L_x^{-1}(a_j(k_x + l_x) + a_j(k_x - l_x)) \tag{56}$$

$$\langle l_x | a_j(x) | \nabla_x k_x \rangle = k_x L_x^{-1}(a_j(l_x + k_x) + a_j(l_x - k_x)). \tag{57}$$

The transformation of equations (31) and (33) into a set of linear secular equations for $a_j(p_x)$ is not quite as straightforward as in the case of magnetic modes. The integration of equations (31) and (33) by means of the Green function (40) yields the derivatives $\nabla_x a_j(x)$ rather than $a_j(x)$, $j = 1, 2$. Applying a Fourier cosine transformation to the resultant equations, we obtain

$$\int_{\text{slab}} \mathrm{d}x \, \nabla_x a_j(x) \cos p_x(x - x_1) = p_x a_j(p_x) + [a_j(x) \cos p_x(x - x_1)]_{x_1}^{x_2}, \tag{58}$$

ie there arise surface terms $a_j(x_1)$ and $a_j(x_2)$ which cannot be expressed in terms of the Fourier sine components $a_j(p_x)$ for a similar reason as in the case of magnetic modes: the Fourier series

$$(a_j(x))_{\text{slab}} = L_x^{-1} \sum_{\pm p_x} a_j(p_x) \sin p_x(x - x_1) \tag{59}$$

represents that function, which results by continuing $a_j(x)$ antisymmetrically across the surfaces x_1 and x_2.

In order to eliminate the surface terms, we apply the Fourier cosine transformation a second time directly to equations (31) and (33) without using the Green function technique. The surface terms arising now can be eliminated by means of those obtained

before and we find

$$-(p_x^2+\pi_x^2)a_1(p_x)+L_x^{-1}\sum_{\pm k_x}\sum_j p_x^{-1}[(p_x+k_x)Q_{1j}-k_xQ_{2j}]a_j(p_x)$$

$$= L_x^{-1}\sum_{\pm k_x}\sum_j \{p_x^{-1}[(p_x+k_x)Q_{1j}-k_xQ_{2j}]$$

$$-p_x\pi_x^{-1}[1-\exp(ip_xL_x-\pi_xL_x)]S_{1j}(p_x+2k_x,\pi_x)\}a_j(p_x+2k_x)\qquad(60)$$

where

$$S_{1j}(p_x,\pi_x) = L_x^{-1}\sum_{\pm k_x}[(p_x+k_x)Q_{1j}-k_xQ_{2j}]\{(p_x^2+\pi_x^2)^{-1}-[(p_x+2k_x)^2+\pi_x^2]^{-1}\}.\qquad(61)$$

The arguments of Q_{ij} in equations (60) and (61) are $Q_{ij}(k_x,p_x+k_x)$. The corresponding secular equations containing $a_2(p_x)$ arise by replacing the kernels $Q_{ij}(k_x,p_x+k_x)$ by the kernels $R_{ij}(k_x,p_x+k_x)$ and $S_{1j}(p_x,\pi_x)$ by $S_{2j}(p_x,\pi_x)$ in equations (60) and (61). Equation (60) together with the corresponding equation for $a_2(p_x)$ represents an explicit secular system for electric bulk and surface modes. Like the respective secular system (52) for magnetic modes, equation (60) contains the factor $1-\exp(ip_xL_x-\pi_xL_x)$ which compares the wavelength and the external extension of the wave with the slab thickness.

A real bulk mode is characterized by the fact that a single Fourier component $a_j(p_x)$ dominates the others. Equating to zero the diagonal terms on the left-hand sides of equations (52) and (60), we recover Lindhard's dielectric functions for longitudinal and transverse bulk modes. The perturbation of these bulk modes by the scattering at the surfaces is given by the off-diagonal terms on the right-hand sides of equations (52) and (60). Applying perturbation theory to the secular systems (52) and (60), we learn that the mutual repulsion of the bulk modes by their interaction at the surfaces is generally proportional to the inverse slab thickness.

