Pramāṇa, Vol. 10, No. 2, February 1978, pp. 179–200, © Printed in India.

Surface exciton modes for plane and spherical semiconductor-metal interfaces

S SRINIVASAN and SUDHANSHU S JHA
Tata Institute of Fundamental Research, Bombay 400 005

MS received 13 October 1977

Abstract. An approximate method is developed for investigating the nature of interface exciton modes in a composite spatially dispersive medium. The method is general enough to be applicable to any composite system, in which each component is described by an arbitrary bulk dielectric function $\epsilon(q, \omega)$. It is based on the extension of the usual electrostatic-image method of solving the Poisson's equation, in the presence of an external point charge in the system. We have applied our general method to a composite system of a finite metal slab surrounded by a semiconductor on one side and the vacuum on the other side. Similarly, we have also considered the case of a metallic sphere of radius R, surrounded by a semiconductor, with a spherical interface between them. With assumed spatially dispersive model dielectric functions for the bulk metal and the bulk semiconductor, the nature of the electron-electron interaction and the interface exciton modes in the metallic region are obtained in both the cases. For the relevant size of the metal large compared to the atomic dimensions over which the bulk dielectric functions are non-local due to the spatial dispersion, it is shown that one can obtain the interface exciton modes by first defining new effective dielectric functions for each of the media making the particular interface, and then using the usual expression which determines the modes in the non-dispersive case.

Keywords. Interface exciton; semiconductor; metal.

1. Introduction

The study of interface exciton modes in a composite system of a semiconductor and a metal is of paramount importance in understanding the nature of effective electron-electron interaction near the junction. The exciton modes are in fact determined by the poles of the modified electron-electron interaction in the vicinity of the interface. Hence, they play a definite role in determining various physical properties of the systems, e.g., in determining the possible existence of the exciton-exchange mechanism of superconductivity (Ginzburg 1970; Ginzburg and Kirzhnits 1972) in composite systems or in explaining the details of Schottky effect (Inkson 1972). Though it is very difficult to obtain (Mills 1972; Ritchie and Marusak 1966; Fuchs and Kliewal 1971; Maradudin and Mills 1973; Agarwal 1972) the nature of these modes exactly, because of the complex nature of the interface, it is often possible to have an understanding about their approximate behaviour near the interface. In the first approximation, this may be enough to answer, for example, whether the exchange of these excitons leads to an attractive interaction between metal electrons, thereby enhancing the superconducting transition temperature, as envisaged by the exciton-exchange mechanism of superconductivity (Rangarajan and Jha 1976; Inkson 1974; Allender *et al* 1973).

In this paper, we obtain the effective electron-electron interaction between metal electrons in a semiconductor-metal system to obtain the surface exciton mode frequencies. The bulk regions of the metal and the semiconductor are described by model dielectric functions. The metal dielectric function represents a spatially dispersive medium with a single plasmon pole, which in the static limit leads to the usual screened static Coulomb interaction. We have considered the situations in which the semiconductor dielectric function is either spatially non-dispersive or spatially dispersive, but we have chosen only a single-oscillator model to describe the bulk semiconductor mode frequency. In the classical image approximation, the electrostatic potential in each region, due to a charge $-e$ at $\mathbf{r}'$ in the metal region, can be written in two parts. The first part is the frequency-dependent screened Coulomb potential due to the charges inside the bulk metal, while the second part arises due to the presence of the other medium. The latter is determined by matching the potentials and the normal components of the displacement vector at the interface. The interaction between electrons at $\mathbf{r}$ and $\mathbf{r}'$ inside the metal region is, then, nothing but the value of the above potential at $\mathbf{r}$ times the electronic charge $-e$.

In section 2, we describe our model dielectric functions which can represent approximately the bulk metal and the bulk semiconductor. These are used here to study the exciton modes in plane as well as spherical interface systems. The exciton mode frequencies in the case of a plane interface are obtained in section 3. The metal is taken to be a slab of width L, with the semi-infinite semiconductor on one side and the vacuum on the other side. Here, $\mathbf{q}_t$, the tangential component of the wave vector of the exciton is still a good quantum number, though its component in the direction normal to the surface is no longer a constant of motion. Hence, we can plot the exciton mode frequencies as a function of q_t. The particular case of a spatially non-dispersive semiconductor in such a composite system has of course already been studied earlier (Rangarajan 1975; Rangarajan and Jha 1976). We consider a spherical interface system consisting of a metallic sphere of radius R inside an infinite semiconductor in section 4. Starting with a semiconductor which is spatially dispersive, we consider the limiting case when the semiconductor becomes spatially non-dispersive. This can be compared with the earlier results of Srinivasan and Jha (1977). In the case of a spherical interface, each of the exciton modes is labelled by its orbital l value, and the frequencies are obtained as a function of the radius of the metallic sphere. A discussion on the salient features of our calculations in the plane as well as the spherical interface systems is presented in section 5.

2. Model dielectric functions for the bulk metal and semiconductor

For many applications, the bulk metal may be represented by a wave vector and frequency dependent dielectric function

$$\epsilon_M(q,\omega)=\epsilon_{M\infty}+Q_s^2\Big/\left[q^2-\frac{\omega^2}{\omega_p^2}Q_s^2\right]=\epsilon_{M\infty}\left[1+q_s^2\Big/\left(q^2-\frac{\omega^2}{\Omega_p^2}q_s^2\right)\right] \tag{1}$$

where $q_s^2=Q_s^2\,\epsilon_{M\infty}^{-1}$, $\Omega_p^2=\omega_p^2\,\epsilon_{M\infty}^{-1}$ and $\epsilon_{M\infty}$ is the contribution from completely full bands, and where the average screening wave vector Q_s due to

the conduction electrons is of the order of the Thomas-Fermi wave vector $q_{\mathrm{TF}} = (6\pi ne^2/E_F)^{\frac{1}{2}}$. Here, $\omega_p = (4\pi ne^2/m)^{\frac{1}{2}}$ is the free electron plasma frequency corresponding to the conduction electrons. In the spatially non-dispersive case, i.e. when $q \ll Q_s$, this function describes the collective plasma mode correctly in that limit, while in the static limit, we get the usual screened Coulomb interaction.

When we look for a representation of the dielectric function for the semiconductor, life is not so simple, if we want to take into account the spatial dispersion as well as the frequency dependence of its dielectric function. Under an isotropic version of the two band model (Penn 1962), this problem can, however, be simplified considerably. In this model, assumed to consist of an empty conduction band and a full valence band, the Bloch states of wave vector $\mathbf{k}$ is taken as the linear combination of two plane waves of wave vector $\mathbf{k}$ and $\mathbf{k}' \equiv (k - 2k_F)\hat{k}$. In other words, the Bloch state of wave vector $\mathbf{k}$ in the band $b(=c$, the conduction band, or $=v$ the valence band) is

$$|\mathbf{k}, b\rangle = [\exp(i\mathbf{k}\cdot\mathbf{r}) + a_k^b \exp(i\mathbf{k}'\cdot\mathbf{r})] / [1 + (a_k^b)^2]^{1/2} \tag{2}$$

with the corresponding energy eigen values

$$E^c(\mathbf{k}) = \frac{1}{2}\left[E_k^0 + E_{k'}^0 + \left\{\left(E_k^0 - E_{k'}^0\right)^2 + E_g^2\right\}^{\frac{1}{2}}\right]$$

$$E^v(\mathbf{k}) = \frac{1}{2}\left[E_k^0 + E_{k'}^0 - \left\{\left(E_k^0 - E_{k'}^0\right)^2 + E_g^2\right\}^{\frac{1}{2}}\right] \tag{3}$$

Here,

$$a_k^b = \frac{1}{2} E_g \Big/ \left(E^b(\mathbf{k}) - \frac{\hbar^2 k'^2}{2m}\right) \tag{4}$$

$E_k^0 = (\hbar^2 k^2/2m)$, and E_g is the energy gap parameter which is adjusted to yield the correct static dielectric constant. The dielectric response function for the semiconductor can then be written as

$$\epsilon_S(\mathbf{q}, \omega) = \epsilon_{S\infty} + (4\pi e^2/q^2 \Omega_c) \sum_{\mathbf{k}} |\langle \mathbf{k}, c \,|\, \mathbf{k}+\mathbf{q}, v\rangle|^2 \times \left\{\frac{1}{E^c(\mathbf{k}) - E^v(\mathbf{k}+\mathbf{q}) - \hbar\omega} + \frac{1}{E^c(\mathbf{k}) - E^v(\mathbf{k}+\mathbf{q}) + \hbar\omega}\right\} \tag{5}$$

where Ω_c is the unit cell volume, and $\mathbf{k}$ runs over the entire first Brillouin zone. For completeness, we have also added the contribution $\epsilon_{S\infty}$ arising from other full bands in the semiconductor. In the zero frequency case, eq. (5) leads to the limiting values

$$\epsilon_S(\mathbf{q}, 0) \xrightarrow[q\to 0]{} \epsilon_{S\infty} + (\hbar\omega_{\mathrm{ps}}/E_g)^2 \tag{6}$$

$$\epsilon_S(\mathbf{q}, 0) \xrightarrow[q\to \infty]{} \epsilon_{S\infty} + (\hbar\omega_{\mathrm{ps}}/E_F)^2 \tag{7}$$

where, ω_{ps} is the plasma frequency corresponding to the free valence-electron density. We can interpolate between these two behaviours to choose, for all $\mathbf{q}$, the form

$$\epsilon_S(\mathbf{q}, 0) = \epsilon_{S\infty} + \frac{(\hbar\omega_{ps})^2}{E_g^2} \frac{1}{1+(E_F/E_g)^2 (q^2/k_F^2)}$$

$$\equiv \epsilon_{S\infty} + (\epsilon_0 - \epsilon_{S\infty})/(1 + q^2/\gamma^2) \tag{8}$$

where

$$\epsilon_0 - \epsilon_{S\infty} = (\hbar\omega_{ps}/E_g)^2; \ \gamma^2 = (\hbar\omega_{ps})^2 k_F^2 \ (\epsilon_0 - \epsilon_{S\infty})/E_F^2 \tag{9}$$

