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Electron spectrum of a semiconductor quantum dot influenced by an interface

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The generalized boundary conditions for the envelope wave function that take into account the real structure of an interface were used to investigate the hole spectrum of the semiconductor quantum dot embedded in an insulator matrix. An essential influnece of the interface levels on the hole spectrum has been demonstrated. Such levels could exist at the top of the valuence band. It is found that boundary conditions usually applied, wherein all components of the envelope wave function vanish at the interface, can be used only in the absence of the interface levels close to the band edge. [S0163-1829(99)51644-5]

To determine the electron states in semiconductor quantum dots, the envelope function approximation is applied.[1] The envelope wave functions are usually supposed to be vanished at the interface in order to describe the quantum confinement. If the intervalley or interband degeneracy of the electron spectrum occurs in the semiconductor, then each component of the envelope wave function is assumed to be vanished at the interface.[1–3] The last statement, however, needs to be justified.

Indeed, the boundary condition $\psi=0$ for the proper (not envelope) wave function arises from the solution of the Schrödinger equation for the infinitely high steplike potential barrier. Such a barrier cannot be considered in the framework of the envelope function approximation, wherein the potential must be smooth on the scale of the lattice constant. This means that the boundary condition $\Psi=0$ is justified if the potential that restricts the electron movement is smooth on the scale of the lattice constant, but sharp on the scale of the electron wavelength. Perhaps this happens at the contacts of chemically similar materials (e.g., GaAs/AlAs),[4] but not at the contacts of significantly different materials (e.g., semiconductor microcrystals embedded in the glass matrix).

The interface influence on the electrons in the quantum dot has to be more complicated if the simple boundary condition $\Psi=0$ does not hold. It is well known that band mixing exists at the interface in the heterojunctions of $A_{\mathrm{III}}B_{\mathrm{V}}$ semiconductors.[5,6] However, this is impossible at the plane interface where $\Psi=0$. The bound electron states are also possible at the interface owing to the interband mixing;[7] in these states the electron wave function behaves roughly as $\psi\propto[\exp(-\gamma_1 r)-\exp(-\gamma_2 r)]$, i.e., the wave function vanishes at the interface and far from it, but has an extremum at a certain distance from the interface.

The band mixing arises when the crystal symmetry that leads to the interband degeneracy in the bulk disappears at the interface. The lattice constant is the size that is characteristic for such symmetry. Therefore, the proper boundary conditions for the envelope wave functions should take into account the real structure of the interface.

In this paper, we propose simplest boundary conditions that take into account these subtle details of the interface influence. We find the conditions under which the boundary condition $\Psi=0$ is applicable at a sharp interface.

Let $z=0$ be the plane interface between a semiconductor ($z>0$) and an insulator ($z<0$). Assume the twofold degeneracy for the electron band of the semiconductor and nondegenerate electron band in the insulator. Then the boundary conditions for the envelope wave functions of the electrons in these bands can be written as follows:[8]

$$\Psi_1(\tau_1^0)=b_{11}\Psi_l(\tau_{11}),$$

$$\Psi_2(\tau_2^0)=b_{22}\Psi_l(\tau_{22}), \tag{1}$$

$$b_{31}\Psi_1(\tau_{31})+b_{32}\Psi_2(\tau_{32})=\Psi_l(\tau_3^0),$$

where Ψ_1 and Ψ_2 are the envelopes that relevant to the degenerate band of the semiconductor, and Ψ_l is the electron envelope in the insulator. To obtain the parameters b_{ij} and τ_{ij} of the boundary conditions (1), the Schrödinger equation has to be solved in the narrow (about a few lattice constants) region at the interface. It is impossible at an arbitrary and rather imperfect interface. Nevertheless, these parameters are independent of the electron energy; they characterize the interface, and estimations of their values (the small width of the interface region is the fact that is important for these estimations) are $b_{ij}\sim 1$ and $|\tau_{ij}|\sim a$, where a is the lattice constant. Thus, the boundary conditions (1) take into account the real structure of the interface.