We expect a real surface mode to decrease exponentially in the interior as well. In that case we cannot single out a distinct Fourier component $a_j(p_x)$, but have to look for additional solutions of the full secular systems (52) and (60). From the theory of electron states it is known that the question of whether real surface states exist depends sensitively on the precise form of the surface potential. This statement holds in the present case, where we consider electromagnetic waves in the pseudopotential caused by the electron transitions. An argument in favour of surface modes is the fact that the eigenvalue spectrum formed by the bulk modes turns out to be rather narrow, which makes the existence of additional states more likely.

9. External modes

Free electromagnetic modes, in contrast to the bulk and surface modes, allow for an arbitrary phase at the surfaces. By making use of equation (37) we do not obtain a secular system but a continuum of allowed frequencies. We are now interested in the phase shift of the free modes at the surfaces. By a direct Fourier cosine transformation of equation (25) in the slab we find

$$(q_x^2-p_x^2)a(p_x)+[\cos p_x(x-x_1)\nabla_x a(x)]_{x_1}^{x_2}$$

$$= L_x^{-1}\sum_{\pm k_x}Q(k_x,k_x+p_x)(a(p_x)-a(2k_x+p_x)).\qquad(62)$$

Equation (62) relates the internal Fourier components $a(p_x)$ to the derivative $\nabla_x a(x)$ at the surface, equation (54) gives $a(x)$ at the surface in terms of the internal Fourier

components $a(p_x)$, and equation (37) relates $\nabla_x a(x)$ and $a(x)$. Solving these equations by iteration we obtain

$$\cot q_x(x_1 - x_0) + \cot \tfrac{1}{2}q_x L_x = L_x^{-1} \sum_{\pm p_x} [2q_x/(q_x^2 - p_x^2)]S(p_x, -iq_x) \tag{63}$$

where $S(p_x, -iq_x)$ is given by equation (53). The off-diagonal terms in the secular system (52), which determine the interaction between the bulk modes, also give rise to the phase shift of the free modes.

The second term on the left-hand side of equation (63) has been obtained by using the representation of $\cot \tfrac{1}{2}q_x L_x$ in terms of its poles, ie

$$L_x^{-1} \sum_{\pm p_x} 2q_x/(q_x^2 - p_x^2) = \cot \tfrac{1}{2}q_x L_x \quad \text{or} \quad \cot \tfrac{1}{2}(q_x L_x + \pi) \tag{64}$$

depending on whether we consider even or odd solutions with respect to the centre, $p_x = \pi N/L_x$, N even or odd. Equation (64) gives the phase of the unperturbed modes at the surfaces $x = x_1, x_2$. If not stated otherwise, we consider the equations referring to the even solutions in the following.

The right-hand term in equation (63) is conveniently summed by dissecting it into partial fractions and using the theorem of residues. This is done in the appendix. We obtain three characteristic contributions: there are terms proportional to $\cot \tfrac{1}{2}q_x L_x$ which compare the wavelength with the slab thickness, terms proportional to $(d/dq_x) \cot \tfrac{1}{2}q_x L_x$ which may be ascribed to a change of the internal wavelength, and there is an integral over $\cot \tfrac{1}{2}p L_x$ where p is the normal wavenumber of the possible electron transitions. This term compares the wavelength of the electron transitions with the slab thickness. The integration over p runs partly along the imaginary axis if the tangential wavenumber q_y exceeds $m\omega/\hbar k_F$, and fully along the imaginary axis if q_y exceeds $2k_F$; $\cot \tfrac{1}{2}p L_x$ then approaches $\pm i$ and the term under consideration takes a constant value.

We conclude: the phase shift of an external magnetic mode with wavenumber $(q_x, q_y, 0)$ changes drastically if the tangential component q_y exceeds two times the Fermi wavenumber k_F. A similar statement holds for the normal component q_x. The main dependence on the normal wavenumber q_x is included in the factor $\cot \tfrac{1}{2}q_x L_x$, which is due to the question of whether the wave under consideration fits into the slab.

The case of electric modes is again somewhat more involved than that of magnetic modes due to the fact that we have to consider two coupled amplitudes $a_1(x)$ and $a_2(x)$ and because the internal Fourier expansion (59) diverges at the surfaces. Both the internal electric amplitude $a_1(x)$ and the internal longitudinal amplitude $a_2(x)$ represent an electric mode externally. The effective external amplitude of the electric mode (28) is given by $a_1(x) - a_2(x)$. A variation of the external amplitudes, which maintains their difference, entails a gauge transformation of the four-potential, but no change of the electric and magnetic fields according to equation (16). Although the Fourier expansion (59) for $(a_j(x))_{slab}$ represents its antisymmetric continuation across the surfaces, we may still use it for calculating $(\nabla_x a_j(x))_{surface}$ if we are able to separate off the discontinuous contribution at the surfaces.