Now, we must incorporate the frequency dependence also. But it can be shown that no simple interpolation procedure works well in all the regions of $\mathbf{q}$ and ω. However, since for $\mathbf{q} = 0$, eq. (5) gives

$$\epsilon_S(0, \omega) = \epsilon_{S\infty} + \hbar^2\omega^2_{ps}/(E_g^2 - \hbar^2\omega^2), \tag{10}$$

we can combine eqs (8) and (10) into a single expression of the form

$$\epsilon_S(\mathbf{q}, \omega) = \epsilon_{S\infty}\left[1 + \frac{(\epsilon_0^* - 1)}{[1 + (q^2/\gamma^2) - (\omega^2/\omega_0^2)]}\right], \quad \epsilon_0^* = \frac{\epsilon_0}{\epsilon_{S\infty}} \tag{11}$$

where

$$\omega_0 = \omega_{ps}(\epsilon_0 - \epsilon_{S\infty})^{1/2} \tag{12}$$

is the usual transverse bulk mode exciton frequency of the semiconductor. Although, expression (11) is very crude, it may be enough for many calculations of interest in physics. The bulk mode longitudinal frequency for the semiconductor is, of course,

$$\omega_L = \omega_0(\epsilon_0/\epsilon_{S\infty})^{1/2}, \quad \gamma \to \infty \tag{13}$$

3. Plane interface exciton modes

We consider a composite system of a semiconductor and a metal with a plane interface taken to be the $z=0$ plane. The bulk semiconductor ($z<0$) is represented by the dielectric function $\epsilon_S(q, \omega)$ given by eq. (11). The metal is assumed to be of finite length L along the positive z-direction, beyond which is the vacuum. The model dielectric function given by eq. (1) represents the metal.

In any medium, the electrostatic potential $\Phi(\mathbf{r},\omega)$ at $\mathbf{r}$ is determined from the solution of Poisson equation

$$\mathbf{D}(\mathbf{r},\omega) = 4\pi \rho_{ext}(\mathbf{r}) \tag{14a}$$

where the displacement vector **D** is given by

$$\mathbf{D}(\mathbf{r}, \omega) = \int d^3r' \, \tilde{\tilde{\epsilon}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{E}(r', \omega) \tag{14b}$$

in terms of the unknown dielectric tensor $\tilde{\tilde{\epsilon}}$ for the whole medium, and where the electric field is

$$\mathbf{E}(\mathbf{r}, \omega) = \vec{\nabla} \Phi(\mathbf{r}, \omega). \tag{14c}$$

Here, $\rho_{\text{ext}}(\mathbf{r})$ is the external charge density within the medium. The general solution of eqs (14) for an arbitrary unbounded composite medium is of course given by

$$\Phi(\mathbf{q}, \omega) = \int \frac{d^3q'}{(2\pi)^3} \frac{4\pi\rho(\mathbf{q}')}{qq'} \epsilon^{-1}(\mathbf{q}, \mathbf{q}', \omega) \tag{15a}$$

$$\Phi(\mathbf{r}, \omega) = \int d^3r' \, K(\mathbf{r}, \mathbf{r}', \omega) \rho(\mathbf{r}') \tag{15b}$$

where $\Phi(\mathbf{q}, \omega)$ is the spatial Fourier transform of the potential $\Phi(\mathbf{r}, \omega)$, and where in terms of the matrix elements of inverse dielectric matrix ϵ^{-1},

$$K(\mathbf{r}, \mathbf{r}', \omega) = \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} \exp(i\mathbf{q}\cdot\mathbf{r}) \exp(-i\mathbf{q}'\cdot\mathbf{r}') \frac{4\pi\epsilon^{-1}(\mathbf{q}, \mathbf{q}')}{q\, q'} \tag{15c}$$

with

$$\epsilon(\mathbf{q}, \mathbf{q}') \equiv \mathbf{q} \cdot \tilde{\tilde{\epsilon}}(\mathbf{q}, \mathbf{q}', \omega) \cdot \mathbf{q}'/qq' \tag{15d}$$

$$\tilde{\tilde{\epsilon}}(\mathbf{r}, \mathbf{r}', \omega) = \int \frac{d^3q}{(2\pi)^3} \int \frac{d^3q'}{(2\pi)^3} \exp(i\mathbf{q}\cdot\mathbf{r}) \exp(-i\mathbf{q}'\cdot\mathbf{r}') \, \tilde{\tilde{\epsilon}}(\mathbf{q}, \mathbf{q}', \omega). \tag{15e}$$

However, the formal solution given above is of not much value since we have no knowledge of $\tilde{\tilde{\epsilon}}(\mathbf{r}, \mathbf{r}', \omega)$ near the interface of a composite medium. We must, therefore, investigate the problem of composite systems in some other way, which may be only approximate. Of course, we may model the bulk metal and the bulk semiconductor fairly well by homogeneous dielectric functions depending only on the difference $\mathbf{r}-\mathbf{r}'$. In such a case, $\epsilon(\mathbf{q}, \mathbf{q}') = \epsilon(\mathbf{q}, \omega)\,(2\pi)^3\,\delta(\mathbf{q}-\mathbf{q}')$; $\epsilon^{-1}(\mathbf{q}, \mathbf{q}') = [1/\epsilon(\mathbf{q}, \omega)]\,(2\pi)^3\,\delta(\mathbf{q}-\mathbf{q}')$, and

$$\Phi(\mathbf{q}, \omega) = \frac{4\pi\rho(\mathbf{q})}{q^2\epsilon(\mathbf{q}, \omega)}. \tag{15f}$$

In other words, for the bulk homogeneous medium, we have

$$\epsilon(\mathbf{r}, \mathbf{r}', \omega) = \epsilon(\mathbf{r} - \mathbf{r}', \omega) \tag{16}$$

and eq. (14a) becomes

$$\int \frac{d^3q}{(2\pi)^3} \exp(i\mathbf{q}\cdot\mathbf{r})\, q^2\, \epsilon(\mathbf{q},\omega)\, \Phi(\mathbf{q},\omega) = 4\pi\, \rho_{\text{ext}}(\mathbf{r}). \tag{17}$$

Since for bulk systems under consideration, $\epsilon(\mathbf{q},\omega)$ is independent of the direction of $\mathbf{q}$, i.e., $\epsilon(\mathbf{q},\omega) \equiv \bar{\epsilon}(q^2,\omega)$, eq. (17) can be rewritten as

$$\nabla^2\, [\bar{\epsilon}(-\nabla^2),\omega]\, \Phi(\mathbf{r},\omega) = 4\pi\, \rho_{\text{ext}}(\mathbf{r}). \tag{18}$$

The usual procedure to determine the potential at any point in a composite system is to solve eq. (17) or analogously eq. (18) in each bulk medium separately, and match the solutions using appropriate boundary conditions determined by the differential equation itself. In the general case, we have the well known continuity conditions, viz.

(i) the potential is continuous at the interface, i.e.,

$$\Phi_1(\mathbf{r},\omega)\,|_{\mathscr{S}} = \Phi_2(\mathbf{r},\omega)\,|_{\mathscr{S}} \tag{19}$$

and (ii) the normal component of the displacement vector is continuous at the interface, i.e.,

$$\hat{n}\cdot\mathbf{D}_1(\mathbf{r},\omega)\,|_{\mathscr{S}} = n\cdot\mathbf{D}_2(\mathbf{r},\omega)\,|_{\mathscr{S}} \tag{20}$$

where $\mathscr{S}$ is the boundary surface between media 1 and 2 and $\hat{n}$ is the normal to the surface $\mathscr{S}$.

