USE OF THE METHOD OF IMAGES IN STUDYING THE ENERGY SPECTRA OF THE SURFACE STATES OF ELECTRONS OR HOLES IN THREE-LAYER SEMICONDUCTOR–DIELECTRIC–CONDUCTOR STRUCTURES

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For the potentials obtained by the method of images, we have found the surface states of an electron or a hole in three-layer semiconductor–dielectric–conductor structures. For the arbitrarily thin layer of a dielectric, we deduced the exact formulas for the energy spectra E_n by the method of effective mass $\left(E_n \sim \frac{1}{n^2}\right)$ and with regard for the discreteness of the crystal lattice of a semiconductor $\left(E_n \sim \sqrt{A + \frac{1}{n^2}}\right)$. The surface states of an electron or a hole can be formed also in the two-layer semiconductor–dielectric structures in the cases where the permittivity of a dielectric is greater than that of a semiconductor. The obtained earlier exact solutions are applicable in this case as well. Other versions of the application of the method of images are discussed.

1. Introduction

The method of images is used in many problems of macroscopic physics: in electro- and magnetostatics, optics, and hydrodynamics [1]– [4]. In the present work, this method is applied to the study of microsystems, namely of the surface states of electrons or holes in semiconductors near the boundary with a conducting medium. The following two circumstances serve the preconditions for the use of the method of images. First, the eigenfrequencies (plasma ones) of the electron subsystem of metals ω_p are of the order of 10–20 eV on the energy scale, whereas the characteristic frequencies of electron-hole excitations are at least one order lower (0.5 eV). If we consider the characteristic frequencies of Wannier–Mott excitons, for which the Rydberg constant $R_{\rm ex}$ is in the interval 0.1–0.01 eV, we may write $\omega_p \gg \omega_{\rm ex}$. Hence, the electron subsystem of a metal is significantly less inertial than the electron-hole one in semiconductors. We assume that the charge induced near the metal surface is mainly formed by electrons near the Fermi level and take into account that the Fermi energy $\hbar\omega_{\rm F}$ varies in the limits 3–7 eV. Even in this case, there is a sufficient reserve to consider that

$$\omega_{\rm F} \gg \omega_{\rm ex}. \tag{1}$$

Hence, in the qualitative study of electron or hole states near the boundary with a metal, we can neglect the inertia of the subsystem with higher frequencies, electrons of a metal, i.e., neglect by a possible retardation and some blur of the image of an electron or a hole.

Secondly, even if a point-like charge approaches slowly the metal surface, its image will be distorted and blurred due to both the discreteness of the crystal structure of a metal and the finiteness of the screening radius λ. However, these distortions become significant at distances of the order of the lattice constant, because the screening radius in metals $\lambda \approx 0.5 \times 10^{-8}$ cm (see, e.g., [5]), which is less than the lattice constant in metals d. Hence, the image will be almost exact at distances $x \gg d$, and the potential energy will be determined by the Coulomb law. It should be noted that an electron or a hole is a quasiparticle and cannot be localized in a volume less than that of the elementary cell. Therefore, the method of images is applicable in the same cases and to the same extent as the method of effective mass for electrons and holes.

If a semiconductor contacts with a metal or other conducting medium, the electrons and holes being present near the boundary will attract to it under the action of the image forces and tunnel through it. Such processes are not accompanied by emission and explain the strong extinction of recombination luminescence near the contact with a metal. In order to exclude the processes of tunneling, we separate a semiconductor and a conductor by the thin layer of a dielectric. In this case, free electrons and holes will form almost stationary surface states. Just such states of an electron

bound with its mirror image near the interface and the analogous states of a hole, as the simplest ones, will be considered in the present work. If the electrons and holes can move along the interface with a definite vector $\vec{k}$, such stationary states can be associated with surface currentless quasiparticles. At $\vec{k} \neq 0$, the motions of an electron and the charge induced by it on the metal surface will be mutually coordinated, and the total transferred charge will be equal to zero.

It is probable that Wannier–Mott excitons can form similar surface states, but the forces of attraction of excitons to the surface will be weaker and will decrease stronger with increase in the distance from the metal surface (by the dipole-dipole law).

2. Energy Operator. The Schrödinger Equation

Consider a three-layer semiconductor–dielectric–conductor structure with plane parallel interfaces. Let a be the thickness of the thin dielectric layer. We choose the Cartesian coordinate system so that the x axis is perpendicular to the interfaces and is directed toward a semiconductor, and the origin of coordinates is at the semiconductor–dielectric interface. Then the y and z axes will be positioned in this plane, and the half-space will be filled by a semiconductor.

If an electron in the conduction band has the scalar effective mass m_e, the operator of its kinetic energy is $\frac{\hbar^2}{2m_e}\Delta$, where Δ is the Laplace operator.

In what follows, the role of the dielectric layer will be mainly reduced to the hindrance to the tunneling of electrons, and its thickness will be assumed to be small. In view of this assumption, the calculations and the form of the potential energy can be simplified, by taking that the permittivity of the dielectric layer ε_d coincides with that of a semiconductor ε. Otherwise, we would consider two images (see Section 4). Let us write the potential energy U of an electron interacting with its mirror image which is located symmetrically relative to the metal–dielectric interface ($x = -a$) and has the charge equal and opposite by sign (see, e.g., [2]): $U = -\frac{e^2}{4\varepsilon(a+x)}$. If we take the top edge of the valence band as the zero-energy reference point, the Hamiltonian of an electron has the form

$$H_e = E_G - \frac{\hbar^2}{2m_e}\Delta - \frac{e^2}{4\varepsilon(a+x)}, \tag{2}$$

where E_G is the forbidden band width.

