

SURFACE EXCITONS AND ELECTROSTATIC IMAGE FORCES AT THE METAL-DIELECTRIC BOUNDARY WITH ALLOWANCE FOR FIELD PENETRATION INTO THE METAL

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A microscopic theory of low-frequency ($\omega \ll E_F/\hbar$, E_F is the metal Fermi energy) surface excitons in a dielectric adjacent to a metal is developed. The electrostatic image forces fundamentally affect the spectrum of these states, the conditions for their formation and the nature of the spectrum being essentially different for vibrational and electron excitations. Penetration into the metal of an electric field produced on propagation of waves in the dielectric leads to "metallic" quenching of excitons. The intensity of this quenching for surface excitons and also for "localized" excitons as a function of their distance from the metal-dielectric boundary is calculated.

1. INTRODUCTION

NUMEROUS experimental investigations of superconductivity of metallic films in contact with dielectrics call urgently for a discussion of the peculiarities of low-frequency ($\omega \ll E_F/\hbar$, E_F is the Fermi energy) surface excitons and optical phonons in a dielectric in contact with a metal. An examination of these states is of interest also in connection with their possible influence on the mechanism of the experimentally observed^[1] surface annihilation of excitons, due to transfer of the exciton energy to the free electrons of the metal ("metallic" quenching of excitons (see^[2,3])).

The presence of a contact between the dielectric and the metal affects radically the spectrum of both the long-wave and short-wave surface excitons. In the case of long-wave excitons, their singularities, as shown in^[4], can be investigated within the framework of macroscopic electrodynamics with allowance for spatial dispersion. On the other hand, a study of short-wave surface excitons calls for the use of microscopic theory and a consistent allowance for the penetration, into the metal, of the electric field produced when waves are excited in the dielectric.

The mechanism whereby the metallic contact influences the spectrum of the surface excitons can be easily understood qualitatively by using as an example a model in which the dielectric contains at the lattice sites dipole oscillators whose frequency is low in comparison with the plasma-oscillation frequency of the metal. In first order of approximation the metal electrons can be assumed to follow adiabatically the distribution of the charges in the dielectric and the quasi-static approximation can be used. If p_n is the dipole moment of an oscillator located at site n of the dielectric at a distance z from the boundary with the metal, then the electrostatic image forces will lower the oscillator energy by an amount $-\alpha p_n^2/(2z)^3$, where α is a positive factor that depends on the orientation of the dipole. This lowering of the potential energy leads to a decrease of the natural frequency of the oscillator.

In quantum language, we can say that the image forces produce for the exciton at the boundary with the metal a potential well $U(z) = -A/z^3$, $A > 0$, in which,

generally speaking, surface-exciton states can be produced.

For the electronic excitations of the dielectric, the foregoing conclusion that their energy is decreased by the image forces is not always valid (see Sec. 3 below). Moreover, the energy of the electronic excitations can in some cases even increase, leading to the occurrence of surface states in an energy region located above the volume-exciton energy band.

In the next sections we develop the theory of small-radius surface excitons in a dielectric with allowance for the penetration of the field into the metal. Within the framework of the theory we consider also "metallic" quenching of "localized" and surface excitons. Since we are interested principally in short-wave excitations of the dielectric, we shall use for the description, in accordance with the foregoing, the microscopic theory. At the same time, the description of the field in the metal will be carried out within the framework of the phenomenological Maxwell's equations. Such an approach is justified since the wavelengths of the considered excitons greatly exceed the average distance between the conduction electrons of the metal.

2. DERIVATION OF FUNDAMENTAL RELATIONS

The total Hamiltonian of the metal + dielectric system considered by us can be represented in the form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{int}^{(1)} + \hat{H}_{int}^{(2)}, \quad (1)$$

where \hat{H}_1 is the Hamiltonian of the metal, \hat{H}_2 is the Hamiltonian of the system of non-interacting molecules, $\hat{H}_{int}^{(1)}$ is the Hamiltonian of the interaction of the molecules with the metal, and $\hat{H}_{int}^{(2)}$ is the Hamiltonian of the intermolecular interaction. If $\varphi(\mathbf{r})$ is the potential of the electric field produced at the point \mathbf{r} of the dielectric ($z > 0$) by a metal filling the half-space $z < 0$, then the Hamiltonian of the interaction of the metal with the dielectric is

$$\hat{H}_{int}^{(1)} = \sum_n \int \varphi(\mathbf{r}) \rho_n(\mathbf{r}) d\mathbf{r}, \quad (2)$$

where $\rho_n(\mathbf{r})$ is the charge-density operator of the molecule located in the n -th site of the crystal lattice. At the same time, the operator $\hat{H}_{int}^{(2)}$ can be expressed

in the following manner:

$$\hat{H}_{int}^{(2)} = \frac{1}{2} \sum_{n \neq m} \hat{W}_{n,m}, \quad (3)$$

where $\hat{W}_{n,m}$ is the operator of the interaction of molecules located in sites n and m . We shall henceforth be interested in excited states of the system, with energies close to the energy of one of the excited states of the isolated molecule. Since the intermolecular interaction, as well as the interaction of the molecules with the metal, is weak in comparison with the intramolecular interaction, the operators $\hat{H}_{int}^{(1)}$ and $\hat{H}_{int}^{(2)}$ can be taken into account within the framework of perturbation theory, as is usually done with respect to $\hat{H}_{int}^{(2)}$ in the theory of small-radius excitons.

The peculiarity of the considered situation lies in the fact that in the presence of a metal there occurs, in addition to the usual intermolecular interaction (3), also an intermolecular interaction due to exchange of virtual excitations of the metal. It is precisely this type of interaction, as is well known (see, for example, [5]) which leads to the occurrence of van der Waals forces on the boundary of two media; at the temperature $T = 0$ these forces are determined principally by the renormalization of the ground state of the system. In our case, on the other hand, the change of the energy and of the excited state of the dielectric also becomes important. In addition, as already noted, the interaction of the molecules with the metal leads to "metallic" quenching of the excitons.

