Surface waveguide States and Nanocatalyst Activity

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Abstract: Spectral problem for Schrödinger operator of half-crystal with surface impurities is considered. We use zero-range potentials model based on the theory of self-adjoint extensions of symmetric operators. The impurities are one-periodic chains of point-like potentials. The impurity leads to appearance of additional bands. The corresponding states are concentrated near the chain, i.e. it looks like a waveguide state. Hence, the electron density near the nanoparticle surface increases. This results in increasing of the catalytic activity of the nanoparticle.
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1 Introduction

Nano catalysts are the most widely used catalysts in modern chemistry (see, e.g., [1]). The main advantage is good surface/volume ratio for nanoparticles. The most important problem is to ensure high catalytic efficiency and to suggest a computational method for determination of characteristics of the corresponding structures. The problem can be considered with using of different (rather complicated) approaches (see, e.g.. [2]), but simple model which allows one to predict the corresponding properties of the system is preferable. Nanoparticle can be treated as a crystal of finite (nano) size. One can mention an interesting phenomenon: the catalytic activity of nanocatalyst increases considerably if there are irregular inclusions at the nanoparticle surface. It was demonstrated in several cases: the electrocatalytic activity of oxygen-modified tungsten carbide [3]; the reaction of ethanol on metallic and oxidized cobalt surfaces [4]; the formation of carbonate

species on alumina [5]; reaction intermediates of methanol synthesis and the water-gas-shift reaction on the ZnO(0001) surface [6]. The presence of substitutional atoms can lead to modified chemical centers on the surface. Particularly, one obtains enhancing the catalytic activity of a nanocluster by designed incorporation (doping)of an impurity on the surface. Doping by a single impurity atom changes significantly the bonding and activation of O_2 compared to the pure gold tetramer [1]. It is interesting to note that even water molecule absorbed on the surface can drastically change the activity - for certain supports moisture is able to increase the activity of gold catalysts by about two order of magnitude. Chen and Goodman [17] have created well-ordered gold mono-layers and bilayers that completely wet (cover) the oxide support, thus eliminating particle shape and direct support effects. High-resolution electron energy loss spectroscopy and carbon monoxide adsorption confirm that the gold atoms are bonded to titanium atoms. Kinetic measurements for the catalytic oxidation of carbon monoxide show that the gold bilayer structure is significantly more active (by more than an order of magnitude) than the monolayer. As for computational approaches, a Monte Carlo simulation technique has been used, e.g., for investigation of the effect of sulphur impurity and ceria support on the surface composition and catalytic activity of Pt-Rh/ceria nanocatalysts [7]

The rise of the surface area is not sufficient to explain this increase. But it is possible to declare additional reasons. Particularly, it is known that other things being equal the catalytic activity increases when the electron density increases at the nanoparticle surface. In [8] we put forward an idea that this effect can be related with the surface irregular inclusion. In the present paper we give one an effective mathematical model for detailed description of surface states related with surface impurities.

We suggest a simple model to explain the growth of surface electron density. Namely, a nanoparticle is considered as a three-dimensional semi-infinite crystal with zero-range potentials [9, 10]. Additional chains of centers on the surface of the half-crystal play a role of impurities. Due to this perturbation of the initial Schröodinger operator for an electron in the half-crystal, additional bands appear in the spectrum. The corresponding band states are concentrated near the chains, i.e. near the nanoparticle surface. It means that one can observe an additional electron density near the surface. As a result, the catalytic activity increases. We investigate the band state characteristics. The situation of such type is observed, for example, when one deals with low-energy electron-induced reactions in thin films of glucose and N-acetyl-glucosamine [11], the influence of the surface state onto the distance distribution of single molecules and small molecular clusters [12], the role of sub-surface oxygen in Cu(100) oxidation [13] and the role of nanocavities at nearly ideal (2?1)Si(100) inner surfaces as nanoreactor [14], etc. We deal with heterogeneous redox catalysis which is related with the electron transfer. That is why the surface electron state is important for this type of catalysis. The catalytic efficiency depends also on the electron interaction between reactants and the surface of the nanocatalysts and other factors. In the present paper we consider only electron density influence. The obtained result is one of important reasons explaining extremely high catalytic activity of the system Zr O2 - Al2O3 in the reaction of hydrogen oxidation. This phenomenon was

observed in [15]. The analogous effect is described in [16] where the influence of nanoscale layers of V and V2O5 on the surface of InP and GaAs on the process of thermal oxidation of these semiconductors is demonstrated.