The energy operator of a hole not interacting with an electron, H_h, differs from (2) only by constants: m_e is changed by m_h, and the energy will be reckoned from the level shifted downward by E_G. In view of this, all the calculations will be performed further for electrons. For holes, the results will be analogous and be reduced to the change of the indicated constants in final formulas.

By solving the stationary Schrödinger equation

$$H_e\Psi = E\Psi, \tag{3}$$

we will find the eigenfunctions and eigenvalues under the following boundary conditions. The ideal dielectric corresponds to the infinitely high potential barrier. Then $\Psi(x, y, z) = 0$ for $x < 0$. This yields the boundary condition at $x = 0$: $\Psi(0, y, z) = 0$. If the system is bounded by the coordinates y and z with some great, but finite sizes, we may impose the standard boundary conditions (zero or periodic ones) on the corresponding boundaries and consider the wave vector $\vec{k}$ ($\vec{k} \perp 0x$) to be quasicontinuous. Since we search for the states localized near the surface $x = 0$, we have one more boundary condition $\lim\limits_{x\to\infty} \Psi(x, y, z) = 0$.

Let us separate the variables by considering that the potential energy depends only on x:

$$\Psi(x, y, z) = Ae^{i(\vec{k},\vec{r})}\varphi(x), \tag{4}$$

where $\vec{r} \perp 0x$. We choose the factor A so that the functions $Ae^{i(\vec{k},\vec{r})}$ are normed. Then $\varphi(x)$ satisfies the condition

$$\int\limits_0^\infty |\varphi(x)|^2 dx = 1. \tag{5}$$

In view of the above-written, Eq. (3) is reduced to the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\frac{d^2\varphi}{dx^2} + \left(\frac{\hbar^2k^2}{2m_e} - \frac{e^2}{4\varepsilon(a+x)} + E_G - E\right)\varphi = 0 \tag{6}$$

with zero boundary conditions

$$\varphi(0) = \varphi(\infty) = 0. \tag{7}$$

We introduce the dimensionless variable $\xi = \mu x$, $\mu = \frac{m_e e^2}{2\varepsilon\hbar^2}$, and denote

$$\alpha = \mu a; \quad \lambda = \frac{1}{\mu^2}\left(-k^2 + \frac{2m_e}{\hbar^2}(E - E_G)\right). \tag{8}$$

Now Eq. (6) takes the form

$$\frac{d^2\varphi}{d\xi^2} + \left(\frac{1}{\alpha+\xi} + \lambda\right)\varphi = 0, \tag{9}$$

and the boundary conditions (7) remain invariable, but for the variable ξ.

If the dielectric thickness tends to zero, and the boundary conditions (7) are satisfied, Eq. (9) takes the form

$$\frac{d^2\varphi}{d\xi^2} + \left(\frac{1}{\xi} + \lambda\right)\varphi = 0. \tag{10}$$

The spectral problem (10), (7) can be solved exactly in terms of antisymmetric functions $\varphi(-x) = -\varphi(x)$. The boundary condition $\varphi(0) = 0$ eliminates all the other solutions and the difficulties related to them. In other words, there occurs the "decimation" of these states (see, e.g., [6]).

3. Energy Spectrum. Eigenfunctions

The one-dimensional Schrödinger equation with the symmetric potential $1/(\alpha + |\xi|)$ and periodic or zero boundary conditions at $\pm\infty$ was analyzed many times [7]– [9]. Both the discrete and continuous parts of the spectrum were investigated. In the last case, the Schrödinger equation can be transformed in the Whittaker equation with imaginary potential [9]). In the present work, we consider the asymmetric potential tending to infinity at negative x. Just this potential hampers the penetration of a particle into the region $x < 0$ and, hence, defines the boundary condition $\varphi(0) = 0$ and the nullification of $\varphi(x)$ for $x < 0$.

Below, we give several eigenfunctions $\varphi_n(\xi)$ and eigenvalues λ_n lowest in energy for the spectral problem (10), (7), by omitting the normalizing factors:

$$\varphi_1 = \xi e^{-\xi/2}; \quad \lambda_1 = -\frac{1}{4}, \tag{11}$$

$$\varphi_2 = \xi\left(1 - \frac{1}{4}\xi\right)e^{-\xi/4}; \quad \lambda_2 = -\frac{1}{4\cdot 2^2} = -\frac{1}{16}, \tag{12}$$

$$\varphi_3 = \xi\left(1 - \frac{1}{3}\xi + \frac{1}{2\cdot 3^3}\xi^2\right)e^{-\xi/6};$$

$$\lambda_3 = -\frac{1}{4\cdot 3^2} = -\frac{1}{36}. \tag{13}$$

$$\varphi_4 = \xi\left(1 - \frac{3}{2^3}\xi + \frac{1}{2^5}\xi^2 - \frac{1}{3\cdot 2^9}\xi^3\right)e^{-\xi/8};$$

$$\lambda_4 = -\frac{1}{4\cdot 4^2} = -\frac{1}{64}. \tag{14}$$

$$\varphi_5 = \xi\left(1 - \frac{2}{5}\xi + \frac{1}{5^2}\xi^2 - \frac{1}{2\cdot 3\cdot 5^3}\xi^3 + \frac{\xi^4}{3\cdot 2^3\cdot 5^5}\right)e^{-\xi/10};$$

$$\lambda_5 = -\frac{1}{4\cdot 5^2}. \tag{15}$$

We present the eigenfunction for any natural n as

$$\varphi_n = \xi(1 + C_{n1}\xi + C_{n2}\xi^2 + ... + C_{n,n-1}\xi^{n-1})e^{-b_n\xi}. \tag{16}$$