In a similar manner to our procedure in the case of magnetic modes, we calculate the phase shift of the electric modes by first expressing the Fourier components $a_j(p_x)$ in terms of the amplitudes $a_j(x)$ at the surface. Then we represent $\nabla_x a_j(x)$ at the surface in terms of the Fourier components $a_j(p_x)$ by means of equation (59). Finally, interrelating

$\nabla_x a_j(x)$ and $a_j(x)$ by means of equation (37), we obtain

$$\tan q_x(x_1 - x_0) + \tan \tfrac{1}{2} q_x L_x = L_x^{-1} \sum_{\pm p_x} [2q_x/(q_x^2 - p_x^2)] T(p_x, -iq_x) \tag{65}$$

where

$$T(p_x, -iq_x) = L_x^{-1} \sum_{\pm k_x} R(k_x, p_x + k_x)\{(p_x^2 - q_x^2)^{-1} - [(p_x + 2k_x)^2 - q_x^2]^{-1}\} \tag{66}$$

$$R(k_x, l_x) = (e^2/2\pi) \iint dk_y\, dk_z\, f_k \sum_{\pm \omega} [1 + (\hbar\omega/mc^2)(k_x^2 - l_x^2)/q_x^2]$$

$$\times [1 + (\hbar\omega/mc^2)(k_y^2 - l_y^2)/q_y^2]/(E_k - E_l + \hbar\omega). \tag{67}$$

The quantities $T(p_x, -iq_x)$ and $R(k_x, l_x)$ are introduced in analogy with the quantities $S(p_x, -iq_x)$ and $Q(k_x, l_x)$ used in the case of magnetic modes. Equations (65) to (67) correspond to equations (63), (53) and (26) respectively. The further evaluation of the phase shift of external electric modes is strictly in line with the procedure used for magnetic modes. The striking difference between the phase shift of electric and magnetic modes is the fact that the effective electric response function $R(k_x, l_x)$ is larger than the magnetic response function $Q(k_x, l_x)$ by the factor $(mc/\hbar k_F)^2$. The electric modes interact with internal longitudinal and transverse modes. The magnetic modes interact with internal transverse modes only. The longitudinal bulk modes push the electric modes strongly out of the slab. The metal slab under investigation is strongly birefringent.

It is now necessary to emphasize that in this and in the preceding section we have used an iteration method up to terms of order one. We have considered the terms linear in the interaction between external and internal modes only. It is the higher-order terms which account for the screening and cause the impenetrability of the slab for particular modes. We have to orthogonalize the external modes with respect to the bulk modes. The present iterative investigations apply to thin slabs only.

10. Macroscopic effects

Among the numerous applications of the present procedure, let us consider the reflectivity and the surface energy of the slab. In order to obtain the reflectivity, we are interested in such solutions of equations (25) and (31), (33) which represent ingoing waves on the left and outgoing waves on both sides. The ratio of the intensity of the outgoing wave to that of the ingoing wave on the left is the reflectivity of the slab. We have to combine the even and odd solutions under consideration in such a manner that the ingoing contribution vanishes on the right. Putting on the left

$$(a(x))_{\text{ext}} = a_{\text{even}} \cos q_x(x - x_{\text{even}}) + a_{\text{odd}} \sin q_x(x - x_{\text{odd}}) \tag{68}$$

and equating to zero the ingoing contribution on the right, we obtain the reflectivity

$$R = \sin^2 q_x(x_{\text{even}} - x_{\text{odd}}). \tag{69}$$

Using the addition theorems for circular functions we are able to represent the reflectivity of the slab fully in terms of the phase shifts discussed in the preceding sections, that is

$$R = \frac{[1 - \cot q_x(x_1 - x_{\text{even}}) \tan q_x(x_1 - x_{\text{odd}})]^2}{[1 + \cot^2 q_x(x_1 - x_{\text{even}})][1 + \tan^2 q_x(x_1 - x_{\text{odd}})]}. \tag{70}$$

The factor $\cot q_x(x_1 - x_{even})$ is given by equations (63) and (65) for the case of magnetic and electric modes respectively; $\tan q_x(x_1 - x_{odd})$ results from these equations by shifting the argument of all circular functions by $\frac{1}{2}\pi$. The reflectivity R thus exhibits mainly the same dependence on frequency, angle of incidence, and Fermi wavenumber as does the phase shift.