In the excited state, the wave function of the dielectric can be represented in the form

$$\Psi = \sum_n u_n \chi_n^f, \quad (4)$$

where χ_n^f is the wave function of the system of non-interacting molecules, in which a molecule located at the site n is in the f -th excited state, and all the remaining molecules are in the ground state. The state f will be assumed, for simplicity, to be nondegenerate. The coefficients u_n satisfy in the first order of perturbation theory in $\hat{H}_{int}^{(2)}$ and in the second in $\hat{H}_{int}^{(1)}$ the following system of equations:

$$(E - \hbar\omega_f) u_n = \sum_m M_{nm} u_m, \quad (5)$$

where $\hbar\omega_f$ is the energy of the f -th excitation in the isolated molecule,

$$M_{nm} = W_{nm}^{0f} + \int \{K(\mathbf{r}', \mathbf{r} - \omega_{0f}) + K(\mathbf{r}, \mathbf{r}', \omega_{0f})\} \rho_n^{f0}(\mathbf{r}') \rho_m^{0f}(\mathbf{r}) d\mathbf{r} d\mathbf{r}', \quad n \neq m, \quad (6)$$

$$M_{nn} = \sum_{i=1}^4 M_{nn}^{(i)}, \quad (7)$$

where

$$M_{nn}^{(1)} = \sum_m (W_{nm}^{f0} - W_{nm}^{000}), \quad M_{nn}^{(2)} = \sum_m \int \{K(\mathbf{r}', \mathbf{r}, 0) + K(\mathbf{r}, \mathbf{r}', 0)\} \cdot [\rho_n^{ff}(\mathbf{r}') - \rho_n^{00}(\mathbf{r}')] \rho_m^{00}(\mathbf{r}) d\mathbf{r} d\mathbf{r}', \quad M_{nn}^{(3)} = \int K(\mathbf{r}, \mathbf{r}', 0) [\rho_n^{ff}(\mathbf{r}') \rho_n^{ff}(\mathbf{r}) - \rho_n^{00}(\mathbf{r}) \rho_n^{00}(\mathbf{r}')] d\mathbf{r} d\mathbf{r}', \quad M_{nn}^{(4)} = \sum_{p \neq f} \int K(\mathbf{r}', \mathbf{r}, -\omega_p) \rho_n^{fp}(\mathbf{r}') \rho_n^{pf}(\mathbf{r}) d\mathbf{r} d\mathbf{r}' - \sum_{p \neq 0} \int K(\mathbf{r}', \mathbf{r}, -\omega_p) \rho_n^{0p}(\mathbf{r}') \rho_n^{p0}(\mathbf{r}) d\mathbf{r} d\mathbf{r}'.$$

In these relations, the matrix elements are

$$W_{nm}^{f'f''f'''} = \langle \psi_n^{f'} \psi_m^{f''} | \hat{W}_{nm} | \psi_n^{f'''} \psi_m^{f''} \rangle, \quad (8)$$

$$\rho_n^{f''}(\mathbf{r}) = \langle \psi_n^{f'} | \hat{\rho}_n(\mathbf{r}) | \psi_n^{f''} \rangle,$$

where ψ_n^f is the wave function of the n -th molecule in the f -th state.

The correlation function K in (6) and (7) is determined by the relation

$$K(\mathbf{r}, \mathbf{r}', \omega) = -i \int_0^{\infty} \langle \varphi(\mathbf{r}, t) \varphi(\mathbf{r}', 0) \rangle e^{i\omega t} dt, \quad (9)$$

and the averaging of the operator under the integral sign is over the ground state of the metal.

The matrix elements of the operators \hat{W}_{nm} and $\hat{\rho}_n$ can be regarded as known, if one knows the wave functions of the isolated molecule. These matrix elements are essentially different for the vibrational and electronic transitions in the molecule, so that the matrices M_{nm} are also different (see (6), (7)). As to the correlation function K , it can be expressed in the phenomenological description of the metal in terms of its dielectric constant.

Let us assume that outside the metal, i.e., at $z > 0$, there is an extraneous charge of density $\rho(\mathbf{r}, t)$. In the linear approximation, the average value of the potential induced by this charge at the point \mathbf{r} is given by (see [5])

$$\langle \varphi^{ind}(\mathbf{r}, t) \rangle = i \int_{-\infty}^t dt' \int d\mathbf{r}' \rho(\mathbf{r}', t') \langle \varphi(\mathbf{r}', t') \varphi(\mathbf{r}, t) - \varphi(\mathbf{r}, t) \varphi(\mathbf{r}', t') \rangle,$$

which in the Fourier representation with respect to time can be written in the form

$$\langle \varphi^{ind}(\mathbf{r}, \omega) \rangle = - \int d\mathbf{r}' \rho(\mathbf{r}', \omega) \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega). \quad (10)$$

In relation (10), the quantity $\mathcal{D}(\mathbf{r}, \mathbf{r}', \omega)$ is the Fourier transform of the retarded Green's function

$$\mathcal{D}(\mathbf{r}, \mathbf{r}', t) = -i\theta(t) \langle \varphi(\mathbf{r}', 0) \varphi(\mathbf{r}, t) - \varphi(\mathbf{r}, t) \varphi(\mathbf{r}', 0) \rangle. \quad (11)$$

The quantity $\mathcal{D}(\mathbf{r}, \mathbf{r}', \omega)$, which is equal to the potential induced at the point \mathbf{r} by a δ -like source situated at the point \mathbf{r}' (see (10)), can be obtained from Maxwell's equations. Indeed, according to [6], the electric field intensity in the metal, if retardation is taken into account, can be represented in the form

$$\mathbf{E}(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{(2\pi)^2} \int \frac{d\mathbf{k}}{k^2} \frac{\mathbf{k} \rho_s(\mathbf{r}', k_{\perp}, \omega)}{\epsilon_l(\omega, \mathbf{k})} e^{i\mathbf{k}\mathbf{r}}, \quad \mathbf{k}_{\perp} = (k_x, k_y), \quad (12)$$