Substituting it in Eq. (10) and nullifying the coefficients of the various degrees of ξ^ν, ($\nu = 0; 1; 2; ..., n$), we obtain the system of $n + 1$ equations for $n + 1$ unknowns: the numbers b_n and λ_n and $n-1$ polynomial coefficients c_{ni}. But if we are interested only in the energy spectrum λ_n, we should not solve the full system of $n+1$ equations. It is sufficient to write only the coefficients of the last two degrees, ξ^{n-1} and ξ^n, in (10):

$$C_{nn-2}b_n^2 - 2nC_{nn-1}b_n + C_{nn-1} + \lambda_n C_{nn-2} = 0, \tag{17}$$

$$C_{nn-1}b_n^2 + \lambda_n C_{nn-1} = 0. \tag{18}$$

The last relation yields $\lambda_n = -b_n^2$. Substituting this relation in (17), we get $b_n = \frac{1}{2n}$. Then

$$\lambda_n = -\frac{1}{4n^2}. \tag{19}$$

Here, we took into account that $C_{nn-1} \neq 0$. Otherwise, we would have φ_{n-1} instead of φ_n in view of formula (16). It is easy to verify that eigenfunctions (16) are determined uniquely from the system of $n+1$ equations. Indeed, if we exclude Eqs. (17), (18) from the full system, whose solutions are unique, then the remaining part of the system for the coefficients c_{ni} will be linear and will possess the unique solution.

Let us rewrite the energy spectrum (19) by using notations (8):

$$E_n(k) = E_G + \frac{\hbar^2k^2}{2m_e} - \frac{R_e}{n^2}; \quad R_e = \frac{m_e e^4}{32\varepsilon^2\hbar^2}. \tag{20}$$

For a hole, we get, respectively, the formulas

$$E_n^h(k_h) = \frac{\hbar^2k_h^2}{2m_h} - \frac{R_h}{n^2}; \quad R_h = \frac{m_h e^4}{32\varepsilon^2\hbar^2}. \tag{21}$$

For an electron (20) and a hole (21) which are located on the surface, interact with their mirror images, and do not interact with each other, the energy spectra have hydrogen-like character as that of a Wannier–Mott exciton. However, there exist the essential differences. First, a Wannier–Mott exciton has 6 degrees of freedom, and its state is determined by 6 quantum numbers: 3 quasicontinuous (k_x, k_y, k_z) and 3 discrete (n, m, l) ones, excluding spin. The superficial electron has 3 degrees of freedom: 2 quasicontinuous (k_y, k_z) and 1 discrete (n) ones. Hence, the levels E_n are not degenerate. Second, the coefficients of k^2 in the dispersion laws (20) and (21) include the effective mass of an electron or a hole, rather than that of an exciton $m_{\rm ex} = m_e + m_h$. Third, the excitonic "Rydberg constant" $R_{\rm ex} = \frac{\mu e^4}{2\varepsilon^2\hbar^2}$ involves the reduced mass $\mu = \frac{m_e m_n}{m_2+m_n}$, whereas formulas (20) and (21) include the effective mass of an electron or a hole and other numerical factors.

We now define the mean value of the coordinate $\bar{x}_1$ in the state φ_1 by the formula $\bar{x}_1 = \frac{\langle\varphi_1|x|\varphi_1\rangle}{\langle\varphi_1|\varphi_1\rangle}$, because states (11)–(16) are not normed. We get

$$\bar{x}_1 = \frac{6\varepsilon\hbar^2}{m_e e^2} = \frac{6\varepsilon m}{m_e} a_{\rm B}, \tag{22}$$

where $a_{\rm B} = \frac{\hbar^2}{me^2}$ is the radius of the first Bohr orbit of a hydrogen atom, and m is the mass of a free electron.

Comparing formula (22) with that of the exciton radius [10] for the first Bohr orbit $r_{\rm ex} = \frac{\varepsilon m}{\mu} a_{\rm B}$, we see that, for $m_e \approx m_h$, the reduced mass $\mu \approx m_e/2$, and $\bar{x}_1 \approx 3r_{\rm ex}$. For example, $r_{\rm ex} \approx 80a_{\rm B}$ for Ge, and then $\bar{x}_1 \approx 240a_{\rm B}$. In this case, the method of effective mass is applicable in the same way as the Coulomb law for the potential. But if $m_h \gg m_e$, then $\mu \approx m_e$, and we get $\bar{x}_1 = 6r_{\rm ex}$.

It is easy to prove that the inertialess approximation for the electron subsystem of a metal, which requires the fulfilment of inequality (1), is valid as well. For well-conducting metals (Cu, Ag, Au, Al), the Fermi energy varies in the limits 5–11 eV [5], and $R_{\rm ex}$ for Ge, e.g., has value of 0.016 eV. Then, for $m_h \approx m_e$, we get $R_e \approx \frac{1}{8}R_{\rm ex} \approx 0.002$ eV. Hence, inequality (1) is fulfilled with high accuracy: $\omega_{\rm F}/\omega_e \approx 10^3$.

The conditions for the method of images to be valid become significantly less strong when the thickness a of the dielectric layer increases. The solution of the spectral problem (9), (7) for $\alpha \neq 0$ is more complicated than that of (10). However, not solving it, we can determine the important properties of the energy spectrum, by basing on the already obtained exact solutions of problem (10), (7).