To determine the potential we use the electrostatic image method. Considering two adjacent media Σ_1 and Σ_2, we note that the effect of one medium on the other is transmitted across the interface $\mathscr{S}$. Hence, we can replace Σ_2 entirely by Σ_1 and a charge distribution at $\mathscr{S}$. Now we have a single medium Σ_1 with some external charges, if any, that were originally in Σ_1 and the surface image charge distribution. Thus, using eq. (15f), the potential inside the medium Σ_1 can be written as

$$\Phi_1(\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3}\, [\exp(i\mathbf{q}.\mathbf{r})]\, \frac{4\pi}{q^2\epsilon_1(\mathbf{q},\omega)}\, [\rho_{1\,\text{ext}}(\mathbf{q}) + \rho_{1\,\text{im}}(\mathbf{q},\omega)]. \tag{21}$$

The displacement vector is given by

$$\mathbf{D}_1(\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3} \exp(i\mathbf{q}.\mathbf{r})(-i\mathbf{q})\, \frac{4\pi}{q^2}\, [\rho_{1\,\text{ext}}(\mathbf{q}) + \rho_{1\,\text{im}}(\mathbf{q},\omega)]. \tag{22}$$

Note that $\rho_{\text{im}}(\mathbf{r},\omega)$ is nonzero only at the interface $\mathscr{S}$. One can write solutions in other media in a similar manner and use the boundary conditions (19) and (20) to determine the unknown image charge densities at each interface. In our problem, an external point charge has to be put only in the medium in which the effective electron-electron interaction has to be obtained.

We consider a semiconductor-metal-vacuum system with plane interfaces and a charge $-e$ at $\mathbf{r}'$ inside the metal region (figure 1a). To obtain the potential at any point inside the metal region, the bulk semiconductor and the vacuum regions are replaced by the image charge distributions at the respective interface surfaces, i.e. at $z = 0$ and $z = L$ planes. The image charge at either of the interfaces, due to the external charge at $\mathbf{r}'$ in the metal, is found to have the form

$$\rho_{\text{im}}\ (\mathbf{r}, \omega) = -e\sigma\ (\ |\mathbf{r}_t - \mathbf{r}_t'\ |, z', \omega)\, \delta(z - z_s) \tag{23}$$

where $\mathbf{r}_t = (x, y)$ is the transverse part of $\mathbf{r}$ and where $z_S = 0$ or L, corresponding to the particular interface. Thus, corresponding to the image charge, distribution at the $z = z_s$ plane, the Fourier transform of eq. (23) is of the form

$$\rho_{\text{im}}\ (\mathbf{q}, \omega) = -e\ [\exp\ (-i\mathbf{q}_z z_s)]\ [\exp\ (-i\mathbf{q}_t.\mathbf{r}_t')]\ \rho_s\ (\mathbf{q}_t, z', \omega) \tag{24}$$

where $\mathbf{q}_t = (q_x, q_y)$. It implies that $\rho_s\ (\mathbf{q}_t, z', \omega)$ is the unknown function which enters at each surface in the finite region in each of the media, which has to be determined using the boundary conditions (19) and (20). Since there is also an external charge $-e$ at $\mathbf{r}'$ inside the metal, in the metal region we have

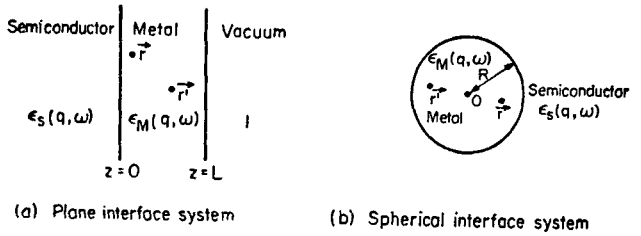
$$\rho_{M\text{ext}}\ (\mathbf{q},\omega) = -e\ \exp\ (-i\mathbf{q}\cdot\mathbf{r}'). \tag{25}$$

Using eqs (21), (24) and (25) the potential inside the metal region can, therefore, be written as

$$\Phi_M\ (\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3} \exp\ (i\mathbf{q}\cdot\mathbf{r})\ \exp\ (-i\mathbf{q}_t.\mathbf{r}_t')\ \frac{-4\pi e}{q^2 \epsilon_M\ (q, \omega)}$$

$$\times\ [\exp\ (-iq_z z') + \rho_{MS}\ (\mathbf{q}_t, z', \omega) + \rho_{MV}\ (\mathbf{q}_t, z', \omega)\ \exp\ (-iq_z L)]. \tag{26}$$

The unknown functions ρ_{ij} corresponds to the image charge distribution at the interface between media i and j, as seen from the i^{th} medium. Here, $i, j = M$ (metal), S (semiconductor), V (vacuum). Similarly, we can write the potential at any point



(a) Plane interface system (b) Spherical interface system

Figure 1. (*a*) A schematic diagram showing the geometry of the semiconductor-metal-vacuum plane interface system. (b) A schematic diagram for the semiconductor-metal spherical interface system.

inside the semiconductor and vacuum regions, respectively, as

$$\Phi_S(\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3} \exp(i\mathbf{q}.\mathbf{r}) \exp(-i\mathbf{q}_t.\mathbf{r}_t') \frac{-4\pi e}{q^2 \epsilon_S(q,\omega)} \rho_{SM}(\mathbf{q}_t, z', \omega) \quad (27)$$

$$\Phi_V(\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3} \exp(i\mathbf{q}.\mathbf{r}) \exp(-i\mathbf{q}_t.\mathbf{r}_t') \frac{-4\pi e}{q^2} \rho_{VM}(\mathbf{q}_t, z', \omega) \exp(-iq_z L). \quad (28)$$

By invoking the boundary conditions given by eqs (19) and (20) and using eqs (1) and (11) for ϵ_M and ϵ_S, we then obtain a system of four equations which determines the four unknown image functions ρ_{MS}, ρ_{MV}, ρ_{SM} and ρ_{VM}. These equations contain integrals of the type

$$\underset{\delta\to 0}{Lt} \int_{-\infty}^{\infty} \frac{dq_z}{2\pi} \frac{\exp(iq_z\delta)}{(q_z^2+q_t^2)\,\epsilon[(q_z^2+q_t^2)^{\frac{1}{2}},\omega]},$$

$$\underset{\delta\to 0^+,\,0^-}{\mathrm{Lt}} \int_{-\infty}^{\infty} \frac{dq_z}{2\pi} \frac{q_z \exp(iq_z\delta)}{q_z^2+q_t^2}, \text{ etc.} \quad (29)$$

which can easily be evaluated by the usual method of contour integration, once the specific forms for $\epsilon(q,\omega)$ are chosen. Instead of going through all the details here, it would be enough for our purpose to write down the final expressions for ρ_{MS} and ρ_{MV} which are obtained in this way, since we are interested in the nature of the electron-electron interaction in the metal region only. We find

$$\begin{aligned}\rho_{MS}(\mathbf{q}_t, z', \omega) = \frac{1}{\Delta(q_t,\omega)}\Big[&\{(\epsilon_{M\mathrm{eff}}+a\epsilon_{S\mathrm{eff}}) \exp(-q_t z') \\ &- (1+a)\,\epsilon_{S\mathrm{eff}} \exp(-Sz')\}(1+\epsilon_{M\mathrm{eff}}) \\ &+ \{(\epsilon_{M\mathrm{eff}}+a\epsilon_{S\mathrm{eff}} \exp(-q_t L) - (1+a)\epsilon_{S\mathrm{eff}} \exp(-SL)\} \\ &\times \{(\epsilon_{M\mathrm{eff}}+a)\exp[-q_t(L-z')] - (1+a)\exp[-S(L-z')]\}\Big] \quad (30)\end{aligned}$$

$$\begin{aligned}\rho_{MV}(\mathbf{q}_t, z', \omega) = \frac{1}{\Delta(q_t,\omega)}\Big[&-(\epsilon_{M\mathrm{eff}}+\epsilon_{S\mathrm{eff}}) \\ &\times \{(\epsilon_{M\mathrm{eff}}+a)\exp[-q_t(L-z')] - (1+a)\exp(-S(L-z')\} \\ &- \{(\epsilon_{M\mathrm{eff}}+a)\exp(-q_t L) - (1+a)\exp(-SL)\} \\ &\times \{(\epsilon_{M\mathrm{eff}}+a\epsilon_{S\mathrm{eff}})\exp(-q_t z') - (1+a)\,\epsilon_{S\mathrm{eff}} \exp(-Sz')\}\Big] \quad (31)\end{aligned}$$

where

$$\Delta(q_t, \omega) = [\epsilon_{M\text{eff}} + \epsilon_{S\text{eff}}]\,[1 + \epsilon_{M\text{eff}}]$$
$$- [(a + \epsilon_{M\text{eff}})\exp(-q_t L) - (1+a)\exp(-SL)]$$
$$\times [(a\epsilon_{S\text{eff}} + \epsilon_{M\text{eff}})\exp(-q_t L) - (1+a)\,\epsilon_{S\text{eff}}\exp(-SL)] \tag{32}$$

$$\epsilon_{M\text{eff}} = \frac{\epsilon_{M\infty}(1-\omega^2/\Omega_p^2)}{(q_t/S - \omega^2/\Omega_p^2)} \tag{33}$$

$$\epsilon_{S\text{eff}} = \frac{\epsilon_{S\infty}(\epsilon_0^* - \omega^2/\omega_0^2)}{[(q_t/Q)(\epsilon^*_0 - 1) + 1 - (\omega^2/\omega_0^2)]} \tag{34}$$

$$a = (\omega^2/\Omega_p^2)/\left[\frac{q_t}{S} - \frac{\omega^2}{\Omega_p^2}\right]. \tag{35}$$