2 Model of Surface Impurities

2.1 Waveguide Band of Infinite Ideal Surface Chain. Single-band Approximation for Crystal

Consider infinite periodic chain of impurity atoms posed along some line (let it be the axis OX) at the surface of ideal crystal (matrix). In chosen coordinates system, the position of $n-$th atom of the chain ($n = 0, \pm 1, \pm 2, \ldots$) is given by a vector $n\mathbf{a} = (na, 0, 0)$, where a is the chain period. To compute the energy spectrum of the chain, we use zero-range potentials model. The initial electron system of the crystal-matrix is considered in a single-band effective mass approximation. It is appropriate if atoms of the chain have no deep levels (i.e. the levels are close to edges of the crystal bands: donor - to the bottom of the conduction band, acceptor - to the top of the valence band). As for zero-range potentials, the background for the model is formed by the theory of self-adjoint extensions of symmetric operators (see, e.g., [9]). Namely, one may start from the self-adjoint Schrödinger operator A in $L_2(\mathbb{R}^3)$ - a sum $-\Delta + W(\mathbf{r})$ of the Laplacian $-\Delta$ with the domain $H^2(\mathbb{R}^3)$ and a bounded potential $W(\mathbf{r})$. Here H^2 is the Sobolev space W_2^2. Let us restrict this operator on the set of smooth functions from $H^2(\mathbb{R}^3)$ vanishing at points $\mathbf{r} = \mathbf{na}$; $\quad \mathbf{n} = \mathbf{0}, \pm\mathbf{1}, \ldots$ The closure B of the restricted operator is a symmetric operator with the domain $D(B) = \{f : f \in H^2(\mathbb{R}^3), \ f(n\mathbf{a}) = 0, n = 0, \pm 1, \ldots\}$ having infinite deficiency indices. Indeed, the resolvent $(A - \lambda I)^{-1}$ for regular λ is the integral operator in $L_2(\mathbb{R}^3)$. The kernel of this operator (the Green function) $G_\lambda(\mathbf{r}, \mathbf{r}')$ has the following property:

$$\int_{\mathbb{R}_3} |G_\lambda(\mathbf{r}, \mathbf{r}')|^2 \, d\mathbf{r} < \infty.$$

Since $G_\lambda(\cdot, n\mathbf{a}) \in L_2(\mathbb{R}^3)$ at least for non-real λ, the difference

$$G_\lambda(\mathbf{r}, \mathbf{r}') - \frac{1}{4\pi} \frac{e^{i\sqrt{\lambda}|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}$$

has no singularity at $\mathbf{r} = \mathbf{r}'$, $G_\lambda(\cdot, n\mathbf{a})$ is orthogonal to the domain of $B - \bar{\lambda}I$ and

$$\lim_{\mathbf{r} \to n\mathbf{a}} |\mathbf{r} - n\mathbf{a}| G_\lambda(\mathbf{r}, n'\mathbf{a}) = \lim_{\mathbf{r} \to n\mathbf{a}} \frac{|\mathbf{r} - n\mathbf{a}|}{4\pi|\mathbf{r} - n'\mathbf{a}|} e^{i\sqrt{\lambda}|\mathbf{r} - n'\mathbf{a}|} = \frac{1}{4\pi} \begin{cases} 1, & n = n', \\ 0, & n \neq n'. \end{cases} \tag{1}$$

Hence, B is a symmetric operator with infinite deficiency indices.

To construct a self-adjoint extension of B, it is more convenient to deal with the initial selfadjoint Schrödinger operator A instead of the adjoint operator B^*. There are several ways of extensions descriptions, e.g., boundary triplets method ([18], von

Neumann formulas ([19]), Krein resolvent formula ([20]). We will use here a variant of the last approach. Having in mind that for regular λ the product $|\mathbf{r} - \mathbf{r}'|G_\lambda(\mathbf{r}, \mathbf{r}')$ is non-singular at $\mathbf{r} = \mathbf{r}'$, put

$$\xi_n(\lambda) = \lim_{\rho_n \to 0} \frac{d}{\rho_n} \rho_n G_\lambda(\mathbf{r}, n\mathbf{a}), \quad \rho_n = |\mathbf{r} - n\mathbf{a}|. \tag{2}$$

and

$$q_{n,n'}(\lambda) := \lim_{\rho_n \to 0} \frac{d}{\rho_n} \rho_n G_\lambda(\mathbf{r}, n'\mathbf{a}) = G_\lambda(n\mathbf{a}, n'\mathbf{a}), \quad n \neq n'. \tag{3}$$

It is worth noting that for $\mathfrak{Im}\lambda \neq 0$

$$\int_{\mathbb{R}_3} |G_\lambda(\mathbf{r}, n\mathbf{a})|^2 \, d\mathbf{r} = \frac{\xi_n(\lambda) - \xi_n(\bar{\lambda})}{\lambda - \bar{\lambda}}, \tag{4}$$

$$\int_{\mathbb{R}_3} G_\lambda(\mathbf{r}, n'\mathbf{a})\overline{G_\lambda(\mathbf{r}, n\mathbf{a})}d\mathbf{r} = \frac{q_{n,n'}(\lambda) - q_{n,n'}(\bar{\lambda})}{\lambda - \bar{\lambda}}. \tag{5}$$