The differential equation (9) can be reduced to (10) with the help of a shift of the variable $\eta = \alpha + \xi$. But, in this case, the boundary condition $\varphi(0) = 0$ will take the form $\lim\limits_{\eta\to\alpha} \varphi(\eta) = 0$. The eigenfunction $\varphi(\eta)$ will be nonzero only for $\eta > \alpha$. It obeys the equation

$$\frac{d^2\varphi}{d\eta^2} + \left(\frac{1}{\eta} + \lambda\right)\varphi = 0 \tag{23}$$

and satisfies the boundary conditions

$$\varphi(\alpha) = \varphi(\infty) = 0. \tag{24}$$

As seen, Eq. (23) coincides with (10) to within the notations. Hence, functions (11)–(16) will be also the solutions of Eq. (23), if we will change ξ by η. However, function (11) $(\varphi_1(\eta))$ cannot satisfy the boundary condition (24) in all cases. On the other hand, all the rest functions (12)–(16) can also satisfy the boundary condition (24) for some fixed values of α. For example, for $\alpha = \eta_0 = 4$, the function $\varphi_2(\eta)$ satisfies Eq. (23) and conditions (24). Hence, for the dielectric thickness $\alpha = \eta_0$, the function $\varphi_2(\eta) = \chi(\eta_0,\infty)\eta(1 - \frac{1}{4}\eta)e^{-\eta/4}$ ($\chi(a,b)$ is the characteristic function of the interval (a,b)) will be one of the exact solutions of the spectral problem (23), (24), and the eigenvalue $\lambda_2 = -\frac{1}{16}$ will be lowest in energy. Function (13), $\varphi_3(\eta)$, has two nodes at the points $\eta_{1,2} = 3(3\pm\sqrt{3})$, $\eta_1 \approx 3.8$, $\eta_2 \approx 14.2$. Hence, for the thicknesses of a dielectric $\alpha = \eta_1$ or $\alpha = \eta_2$, the function $\varphi_3(\eta)$ is the exact solution of problem (23), (24) with the eigenvalue $\lambda_3 = -\frac{1}{36}$. Now for $\alpha = \eta_2$, the function $\varphi_{31} = \chi(\eta_2,\infty)\varphi_3(\eta)$ has no nodes in the interval (η_2,∞) and corresponds to the eigenvalue $\lambda_3 = -\frac{1}{36}$ lowest in energy. But if $\alpha = \eta_1$, then the function $\varphi_{32} = \chi(\eta_1,\infty)\varphi_3(\eta)$ has one node in (η_1,∞), and the level $\lambda_3 = -\frac{1}{36}$ will be the second one. We do not know the position of the first level, but can find it by interpolation with regard for the facts that the numbers $\eta_1 = 3.8$ and $\eta_0 = 4$ are close to each other, and the level for $\alpha = \eta_0$ is known. Analogously, we can determine the nodes η_i of function (14): $\eta_3 = 16\left(1 - \cos\frac{\pi}{9}\right) \approx 3.74$, $\eta_4 = 16\left(1 - \cos\frac{2\pi}{9}\right) \approx 13.2$, and $\eta_5 = 16\left(1 + \cos\frac{\pi}{18}\right) \approx 31.0$. We may assert now that, for $\alpha = \eta_i$, there exist three exact solutions of problem (23), (24). For $\alpha = \eta_5$, the eigenfunction $\varphi_{45} = \chi(\eta_5,\infty)\varphi_4(\eta)$ has no nodes in the interval (η_5,∞), and the value of $\lambda_4 = -\frac{1}{64}$ corresponds to the lowest level of the spectrum. For the thicknesses of a dielectric $\alpha = \eta_4$ and $\alpha = \eta_3$, the same value of λ_4 will be, respectively, the second and third eigenvalues. By determining the nodes $\eta_i (i = 6; 7; ...)$ of the rest functions (15) and (16), we get a series of exact solutions of the spectral problem (23),

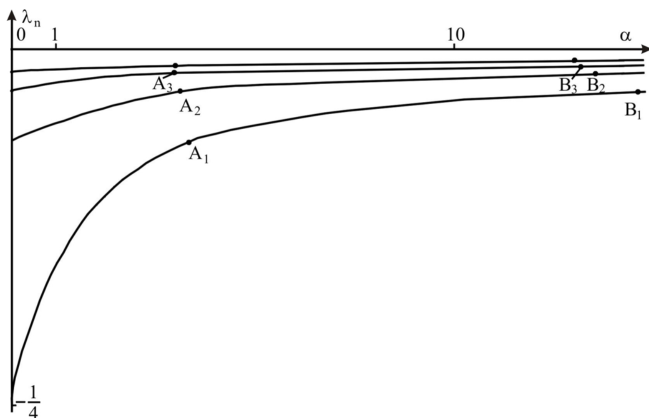

Fig. 1

(24) for some discrete values of the parameter $\alpha = \eta_i$. By the points obtained, we can construct the approximate plots of the dependences $\lambda_n(\alpha)$. These dependences can be corrected, by using the variation method. While determining the state lowest in energy for the spectral problem (7), (9), we can use the normed trial function $\varphi_{tr} = 2b\sqrt{b}\xi e^{-b\xi}$ with variational parameter b. By minimizing the mean value $\bar{\lambda}_1(\alpha, b) = \int\limits_0^\infty \varphi_{tr} F \varphi_{tr} d\xi$ of the operator $F = \frac{d^2}{d\xi^2} + \frac{1}{\xi+\alpha}$ in the parameter b, we obtain the dependence $\lambda_1(\alpha)$ which becomes linear $\bar{\lambda}_1(\alpha) = -\frac{1}{4} + \frac{1}{2}\alpha$ in the limit $\alpha \ll 1$. Then the dependence $\lambda_1(\alpha)$ (curve *1* in Fig. 1) will possess the same asymptotics and pass through the points $A_1, B_1, ...$, corresponding to the exact solutions.

For greater values of n such that $\bar{\xi}_n \gg \alpha$, the dependence λ_n on n becomes approximately "hydrogen-like": $\lambda_n \sim \frac{1}{n^2}$.