In the above expressions,

$$S = \left[q_t^2 + q_s^2\left(1 - \frac{\omega^2}{\Omega_p^2}\right)\right]^{\frac{1}{2}}, \quad \text{if } \omega^2 < \Omega_p^2\left(1 + \frac{q_t^2}{q_s^2}\right) \tag{36a}$$

$$= \mp i\left[q_s^2\left(\frac{\omega^2}{\Omega_p^2} - 1\right) - q_t^2\right]^{\frac{1}{2}}, \quad \text{if } \omega^2 > \Omega_p^2\left(1 + \frac{q_t^2}{q_s^2}\right) \tag{36b}$$

$$Q = [q_t^2 + \gamma^2(\epsilon_0^* - \omega^2/\omega_0^2)]^{\frac{1}{2}}, \quad \text{if } \omega^2 < \omega_0^2\left(\epsilon_0^* + \frac{q_t^2}{\gamma^2}\right) \tag{37a}$$

$$= \mp i\left[\gamma^2\left(\frac{\omega^2}{\omega_0^2} - \epsilon_0^*\right) - q_t^2\right]^{\frac{1}{2}}, \quad \text{if } \omega^2 > \omega_0^2\left(\epsilon_0^* + \frac{q_t^2}{\gamma^2}\right) \tag{37b}$$

where, in the complex ω-plane, $(-)$ sign corresponds to frequencies $\pm(\omega + i\delta)$, while $(+)$ sign corresponds to frequencies $\pm(\omega - i\delta)$ where ω is the real positive frequency and $\delta \to 0^+$. From eqs (30) and (31), it can be seen that the zeroes of $\Delta(q_t, \omega)$ determine the poles of ρ_{MS} and ρ_{MV}. The expression (26) then implies that these zeroes determine all the interface modes at either of the surfaces in the metal, since the bulk mode is determined by the zeroes of $\epsilon_M(q, \omega)$ in eq. (26). Indeed for a very thick metal, i.e. when $q_t L \gg 1$, the equation $\Delta(q_t, \omega) = 0$ reduces to the simple form $[\epsilon_{M\text{eff}} + \epsilon_{S\text{eff}}]\,[1 + \epsilon_{M\text{eff}}] = 0$. The expression $\epsilon_{M\text{eff}} = -\epsilon_{S\text{eff}}$ then gives the interface modes localized at the metal-semiconductor interface (poles of ρ_{MS}), and $\epsilon_{M\text{eff}} = -1$ gives the modes localized at the metal-vacuum interface (poles of ρ_{MV}). In the spatially non-dispersive case, these results reduce to the usual interface mode dispersion relations. The interaction between two electrons at $\mathbf{r}$, $\mathbf{r}'$ inside the metal region is of course obtained from eq. (26), by multiplying it by $-e$. After inte-

grating over the polar coordinate φ_q, this is given by

$$V_M(\mathbf{r}, \mathbf{r}', \omega) = -e\Phi_M = 2e^2 \int_0^\infty dq_t \, q_t \frac{J_0(q_t | \mathbf{r}_t - \mathbf{r}'_t|)}{\Omega_p^2 - \omega^2}$$

$$\times \left[\left\{ \frac{\Omega_p^2}{S} \exp(-S|z-z'|) - \frac{\omega^2}{q_t} \exp(-q_t|z-z'|) \right\} \right.$$

$$+ \left(\frac{\Omega_p^2}{S} \exp(-Sz) - \frac{\omega^2}{q_t} \exp(-q_t z) \right) \rho_{MS}(\mathbf{q}_t, z', \omega)$$

$$\left. + \left(\frac{\Omega_p^2}{S} \exp\left[-S(L-z)\right] - \frac{\omega^2}{q_t} \exp\left[-q_t(L-z)\right] \right) \rho_{MV}(\mathbf{q}_t, z', \omega) \right]. \quad (38)$$

We observe that the interaction in the metal region consists of two parts. The terms in the curly brackets in the integrand of eq. (38) form the direct part corresponding to the bulk dynamically screened Coulomb interaction, while the rest of the terms form the image part arising due to the presence of other media. In fact, when the metal dielectric function is spatially non-dispersive, i.e. when q_s and hence $S \to \infty$, the direct term leads to the usual Coulomb interaction $e^2/|\mathbf{r}-\mathbf{r}'|\epsilon_M$. In the absence of spatial dispersion in both ϵ_M and ϵ_S, i.e. when $q_s \to \infty$, $\gamma \to \infty$, it can be shown after some involved algebra that the image part is just the usual electrostatic-image interaction in the presence of two different media of dielectric constants ϵ_S and 1, on either side.

As already stated, all the interface modes are determined by the poles of ρ_{MS} and ρ_{MV}, i.e. from the solution of the equation

$$\Delta(q_t, \omega) = 0 \quad (39)$$

where Δ is defined by eq. (32). Because of the complicated nature of $\Delta(q_t, \omega)$, it is not easy in general, to obtain its solutions in terms of q_t, analytically. However, we can look at some of the limiting cases analytically to get an idea about the nature of the interface exciton modes. These are discussed below.

3.1. *The case of a thick metal slab* (*Large* L)

In the limit $q_t L \gg 1$, which also implies $SL \gg 1$, eqs (39) and (32) give

$$\Delta(q_t, \omega) \xrightarrow[q_t L \gg 1]{} [\epsilon_{M\text{eff}} + \epsilon_{S\text{eff}}][1 + \epsilon_{M\text{eff}}] = 0. \quad (40)$$

From eqs (30) and (31), it is clear that in this limit, the interface modes localized at the metal-semiconductor interface (poles of ρ_{MS}) come from

$$\epsilon_{M\text{eff}} + \epsilon_{S\text{eff}} = 0 \quad (41)$$

since the factor $(1+\epsilon_{M\text{eff}})$ cancels out in ρ_{MS}. The zeroes of $(1+\epsilon_{M\text{eff}})$ give the

poles of ρ_{VS}, i.e. the interface modes localized at the metal-vacuum interface. In this limit (i.e. when $q_t L \gg 1$), these two types of interface modes are distinct, as it should be. Here, we are of course primarily interested in the interface modes localized at the metal-semiconductor interface. Equation (41) can be rewritten as

$$\epsilon_{M\infty}\left(1-\frac{\omega^2}{\Omega_p{}^2}\right)\left[\frac{q_t}{Q}(\epsilon_0{}^*-1)+1-\frac{\omega^2}{\omega_0{}^2}\right]+\epsilon_{S\infty}\left(\frac{q_t}{S}-\frac{\omega^2}{\Omega_p{}^2}\right)\left(\epsilon_0{}^*-\frac{\omega^2}{\omega_0{}^2}\right)=0. \tag{42}$$

For this case, the long wavelength modes ($q_t \to 0$) are determined by the equation

$$\epsilon_{M\infty}\left(1-\frac{\Omega_p{}^2}{\omega^2}\right)\left(1-\frac{\omega^2}{\omega_0{}^2}\right)+\epsilon_{S\infty}\left(\epsilon_0{}^*-\frac{\omega^2}{\omega_0{}^2}\right)=0. \tag{43}$$

This leads to two distinct long wavelength modes, with frequencies

$$\frac{\omega^2}{\omega_0{}^2}=\frac{1}{2(\epsilon_{M\infty}+\epsilon_{S\infty})}\left[\epsilon_{M\infty}+\epsilon_0+\epsilon_{M\infty}\frac{\Omega_p{}^2}{\omega_0{}^2}\right.$$

$$\left.\pm\left\{\left(\epsilon_{M\infty}+\epsilon_0+\epsilon_{M\infty}\frac{\Omega_p{}^2}{\omega_0{}^2}\right)^2-4\epsilon_{M\infty}(\epsilon_{M\infty}+\epsilon_{S\infty})\frac{\Omega_p{}^2}{\omega_0{}^2}\right\}^{\frac{1}{2}}\right]. \tag{44}$$

When $\Omega_p \gg \omega_0$, the surface metal plasmon mode gets decoupled from the surface semiconductor exciton mode. For $\epsilon_{M\infty}=\epsilon_{S\infty}=1$, the frequencies of these two modes are given by $\omega_1=\Omega_p/\sqrt{2}$ and $\omega_2=\omega_0$, respectively. In the limit $q_t/q_s \gg 1$ and $q_t/\gamma \gg 1$, eq. (42) becomes

$$\left(1-\frac{\omega^2}{\Omega_p{}^2}\right)\left(\epsilon_0{}^*-\frac{\omega^2}{\omega_0{}^2}\right)=0. \tag{45}$$