$\epsilon_l(\omega, \mathbf{k})$ is the "longitudinal" dielectric constant of the metal, and $\rho_s(\mathbf{r}', \mathbf{k}_{\perp}, \omega)$ is the Fourier component of the density of the induced surface charges on the interface. The field outside the metal is determined by the potential

$$\varphi(\mathbf{r}, \mathbf{r}', \omega) = \varphi^{so}(\mathbf{r}, \mathbf{r}', \omega) + \varphi^{ind}(\mathbf{r}, \mathbf{r}', \omega), \quad (13)$$

where

$$\varphi^{so}(\mathbf{r}, \omega) = \frac{e}{|\mathbf{r} - \mathbf{r}'|} = \frac{e}{2\pi^2} \int \frac{d\mathbf{k}}{k^2} e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')},$$

whereas the potential due to the presence of induced surface charges, occurring under the influence of the δ -like source at the point \mathbf{r}' , can be expressed in the form

$$\varphi^{so}(\mathbf{r}, \mathbf{r}', \omega) = \int c(\mathbf{r}', \mathbf{k}_{\perp}, \omega) e^{i\mathbf{k}_{\perp} \cdot \mathbf{r}' - i|\mathbf{k}_{\perp}|z} d\mathbf{k}_{\perp}.$$

The function $c(\mathbf{r}', \mathbf{k}_\perp, \omega)$ and the surface-charge density $\rho_S(\mathbf{r}', \mathbf{k}_\perp, \omega)$ can be obtained, using (12) and (13), from the boundary conditions for the tangential and normal components of the vectors of the field \mathbf{E} and of the induction \mathbf{D} :

$$E_t(+0) = E_t(-0), \quad E_n(+0) = D_n(-0).$$

On the other hand, knowledge of the function $c(\mathbf{r}', \mathbf{k}_\perp, \omega)$ makes it possible to determine, in accordance with (10), also the value of $\mathcal{D}(\mathbf{r}', \mathbf{r}, \omega)$. Simple manipulations lead to the following relation:

$$\mathcal{D}(\mathbf{r}', \mathbf{r}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{dk_\perp}{k_\perp} \left(\frac{1-f(\omega, k_\perp)}{1+f(\omega, k_\perp)} \right) \exp(ik_\perp(\mathbf{r}-\mathbf{r}') - |k_\perp|(z+z')), \quad (14)$$

where

$$f(\omega, k_\perp) = \frac{k_\perp}{\pi} \int_{-\infty}^{+\infty} \frac{dk_s}{k^2 \epsilon_t(\omega, \mathbf{k})}. \quad (15a)$$

It can be shown that relation (14) retains its form also when retardation is taken into account. However, the more general relation¹⁾

$$f(\omega, k_\perp) = -i \frac{\omega}{ck_\perp} Z(\omega, k_\perp) \quad (15b)$$

is then satisfied in place of (15a), where $Z(\omega, k_\perp)$ is the surface impedance of the metal when retardation is taken into account (see [7]):

$$Z(\omega, k_\perp) = \frac{i\omega}{\pi c} \int_{-\infty}^{+\infty} \frac{dk_s}{k^2} \left[\frac{k_\perp^2}{(\omega^2/c^2) \epsilon_l(\omega, \mathbf{k})} + \frac{k_s^2}{(\omega^2/c^2) \epsilon_t(\omega, \mathbf{k}) - k^2} \right]. \quad (15c)$$

This relation contains besides the "longitudinal" dielectric constant $\epsilon_l(\omega, \mathbf{k})$ also the "transverse" dielectric constant of the metal $\epsilon_t(\omega, \mathbf{k})$.

Using the spectral expansions for the functions K and \mathcal{D} , we can easily show that the sought correlation function $K(\mathbf{r}, \mathbf{r}', \omega)$ can be expressed in terms of the imaginary part of the function $\mathcal{D}(\mathbf{r}, \mathbf{r}', \omega)$:

$$K(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\pi} \int_0^{\infty} \frac{\text{Im } \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega')}{\omega - \omega' + i\delta} d\omega', \quad \delta > 0, \quad (16)$$

with

$$\text{Re } \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im } \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega')}{\omega' - \omega} d\omega'.$$

If it is recognized that the frequencies of the surface plasmons in a metal satisfy the relation (see [6])

$$1 + f(\omega, k_\perp) = 0, \quad (17)$$

then it follows from the expression for the function $\mathcal{D}(\mathbf{r}, \mathbf{r}', \omega)$ (see (14)) that $\text{Im } \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega)$ has a sharp maximum at the surface-plasmon frequencies. Therefore, if the frequency ω is small in comparison with the plasma frequency, then we can neglect in first order (see (16)) the dependence of $K(\mathbf{r}, \mathbf{r}', \omega)$ on ω , putting $\omega = 0$. Such an approximation is not suitable, however, for the estimate of $\text{Im } K$, which, as follows from (16), is described by the relation

$$\text{Im } K(\mathbf{r}, \mathbf{r}', \omega) = \begin{cases} -\text{Im } \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega), & \omega > 0, \\ 0, & \omega \leq 0. \end{cases} \quad (18)$$

¹⁾As before, we do not take retardation in the dielectric into account; this is valid if $k_\perp > c/\omega$. In a metal, on the other hand, neglect of the retardation leads to neglect of the damping due to excitation of the transverse waves excited in the metal (see Sec. 3 below, formula (41b)).

As to $\text{Re } K$, in the indicated case of low frequencies we have

$$\text{Re } K(\mathbf{r}, \mathbf{r}', \omega) \approx \text{Re } K(\mathbf{r}, \mathbf{r}', 0) = -1/2 \text{Re } \mathcal{D}(\mathbf{r}, \mathbf{r}', 0). \quad (19)$$

Since the functions $K(\mathbf{r}, \mathbf{r}', \omega)$ (see (6) and (7)) which determine the effective intermolecular interaction are complex, the exciton states in a dielectric turn out to be damped. Generally speaking, however, this damping is weak at small ω and can be disregarded in first order when the excited states of the dielectric are determined. However, even in the next higher order, we get from (5) that $\mathbf{E} \rightarrow \mathbf{E} + i\Gamma$, with

$$\Gamma(E) = \sum_{nm} u_n^* u_m \text{Im } M_{nm}, \quad (20)$$

where the quantities u_n satisfy the system (5) when damping is not taken into account.