We assume the effective-mass approximation holds in the bulk of each material, so that $\Psi(\tau)=\Psi(0)+\tau\Psi'(0)$. The large bands offset at the interface restricts the electron movement. If so, then $\Psi_l\propto\exp(\gamma_l z)$ and $\Psi_l'=\gamma_l\Psi_l$, where the γ_l value can be considered as independent of the electron energy. Eliminating Ψ_l from the Eqs. (1) yields

$$\Psi_1(\tilde{\tau}_{11})+\tilde{b}_{12}\Psi_2(\tilde{\tau}_{12})=0, \tag{2}$$

$$\tilde{b}_{21}\Psi_1(\tilde{\tau}_{21})+\Psi_2(\tilde{\tau}_{22})=0,$$

where $\tilde{b}_{ij}\sim b_{ij}$ and $\tilde{\tau}_{ij}\sim\tau_{ij}$ are known functions of b_{ij}, τ_{ij}, and γ_l. To ensure the probability flux conservation at the interface, we have to assume

$$\frac{\tilde{b}_{12}(\tilde{\tau}_{22}-\tilde{\tau}_{12})}{m_1}=\frac{\tilde{b}_{21}(\tilde{\tau}_{11}-\tilde{\tau}_{21})}{m_2}, \tag{3}$$

where m_1 and m_2 are effective masses of the appropriate bands.

Equations (2) are the general form of the boundary conditions that should be written instead of $\Psi=0$ at a sharp semiconductor/insulator interface. The most general boundary conditions that are applicable at such interface have been considered in Ref. 7. Ours, shown in Eqs. (2), hold in the effective-mass approximation. This approximation has been used in Ref. 8 to obtain Eqs.(1) and to estimate the parameters b_{ij} and τ_{ij}.

It is important that the boundary conditions (2) are nonlocal; they relate the envelopes at the different points $\tilde{\tau}_{ij}$ near the interface. However, the mean width of the ''nonlocality region'' is small in comparison with the electron wavelength λ ($|\tilde{\tau}_{ij}|\sim a\ll\lambda$). To understand consequences of this nonlocality, let us, at first, assume $\tilde{\tau}_{ij}=0$. Then Eqs. (2) become homogeneous in $\Psi_{1,2}$, and so their nonzero solutions exist only when

$$1-\tilde{b}_{21}\tilde{b}_{12}=0. \tag{4}$$

To be precise, for the parameters $\tilde{b}_{ij}$ that do not obey Eq. (4), the envelopes $\Psi_{1,2}(0)$ are as small as $\tau\Psi'(0)$, i.e., $\Psi_{1,2}(0)\sim a/\lambda\to 0$; this is the accuracy under which the simple boundary conditions $\Psi_{1,2}(0)=0$ are applicable. They are not applicable if Eq. (4) holds. It can be shown that condition (4) means the proximity of a certain interface level to the band edge. The energy position of this level is determined by the parameters $\tilde{b}_{ij}$ and $\tilde{\boldsymbol{\tau}}_{ij}$, i.e., by structure of the interface.

Thus, the simple boundary conditions $\Psi_{1,2}(0)=0$ can be used at a sharp interface in the absence of interface levels close to the band edge. Otherwise, the general boundary conditions (2) should be used.

It should be noted that assumption of the large bands offset at the interface is not important for our consideration. The boundary conditions (1) could be used in that case. This means that the simple boundary conditions $\Psi_{1,2}=0$ can be used at a sharp interface even in the absence of real potential barrier there, provided that the interface levels are not close to the band edge. In that case, the quantum confinement arises because the resonant tunneling of electrons is no longer possible through the interface.[9]

It is possible to rewrite Eqs. (2) in a more simple form:

$$\begin{pmatrix}\Psi_1\\ \Psi_1'\end{pmatrix}=\begin{pmatrix}t_{11} & t_{12}\\ t_{21} & t_{22}\end{pmatrix}\begin{pmatrix}\Psi_2\\ \Psi_2'\end{pmatrix}, \tag{5}$$

where

$$t_{11}=\frac{\tilde{b}_{12}\tilde{b}_{21}\tilde{\tau}_{21}-\tilde{\tau}_{11}}{\tilde{b}_{21}(\tilde{\tau}_{11}-\tilde{\tau}_{21})},\quad t_{12}=\frac{\tilde{b}_{12}\tilde{b}_{21}\tilde{\tau}_{12}\tilde{\tau}_{21}-\tilde{\tau}_{11}\tilde{\tau}_{22}}{\tilde{b}_{21}(\tilde{\tau}_{11}-\tilde{\tau}_{21})},$$