In order to obtain the surface energy of the slab under investigation we compare a slab with thickness $2(\xi_2 - \xi_1)$ with two slabs with thickness $\xi_2 - \xi_1$ at infinite separation. The resultant change in total free energy of the electromagnetic modes yields twice the surface energy of the slab. Let us first consider two slabs with thickness $\xi_2 - \xi_1$ at finite separation and introduce a large, perfectly reflecting cavity at $\pm x_C$, which singles out a discrete spectrum of possible frequencies of the electromagnetic modes and thus makes possible the integration of the total free energy. In that case we have to compose the even and odd solutions (68) corresponding to the individual slabs in such a way that even or odd solutions with respect to the centre and zero amplitude at $x = x_C$ arise. We obtain

$$\cos q_x[x_C - \tfrac{1}{2}(x_1 + x_2) + \Delta_{even}]\{\cos, \sin\}q_x(\tfrac{1}{2}(x_1 + x_2) + \Delta_{odd})$$
$$+ \sin q_x(x_C - \tfrac{1}{2}(x_1 + x_2) + \Delta_{odd})\{-\sin, \cos\}q_x(\tfrac{1}{2}(x_1 + x_2) + \Delta_{even}) = 0 \quad (71)$$

where Δ_{even} and Δ_{odd} are the phase shifts of the modes even and odd with respect to the individual slabs, whereas the braces $\{\cos, \sin\}$ and $\{-\sin, \cos\}$ refer to the modes even and odd with respect to the coupled system.

In the second case of interest, when the two slabs are in contact, we denote the resulting phase shifts by Γ_{even} and Γ_{odd}. We obtain the dispersion relations

$$\cos q_x(x_C + \Gamma_{even}) = 0$$
$$\sin q_x(x_C + \Gamma_{odd}) = 0. \tag{72}$$

The surface energy of the slab is obtained by providing all electromagnetic modes allowed according to dispersion relations (71) and (72) with the free energy of bosons and summing the change in free energy in the case of contact and infinite separation, ie

$$2E_{surface} = \sum_{all\ modes} [kT \ln 2 \sinh(\hbar\omega/2kT)]_{sep}^{con}. \tag{73}$$

From the theory of van der Waals attraction it is known that the sum in equation (73) can be calculated without explicitly solving dispersion relations (71) and (72) for the allowed frequencies. We may replace the summation over all zeros of these dispersion functions by a contour integral around the poles of the logarithmic derivative of the dispersion functions (van Kampen *et al* 1968, Richmond and Ninham 1971, Langbein 1974), yielding

$$2E_{surface}/L_y L_z = \sum_{el,\ mag} (2\pi)^{-2} \iint dq_y\, dq_z(\hbar/4\pi i) \oint_{-i\infty}^{+i\infty} d\omega\, \cot(\hbar\omega/2kT) \ln G(\omega). \tag{74}$$

The summation in equation (74) extends over electric and magnetic modes. The hyperbolic cotangent results from shifting by partial integration the derivative with respect to frequency from the dispersion function over to the free energy. $G(\omega)$ is the ratio of dispersion functions (72) and (71) when the slabs are in contact and at infinite separation.