Here again, the interface exciton modes get decoupled. The surface metal plasmon mode has a frequency $\omega=\Omega_p$. The frequency of the surface semiconductor exciton mode for finite γ is $\omega=\omega_0(\epsilon_0{}^*)^{\frac{1}{2}}$, which is just the frequency of the longitudinal bulk mode of the semiconductor. However, when the semiconductor is spatially non-dispersive, i.e. when $\gamma=\infty$, eq. (42) becomes

$$\epsilon_{M\infty}\left(1-\frac{\omega^2}{\Omega_p{}^2}\right)(1-\omega^2/\omega_0{}^2)-\left(\frac{q_t}{S}-\frac{\omega^2}{\Omega_p{}^2}\right)\left(\epsilon_0{}^*-\frac{\omega^2}{\omega_0{}^2}\right)=0. \tag{46}$$

The surface exciton mode frequency for large q_t is then equal to $\omega_0[(\epsilon_0+1)/(\epsilon_{S\infty}+1)]^{\frac{1}{2}}$ which is the interface exciton frequency for a semiconductor-vacuum plane interface system. For a spatially nondispersive metal, the interface exciton frequencies are obtained by solving the $q_s \to \infty$ limit of eq. (42). In this case, we have

$$\frac{q_t}{Q}-\left(\frac{q_t}{Q}-1\right)\left(\frac{1-\omega^2/\omega_0{}^2}{\epsilon_0{}^*-\omega^2/\omega_0{}^2}\right)+\frac{\epsilon_{S\infty}/\epsilon_{M\infty}}{(1-\Omega_p{}^2/\omega^2)}=0 \tag{47}$$

which is in agreement with the results of Rangarajan (1973). To obtain the interface exciton frequencies for general q_t when both the metal and the semiconductor are spatially dispersive, one has to solve eq. (42). Inkson (1972) has obtained the dispersion curves in this case, by solving eq. (42) numerically.

3.2. *The case of a finite metal slab, with* $\Omega_p \gg \omega_0$

When $\Omega_p \gg \omega_0$, the interface exciton frequencies can be obtained by seeking the solutions of eq. (39) separately in the region $\omega \sim \Omega_p$ and in the region $\omega \ll \Omega_p$. Looking for solutions in the region $\omega \sim \Omega_p$, eq. (39) can be written as

$$(\epsilon_{M\text{eff}} + \epsilon_{S\infty})(1 + \epsilon_{M\text{eff}}) - [(\epsilon_{M\text{eff}} + a)\exp(-q_tL) - (1 + a)\exp(-SL)]$$
$$[(\epsilon_{M\text{eff}} + a\epsilon_{S\infty})\exp(-q_tL) - (1 + a)\epsilon_{S\infty}\exp(-SL)] = 0. \quad (48)$$

For $q_tL \gg 1$, eq. (48) leads to two interface exciton modes given by $\epsilon_{M\text{eff}} + \epsilon_{S\infty} = 0$ localized near the metal-semiconductor interface and $\epsilon_{M\text{eff}} + 1 = 0$ localized near the metal vacuum interface. Our main interest, however, is on the low energy excitons, i.e. in the region $\omega \ll \Omega_p$, in which case eq. (39) can be rewritten as

$$\left(\frac{S_\infty \epsilon_{M\infty}}{q_t} + \epsilon_{S\text{eff}}\right)\left(\frac{S_\infty \epsilon_{M\infty}}{q_t} + 1\right) - \left(\frac{S_\infty \epsilon_{M\infty}}{q_t}\exp(-q_tL) - \exp(-S_\infty L)\right)$$
$$\left(\frac{S_\infty \epsilon_{M\infty}}{q_t}\exp(-q_tL) - \epsilon_{S\text{eff}}\exp(-S_\infty L)\right) = 0 \quad (49)$$

where $S_\infty = (q_t^2 + q_s^2)^{1/2}$. To obtain the interface exciton mode frequencies, eq. (49) is rearranged and converted by squaring into a cubic equation in ω^2 which will have three roots. All these three roots may be real or one of them will be real with the other two forming a complex conjugate pair. It must be noticed that not all these three roots are necessarily the solution of eq. (49). However, there always exists one solution with real interface exciton frequencies (mode 1), which goes over to the only mode possible for $\gamma \to \infty$. For very small q_t, the frequency of mode 1 tends to the limit $\omega = \omega_0$, the bulk transverse mode frequency of the semiconductor. For large q_t, in the case of finite γ, eq. (49) has a solution $\omega = \omega_0 (\epsilon_0^*)^{\frac{1}{2}}$ which is the bulk longitudinal mode frequency of the semiconductor. For the case when $\gamma = \infty$, eq. (49) can be solved to yield

$$\frac{\omega^2}{\omega_0^2} = \left[\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} + \epsilon_0\right)\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} + 1\right)\right.$$

$$-\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} \exp(-q_t L) - \epsilon_0 \exp(-S_\infty L)\right)$$

$$\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} \exp(-q_t L) - \exp(-S_\infty L)\right)\Bigg]$$

$$\Bigg[\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} + \epsilon_{S\infty}\right)\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} + 1\right)$$

$$-\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} \exp(-q_t L) - \epsilon_{S\infty} \exp(-S_\infty L)\right)$$

$$\left(\frac{\epsilon_{M\infty} S_\infty}{q_t} \exp(-q_t L) \exp(-S_\infty L)\right)\Bigg]^{-1} \tag{50}$$

which for large q_t becomes $\omega^2/\omega_0^2 = (\epsilon_0 + 1)/(\epsilon_{S\infty} + 1)$, corresponding to the plane interface semiconductor-vacuum exciton frequency. In figure 2, we have plotted (ω/ω_0) corresponding to mode 1 as a function of (q_t/q_s) for three different values of $\gamma(=10q_s, 100q_s$ and $\infty)$. We have taken $\epsilon_{M\infty} = \epsilon_{S\infty} = 1$ and $q_s L = 1$, $\epsilon_0 = 16{\cdot}3$ corresponding to germanium. The bulk longitudinal and the bulk transverse modes of the semiconductor have also been plotted for comparison.

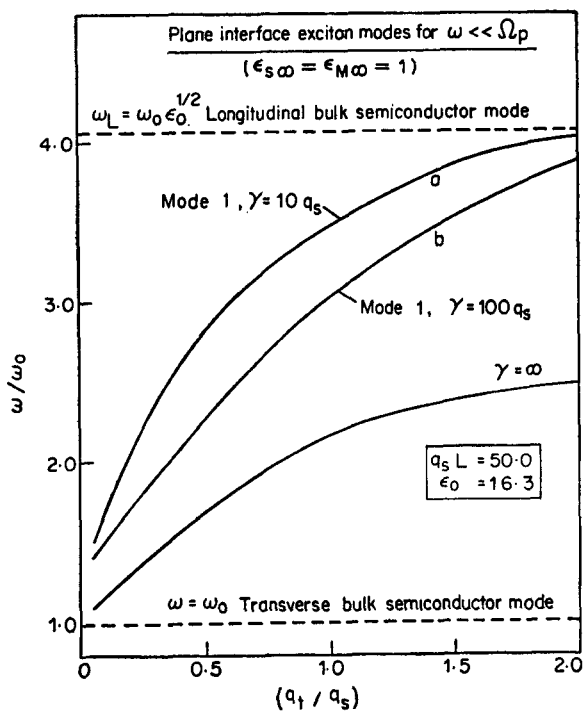


Figure 2. Dependence of the surface exciton mode frequencies localized at the metal-semiconductor interface on q_t/q_s, for different values of γ, when the bulk exciton frequency is small compared to the bulk metal plasma frequency. Here q_t is the magnitude of the wavevector transverse to the interface, and q_s and γ are parameters relating to the spatial dispersion of the bulk modes in the metal and semiconductor, respectively.

4. Exciton modes in spherical interface systems

Though the study of a plane interface metal-semiconductor system considered in the last section is quite rewarding, most of the practical systems have more complex interfaces. We, therefore, consider the case of the spherical interface also, which is often found, e.g., in systems with metal granules in a semiconductor matrix. For the sake of simplicity, we consider a metallic sphere of finite radius R, embedded in an infinite semiconductor. The bulk metal and the bulk semiconductor are represented by the model dielectric functions given by eqs (1) and (11), respectively.