It follows from (6), (7), and (18) that the quantity $\Gamma(E)$ is determined entirely by the values of the imaginary part of the Green's function $\mathcal{D}(\mathbf{r}, \mathbf{r}', \omega)$, which can be represented at frequencies $\omega \ll E_F/\hbar$ (see (14); in this case $|f(\omega, k_\perp)| \ll 1$) in the following manner:

$$\text{Im } \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\pi^2} \int \left\{ \frac{\epsilon_t''(\omega, \mathbf{k})}{|\epsilon_t(\omega, \mathbf{k})|^2} + \frac{k_s^2}{k_\perp^2 |\epsilon_t(\omega, \mathbf{k}) - c^2 k^2/\omega^2|^2} \right\} \times \exp(ik_\perp(\mathbf{r}-\mathbf{r}') - |k_\perp|(z+z')) \frac{dk}{k^2}$$

Although relations (5)–(8), (14)–(16), and 20, which determine the effect of the metallic contact on the properties of both the volume and the surface small-radius excitons, were obtained using the molecular-crystal model, their range of applicability is actually much larger. These relations can be used, in particular, also to investigate the influence of a metallic contact in dielectrics on the spectrum of the high-frequency optical phonons, for which the width of the energy band is small in comparison with their energy.

Before we proceed to a direct solution of the system (5) for the spectral region corresponding to vibrational excitations of the molecule, we make a few remarks concerning the spectrum of the long-wave surface states. The spectrum of these states, disregarding the penetration of the field into the metal, was discussed in [4]. To obtain a dispersion equation for the surface states with allowance for the penetration of the field into the metal, we use an expression of type (12) for the electric field intensity not only in a metal, but also in a dielectric (for simplicity, we disregard the anisotropy of the dielectric). We can then obtain easily with the aid of the boundary conditions for the fields the following equation:

$$-\frac{k_\perp}{\pi} \int_{(z \rightarrow -0)}^{+\infty} \frac{e^{ik_s z} dk_s}{k^2 \epsilon_l(\omega, \mathbf{k})} = \frac{k_\perp}{\pi} \int_{(z \rightarrow +0)}^{+\infty} \frac{e^{ik_s z} dk_s}{k^2 \epsilon_t(\omega, \mathbf{k})}, \quad (21)$$

where $\epsilon_l^d(\omega, \mathbf{k})$ is the "longitudinal" dielectric constant of the dielectric, which determines the relation $\omega = \omega(\mathbf{k}_\perp)$ for the frequencies of the surface states.

If the dielectric borders on a vacuum (in this case $\epsilon_l(\omega, \mathbf{k}) \rightarrow 1$), then the left-hand side of (21) becomes equal to minus unity, so that if spatial dispersion is disregarded the equation for the surface-wave frequencies takes on the known form

$$\varepsilon^{\pi}(\omega) = -1. \quad (21a)$$

On the other hand, if the dielectric borders on a metal then, since the metal has at low frequencies ($\omega \ll E_F/\hbar$) a dielectric constant $\varepsilon(\omega, \mathbf{k}) \approx 1 + k_0^2/k^2$, where k_0 is the reciprocal of the Debye screening radius in the metal, the integral in the left-hand side of (2) turns out to equal $k_{\perp}/(k_0^2 + k_{\perp}^2)^{1/2} \approx k_{\perp}/k_0$. In this case we obtain in place of (21a)

$$\varepsilon^d(\omega) = -k_0/k_{\perp}. \quad (22)$$

Since $k_0/k_{\perp} \gg 1$ for macroscopic states, it follows from (22) that the frequencies of the long-wave surface states are quite close to the frequencies of the volume transverse waves (for which $\varepsilon^d(\omega) = \pm\infty$), so that, strictly speaking, in the study of the surface wave one must take into account the spatial dispersion not only in the metal but also in the dielectric. In addition, it follows from the foregoing that at low ω the onset of surface wave is hindered also by the presence of damping processes.

We can consider analogously the surface-state spectrum of anisotropic dielectrics. It is easy to verify that in this case the conditions for the onset of surface states, as incidentally also in the case of contact with vacuum (see^[8]), become even more favorable. We note also that unlike the "macroscopic" surface waves, the short-wave surface excitations should be quite sensitive to violations of the "ideal" structure of the surface layer. We shall henceforth, however, disregard the "defects" of the surface, since it follows from^[9] that at sufficiently low temperatures appreciable sections of a crystal surface can be quite close to ideal.

3. SURFACE STATES IN THE REGION OF INTERMOLECULAR-TRANSITION FREQUENCIES

When excited states of a dielectric are considered in the region of the spectrum of the electronic and vibrational transitions, it must be recognized that an appreciable contribution to the exciton energy is made generally speaking, not only by the dipole-dipole interactions but also by intermolecular interactions of higher multipolarity. Therefore, to simplify the discussion that follows, we assume the dielectric molecules to have an inversion center. For such molecule, the dipole moment operator can only off-diagonal non-zero matrix elements, so that the quantities W_{nm}^{if00} , W_{nm}^{0000} and $\rho_n^{00}(\mathbf{r})$, $\rho_n^{ff}(\mathbf{r})$ turn out to depend only on the mean values of the quadrupole moment and on the higher-multipolarity moments of a molecule that is in the ground or excited state. By virtue of the foregoing, the quantities W_{nm}^{if00} and W_{nm}^{0000} decrease rapidly with increasing $|\mathbf{n} - \mathbf{m}|$, so that to calculate their contribution to the exciton energy it suffices to take into account the nearest-neighbor interaction. In this approximation, the first term in (7) does not depend on n_3 provided that $n_3 \geq 2$. As to the second term in (7), it should not be included at all in the nearest-neighbor approximation. For molecules with $n_3 = 1$, the first term in (7) differs from its "volume" value by an amount equal to the energy of interaction with one missing nearest neighbor. In place of this interaction, Eq. (7) contains a third term due to the change occur-

ring in the energy of interaction of the molecule with its electrostatic image in the metal as $0 \rightarrow f$.