Since we are now integrating along the imaginary frequency axis, we need $G(\omega)$ at imaginary frequencies only. We find that q_x also becomes imaginary according to equation (27). Putting $q_x = i\pi_x$ we may readily increase the size of the cavity and the separation of the slabs to infinity, $x_C \to \infty$ and $\frac{1}{2}(x_1 + x_2) \to \infty$, yielding

$$\ln G(\omega) = \pi_x[\Gamma_{even} + \Gamma_{odd} - 2(\Delta_{even} + \Delta_{odd})]. \tag{75}$$

The surface energy of the slab is obtained by integrating along the imaginary frequency axis the difference in phase shift between the slabs in contact and at infinite separation. There are generally two different contributions to the surface energy:

(i) In § 9 we considered the phase shift of the external modes up to iteration terms of order one only. A slab with double thickness causes twice the phase shift within this limit, suggesting that the surface energy would vanish. However, there is a difference in phase shifts left owing to the fact that a slab with thickness $2(\xi_2 - \xi_1)$ does not exhibit exactly twice the effective thickness L_x according to equation (47). The extension $\xi_1 - x_1$ of the electron states to the exterior is removed at the surfaces in contact. This contribution to the surface energy has been considered explicitly by Lang and Kohn (1970). We learn that it arises automatically also in van der Waals-type investigations into the surface energy.

(ii) The screening of the external electromagnetic waves is covered by the neglected iteration terms of order two. These terms decouple the distortion of the electromagnetic waves at the left-hand surface from that at the right-hand surface. Taking screening into account, we expect the phase shift and the surface energy to approach a constant value as a function of the slab thickness.

Finally, we should emphasize that the procedure used in this section is not limited to the contribution of the free electromagnetic modes to the surface energy. The dispersion functions (71) and (72) also include the bulk and surface modes which decrease exponentially in the exterior and are therefore not affected by the cavity at all. We have already noted in the preceding sections that it is the scattering terms at the surfaces which give rise to the confinement of the internal modes and the phase shift of the external modes.

11. Conclusions

The present investigations are basically semiclassical. We accounted for quantum theory merely by calculating the response of the electrons from the Schrödinger equation. Most of the above results hold if another means of calculating the response, such as the Boltzmann equation, is used. The Schrödinger equation provides the specific information on the energy of the single-electron excitations. Within this semiclassical limit we find full analogy between electromagnetic waves and electrons. The electromagnetic waves cause the potential in the Schrödinger equation which determines the properties and the energy of the electron states, and the electrons cause the pseudopotential in the Helmholtz equation which determines the properties and the energy of the electromagnetic waves. We find bulk, surface and free states in both cases. In the exterior the bulk states drop off exponentially, while the free states become plane waves.

The potential exerted by the electrons on the electromagnetic waves is a non-local pseudopotential which depends on the frequency and wavenumber of the electromagnetic wave and is confined to the region of non-vanishing electron density. We have derived

the secular equations for the bulk electromagnetic modes and have calculated the phase shift of the free electromagnetic modes. In the bulk we find both longitudinal and trans- . verse modes. The longitudinal bulk modes are the well known plasmons, ie they are many-electron states, which are confined to the slab by the pseudopotential caused by coherent single-electron oscillations. The transverse bulk modes are many-photon states, which are confined to the slab by the pseudopotential caused by coherent current oscillations.

The scattering at the surfaces causes a coupling between longitudinal and transverse modes. The normal current density must vanish. The magnetic bulk modes exhibit a current density tangential to the surface only. The surfaces cause a coupling between the magnetic bulk modes which is inversely proportional to the slab thickness. The electric bulk modes and the longitudinal modes exhibit a current density normal to the surface; they are mutually coupled. We obtain a secular system which contains the dielectric function of the bulk modes along the diagonal, whereas the off-diagonal elements are caused by the surface. Externally only electric and magnetic modes exist; they are orthogonal to the bulk modes. The phase shift of the magnetic modes is governed by the internal transverse dielectric function, whereas the phase shift of the electric modes is governed by the internal longitudinal dielectric function; the latter is larger than the former by a factor $(mc/\hbar k_F)^2$. The phase shift of the external modes found by means of the present procedure differs from that obtained on the basis of the usual permeability concept by the term which compares the normal wavelength of the single-electron transitions with the slab thickness. This normal wavelength becomes imaginary, ie we obtain an exponential decrease of the interaction internally, if the tangential wavenumber of the wave under consideration exceeds two times the Fermi wavenumber. The phase shift of the external modes depends drastically on the angle of incidence.