The electrostatic potential $\Phi(\mathbf{r}, \omega)$ at any point $\mathbf{r}$ due to a charge $-e$ at $\mathbf{r}'$ inside the metal region (figure 1b) is determined by eqs (14a) to (14c). The boundary conditions to be used are given by eqs (19) and (20) which demand the continuity of the potential and the normal component of the displacement vector, respectively, at the interface. To obtain the potential, we again use the method of images, already described in the last section. The two different induced image charge distributions at the surface $r = R$, which one introduces to determine the potentials in the metal and semiconductor regions can both be expanded in the form

$$\rho_{\text{im}}(\mathbf{r}, \omega) = -\frac{e}{R^2}\delta(r - R)\,\sigma(\theta, \varphi, \mathbf{r}', \omega)$$

$$= -\frac{e}{R^2}\delta(r - R)\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sigma_{lm}(\mathbf{r}', \omega)\,Y_{lm}(\theta, \varphi) \qquad (51)$$

where Y_{lm}'s are the spherical harmonics. Because of the symmetry of the problem, each of the surface charge distributions are found to be of the simplified form

$$\rho_{\text{im}}(\mathbf{r}, \omega) = -\frac{e}{R^2}\delta(r-R)\sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_{lm}(r', \omega)$$

$$Y_{lm}^*(\theta', \varphi')\,Y_{lm}(\theta, \varphi) \qquad (52)$$

whose Fourier transform is

$$\rho_{\text{im}}(\mathbf{q}, \omega) =$$

$$-4\pi e\sum_{l=0}^{\infty}\sum_{m=-l}^{l} a_{lm}(r', \omega)\,j_l(qR)\,Y_{lm}^*(\theta', \varphi')\,Y_{lm}(\theta_q, \varphi_q) \qquad (53)$$

where j_l's are the spherical Bessel functions of the first kind. The unknown coefficients a_{lm}'s are, of course, different for the metal and the semiconductor regions. The Fourier transform of the external charge distribution function in the metal region is

$$\rho_{M\text{ext}}(\mathbf{q}, \omega) = -e\exp(-i\mathbf{q}.\mathbf{r}'). \qquad (54)$$

Using eqs (21), (53) and (54), the potential $\Phi(\mathbf{r}, \omega)$ at any point $\mathbf{r}$ inside the metal region can be written in the form

$$\Phi_M(\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3} \exp(i\mathbf{q}.\mathbf{r}) \frac{-4\pi e}{q^2} \frac{1}{\epsilon_M(q,\omega)}$$
$$\times \left[\exp(-i\mathbf{q}.\mathbf{r}') + 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm}(r',\omega) j_l(qR)\right.$$
$$\left. Y_{lm}^*(\theta',\varphi')\, Y_{lm}(\theta_q,\varphi_q)\right]. \tag{55}$$

Similarly, the potential at any point $\mathbf{r}$ inside the semiconductor region is written as

$$\Phi_S(\mathbf{r},\omega) = \int \frac{d^3q}{(2\pi)^3} \exp(i\mathbf{q}.\mathbf{r}) \frac{-4\pi e}{q^2} \frac{1}{\epsilon_S(q,\omega)}$$
$$\times \left[4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} b_{lm}(r',\omega) j_l(qR)\right.$$
$$\left. Y^*_{lm}(\theta',\varphi')\, Y_{lm}(\theta_q,\varphi_q)\right]. \tag{56}$$

After carrying out the integration over the angular coordinates θ_q and φ_q, eqs (55) and (56) can be rewritten as

$$\Phi_M(\mathbf{r},\omega) = -8e \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y^*_{lm}(\theta',\varphi')\, Y_{lm}(\theta,\varphi)$$
$$\left[\int_0^{\infty} \frac{j_l(qr)\, j_l(qr')}{\epsilon_M(q,\omega)} dq + a_{lm}(r',\omega) \int_0^{\infty} dq \frac{j_l(qr)\, j_l(qR)}{\epsilon_M(q,\omega)}\right] \tag{57}$$

$$\Phi_S(\mathbf{r},\omega) = -8e \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y^*_{lm}(\theta',\varphi')\, Y_{lm}(\theta,\varphi)$$
$$\left[b_{lm}(r',\omega) \int_0^{\infty} dq \frac{j_l(qr)\, j_l(qR)}{\epsilon_S(q,\omega)}\right] \tag{58}$$

The displacement vector $\mathbf{D}_M(\mathbf{r},\omega)$ in the metal region can be obtained from eq. (22) using eqs (53) and (54). After carrying out the integration over $\mathbf{q}$, the normal component of $\mathbf{D}(\mathbf{r},\omega)$, i.e. the component along $\hat{r}$, in the metal region can be written in the form

$$D_{Mn}(\mathbf{r},\omega) = -8e \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y^*_{lm}(\theta',\varphi')\, Y_{lm}(\theta,\varphi) \left(\frac{\pi}{2} \frac{1}{2l+1}\right)$$
$$\left[(l+1) \frac{r'^l}{r^{l+2}} \Theta(r-r') - l \frac{r^{l-1}}{r'^{l+1}} \Theta(r'-r) - l \frac{r^{l-1}}{R^{l+1}} a_{lm}(r',\omega)\right] \tag{59}$$

where $\Theta(r-r')$ is the usual step function. In a similar manner, the normal component of $\mathbf{D}$ in the semiconductor region can be written as

$$D_{Sn}(\mathbf{r},\omega) = -8e \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y^*_{lm}(\theta',\varphi')\, Y_{lm}(\theta,\varphi) \left(\frac{\pi}{2} \frac{1}{2l+1}\right)$$
$$\left[(l+1) \frac{R^l}{r^{l+2}} b_{lm}(r',\omega)\right] \tag{60}$$

Applying the boundary conditions given by eqs 19 and 20, on eqs. 57–60, we obtain a pair of equations to be solved for $a_{lm}(r', \omega)$ and $b_{lm}(r', \omega)$. The solutions are

$$a_{lm}(r', \omega) = \frac{-(l+1)\epsilon_{M\text{eff}}(l, R, \omega)\,[f_l(r', R\,\omega)\,\epsilon_{s\text{eff}}(l, R, \omega) - (r'^l/R^l)]}{l\epsilon_{M\text{eff}}(l, r, \omega) + (l+1)\epsilon_{s\text{eff}}(l, R, \omega)} \tag{61}$$

$$b_{lm}(r', \omega) = \frac{\epsilon_{s\text{eff}}(l, R, \omega)\,[lf_l(r', R, \omega)\,\epsilon_{M\text{eff}}(l, R, \omega) + (l+1)(r'^l/R^l)]}{l\epsilon_{M\text{eff}}(l, R, \omega) + (l+1)\epsilon_{s\text{eff}}(l, R, \omega)} \tag{62}$$

where

$$f_l(r', R, \omega) = \frac{\int_0^\infty dq \frac{j_l(qR)\, j_l(qr')}{\epsilon_M(q, \omega)}}{\int_0^\infty dq\, j_l(qR)\, j_l(qR)}$$

$$= \left(\frac{\pi}{2}\frac{1}{2l+1}\frac{1}{R}\right)^{-1} \int_0^\infty dq \frac{j_l(qR)\, j_l(qr')}{\epsilon_M(q, \omega)} \tag{63}$$

$$\epsilon^{-1}_{M\text{eff}}(l, R, \omega) = \frac{\int_0^\infty dq \frac{j_l(qR)\, j_l(qR)}{\epsilon_M(q, \omega)}}{\int_0^\infty dq\, j_l(qR)\, j_l(qR)}$$

$$= \left(\frac{\pi}{2}\frac{1}{2l+1}\frac{1}{R}\right)^{-1} \int_0^\infty dq \frac{j_l(qR)\, j_l(qR)}{\epsilon_M(q, \omega)} \tag{64}$$

$$\epsilon^{-1}_{s\text{eff}}(l, R, \omega) = \frac{\int_0^\infty dq \frac{j_l(qR)\, j_l(qR)}{\epsilon_S(q, \omega)}}{\int_0^\infty dq\, j_l(qR)\, j_l(qR)}$$

$$= \left(\frac{\pi}{2}\frac{1}{2l+1}\frac{1}{R}\right)^{-1} \int_0^\infty dq \frac{j_l(qR)\, j_l(qR)}{\epsilon_S(q, \omega)}. \tag{65}$$

Here, $\epsilon_{M\text{eff}}$ and $\epsilon_{s\text{eff}}$ can be recognised as the effective dielectric functions of the bulk metal and the bulk semiconductor. In the limit when both the media become spatially nondispersive the effective dielectric functions become just the corresponding bulk dielectric functions. The interaction between two electrons at $\mathbf{r}$ and $\mathbf{r}'$ inside the metal region is given by

$$V_M(\mathbf{r}, \mathbf{r}', \omega) = -e\,\Phi_M$$

$$= 8e^2 \sum_{l=0}^{\infty} \sum_{m=-l}^{l} Y_{lm}^{*}(\theta', \varphi)\, Y_{lm}(\theta, \varphi) \Bigg[\int_0^{\infty} dq\, \frac{j_l(qr)\, j_l(qr')}{\epsilon_M(q,\omega)}$$

$$- \left\{ \frac{(l+1)\, \epsilon_{M\text{eff}}(l, R, \omega)\, (f_l(r', R, \omega)\, \epsilon_{S\text{eff}}(l, R, \omega) - (r'^l/R^l)}{l\, \epsilon_{M\text{eff}}(l, R, \omega) + (l+1)\, \epsilon_{S\text{eff}}(l, R, \omega)} \right\}$$

$$\int_0^{\infty} dq\, \frac{j_l(qr)\, j_l(qR)}{\epsilon_S(q, \omega)} \Bigg] \tag{66}$$

where f_l, $\epsilon_{M\text{eff}}$ and $\epsilon_{S\text{eff}}$ are defined by eqs (63)-(65). Just as in the case of a plane interface, the interaction divides itself into two parts. The first term in the square brackets in eq. (66) is the direct part describing the dynamically repulsive screened Coulomb interaction, the poles of which will give the bulk metal plasmon modes. The second term is the image part arising due to the presence of the semiconductor. This term contains additional poles, incorporated in the terms in curly brackets in eq. (66), which give rise to the interfeace exciton modes. The longitudinal interface exciton frequencies are obtained by solving the equation

$$l\epsilon_{M\text{eff}}(l, R, \omega) + (l+1)\, \epsilon_{S\text{eff}}(l, R, \omega) = 0. \tag{67}$$

It is evident that the exciton frequencies are independent of m but there are different exciton modes corresponding to different l-values.