We note also that in the considered case of planar geometry, the quantities u_n contained in (5) are conveniently sought in the form

$$u_n = u_{\mathbf{k}_{\perp}(n_3)} e^{i\mathbf{k}_{\perp} \cdot \mathbf{n}}, \quad (23)$$

where \mathbf{k}_{\perp} is the wave vector with $k_3 = 0$, and $n_3 = 1, 2, \dots$. For simplicity, we assume here that the crystal occupying the half-space $z > 0$ has a primitive cubic lattice (lattice constant a) with one molecule per unit cell, with the z axis directed along an edge of the cube. Therefore, taking the foregoing into account, we can represent the system (5) in the form

$$\begin{aligned} [E - \hbar\omega_{f_0} - D^{(0)} - \Gamma_{\mathbf{k}_{\perp}}(0) - D^{(1)}\delta_{ln_3}]u(n_3) - \sum_{m_3} \tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 - m_3)u(m_3) \\ - \sum_{m_3} \tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 + m_3)u(m_3) = A(n_3)u(n_3). \end{aligned} \quad (24)$$

Here $D^{(0)}$ is the value of the first term in (7) for an unbounded crystal, while

$$\begin{aligned} D^{(1)} = \int \frac{\rho_n^{00}(\mathbf{r})\rho_n^{00}(\mathbf{r}') - \rho_n^{ff}(\mathbf{r})\rho_n^{ff}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ + \int \frac{\rho_n^{00}(\mathbf{r}) - \rho_n^{ff}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \rho_n^{00}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (25)$$

where $\mathbf{n} \equiv (n_1 n_2 1)$, $\mathbf{m} \equiv (m_1 m_2 0)$, $\tilde{\mathbf{r}}' = (x', y', -z')$.

Unlike $D^{(0)}$ and $D^{(1)}$, the quantities $A(n_3)$, $\Gamma_{\mathbf{k}_{\perp}}$, and $\tilde{\Gamma}_{\mathbf{k}_{\perp}}$ are expressed in terms of the off-diagonal matrix element of the charge-density operator $\hat{\rho}_n(\mathbf{r})$ and do not vanish even in the dipole approximation. Confining ourselves to this approximation and recognizing that $\rho_n^{ff}(\mathbf{r}) = -\mathbf{p}^{ff} \nabla \delta(\mathbf{r} - \mathbf{n})$, where \mathbf{p}^{ff} is the dipole moment of the $f \rightarrow f'$ transition, we obtain for the indicated quantities

$$\begin{aligned} A(n_3) = M_{nn}^{(1)} - \int \mathcal{D}(\mathbf{r}, \mathbf{r}', \omega_{f_0}) \rho_n^{0f}(\mathbf{r}) \rho_n^{f'0}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \\ \Gamma_{\mathbf{k}_{\perp}}(m_3 - n_3) = \sum_{\mathbf{m}_{\perp}} W_{nm}^{0f'f_0} e^{i\mathbf{k}_{\perp} \cdot (\mathbf{m} - \mathbf{n})}, \end{aligned} \quad (26)$$

$$\tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 + m_3) = \sum_{\mathbf{m}_{\perp}} \int \mathcal{D}(\mathbf{r}', \mathbf{r}, \omega_{f_0}) \rho_n^{f'0}(\mathbf{r}') \rho_m^{0f}(\mathbf{r}) e^{i\mathbf{k}_{\perp} \cdot (\mathbf{m} - \mathbf{n})} d\mathbf{r} d\mathbf{r}'.$$

The last two expressions, as shown for example in^[4], can be represented also in the form

$$\begin{aligned} \Gamma_{\mathbf{k}_{\perp}}(m_3 - n_3) = \Gamma_{\mathbf{k}_{\perp}}^*(n_3 - m_3) = \frac{2\pi}{a^2} \sum_{\mathbf{g}_{\perp}} \frac{[(\mathbf{p}^{0f}, \mathbf{g}_{\perp} + \mathbf{k}_{\perp}) + ip_s |\mathbf{g}_{\perp} + \mathbf{k}_{\perp}|]^2}{|\mathbf{g}_{\perp} + \mathbf{k}_{\perp}|} \\ \times \exp\{-|\mathbf{g}_{\perp} + \mathbf{k}_{\perp}| \cdot |m_3 - n_3|a\}, \quad m_3 > n_3 \end{aligned} \quad (27)$$

$$\begin{aligned} \tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 + m_3) = -\frac{2\pi}{a^2} \sum_{\mathbf{g}_{\perp}} \frac{[(\mathbf{p}^{0f}, \mathbf{g}_{\perp} + \mathbf{k}_{\perp})^2 + (p_s^{0f})^2 |\mathbf{g}_{\perp} + \mathbf{k}_{\perp}|^2]}{|\mathbf{g}_{\perp} + \mathbf{k}_{\perp}|} \\ \times \frac{1 - f(\mathbf{g}_{\perp} + \mathbf{k}_{\perp}, \omega_{f_0})}{1 + f(\mathbf{g}_{\perp} + \mathbf{k}_{\perp}, \omega_{f_0})} \exp\{-|\mathbf{g}_{\perp} + \mathbf{k}_{\perp}| [(n_3 + m_3)a + 2(d - a)]\}. \end{aligned} \quad (28)$$

The summation in (27) and (28) is over all the possible projections of the reciprocal-lattice vectors on the (x, y) plane, and d is equal to the distance from the plane $n_3 = 1$ to the surface of the metal. The minimal value of d in the case of good contact between the dielectric and the metal can probably be assumed equal to $d \approx a/2$.

The quantity $\Gamma_{\mathbf{k}_{\perp}}(m_3 - n_3)$ (see (27)) is equal to the interaction energy of a dipole \mathbf{p}^{0f} located at site \mathbf{n}

with a plane grid of dipoles $p^{\text{of}} \exp(i\mathbf{k}_{\perp} \cdot \mathbf{m})$ located at the lattice sites with constant m_3 . At the same time, the quantity $\tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 + m_3)$ with $m_3 \neq n_3$ is equal to the interaction energy of the same dipole with the image of the dipole grid $m_3 = \text{const}$, obtained with allowance for the penetration of the field into the metal. If $m_3 = n_3$, then (28) does not account for the entire interaction energy of the moment of transition in the molecule n with the mirror image of the dipole grid, but only part of this energy. The reason is that the interaction energy of the transition dipole with its own image (the quantity $M_{nn}^{(4)}$, see (7), which is determined by the entire aggregate of the excited states of the molecule, differs generally speaking from the energy of interaction with a foreign image (the second term in the right-hand side of (6)), even if we put in this term $m = n$. This is precisely the reason why the equations in (24) contain a term with $A(n_3)$, which takes into account the part of the interaction energy not included in $\tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 + m_3)$. It follows from (26) that the quantity $A(n_3)$ decreases with increasing n_3 like $A(n_3) \sim (2z_n)^{-3}$, where $z_n = n_3 a + d - a$ (see also below).