4. Account of the Discreteness of the Crystal Lattice of a Semiconductor

When the value of $\bar{x}_1$ determined by formula (22) turns out to be comparable with the lattice constant d, the method of effective mass becomes inapplicable. In this case, we must use other methods taking the discreteness of the crystal lattice into account.

Consider a semiconductor crystal with the cubic crystal lattice and the lattice constant d. The radius vectors of nodes of the lattice are

$$\vec{r}_{l,m,p} = d(\vec{i}\,l + \vec{j}\,m + \vec{k}p), \tag{25}$$

where $\vec{i}$, $\vec{j}$, $\vec{k}$ are the unit vectors of the Cartesian coordinate system, and l, m, p are the integers enumerating the lattice nodes. Let, at $x = 0$, the semiconductor be in contact with a thin dielectric layer, and let a metal occupy the region $x < 0$. Then the number l in (25) will be bounded from the left: l=1,2,... The distance from an electron being at the node of the lattice l, m, p to its image in a conductor is $2ld$, and the potential energy of the Coulomb interaction $U_l = -\frac{e^2}{4\varepsilon\ ld}$. The probability of the transition of an electron from node to node is defined by the exchange interaction energy $I(l - l', m - m', p - p')$ calculated in terms of the overlap integrals of the electron wave functions centered at the nodes (l, m, p) and (l', m', p'). Because the exchange interaction is short-range (the overlap integrals decrease exponentially with increase in the distance), we may account only the exchange interaction between the nearest neighbors. We denote the energy of this interaction as I (and that for a hole as J). The electron energy operator in the conduction band looks as

$$H_e = \sum_{l=1}^{\infty}\sum_{m,p}\Bigg\{ I(a^+_{l,m,p}(a_{l+1,m,p} + a_{l,m+1,p} + a_{l,m,p+1}) + $$

$$+\mathrm{h.c.}) + \left(\mathrm{E}_0 - \frac{\mathrm{e}^2}{2\varepsilon \mathrm{ld}}\right) \mathrm{a}^+_{\mathrm{l,m,p}} \mathrm{a}_{\mathrm{l,m,p}} \Bigg\}, \tag{26}$$

where $a^+_{l,m,p}$, $a_{l,m,p}$ are the Fermi operators of creation and annihilation of an electron at the lattice node l, m, p, E_0 is some parameter of the order of the forbidden band width. The Hamiltonian for a hole, which is located in the conduction band and does not interact with the electron, can be also written in form (26), where I should be changed by J, the operators a^+, a by the Fermi operators b^+, b, and the constant E_0 should be dropped.

Solving the stationary Schrödinger equation $H_e|\Psi\rangle = E|\Psi\rangle$ on the one-particle wave functions $|\Psi\rangle = \sum\limits_{l,m,p} C_{lmp} a^+_{lmp}|0\rangle$, we obtain the system of difference equations for the coefficients $C_{l,m,p}$:

$$I(C_{l+1,m,p} + (1 - \delta_{l1})C_{l-1,m,p} + C_{l,m+1,p} + C_{l,m-1,p} +$$

$$+C_{l,m,p+1} + C_{l,m,p-1}) + (U_l - E)C_{lmp} = 0. \tag{27}$$

Here, $l = 1, 2, 3, ...$, and the Kronecker symbol δ indicates that only a neighbor on the right is present in the boundary layer of the semiconductor (l=1). This also yields the boundary condition $C_{0,m,p} = 0$. Further, we will be interested only in the discrete part of the spectrum. Therefore, we get one more boundary

condition in the form $\lim_{l\to\infty} C_{l,m,p} = 0$. The positive effective mass of the electron corresponds to the negative value of the parameter I. Since $U_l < 0$, the dimensionless quantities $V_l = \frac{U_l}{I}$ are positive. Denoting $V = -\frac{e^2}{4\varepsilon Id}$, we have $V_l = \frac{V}{l}$. The potential energy U_l depends only on l. Hence, the variables in $C_{l,m,p}$ can be separated:

$$C_{l,m,p} = Ae^{i(q_y m + q_z p)}\varphi(l). \tag{28}$$

Here, q_y and q_z are the components of the superficial dimensionless wave vector $\vec{q}$, and A is the normalizing factor. If we impose periodic (or zero) boundary conditions on the functions (28) in the variables m, p ($m, p = 0; \pm 1; \pm ... \pm N$), and if $N \gg 1$, we obtain a quasicontinuous spectrum in the quantum numbers q_y and q_z. In this case, relation (27) yields the following difference equations for the function $\varphi(l)$:

$$\varphi(l+1) + (1-\delta_{l1})\varphi(l-1) + \left(\lambda + \frac{V}{l}\right)\varphi(l) = 0;$$

$$l = 1; 2; ..., \tag{29}$$

where $\lambda = (E_0 + 2I(\cos q_y + \cos q_z) - E)/I$, and the boundary conditions take the form

$$\varphi(0) = 0; \quad \lim_{l\to\infty} \varphi(l) = 0. \tag{30}$$

In a semiconductor crystal, whose all six faces contact with vacuum, the eigenfunctions and the electron energy spectrum are, respectively, $C_{l,m,p} = Ae^{i(q_z l + q_y m + q_z p)}$ and $E_e(k) = E_0 + 2I(\cos q_x + \cos q_y + \cos q_z)$. Hence, in the one-electron approximation of strong coupling and the approximation of nearest neighbors, the conduction band width is $12|I|$, and its bottom corresponds to the level $E_e = E_0 + 6I < E_0$. Using the analogous formula for a hole with the wave vector q', we get $E_h = 2J(\cos q'_x + \cos q'_y + \cos q'_z)$. Hence, the valence band width is $12|J|$, and its upper edge corresponds to $6|J|$. This yields the connection between the forbidden band width E_G and the parameter E_0: $E_G = E_0 - 6(|I| + |J|)$.