The electron-electron interaction and the equation for the interface exciton frequencies given by eqs (66) and (67) are, in fact, true for arbitrary $\epsilon_M(q, \omega)$ and $\epsilon_S(q, \omega)$. For the particular choice of the model dielectric functions given by eqs (1) and (11), evaluation of the integrals in eqs (63)-(65) leads to

$$f_l(r', R, \omega) = \frac{1}{\epsilon_{M\infty}} \frac{\omega^2}{\omega^2 - \Omega_p^2}$$

$$- \frac{1}{\epsilon_{M\infty}} \frac{\Omega_p^2}{\omega^2 - \Omega_p^2} S_0\, \tilde{I}_l(S_0 r') \tilde{K}_l(S_0 R) \left(\frac{\pi}{2} \frac{1}{2l+1} \frac{1}{R} \right)^{-1} \tag{68}$$

$$\epsilon_{M\text{eff}}^{-1}(l, R, \omega) = \frac{1}{\epsilon_{M\infty}} \frac{\omega^2}{\omega^2 - \Omega_p^2}$$

$$- \frac{1}{\epsilon_{M\infty}} \frac{\Omega_p^2}{\omega^2 - \Omega_p^2} S_0 \tilde{I}_l(S_0 R) \tilde{K}_l(S_0 R) \left(\frac{\pi}{2} \frac{1}{2l+1} \frac{1}{R} \right)^{-1} \tag{69}$$

$$\epsilon_{S\text{eff}}^{-1}(l, R, \omega) = \frac{1}{\epsilon_{S\infty}} \frac{1 - \omega^2/\omega_0^2}{\epsilon_0^* - \omega^2/\omega_0^2}$$

$$+ \frac{1}{\epsilon_{S\infty}} \frac{\epsilon_0^* - 1}{\epsilon_0^* - \omega^2/\omega_0^2} Q_0 \tilde{I}_l(Q_0 R) \tilde{K}_l(Q_0 R) \left(\frac{\pi}{2} \frac{1}{2l+1} \frac{1}{R} \right)^{-1} \tag{70}$$

where

$$S_0=q_s\left(1-\frac{\omega^2}{\Omega_p{}^2}\right)^{1/2}, \quad Q_0=\gamma\left(\epsilon_0{}^*-\frac{\omega^2}{\omega_0{}^2}\right)^{1/2} \tag{71}$$

$$\tilde{I}_l(z)=\left(\frac{\pi}{2z}\right)^{1/2} I_{l+1/2}(z), \quad \tilde{K}_l(z)=\left(\frac{\pi}{2z}\right)^{1/2} K_{l+1/2}(z) \tag{72}$$

and where $I_n(z)$ and $K_n(z)$ are the usual modified Bessel functions. The interface exciton frequencies are obtained by eq. (67) which, using eqs (69) and (70), is written as

$$\frac{l}{\epsilon_{S\infty}}\left[\frac{1-\omega^2/\omega_0{}^2}{\epsilon_0{}^*-\omega^2/\omega_0{}^2}+\frac{\epsilon_0{}^*-1}{\epsilon_0{}^*-\omega^2/\omega_0{}^2}\, Q_0\tilde{I}_l(Q_0R)\tilde{K}_l(Q_0R)\left(\frac{\pi}{2}\,\frac{1}{2l+1}\,\frac{1}{R}\right)^{-1}\right]$$

$$+\frac{l+1}{\epsilon_{M\infty}}\left[\frac{\omega^2}{\omega^2-\Omega_p{}^2}-\frac{\Omega_p{}^2}{\omega^2-\Omega_p{}^2}\, S_0\tilde{I}_l(S_0R)\tilde{K}_l(S_0R)\left(\frac{\pi}{2}\,\frac{1}{2l+2}\,\frac{1}{R}\right)^{-1}\right]=0. \tag{73}$$

Because of the coupling of different modes corresponding to the bulk plasmons and the bulk excitons, the interface exciton modes have a complicated structure. However, for the case when $\Omega_p \gg \omega_0$, the surface exciton modes corresponding to the metal plasmon mode get decoupled form the surface exciton modes corresponding to the semiconductor mode. The plasmon type interface modes are obtained by seeking the solution of eq. (73) in the region $\omega \sim \Omega_p$, with $\omega_0 \ll \Omega_p$. In this case eq. (73) becomes

$$l\epsilon_{S\infty}^{-1}+(l+1)\epsilon_{M\text{eff}}^{-1}(l, R, \omega)=0 \tag{74}$$

where $\epsilon_{M\text{eff}}$ is given by eq. (69). Now, let us look at the low frequency semiconductor exciton like modes whose frequencies lie in the $\omega \sim \omega_0$ region. In the limit $\omega_0 \ll \Omega_p$, for these modes, eq. (73) simplifies to

$$l\epsilon_{S\text{eff}}^{-1}(l, R, \omega)+\frac{(l+1)}{\epsilon_{M\infty}}\left[q_s\tilde{I}_l(q_sR)\tilde{K}_l(q_sR)\left(\frac{\pi}{2}\,\frac{1}{2l+1}\,\frac{1}{R}\right)^{-1}\right]=0. \tag{75}$$

Equation (75) can easily be solved in the limiting case when the semiconductor becomes spatially non-dispersive. In this limit, i.e., when $\gamma \to \infty$, eq. (75) reduces to

$$\frac{\epsilon_0\omega_0{}^2-\epsilon_{S\infty}\omega^2}{\omega_0{}^2-\omega^2}+\frac{l}{l+1}\,\frac{(\pi/2)\,(1/R)\,[1/(2l+1)]}{q_s\tilde{I}_l(q_sR)\tilde{K}_l(q_sR)}\,\epsilon_{M\infty}=0. \tag{76}$$

The solution for a few l-values are given in figure 3 where $\Omega_l{}^2=\{[(\omega_l{}^2/\omega_0{}^2)-1]/(\epsilon_0-1)\}$ is plotted as a function q_sR. While evaluating the frequencies, we have assumed $\epsilon_{M\infty}=1$ and $\epsilon_{S\infty}=1$. The longitudinal bulk semiconductor exciton mode, given by $\Omega^2=1{\cdot}0$ and the semiconductor-vacuum plane interface exciton mode, given by $\Omega^2=0{\cdot}5$ are also plotted for comparison. It can be seen directly from eq. (76)

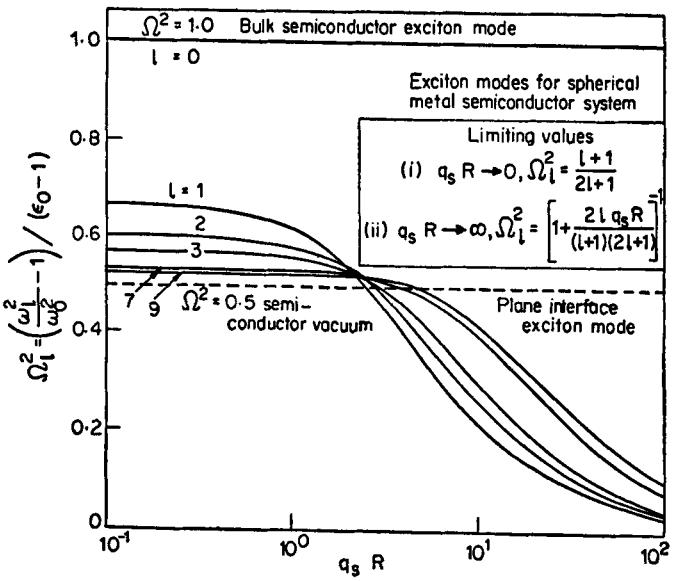


Figure 3. Dependence of the surface exciton mode frequencies for the spherica metal-semiconductor interface on $q_s R$, for different values of orbital l. Here R is the radius of the metal sphere.

that for $l=0$, the interface exciton mode frequency is equal to the bulk longitudinal mode frequency, i.e, $\Omega_0^2=1$, for all values of q_sR. For small q_sR values, i.e. $q_sR \ll 1$, $\Omega_l^2=(l+1)/(2l+1)$. This limit is equivalent to taking the metal region also to be spatially nondispersive and the result is in agreement with the case of a spherical interface system between two spatially non-dispersive media. For $q_sR \gg 1$, $\Omega_l^2 \to (l+1)(2l+1)/[(l+1)(2l+1)+2lq_sR]$. For $l \gg 1$, this is in agreement with the earlier results of Srinivasan and Jha (1977), which were obtained by using the continuity condition of the normal component of derivative of the potential instead of the continuity of the normal component of the displacement vector as used in this paper.