$$t_{21}=\frac{1-\tilde{b}_{12}\tilde{b}_{21}}{\tilde{b}_{21}(\tilde{\tau}_{11}-\tilde{\tau}_{21})},\quad t_{22}=-\frac{\tilde{b}_{12}\tilde{b}_{21}\tilde{\tau}_{12}-\tilde{\tau}_{22}}{\tilde{b}_{21}(\tilde{\tau}_{11}-\tilde{\tau}_{21})}.$$

Then Eq.(4) takes the form $t_{21}=0$.

The interface influence on the electrons is determined by the parameters t_{ij}. They are not independent. It follows from Eq. (3) that the determinant of the $||t_{ij}||$ matrix is equal to m_1/m_2. Moreover, $t_{12}\sim a$, and so it is possible to assume $t_{12}=0$ by the appropriate choice of the position of the plane $z=0$ within the unit cell at the interface.

Thus, there are two parameters, $t_{11}\sim 1$ and $t_{21}\sim a^{-1}$, that determine the interface influence on the electron. One of them, t_{21}, is sensitive to the position of the interface level: it vanishes when this level coincides with the band edge. Another one, t_{11}, can be considered as a trial parameter.

To consider the hole states in the spherical quantum dot, we write the Luttinger Hamiltonian in the spherical approximation as follows:[10]

$$\hat{H}=\left(\gamma_1+\frac{5}{2}\gamma\right)\frac{\hat{p}^2}{2m_0}-\frac{\gamma}{m_0}(\hat{\mathbf{p}}\mathbf{J})^2, \tag{6}$$

where $\hat{\mathbf{p}}$ is the momentum and $\mathbf{J}$ are the 4×4 matrices of the angular moment J=3/2; $\gamma>0$ and γ_1 are the Luttinger parameters that are relevant to the light and heavy effective masses of the holes: $m_l=m_0(\gamma_1+2\gamma)^{-1}$ and $m_h=m_0(\gamma_1-2\gamma)^{-1}$, m_0 is mass of the free electron.

The moment $F=1/2, 3/2, \ldots,$ and its projection M are good quantum numbers due to the spherical symmetry. Solutions of the Schrödinger equation with the Hamiltonian (6) are of the form[11]

$$\psi_{EM}(r,\theta,\varphi)=\sqrt{2F+1}\sum_l(-1)^{l-3/2+M}R_{Fl}(r)\times\sum_{m\mu}\begin{pmatrix}l & 3/2 & F\\ m & \mu & -M\end{pmatrix}Y_{lm}(\theta,\varphi)\chi_\mu,$$

where

$$\begin{pmatrix}l & 3/2 & F\\ m & \mu & -M\end{pmatrix}$$

are the Wigner symbols, and χ_μ is the eigenvector of the J_z matrix. The radial functions $R_{F,F+1/2}$ and $R_{F,F-3/2}$ that are relevant to the even solutions obey the equations [11]

$$\begin{aligned}&(\gamma_1-2\gamma\cos\alpha_F)P_F^+P_FR_{F,F+1/2}\\ &\quad+2\gamma\sin\alpha_FP_F^+P_{-F}R_{F,F-3/2}\\ &\quad+\frac{2m_0}{\hbar^2}[E-U(r)]R_{F,F+1/2}=0,\\ &(\gamma_1+2\gamma\cos\alpha_F)P_{-F}^+P_{-F}R_{F,F-3/2}\\ &\quad+2\gamma\sin\alpha_FP_{-F}^+P_FR_{F,F+1/2}\\ &\quad+\frac{2m_0}{\hbar^2}[E-U(r)]R_{F,F-3/2}=0,\end{aligned} \tag{7}$$

where

$$\cos\alpha_F=\frac{2F-3}{4F},\quad \sin\alpha_F\geqslant 0,\quad P_F=\frac{d}{dr}+\frac{F+3/2}{r},$$