Proceeding to solve the system (24), we consider first the surface states in a dielectric in the region of the fundamental-tone frequency ($f = 1$) of the dipole-active nondegenerate intramolecular vibration. For excitations of this kind, the matrix elements $p_{\mathbf{n}}^{\text{ff}'}(\mathbf{r})$ differ from zero only if $f' = f + 1$, with

$$\rho_n^{f+1,f}(\mathbf{r}) = \rho_n^{f,f+1}(\mathbf{r}) = -\nabla f + 1(p^{\text{of}} \nabla \delta(\mathbf{r} - \mathbf{n})). \quad (29)$$

Taking (19) and (26) into account, we find that the quantity

$$A(n_3) = \int \mathbf{K}(\mathbf{r}', \mathbf{r}, 0) \left\{ \sum_{p \neq 1} \rho_n^{1p}(\mathbf{r}') \rho_n^{p1}(\mathbf{r}) - \sum_{p \neq 0} \rho_n^{0p}(\mathbf{r}') \rho_n^{p0}(\mathbf{r}) - 2\rho_n^{01}(\mathbf{r}') \rho_n^{10}(\mathbf{r}) \right\} d\mathbf{r} d\mathbf{r}'$$

vanishes identically if (29) is taken into account. The vanishing of $A(n_3)$ which is a characteristic of the oscillator spectrum, makes the system (24) equivalent to the system (28) of [4]. The only difference is that in (24) the quantity $\tilde{\Gamma}_{\mathbf{k}_{\perp}}(n_3 + m_3)$ differs somewhat from that in [4], owing to the allowance for the penetration of the field into the metal (this difference vanishes if $\epsilon(\omega, \mathbf{k}) \rightarrow \infty$; in this case $f(\mathbf{k}_{\perp}, \omega) \rightarrow 0$).

It follows from (27) and (28) that at $\mathbf{k}_{\perp} = 0$, and also at $|\mathbf{k}_{\perp}| \lesssim \pi/a$, the quantities $\Gamma_{\mathbf{k}_{\perp}}(z)$ and $\tilde{\Gamma}_{\mathbf{k}_{\perp}}(z)$ decrease exponentially with increasing z . Therefore, when considering the system (24) with $\mathbf{k}_{\perp} = 0$ and with $\mathbf{k}_{\perp} \lesssim \pi/a$, we can use the nearest-neighbor approximation. In this approximation we have for the corresponding surface states

$$u(n_3) = e^{-\kappa n_3}, \quad E(\mathbf{k}_{\perp}) = \hbar\omega_{f0} + D^{(0)} + \Gamma_{\mathbf{k}_{\perp}}(0) + 2\Gamma_{\mathbf{k}_{\perp}}(1) \cos \kappa a, \\ e^{-\kappa} = \Gamma_{\mathbf{k}_{\perp}}(1) / [D^{(1)} + \tilde{\Gamma}_{\mathbf{k}_{\perp}}(2)]. \quad (30)$$

According to (27) and (28), the quantities $\Gamma_{\mathbf{k}_{\perp}}$ and $\tilde{\Gamma}_{\mathbf{k}_{\perp}}$ depend on the direction of the dipole p^{of} . The surface states of this type are therefore possible only at molecule orientations for which $|e^{-\kappa}| < 1$. Since at the same values of \mathbf{k}_{\perp} the energy for the volume states is

$$E(\mathbf{k}_{\perp}, k_3) = \hbar\omega_{f0} + D^{(0)} + \Gamma_{\mathbf{k}_{\perp}}(0) + 2\Gamma_{\mathbf{k}_{\perp}}(1) \cos k_3 a,$$

it follows that the depth of the surface levels is

$$\Delta = [D^{(1)} + \tilde{\Gamma}_{\mathbf{k}_{\perp}}(2) - \Gamma_{\mathbf{k}_{\perp}}(1)]^2 / [D^{(1)} + \tilde{\Gamma}_{\mathbf{k}_{\perp}}(2)]. \quad (31)$$

In those cases when $\text{Re } \kappa \ll 1$, the surface states with $\mathbf{k}_{\perp} = 0$ are macroscopic. As shown in [4], these states can be obtained also in the framework of the phenomenological Maxwell equations with allowance for spatial dispersion, and it turns out that it is necessary to introduce additional boundary conditions.

We note in addition that at small $|D^{(1)}|$ the total width of the energy band of the volume states (i.e., of the energies at arbitrary \mathbf{k}) can be larger than Δ . In this case the surface-exciton states obtained above lie below the energy band of all the volume states only at such dipole orientations at which the absolute minimum of the energies of the volume excitons corresponds to $\mathbf{k}_{\perp} = 0$, or else $|\mathbf{k}_{\perp}| \lesssim \pi/a$.

We proceed now to consider the surface states in the region of the frequencies of the intramolecular electronic transitions. In this case relations (29) no longer hold, and $A(n_3)$ does not vanish in general. To estimate $A(n_3)$ we consider the dependence of the functions \mathbf{K} and \mathcal{D} on the frequency ω .

Inasmuch as in this case $ak_0 > 1$, the main contribution to the integral (14) at $z' \gtrsim a$ is made by small \mathbf{k}_{\perp} . Therefore

$$\mathcal{D}(\mathbf{r}', \mathbf{r}, \omega) \approx F(\omega) / |\mathbf{r} - \tilde{\mathbf{r}}'|, \quad (32)$$

where $\tilde{\mathbf{r}}' \equiv (\mathbf{x}', \mathbf{y}', -z')$,

$$F(\omega) = \frac{1 - f(\omega, \mathbf{k}_{\perp})}{1 + f(\omega, \mathbf{k}_{\perp})} \Big|_{\mathbf{k}_{\perp} \rightarrow 0},$$

so that

$$\mathbf{K}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\Phi(\omega)}{|\mathbf{r} - \mathbf{r}'|}, \quad \Phi(\omega) = \frac{1}{\pi} \int_0^{\infty} \frac{\text{Im } F(\omega')}{\omega - \omega' + i\delta} d\omega'. \quad (33)$$