The discrete spectral problem (29), (30) has solutions analogous to (11)–(16). Omitting the normalizing factors, we write the solutions of problem (29), (30) which depend on the natural quantum number n as

$$\varphi_1(l) = le^{-b_1 l}, \quad b_1 = \mathrm{Arsh}\frac{\mathrm{V}}{2}, \quad \lambda_1 = -\sqrt{4 + \mathrm{V}^2}, \tag{31}$$

$$\varphi_2(l) = l(1 + \beta_{12} l)e^{-b_2 l}; \quad \beta_{12} = -\frac{V}{\sqrt{16 + V^2}};$$

$$b_2 = \mathrm{Arsh}\frac{\mathrm{V}}{4}; \quad \lambda_2 = -\sqrt{4 + \frac{\mathrm{V}^2}{2^2}}, \tag{32}$$

$$\varphi_3(l) = l(1 + \beta_{13} l + \beta_{23} l^2)e^{-b_3 l}; \quad \beta_{13} = -\frac{3V\sqrt{36 + V^2}}{2(27 + V^2)};$$

$$\beta_{23} = \frac{V^2}{2(27 + V^2)}; \quad b_3 = \mathrm{Arsh}\,\frac{\mathrm{V}}{6}; \quad \lambda_3 = -\sqrt{4 + \frac{\mathrm{V}^2}{3^2}}, \tag{33}$$

$$\varphi_n(l) = l(1 + \beta_{1n} l + \beta_{2n} l^2 + ... + \beta_{n-1,n} l^{n-1})e^{-b_n l};$$

$$b_n = \mathrm{Arsh}\,\frac{V}{2n}; \quad \lambda_n = -\sqrt{4 + \frac{V^2}{n^2}}. \tag{34}$$

The method of derivation of spectrum (34) is identical to that used in the construction of spectrum (19).

We rewrite formula (34) in the previous notations as

$$E_n(q) = E_0 + 4I - 2Iq^2 + I\sqrt{4 + \frac{V^2}{n^2}}; \quad (I < 0). \tag{35}$$

For $V^2 \ll 4$, the last term in (35) can be represented in the approximation linear in a small parameter as

$$E_n(q) \approx E_0 + 6I - 2Iq^2 + \frac{e^4}{64\varepsilon^2 Id^2 n^2}. \tag{36}$$

Since $q = kd$, $E_G = E_0 - 6(|I| + |J|)$, and $2I = -\frac{\hbar^2}{m_e d^2}$, we see that formula (36) coincides with formula (20). The analogous result (21) can be obtained for a hole if the inequality $V_h^2 \ll 4$ holds, where $V_h = -\frac{e^2}{4\varepsilon Jd}$.

In the opposite limiting case $V^2 \gg 4$ for small values of n, for which the inequality $\frac{V^2}{n^2} \gg 4$ holds, formula (35) yields

$$E_n(q) \approx E_0 + 4I - 2Iq^2 - \frac{e^2}{4\varepsilon dn} - \frac{8I^2\varepsilon d}{e^2}n. \tag{37}$$

The energy spectrum (37) has simple physical sense: if the exchange interaction $I = 0$, the stationary states correspond to the states of an electron localized at some lattice node with the energy $E_n = E_0 - \frac{e^2}{4\varepsilon dn}$ corresponding to the Coulomb interaction of the electron with its mirror image positioned at a distance of $2nd$. For small, but nonzero I, we get both a narrow band of surface states with a width of $8|I|$ and a small negative correction to the spectrum due to the exchange

interaction which is proportional to I^2 and n. However in this case ($V^2 \gg 4$) for sufficiently large n, the inequality $\frac{V^2}{n^2} \ll 1$ can be satisfied, and we get a spectrum similar to (36). With increase in n, the energy spectrum will be smoothly varied from the approximate dependence $E_n \sim 1/n$ to the hydrogen-like one $E_n \sim 1/n^2$.

5. Other Applications of the Method of Images

The method of images can be also used in the calculation of the energy spectrum of surface states of a charged particle in the case where a metal contacts with vacuum. However, the characteristic frequencies calculated by this method for an electron, for example, turn out comparable with the frequencies $\omega_{\rm F}$ of electrons of a metal near the Fermi level, and the method of images is already inapplicable. But if we consider a more massive particle, for example, an ion with charge q, the inequality $\omega_{\rm F} \gg \omega_q$ is satisfied, and all the above-obtained results are true for ions. Though the ions cannot penetrate into a metal, so that the zero boundary conditions will be satisfied, the dielectric layer between a metal and vacuum is necessary in order to hamper the neutralization of an ion by a metal.

But if we replace a metal by an ionic conductor (a liquid or solid electrolyte, e.g.), the image in the conductor will be blurred due to a great mass of ions: the surface ions will not manage to "trace" the fast virtual movements of an electron or a hole in the semiconductor, by averaging these movements in a certain way. If the inverse inequality $\omega_{\rm F} \gg \omega_e$ holds, then the image of an electron in a stationary state $\Psi(x,y,z)$ in the ionic conductor will be distributed with density $\rho = +e|\Psi(-x,y,z)|^2$ rather than be point-like. The potential energy of an electron, which is at a point (x,y,z) of the semiconductor and interacts with the blurred mirror image, can be calculated by the formula

$$U(x,y,z) = -\frac{e^2}{2\varepsilon}\int\limits_{-\infty}^{0} dx' \int\limits_{-L}^{L} dy' \int\limits_{-L}^{L} dz' \times$$

$$\times \frac{|\Psi(x',y',z')|^2}{\sqrt{(x-x'+2a)^2+(y-y')^2+(z-z')^2}}, \qquad (38)$$

where ε is the permittivity of both the semiconductor and the dielectric layer with thickness a. We assume that the sizes L in the variables y,z are great ($L \gg a$) or infinite. In this case, Eq. (6) becomes the integro-differential equation with potential (38)

$$-\frac{\hbar^2}{2m_e}\Delta\Psi + U\Psi = E\Psi \qquad (39)$$

and the boundary conditions $\Psi(0,y,z) = 0$, $\Psi(\infty,y,z) = 0$. By the variables y,z, the boundary conditions can be chosen periodic or zero.