$$P_F^+=\frac{d}{dr}-\frac{F-1/2}{r}.$$

Let us, at first, suppose that Eqs. (7) also hold at the interface where the potential $U(r)$ restricts the hole movement. Then we can obtain the boundary conditions for the radial wave functions. Two of them arise after integration of Eqs. (7) over the narrow region $|r-r_0|<w/2$ ($a \ll w \ll \lambda$) at the interface. To obtain another two boundary conditions, we have to multiply Eqs. (7) by $r-r_0$ before the integration. After elimination of $R_{F,F+1/2}(r_0+w/2) \propto \exp(-\gamma_{F+1/2} r)$ and $R_{F,F-3/2}(r_0+w/2) \propto \exp(-\gamma_{F-3/2} r)$ (where $\gamma_{F+1/2}>0$ and $\gamma_{F-3/2}>0$ are the decay exponents of the wave functions off the dot boundary) from the derived equations, we obtain

$$-\gamma_{F+1/2} R_{F,F+1/2} + R'_{F,F+1/2} = \frac{(\gamma_{F+1/2} W_+ + V_+)(\gamma_1 + 2\gamma \cos\alpha_F) - 2\gamma \sin\lambda_F (\gamma_{F+1/2} W_- + V_-)}{\gamma_1^2 - 4\gamma^2},$$
$$-\gamma_{F-3/2} R_{F,F-3/2} + R'_{F,F-3/2} = \frac{(\gamma_{F-3/2} W_- + V_-)(\gamma_1 - 2\gamma \cos\alpha_F) - 2\gamma \sin\lambda_F (\gamma_{F-3/2} W_+ + V_+)}{\gamma_1^2 - 4\gamma^2}. \tag{8}$$

where $V_+ = 2m_0 \int_{-w/2}^{w/2} U(r-r_0) R_{F,F+1/2} dr$, $V_- = 2m_0 \int_{-w/2}^{w/2} U(r-r_0) R_{F,F-3/2} dr$, $W_+ = -2m_0 \int_{-w/2}^{w/2} (r-r_0) U(r-r_0) R_{F,F+1/2} dr$, and $W_- = -2m_0 \int_{-w/2}^{w/2} (r-r_0) U(r-r_0) R_{F,F-3/2} dr$. These values vanish when $w \to 0$, if the potential $U(r)$ has not any singularity at the interface. This leads to the simple boundary conditions $R_{F,F+1/2}(-\hbar/\gamma_{F+1/2}) = R_{F,F-3/2}(-\hbar/\gamma_{F-3/2}) = 0$.

The values of $V_\pm$ and $W_\pm$ don't vanish at a sharp interface where the potential $U(r)$ changes essentially on the scale of the lattice constant. In particular, this is possible at a strain interface due to mismatch of the lattice constants of the bordering materials (e.g., at the Ge/Si interface). Then $U(r)$ can be estimated as $U \sim D(\delta a/a)$ for $|r-r_0|<a$, where $D \sim 10$ eV is the constant of the deformational potential and δa is the lattice mismatch. So that $W \sim \delta a/a \sim 1$ and $V \sim \delta a/a^2$. The boundary conditions (8) accept the form of Eqs. (2) after expansion of the radial wave functions in the integrands. This is the case even when $\gamma_{F-3/2} \to \infty$ and $\gamma_{F+1/2} \to \infty$.

We shall use the boundary conditions (2) in the form (5) to obtain the hole spectrum of the quantum dot. The radial wave functions in the free space ($U=0$) are[3]

$$R_{F,F+1/2}(r) = A j_{F+1/2}(kr) + B j_{F+1/2}(kr\sqrt{\beta}),$$
$$R_{F,F-3/2}(r) = A_1 j_{F-3/2}(kr) + B_1 j_{F-3/2}(kr\sqrt{\beta}), \tag{9}$$

where $j_l(z)$ are the spherical Bessel functions, $A_1 = A \tan(\alpha_F/2)$, $B_1 = B \cot(\alpha_F/2)$, $\cos\alpha_F = (2F-3)/(4F)$, $\sin\alpha_F \geqslant 0$, $\beta = m_l/m_h$; A and B are the constants that are determined by the boundary conditions at $r=r_0$.