Both the reflectivity and the surface energy of the slab can be represented in terms of the phase shift of the external modes. The reflectivity exhibits mainly the same dependence on frequency, angle of incidence and Fermi wavenumber as does the phase shift. The surface energy is given by the phase shift at a slab of double thickness minus twice the phase shift at a slab of regular thickness at imaginary frequencies. It exhibits a contribution resulting from the extension of the electron states to the exterior and a contribution describing the lacking correlation of the electrons with the exterior. The controversy (Feibelman 1973, Kohn 1973, Budd and Vannimenus 1973, Barrera and Gerlach 1974) which has arisen over the papers of Lang and Kohn on the one hand, and of Schmit and Lucas on the other hand, is irrelevant. Van der Waals-type calculations on surface energy cover the extension of the electron states across the surfaces if allowance is made for the smooth variation of the dielectric function from the interior to the exterior. On the other hand, in the investigations reported by Lang and Kohn, we must stipulate that the correlation terms at the surface are adequately described by a one-electron pseudopotential.

Appendix. Evaluation of phase shift

The right-hand term in equation (63) is conveniently evaluated by dissecting it into partial fractions; $S(p_x, -iq_x)$ exhibits poles at $p_x = \pm q_x$, $p_x + 2k_x = \pm q_x$, and poles arising from the energy denominators of $Q(k_x, p_x + k_x)$ according to equation (26). Substituting

$$
\frac{2q_x}{p_x^2 - q_x^2}\left(\frac{1}{p_x^2 - q_x^2} - \frac{1}{(p_x + 2k_x)^2 - q_x^2}\right)
$$

$$
= \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}q_x}\frac{1}{q_x}\left(\frac{1}{p_x - q_x} - \frac{1}{p_x + q_x}\right) - \frac{1}{4k_x(k_x + q_x)}\left(\frac{1}{p_x - q_x} - \frac{1}{p_x + 2k_x + q_x}\right)
$$

$$
+ \frac{1}{4k_x(k_x - q_x)}\left(\frac{1}{p_x + q_x} - \frac{1}{p_x + 2k_x - q_x}\right) \tag{A.1}
$$

and re-labelling the summation over p_x in the terms containing $p_x + 2k_x$, we obtain

$$
\cot q_x(x_1 - x_0) + \cot \tfrac{1}{2}q_x L_x = -L_x^{-2}\sum_{\pm k_x}\left(\frac{\mathrm{d}}{\mathrm{d}q_x}\frac{1}{q_x} - \frac{1}{k_x(k_x + q_x)}\right)\sum_{\pm p_x}\frac{Q(k_x, p_x + k_x)}{p_x - q_x}. \tag{A.2}
$$

Summing first over p_x we denote the poles of $Q(k_x, p_x + k_x)$ with respect to p_x by p, ie

$$
p = \pm[k_x^2 + k_y^2 - (k_y + q_y)^2 \pm 2m\omega/\hbar]^{1/2} - k_x. \tag{A.3}
$$

Now breaking up also $Q(k_x, p_x + k_x)$ into partial fractions, summing over p_x and finally replacing the integration over k_y in $Q(k_x, p_x + k_x)$ by that over p, we obtain

$$
-L_x^{-1}\sum_{\pm p_x} Q(k_x, p_x + k_x)/(p_x - q_x)
$$

$$
= (e^2/4\pi mc^2)\left(\iint \mathrm{d}p\, q_y^{-1}\,\mathrm{d}k_z\, k_z^2 f_k \sum_{+,-}(\cot \tfrac{1}{2}pL_x - \cot \tfrac{1}{2}q_x L_x)/(p - q_x)\right.
$$

$$
\left. + \iint \mathrm{d}k_y\,\mathrm{d}k_z\, f_k \cot \tfrac{1}{2}q_x L_x\right). \tag{A.4}
$$

The integration over p in equation (A.4), as was the integration over k_y, is limited to the Fermi sphere $k \leqslant k_F$ by the occupation number f_k. This yields generally two different regions of integration corresponding to the two signs of the square root in equation (A.3). Difficulties in the above summations and integrations, which may arise by crossing a pole, can generally be overcome by slowly switching on the electromagnetic fields with a time constant α, ie $\omega \to \omega + i\alpha$. Inserting equation (A.4) into equation (A.2), we split the phase shift into three terms. Mainly for mathematical reasons we put

$$
\cot q_x(x_1 - x_0) + \cot \tfrac{1}{2}q_x L_x = (e^2/4\pi mc^2)(A_1 + A_2 + A_3) \tag{A.5}
$$

where

A_1 results by applying $L_x^{-1}\Sigma\,(\mathrm{d}/\mathrm{d}q_x)q_x^{-1}$ to the first integral on the right-hand side of equation (A.4);