Using now the relations (26), (7), (32), and (33), we find that

$$\text{Im } A(n_3) = -\frac{[|\mathbf{p}^{\text{of}}|^2 + (\mathbf{p}_s^{\text{of}})^2]}{8z_n^3} \text{Im } F(\omega_{f0}), \quad \text{Re } A(n_3) = \frac{1}{16z_n^3} R_f, \\ R_f = \sum_{f' \neq 0, f} \{ \Phi(\omega_{f'}) [|\mathbf{p}^{\text{of}'}|^2 + (\mathbf{p}_s^{\text{of}'})^2] - [|\mathbf{p}^{\text{of}}|^2 + (\mathbf{p}_s^{\text{of}})^2] \Phi(\omega_{f'}) \} \\ - 2 \text{Re } \Phi(\omega_{f0}) [|\mathbf{p}^{\text{of}}|^2 + (\mathbf{p}_s^{\text{of}})^2]. \quad (34)$$

The sign of $\text{Re } A(n_3)$ depends significantly on the structure of the spectrum of the electronic excitations of the molecule. If we take into account only the two molecular states 0 and f , then $\text{Re } A(n_3) > 0$. Allowance for the other molecular excitations, on the other hand, can lead also to $\text{Re } A(n_3) < 0$.

If $|\mathbf{R}_f| \ll |\mathbf{p}^{\text{of}}|^2$, then the term with $A(n_3)$ in the system (24) can be omitted. In this case we arrive at the situation considered earlier for the vibrational surface excitons.

The most interesting features of the spectrum of the electronic surface states occur if

$$|\mathbf{R}_f| \gg |\mathbf{p}^{\text{of}}|^2,$$

when the depth of the potential well (or the height of the potential hump if $\text{Re } A(n_3) > 0$) is large in comparison with the width of the energy band of the volume excitons. In this case, at small n_3 and at any rate for $\mathbf{k}_{\perp} = 0$ or $\mathbf{k}_{\perp} \lesssim \pi/a$ (in which case Γ and $\tilde{\Gamma}$ are exponen-

tially small, see (27) and (28)), the following inequalities hold:

$$|\operatorname{Re} A(n_3)| \gg |\Gamma_{k_{\perp}}(n_3 - m_3)|, |\tilde{\Gamma}_{k_{\perp}}(n_3 + m_3)|.$$

Therefore, at the indicated values of n_3 , the terms of order $\Gamma_{k_{\perp}}$ and $\tilde{\Gamma}_{k_{\perp}}$ can be left out from the system (24) in the first-order approximation. On the other hand, the presence of the term with $A(n_3)$ leads to surface states with energy values

$$E_{n_3}(k_{\perp}) = \hbar\omega_{j_0} + D^{(0)} + \delta_{n_3} D^{(1)} + \operatorname{Re} A(n_3) \quad (35a)$$

and wave functions

$$\Psi(k_{\perp}, n_3) = \frac{1}{\sqrt{N_1 N_2}} \sum_{n_1, n_2} e^{ik_{\perp} n_1} \chi_{n_1, n_2, n_3} \quad (35b)$$

Each such state extends in practice over only one crystal plane $n_3 = \text{const}$. Their number, however, is small and does not exceed two ($n_3 \leq 2$) even at $|\operatorname{Re} A| = 10|\rho^{\text{of}}|^2$. We note that in addition to the considered surface states of type (35), "macroscopic" surface states are also possible, subtending over a large number of near-surface planes of molecules. Since, however, $A(n_3) \sim z_n^{-3}$, the number of such states is also finite, and they are similar in their properties to those considered in^[4] within the framework of the phenomenological approach.

In conclusion, we shall touch upon again on the observed appreciable difference between the spectra of the surface states of a dielectric, which correspond to electronic and vibrational intramolecular excitations. As was already emphasized, these surface states are due to interaction between an intramolecular excitation and the surface of the metal. Naturally, the energy of this interaction, which is equal to the difference between the shifts of the terms of the ground and excited states of the molecule, depends on the spectrum of the molecule spectrum and on the wave functions of the stationary states, as is indeed reflected in relations (6) and (7). At the same time, the surface states considered above lie in the energy region of the lowest molecular excitations, where the quantum features are most strongly pronounced. It is therefore not surprising that if the spectra of the intramolecular excitations differ in character, the structures of the corresponding surface states are also different.

4. "METALLIC" QUENCHING OF "LOCALIZED" AND SURFACE EXCITONS

We now proceed to estimate the damping of the exciton states, due to the presence of the metallic contact.

For an excitation localized at the site n ("localized" Frenkel exciton; this is precisely the case investigated in various experiments, and also in^[3]), it follows from (20) (see (18)) that

$$\Gamma_n = \operatorname{Im} M_{nn} = \operatorname{Im} M_{nn}^{(4)} = \Gamma_n^l + \Gamma_n^t, \quad (36)$$

$$\Gamma_n^l = \frac{1}{\pi^2} \int \frac{dk}{k^2} \frac{\epsilon_t''(\omega, k)}{|\epsilon_t(\omega, k)|^2} |\rho^{\text{of}} \mathbf{K}|^2 e^{-2k_{\perp} z_n}, \quad (36a)$$

$$\Gamma_n^t = \frac{1}{\pi^2} \int \frac{dk}{k^2} \frac{k_z^2}{k_{\perp}^2} \frac{\epsilon_t''(\omega, k)}{|\epsilon_t(\omega, k) - k^2 c^2 / \omega^2|^2} |\rho^{\text{of}} \mathbf{K}|^2 e^{-2k_{\perp} z_n}, \quad (36b)$$

where $\mathbf{K} \equiv (k_{\perp}, ik)$ and z_n is the distance from the molecule n to the metal-dielectric interface. The

quantities Γ_n^l and Γ_n^t are due to the excitation in the metal of longitudinal and transverse induced oscillations, respectively, with $\Gamma_n^t \rightarrow 0$ as $c \rightarrow \infty$. We consider first the expression for Γ_n^l . Since the value of $\epsilon_l(\omega, \mathbf{k})$ at small ω gives the Debye screening of the interaction, and since the function \mathbf{k} varies appreciably in the interval of the values $k \sim k_0$, we can replace the function $\epsilon_l''|\epsilon_l|^2$ under the integral sign in (36a), when $z_n \gg 1/k_0$, by its value at $k_{\perp} = 0$. In this approximation we have

$$\Gamma_n^l = \Gamma_l / z_n^4, \quad (37)$$

where

$$\Gamma_l = \frac{3}{8\pi} [|\rho^{\text{of}}|^2 + (p_s^{\text{of}})^2] \int_{-\infty}^{\infty} \frac{\epsilon_t''(\omega, k_s, k_{\perp} = 0) dk_s}{k_s^2 |\epsilon_t(\omega, k_s, k_{\perp} = 0)|^2}.$$