By substituting Eq. (9) into the boundary conditions (5), we obtain the system of equations which is homogeneous in A and B. Its nonzero solutions exist only when the determinant vanishes, i.e.,

$$\left[t_{11} j_{F+1/2}(kr_0) - \tan\frac{\alpha_F}{2} j_{F-3/2}(kr_0) \right] \left[t_{21} j_{F+1/2}(kr_0\sqrt{\beta}) + t_{22} j'_{F+1/2}(kr_0\sqrt{\beta}) + \cot\frac{\alpha_F}{2} j'_{F-3/2}(kr_0\sqrt{\beta}) \right]$$
$$- \left[t_{21} j_{F+1/2}(kr_0) + t_{22} j'_{F+1/2}(kr_0) - \tan\frac{\alpha_F}{2} j'_{F-3/2}(kr_0) \right]$$
$$\times \left[t_{11} j_{F+1/2}(kr_0\sqrt{\beta}) + \cot\frac{\alpha_F}{2} j_{F-3/2}(kr_0\sqrt{\beta}) \right] = 0. \tag{10}$$

where $j' \equiv dj/dr$. Equation (10) determines the hole spectrum of the quantum dot: $E_n = (\gamma_1 - 2\gamma)\hbar^2 k_n^2/2m_0$, where k_n are the roots of Eq. (10). Influence of the interface on this spectrum is determined by the parameters t_{ij}. To estimate the energy E_0 of the interface hole state, we assume $k = i\kappa$, where $\kappa r_0 \gg 1$. Then, from the Eq. (10) we obtain

$$\kappa \simeq \frac{t_{21}\left(\tan\frac{\alpha_F}{2} + \cot\frac{\alpha_F}{2} \right)}{(t_{11}t_{22}-1)(1-\sqrt{\beta}) + t_{11}\left(\sqrt{\beta}\cot\frac{\alpha_F}{2} + \tan\frac{\alpha_F}{2} \right) - t_{22}\left(\sqrt{\beta}\tan\frac{\alpha_F}{2} + \cot\frac{\alpha_F}{2} \right)}, \tag{11}$$

so that $E_0 = -\hbar^2\kappa^2/2m_h$. The simple case that corresponds to $\Psi_{1,2}(0)=0$ follows from Eq. (10) if we assume that $t_{21} \to \infty$. This is possible when $t_{21} \gg k$. The value of t_{21} can be estimated from Eq. (11), $t_{21} \sim \kappa = \hbar^{-1}\sqrt{2m_h|E_0|}$. Therefore the boundary conditions $\Psi_{1,2}(0)=0$ are applicable at a sharp interface, if $|E_0| \gg \hbar^2 k^2/2m_h$, i.e., when the energy of the interface level much exceeds the energy of the hole. Otherwise, the general boundary conditions (5) should be used.

Figure 1 displays the left side of Eq. (10) as a function of kr_0. We assume $t_{11}=1$, $m_h=m_0$, $\beta=0.1$, and obtain t_{21}

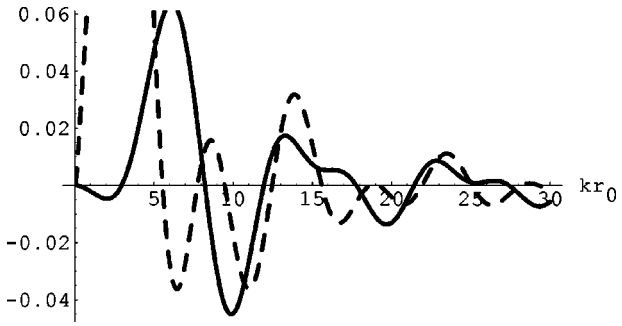

FIG. 1. Left side of Eq. (10) as a function of kr_0 (bold curve). Similar dependence which is relevant to the boundary conditions $\Psi_{1,2}(0)=0$ (dashed curve).

from Eq. (10), provided $E_0=0.01$ eV. The dashed curve presents the similar dependence that follows from the simple boundary conditions $\Psi_{1,2}(0)=0$.[3] We reveal an essential difference between the hole spectra. Apart from an essential change of the position of the roots of Eq. (10), we find that some of them become complex ($kr_0=15.5\pm1.3i$ and $kr_0=25.3\pm0.7i$ on Fig. 1), and so the relevant hole states become quasistationary and bounded at the interface. This could be essential for the optical properties of the quantum dot. Moreover, such states affect the electron transport in the array of the quantum dots; they increase the effective cross section of the quantum dot. Note that the solid curve becomes close to the dashed one when E_0 is about a few eV.