It is easy to verify that the significant gain in energy can be obtained only under the localization of $\Psi(x,y,z)$ in all three variables. Indeed, let us represent Ψ in form (4) with the localization only in the variable x, and let us calculate the mean value of the potential energy (38): $\bar{U} = \langle\Psi|U|\Psi\rangle$. For the strong localization of the function $\varphi(x)$ so that $\bar{x} \ll a$, the energy gain $\bar{U}$ will be maximum. Moreover, the calculation of $\bar{U}$ is reduced to the calculation of the energy of a plane capacitor $\frac{e^2}{2C}$, $C = \frac{\varepsilon S}{a}$, $S = 4L^2$. If $L \to \infty$, then $\bar{U} \to 0$.

Problem (39) has some similarity with the polaron problem [10], and we can suppose that the properties of a superficial quasiparticle under consideration will be similar to those of polarons. First, the effective mass of a superficial quasiparticle will be greater (and, possibly, much more greater) than m_e. Second, the degree of localization of the quasiparticle will be higher and its connection with the surface will be stronger with increase in m_e and with decrease in a.

In the construction of Hamiltonian (2), we assumed that the permittivities of the semiconductor ε and the insulating layer ε_d are the same. We will now analyze the situation where these quantities differ significantly from each other. Let the semiconductor and the dielectric have a plane interface, and let a charge e be located in the semiconductor at a distance x from the interface. Then the field in the semiconductor is the superposition of two fields: those of the charge e and its image $e' = e\frac{\varepsilon-\varepsilon_d}{\varepsilon+\varepsilon_d}$ located symmetrically, i.e. at the distance of $2x$ from e. If the dielectric layer with thickness a is followed by a conductor, then its boundary with the dielectric gives one more image and, respectively, the additional term to the potential energy of the charge e:

$$U = U_1 + U_2; \quad U_1 = -\frac{e^2\varepsilon_d}{(\varepsilon+\varepsilon_d)^2(x+a)},$$

$$U_2 = \frac{e^2(\varepsilon-\varepsilon_d)}{4\varepsilon(\varepsilon+\varepsilon_d)x}. \qquad (40)$$

In fact, the above-described situation is characterized by the formation of the infinite series of charges-images q_i like those of an object positioned between two mirrors, one of which (the front one) is semitransparent. The

distances from an electron in the semiconductor to its images q_i will increase, and $\mid q_i \mid$ will decrease by a geometric progression. In potential (40), we consider the interaction only with the two nearest images.

Repeating the calculation given in Section 1, we get, instead of (9), the equation

$$\frac{d^2\varphi}{d\xi^2} + \lambda\varphi + \left(\frac{1}{\xi+\alpha} + \frac{\gamma}{\xi}\right)\varphi = 0 \tag{41}$$

for potential (40) with boundary conditions (7). Here, $\gamma = \frac{\varepsilon_d^2-\varepsilon^2}{2\varepsilon\varepsilon_d}$, but the parameter μ takes the form, $\mu = \frac{2m_e e^2\varepsilon_d}{\hbar^2(\varepsilon+\varepsilon_d)^2}$, different from (9). If $\varepsilon_d = \varepsilon$, the parameter γ becomes zero, and Eq. (41) passes into (9). In the case of only two media, a semiconductor and a dielectric, the surface states of an electron or a hole can be formed only if $\varepsilon_d > \varepsilon$. Just in this case, the image charge $e' = e\,\frac{\varepsilon-\varepsilon_d}{\varepsilon+\varepsilon_d}$ is opposite in sign to the electron charge (or the hole charge), and the forces of attraction arise. In this case, Eq. (41) passes into Eq. (10), where all the quantities, except for μ, are defined as in (8), but $\mu = \frac{m_e e^2(\varepsilon_d-\varepsilon)}{2\hbar^2\varepsilon(\varepsilon_d+\varepsilon)}>0$. Then the energy spectra of the surface states of an electron or a hole near the boundary with the dielectric are given by formula (20) or (21), where R_e and R_h should be replaced by formulas $R_e = \frac{m_e e^4(\varepsilon_d-\varepsilon)^2}{32\hbar^2\varepsilon^2(\varepsilon_d+\varepsilon)^2}$ and $R_h = \frac{m_h}{m_e}R_e$. If $\varepsilon_d \approx \varepsilon$, then the hydrogen-like structure of the spectrum will be shallow and will be blurred by thermal oscillations even at low temperatures. But if, for example, $\varepsilon_d = 2\varepsilon$, then $R_e = \frac{m_e e^4}{288\hbar^2\varepsilon^2}$. This value is less by almost one order than that in (20). For $\varepsilon_d \gg \varepsilon$, $R_e \approx \frac{m_e e^4}{32\hbar^2\varepsilon^2}$, which coincides with (20). However, it is impossible, most likely, to select a semiconductor–dielectric pair, for which the inequality $\varepsilon_d \gg \varepsilon$ will hold. In addition, it is necessary that the condition analogous to (1), $\omega_d \gg R_e/\hbar$, where ω_d are the characteristic frequencies of a dielectric, be satisfied.