5. Discussion

In the preceding analysis of the nature of the interface modes in spatially dispersive composite semiconductor-metal system, we have been able to present here a very unified, and at the same time very general, method of investigating such problems. Our method is based on the electrostatic-image approximation for calculating the electron-electron interaction in the metal region, in presence of other media on the either side. It can be used for arbitrary physical models of the homogeneous bulk dielectric functions $\epsilon(q, \omega)$ for each of the medium, zeroes of which determine bulk longitudinal (exciton) modes in the respective media. Our procedure involves the calculation of electrostatic potentials in each of the individual media, with arbitrary unknown induced surface charges at their interfaces in the finite region. The external point charge is of course placed in the metal region since the calculation of the electron-electron interaction in the metal region is enough to give the additional modes at the metal interface(s). The functions entering the unknown induced surface charge

densities are obtained by using the usual boundary conditions involving the continuity of the electrostatic potential and the continuity of the normal component of the displacement vector D at each interface. This gives the complete solution. The poles of the interaction function in the metal region then determine both the bulk modes and the interface modes. The interface modes actually arise from the poles of the induced surface charge densities, discussed earlier.

At a first glance, one can criticize our calculations of the interface values of the displacement vector **D** in each media when the bulk dielectric functions are spatially dispersive, and hence our method of investigating the interface modes itself. Because of the spatial dispersion, the relation between **D** (**r**) and the electric field $\mathbf{E}(\mathbf{r}) = -\vec{\nabla}\,\Phi(\mathbf{r})$ becomes nonlocal. But we continue to use this nonlocal relation to evaluate **D** (**r**, ω) even at the interface of a medium, as if the solution fot Φ written down for this particular medium can be extended to all space. However, the nonlocality of the relation between **D** and **E** in reality extends only for small distances (atomic distances), and it is expected that our approximate method will be excellent for dimensions of the media larger than such distances. In fact, as expected, in the limiting case, our method gives the usual solutions for potentials when the dielectric function of each of the media is spatially non-dispersive. For a charge $-e$ at $\mathbf{r}'$ in a medium with dielectric function $\epsilon_M(\omega)$ surrounded by two media of dielectric functions $\epsilon_S(\omega)$ and $\epsilon_V(\omega)$ on either side, with plane interfaces at $z = 0$ and $z = L$, respectively, we find

$$\Phi_M(r, \omega) = \frac{-e}{\epsilon_M}\Bigg[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \int \frac{d^3q}{(2\pi)^3}\,\frac{\exp(i\mathbf{q}.\mathbf{r})\,\exp(-i\mathbf{q}_t.\mathbf{r}'_t)}{q^2}\,4\pi\,\rho_{MS}(q_t, z', \omega) + \int \frac{d^3q}{(2\pi)^3}\,\frac{\exp(i\mathbf{q}.\mathbf{r})\,\exp(-i\mathbf{q}_t.\mathbf{r}'_t)}{q^2}\,4\pi\,\rho_{MV}(q_t, z', \omega)\exp(-iq_z L)\Bigg] \tag{77}$$

where

$$\rho_{MS}(q_t, z', \omega) = \frac{(\epsilon_M-\epsilon_S)(\epsilon_V+\epsilon_M)\exp(-q_t z') + (\epsilon_V-\epsilon_M)(\epsilon_S-\epsilon_M)\exp(-q_t L)\exp[-q_t(L-z')]}{(\epsilon_S+\epsilon_M)(\epsilon_V+\epsilon_M) - (\epsilon_M-\epsilon_M)(\epsilon_V-\epsilon_M)\exp(-2q_t L)} \tag{78}$$

$$\rho_{MV}(q_t, z', \omega) = \frac{(\epsilon_M-\epsilon_S)(\epsilon_V-\epsilon_M)\exp(-q_t(L+z')) + (\epsilon_V-\epsilon_M)(\epsilon_S+\epsilon_M)\exp(-q_t(L-z'))}{(\epsilon_S+\epsilon_M)(\epsilon_V+\epsilon_M) - (\epsilon_S-\epsilon_M)(\epsilon_V-\epsilon_M)\exp(-2q_t L)} \tag{79}$$

For $q_t L \gg 1$, the poles of ρ_{MS} and ρ_{MV} indeed give the usual interface modes determined by the relations

$$\epsilon_S(\omega) = -\epsilon_M(\omega);\ \epsilon_M(\omega) = -\epsilon_V(\omega) \tag{80}$$

which are localized at the MS and MV interfaces, respectively. As already stated, even with finite spatial dispersion, the exact validity of our method can be questioned only for L of the order of the atomic dimensions over which the bulk dielectric functions are nonlocal. At such distances, any true interface is known to be very complicated object, and there is no point then in talking about interfaces with sharp boundaries, as we have done here. Any extension of our method to make it more exact even for atomic dimensions is, therefore, beyond the scope of this invetsigation.

It is interesting to note that for large $q_t L$, the nature of the interface modes localized at the plane interface between medium 1 and 2 can be obtained from a relation of the type similar to the case of the non-dispersive media, i.e. from the equation

$$\epsilon_{1\text{eff}}(q_t, \omega) = -\epsilon_{2\text{eff}}(q_t, \omega) \tag{81}$$

Where $\epsilon_{1\text{eff}}$ and $\epsilon_{2\text{eff}}$ are suitably defined effective dielectric functions of the spatially dispersive media. For the model dielectric functions $\epsilon_M(q, \omega)$ and $\epsilon_S(q, \omega)$ given by eqs (1) and (11), these effective dielectric functions for the metal and the semiconductor are given by eqs (33) and (34), respectively. In general for the case of a plane interface, taken to be the x–y plane, the effective dielectric function $\epsilon_{\text{eff}}(q_t, \omega)$ corresponding to an arbitrary bulk dielectric function $\epsilon(q, \omega)$ can be obtained from the relation

$$\frac{1}{\epsilon_{\text{eff}}(q_t, \omega)} = \int_{-\infty}^{\infty} \frac{dq_z}{2\pi} \frac{2q_t}{\epsilon(q, \omega) q^2},\ q^2 = q_z^2 + q_t^2 \tag{82}$$

which can be used in eq. (81) to find the dispersion relations for the interface modes. Similar analysis can be carried through for the case of a spherical interface with spatially dispersive bulk dielectric functions. In that case, instead of q_t, the orbital constant l=0, 1, 2 ..., corresponding to the spherical harmonics $Y_{lm}(\theta, \varphi)$, and the radius R of the interface enter in defining $\epsilon_{\text{eff}}(l, R, \omega)$. For any medium described by the bulk dielectric functions $\epsilon(q, \omega)$ this is given by

$$\epsilon_{\text{eff}}(l, R, \omega) = \int_0^{\infty} dq\, j_l^2(qR) \left[\int_0^{\infty} dq\, j_l^2(qR)/\epsilon(q, \omega)\right]^{-1}$$

$$= \frac{\pi}{2(2l+1)R}\left[\int_0^{\infty} dq\, j_l^2(qR)/\epsilon(q, \omega)\right]^{-1}. \tag{83}$$

For a single spherical interface for which the medium 1 is the interior region and the medium 2 is the exterior region, the modes are then determined by the equation

$$\epsilon_{2\text{eff}}(l, R, \omega) = (-)\frac{l}{l+1}\epsilon_{1\text{eff}}(l, R\,\omega) \tag{84}$$

as in the spatially non-dispersive case.

References

Agarwal G S 1972 *Opt. Commun.* **6** 221
Allender D, Bray J and Bardeen J 1973 *Phys. Rev.* **B7** 1020
Fuchs R and Kliewar K L 1971 *Phys. Rev.* **B3** 2270
Ginzburg V L 1970 *Sov. Phys. Usp.* **13** 335
Ginzburg V L and Kirzhnits D A 1972 *Phys. Rep.* **4C** 334
Inkson J C 1972 *J. Phys.* **C5** 2599
Inkson J C Preprint No. TCM/52/1974 Cambridge Univ.
Maradudin A A and Mills D L 1973 *Phys. Rev.* **B7** 2787
Mills D L 1972 *Polaritons, Proc. of the first Taormina Research Conference on the Structure of Matter* eds E Burstein and F De Martini (New York: Pergamon) p. 147
Penn D R 1962 *Phys. Rev.* **128** 2093
Philips J C 1970 *Phys. Rev.* **B1** 3304
Rangarajan S 1973 *Nucl. Phys. Solid State Phys. Symp.* **C16** 17
Rangarajan S 1975 Ph.D. Thesis Univ. of Bombay Ch. IV
Rangarajan S and Jha S S 1976 *Pramana* **6** 161
Ritchie R H and Marusak A L 1966 *Surface Sci.* **4** 234
Srinivasan S and Jha S S 1977 *Phys. Rev.* **B16**