The hole spectrum was found to be sensitive to the energy position of the interface level; namely, whether or not it is close to the band edge. Such levels really exist at the top of the valence band in some semiconductor/insulator contacts;[12] they are responsible for the Fermi-level pinning. It seems that the electron interface level should be close to the valence band, at least in wide-gap semiconductors. If the interface level is shifted too far off the top of the valence band, then it becomes empty. This results in a large surface charge and a strong band bending that is not favorable from the energetical point of view. Nevertheless, the interface level can be shifted as the result of the structure reconstruction of the interface. Such reconstruction does not essentially affect the interatomic spaces or angles, but it makes the interface level closer to the top of the valence band.

In conclusion, we propose the general boundary conditions for the envelope wave functions to investigate the hole spectrum of the spherical quantum dot. We show that usually applicable boundary conditions $\Psi_{1,2}(0)=0$ can be used at a smooth interface or at a sharp one, provided that the energy separation nearest to the band edge interface level much exceeds the energy of the hole under consideration. Two real parameters are sufficient to determine an interface influence on the hole spectrum. They could be measured in optical experiments or estimated theoretically [e.g., from Eq. (8)] for a certain model of the interface structure. The boundary conditions (5) can be used also to describe the intervalley mixing of the electron in the conduction band.

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[1] U. Woggon, *Optical Properties of Semiconductor Quantum Dots*, Springer Series in Modern Physics, Vol. 136 (Springer-Verlag, Berlin, 1997).

[2] J-B. Xia, Phys. Rev. B **40**, 8500 (1989); B. Szafran, J. Adamovsky, and S. Bednereck, Physica E (Amsterdam) **4**, 1 (1999).

[3] A. I. Ekimov *et al.*, Zh. Eksp. Teor. Phys. **88**, 1490 (1985) [Sov. Phys. JETP **61**, 891 (1985)].

[4] E. E. Tachtamirov and V. A. Volkov, Semicond. Sci. Technol. **12**, 77 (1997).

[5] I. L. Aleiner and E. L. Ivchenko, Pis'ma Zh. Éksp. Teor. Fiz. **55**, 662 (1992) [JETP Lett. **55**, 692 (1992)]; E. L. Ivchenko, A. Yu. Kaminsky, and U. Rössler, Phys. Rev. B **54**, 5852 (1996).

[6] B. A. Foreman, Phys. Rev. Lett. **81**, 425 (1998); M. G. Burt and B. A. Foreman, in Proceedings of the 24th International Conference on the Physics of Semiconductors (World Scientific, Singapore, in press).

[7] V. A. Volkov and T. N. Pinsker, Zh. Éksp. Teor. Phys. **70**, 2268 (1976), [Sov. Phys. JETP **43**, 1183 (1976)]; **72**, 1087 (1977) **45**, 568 (1977)].

[8] L. Braginsky, Phys. Rev. B **57**, R6870 (1998).

[9] Qi-Gao Zhu and Herbert Kroemer, Phys. Rev. B **27**, 3519 (1983); L. Braginsky and D. Romanov, Fiz. Tverd. Tela (St. Petersburg) **37**, 2122 (1995) [Phys. Solid State **37**, 1154 (1995)].

[10] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

[11] B. G. Gel'mont and M. I. Diakonov, Fiz. Tekh. Poluprovodn. **5**, 2191 (1971) [Sov. Phys. Semicond. **5**, (1971)].

[12] H. Fujitani and S. Asano, Phys. Rev. B **40**, 8357 (1989); A. B. McLean and F. J. Himpsel, *ibid.* **39**, 1457 (1989); J. L. Batstone, J. M. Philips, and E. C. Hunke, Phys. Rev. Lett. **60**, 1394 (1988).