The problem involving a semiconductor–dielectric pair can be solved in the discrete version. Then, if $\varepsilon_d > \varepsilon$, we get spectrum (34). For a polar dielectric, whose polarization is related to the displacements of nuclei, we may expect that the inequality $\omega_d \ll R_e/\hbar$ is satisfied. In this case, we arrive at a potential of form (38), in which a=0 and the factor $1/\varepsilon$ is replaced by $\frac{\varepsilon_d-\varepsilon}{2\varepsilon(\varepsilon_d+\varepsilon)}$.

For the three-layer semiconductor–dielectric–conductor structures with $\varepsilon_d \neq \varepsilon$, the following versions are possible. If $\varepsilon_d > \varepsilon$, then both terms in (40) are negative, and the surface states of the electron and the hole must exist with the asymptotics of the spectrum $\sim \frac{1}{n^2}$ at great values of n. Depending on the value of $\bar{\xi}_1$, the spectral problem can be solved in the continuum approximation for $\bar{\xi}_1 \gg d$ or in the discrete version if $\bar{\xi} \sim d$. The formula for $\bar{\xi}_1$ can be obtained, if the solution of problem (41), (7) lowest in energy is determined. But if $\varepsilon_d < \varepsilon$, the possibility for the surface states to exist depends on the ratio of the constants a, ε, and ε_d.

The formation of the surface states of an electron or a hole can occur by two ways.

1. In the bulk of a semiconductor, a dissociated electron–hole pair is excited. While migrating in the crystal and attracting to the own image, the quasiparticle occupies one of the surface levels E_n, by releasing the energy excess in the form of phonons. In this case, the presence of the electron near the surface does not guarantee the presence of the hole there: the processes of binding them with the surface are independent.

2. Light can excite at once the surface states of the electron–hole pair. In this case, the energies of absorbed light quanta will be determined by the combination principle

$$E_{nn'} = E_n^e + E_{n'}^h + E_G + \frac{\hbar^2}{2}\left(\frac{k_e^2}{m_e} + \frac{k_h^2}{m_h}\right) - \frac{R_e}{n} - \frac{R_h}{n'}, \tag{42}$$

where n, n' are natural numbers. Of course, the conservation law for the quasimomentum must be fulfilled.

Let us consider the question about the possibility to bind the superficial pair of an electron and a hole, as a two-dimensional analog of a Wannier–Mott exciton. It is known that the tangent component of the electric field is suppressed near the metal surface. Therefore, while being near the surface, the electron and the hole attract quite weakly each other, as two antiparallel dipoles with the dipole moments $P_e = -2e(a+\bar{\xi}_n)$ and $P_h = 2e(a+\bar{\xi}_{n'})$. If the coupling with a metal is great, then $\bar{\xi}$ are small, and the attraction forces are small as well. The binding energy will be also low. If the coupling with a metal decreases, the mean values of $\bar{\xi}$ increase. Then the electron–hole coupling increases, and the attraction to the metal becomes else less, because the dipole moment of the electron–hole pair is not great, and the distance to the metal is large.

The method of images can be used also for some curvilinear interfaces, in particular, for the problems involving a sphere or a cylinder. This can be useful in the study, for example, of quantum dots and lines in various versions (a semiconductor inside a dielectric or vice versa), three-layer structures of spherical or cylindrical form, *etc.*

1. W.R. Smythe, *Static and Dynamic Electricity* (Hemisphere, New York, 1989).
2. L.D. Landau and E.M. Lifshits, *Electrodynamics of Continuous Media* (Pergamon, New York, 1984).
3. N.E. Kochin, I.A. Kibel, and N.V. Roze, *Theoretical Hydromechanics* (Gostekhizdat, Moscow, 1963), Vol. 1 (in Russian).
4. L.M. Brekhovsky, *Waves in Layered Media* (Nauka, Moscow, 1982) (in Russian).
5. Ch. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
6. I.O. Vakarchuk, *Quantum Mechanics* (L'viv University, L'viv, 2004) (in Ukrainian).
7. R. Loudon, Amer. J. Phys. **27**, 649 (1959).
8. R.J. Elliott and R. Loudon, J. Phys. Chem. Sol. **8**, 382 (1959).
9. T. Ogawa and T. Takagara, Phys. Rev. B **47**, 14325 (1991).
10. A.S. Davydov, *Solid State Theory* (Nauka, Moscow, 1976) (in Russian).

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ВИКОРИСТАННЯ МЕТОДУ ЗОБРАЖЕНЬ ПРИ ДОСЛІДЖЕННІ СПЕКТРІВ ЕНЕРГІЙ ПОВЕРХНЕВИХ СТАНІВ ЕЛЕКТРОНІВ ЧИ ДІРОК В ТРИШАРОВИХ СТРУКТУРАХ НАПІВПРОВІДНИК–ДІЕЛЕКТРИК–ПРОВІДНИК

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Р е з ю м е

Для потенціалів, які отримані методом зображень, було знайдено поверхневі стани електрона або дірки в тришаровій структурі напівпровідник – діелектрик – провідник. При нескінченно тонкому шарі діелектрика отримані точні формули спектрів енергій E_n як методом ефективної маси $\left(E_n \sim \frac{1}{n^2}\right)$, так і з урахуванням дискретності кристалічної ґратки напівпровідника $\left(E_n \sim \sqrt{A + \frac{1}{n^2}}\right)$. Поверхневі стани електрона або дірки можуть створюватися і в двошарових структурах напівпровідник – діелектрик, коли діелектрична проникність діелектрика більша, ніж у напівпровідника. Точні розв'язки, які отримано вище, можуть застосовуватися і в цьому випадку. Обговорено інші варіанти застосування методу зображень.