For example, in the dense electron gas approximation

$$\epsilon_t'(\omega, k_s) = 1 + k_s^2 / k_0^2, \quad \epsilon_t''(\omega, k_s) = e^2 k_0^4 \hbar\omega / 2k_s^2 E_F^2$$

if $k < 2k_0$ and $\hbar\omega < k(2k_0 - k)E_F/k_0^2$ (in the remaining cases, $\epsilon_t'' = 0$; see^[10]), and we obtain for Γ_l the estimate

$$\Gamma_l \approx \frac{e^2 \hbar\omega}{30E_F^2} |\rho^{\text{of}}|^2 \ln \frac{E_F}{\hbar\omega}.$$

Thus, if $E_F = 10$ eV and $|\rho^{\text{of}}| = e \text{ \AA}$, then at $z_n = 5 \text{ \AA}$ and $\hbar\omega = 2$ eV we obtain $\Gamma_n^l \approx 1 \text{ cm}^{-1}$, whereas at $z_n = 100 \text{ \AA}$ we have already $\Gamma_n^l \approx 10^{-5} \text{ cm}^{-1}$.

For the estimate of Γ_n^t we shall disregard the dependence of ϵ_t on k (as in the normal skin effect). In this approximation

$$\Gamma_n^t = \frac{\delta^3 \epsilon_t''(\omega)}{2|\epsilon_t(\omega)|^2} [|\rho^{\text{of}}|^2 + (p_s^{\text{of}})^2] \int_0^{\infty} \frac{x(x - \sqrt{x^2 + 1})^2}{(x^2 + 1)^{3/2}} e^{-2x z_n} dx, \quad (38)$$

where $\delta \equiv (\omega/c)\sqrt{|\epsilon_t'(\omega)|}$ is the wave vector of the light wave in the metal at the frequency ω . It follows from (38) that at $z_n \ll 1/\delta$ the value of Γ_n^t is practically independent of z_n :

$$\Gamma_n^t \approx \frac{\delta^3 \epsilon_t''(\omega)}{6|\epsilon_t(\omega)|^2} [|\rho^{\text{of}}|^2 + (p_s^{\text{of}})^2] + O(z_n \delta).$$

On the other hand, if $z_n \gg 1/\delta$ (and, as before, $z_n < c/\omega$), then

$$\Gamma_n^t \approx \frac{\delta^3 \epsilon_t''(\omega)}{8|\epsilon_t(\omega)|^2} [|\rho^{\text{of}}|^2 + (p_s^{\text{of}})^2] (z_n \delta)^{-2}.$$

Since $\epsilon_t'' = 2n\kappa$ and $|\epsilon_t| = (n^2 + \kappa^2)^{1/2}$, where n and κ are the refractive index and the extinction coefficient of the light in the metal, for example at $n = 5$, $\kappa = 1$, $|\rho^{\text{of}}| = e \text{ \AA}$, and $\lambda = 2\pi c/\omega = 5 \times 10^3 \text{ \AA}$ we obtain for Γ_n^t at $z_n \lesssim 1/\delta$ the value $\Gamma_n^t = 10^{-4} \text{ cm}^{-1}$.

Comparing the estimates of Γ_n^l and Γ_n^t , we arrive at the conclusion that at small $z_n < 1/\delta$ the main contribution to the damping of the "localized" electrons is made by the term $\Gamma_n^l \sim z_n^{-4}$. On the other hand, the contribution of Γ_n^t can be appreciable only if $z_n \gtrsim 1/\delta$. Thus, at small z_n the exciton damping, as seen from (37), is determined only by the "longitudinal" dielectric constant and therefore, unlike Γ_n^l , it cannot be expressed in terms of the optical constant of the metal in the case of normal incident of light, in contradiction to the statement made in^[3].

It follows also from the foregoing comparison of Γ_n^l and Γ_n^t that those terms of the surface impedance Z

(see (15c)) which depend on $\epsilon_t(\omega, \mathbf{k})$ can be omitted in the analysis of the damping of surface states having in the dielectric a penetration depth smaller than the skin-layer depth. In particular, for the states (35) the use of (20) yields in this approximation (neglect of retardation) a damping constant

$$\Gamma(\mathbf{k}_\perp, n_s) = \frac{1}{a^2} \sum_{\mathbf{k}_\perp} \int \frac{\epsilon_i''(\omega, k_s, \mathbf{k}_\perp + \mathbf{g}_\perp) |\mathbf{p}^0 \mathbf{K}(\mathbf{g}_\perp)|^2}{[k_s^2 + (\mathbf{k}_\perp + \mathbf{k}_\perp)^2] |\epsilon_i(\omega, k_s, \mathbf{k}_\perp + \mathbf{g}_\perp)|^2} \times \exp\{-2z_n |\mathbf{k}_\perp + \mathbf{g}_\perp|\} dk_s,$$

where $\mathbf{K}(\mathbf{g}_\perp) \equiv (\mathbf{k}_\perp + \mathbf{g}_\perp, i |\mathbf{k}_\perp + \mathbf{g}_\perp|)$. Thus, unlike the case of "localized" excitons, the value of Γ for surface states decreases exponentially with increasing n_s , which may be of importance in the experimental study of the luminescence from these states.

We note in conclusion that the surface states (35) obtained in this paper make the decisive contribution to the energy of electron-electron interactions in a metal; this energy is due to exchange of virtual excitons of the dielectric. This circumstance should be taken into account when considering the influence of dielectric coatings on the temperature of the superconducting transitions of metallic films, both in the case of the usual "bulk" superconductivity, and, in particular, in the case of "surface" superconductivity.^[11] In addition, the aforementioned surface states, and also the strong dependence of their spectrum on the width of the gap d between the metal and the dielectric, exerts at small d a noticeable influence on the adhesion forces acting on the metal-dielectric boundary. These questions, however, lie outside the scope of the present article and will be considered separately.

We note that the influence of the electrostatic image forces on the spectrum of large-radius exciton on a semiconductor-metal interface is also worthy of special attention.

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