A_2 results by applying $L_x^{-1}\Sigma\, k_x^{-1}(k_x + q_x)^{-1}$ to that integral; and

A_3 results by applying $L_x^{-1}\Sigma\,[(\mathrm{d}/\mathrm{d}q_x)q_x^{-1} - k_x^{-1}(k_x + q_x)^{-1}]$ to the second integral on the right-hand side of equation (A.4).

Provided that the slab thickness allows the replacement of the summation over k_x by an integration, it turns out convenient to interchange the k_x and p integrations in A_1 and A_2. Eliminating k_y from $k_x^2 + k_y^2 \leqslant k_F^2$ by means of equation (A.3), we find the region of integration with respect to k_x given by

$$\{k_x + \tfrac{1}{2}p[1 \mp 2m\omega/\hbar(p^2 + q_y^2)]\}^2 \leqslant q_y^2\{k_F^2/(p + q_y^2) - \tfrac{1}{4}[1 \mp 2m\omega/\hbar(p^2 + q_y^2)]^2\}. \tag{A.6}$$

The integrations over k_x and k_z in A_1 and A_2 are elementary. We obtain

$$A_1 = \tfrac{1}{4} \sum_{+,-} \int dp(p^2 + q_y^2)^{-1/2}\{k_F^2 - \tfrac{1}{4}(p^2 + q_y^2)[1 \mp 2m\omega/\hbar(p^2 + q_y^2)]^2\}^2$$

$$\times (d/dq_x)q_x^{-1}(\cot \tfrac{1}{2}pL_x - \cot \tfrac{1}{2}q_xL_x)/(p - q_x) \tag{A.7}$$

and a similar, somewhat more lengthy expression for the second contribution A_2. The integration over p in equation (A.7) extends over that region, where the expression in the brackets is positive, that is

$$[\tfrac{1}{2}(p^2 + q_y^2) - (k_F^2 \pm m\omega/\hbar)]^2 \leqslant k_F^2(k_F^2 \pm 2m\omega/\hbar) \tag{A.8}$$

and over both signs of p.

The third term A_3 can be integrated directly, yielding

$$A_3 = \left(\frac{4}{3}k_F^3 \frac{d}{dq_x} \frac{1}{q_x} + 2k_F + \frac{k_F^2 - q_x^2}{q_x} \ln \left| \frac{k_F + q_x}{k_F - q_x} \right| \right) \cot \tfrac{1}{2}q_xL_x. \tag{A.9}$$

We have now reduced the phase shift according to equation (A.5) to a single integration over p. The integrand in equation (A.7) vanishes at both boundaries according to equation (A.8). The pole $p = q_x$ is not crossed in the course of the integration; it lies below the lower integration limit. Thus we may break up integral (A.7) into two integrals containing either $\cot \tfrac{1}{2}pL_x$ or $\cot \tfrac{1}{2}q_xL_x$. The latter cotangent is not affected by the integration, so this integral is elementary. The factor $\cot \tfrac{1}{2}pL_x$ in the first integral oscillates rapidly. We have to take the principal value, which vanishes with increasing slab thickness L_x. However, there are no oscillations of $\cot \tfrac{1}{2}pL_x$ if the wavenumber tangential to the surface becomes large. By expanding the limits of the $p^2 + q_y^2$ integration according to equation (A.8) with respect to $2m\omega/\hbar k_F^2$, we obtain

$$(m\omega/\hbar k_F)^2 \leqslant p^2 + q_y^2 \leqslant (2k_F)^2 \pm 4m\omega/\hbar. \tag{A.10}$$

We find that the integration over p runs partly along the imaginary axis if q_y exceeds $m\omega/\hbar k_F$, and runs fully along the imaginary axis if q_y exceeds $2k_F$; $\cot \tfrac{1}{2}pL_x$ now approaches $\pm i$, so the integral over p takes on a constant value.

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