Taking into account that the independent vectors

$$G_\lambda(., n\mathbf{a}) = \int_{E_3} G_\lambda(., n\mathbf{r}')\delta(\mathbf{r}' - n\mathbf{a})d\mathbf{r}' = (A - \bar{\lambda})^{-1}\delta(\cdot - n\mathbf{a}), \quad \mathrm{Im}\lambda \neq 0,$$

form a basis of deficiency subspace $\left[\left(B - \bar{\lambda}I\right)\overset{\circ}{H}^2(\mathbb{R}^3)\right]^\perp$, one can write down a formal expression of the Krein resolvent formula directly for the set of Green functions $G_\lambda^M(\mathbf{r}, \mathbf{r}')$ of selfadjoint extensions A_M of B [21], [22]:

$$G_\lambda^M(\mathbf{r}, \mathbf{r}') = G_\lambda(\mathbf{r}, \mathbf{r}') - \sum_{n,n'} G_\lambda(\mathbf{r}, n\mathbf{a}) \left([Q(\lambda) + M]^{-1}\right)_{n,n'} G_\lambda(n'\mathbf{a}, \mathbf{r}'), \tag{6}$$

where $Q(\lambda)$ is a Nevanlinna infinite matrix function with inputs

$$Q_{n,n'}(\lambda) = \begin{cases} \xi_n(\lambda), & n = n'; \\ G_\lambda(n\mathbf{a}, n'\mathbf{a})(\lambda), & n \neq n', \end{cases} \tag{7}$$

and M runs through the set of infinite Hermitian matrices generating selfadjoint operators in the space of bilateral sequences $\mathbf{l}_2$. [2]

By (6),(1)(2) and (3) for $\mathbf{r}' \neq n\mathbf{a}, n = 0, \pm 1, \dots$ one has

$$\lim_{\rho_n \to 0} \rho_n G_\lambda^M(\mathbf{r}, n\mathbf{r}') = -\frac{1}{4\pi} \sum_{n'} \left([Q(\lambda) + M]^{-1}\right)_{n,n'} G_\lambda(n'\mathbf{a}, \mathbf{r}'),, \quad \rho_n = |\mathbf{r} - n\mathbf{a}|,$$

$$\lim_{\rho_n \to 0} \frac{d}{\rho_n} \rho_n G_\lambda^M(\mathbf{r}, \mathbf{r}') = \sum_{n'} \left(M \cdot [Q(\lambda) + M]^{-1}\right)_{n,n'} G_\lambda(n'\mathbf{a}, \mathbf{r}').$$

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[2] To avoid the overburdening of the paper by minor questions, we omit here a discussion of technical details arising from the case of infinite deficiency spaces as irrelevant for the simple versions of the Krein formula used below.

Hence, each function $f(\mathbf{r})$ from the domain of self-adjoint extension A_M of B satisfies the set of boundary conditions

$$\lim_{\rho_n \to 0} \frac{d}{d\rho_n}(\rho_n f)(\mathbf{r}) + 4\pi \sum_{n'} M_{n,n'} \lim_{\rho_{n'} \to 0}(\rho_{n'} f)(\mathbf{r}) = 0. \tag{8}$$

Within the scope of this paper we will consider only the simplest class of extensions corresponding to matrices M being multiple of the unit matrix, $M = b \cdot I$, that is we will consider the self-adjoint extensions A_b of B, which are associated with the boundary conditions

$$\lim_{\rho_n \to 0} \left\{ \frac{d}{d\rho_n}(\rho_n f)(\mathbf{r}) + 4\pi b \rho_n f(\mathbf{r}) \right\} = 0, \tag{9}$$

with any real b.

We will assume further that the potential $W(\mathbf{r})$ of the initial Schrödinger operator A doesn't depend on variable x. By virtue of this assumption, $G_\lambda(x, y, z; x', y', z') = G_\lambda(x - x', y, z; 0, y', z') = G_\lambda(|x - x'|, y, z; 0, y', z')$ and, hence, $Q(\lambda) + bI$ is a Töplitz matrix,

$$[Q(\lambda) + bI]_{n,n'} = [Q(\lambda) + bI]_{n-n',0} = \begin{cases} \xi_0(\lambda) + b, & n = n'; \\ G_\lambda((n - n')\mathbf{a}, \mathbf{0}), & n \neq n', \end{cases} \quad -\infty < n, n' < \infty, \tag{10}$$

with the symbol

$$\begin{aligned} D(k, \lambda) &= \xi_0(\lambda) + b + \sum_{n \neq 0} G_\lambda(n\mathbf{a}, \mathbf{0}) e^{inka} \\ &= \xi_0(\lambda) + b + 2 \sum_{n=1}^{\infty} G_\lambda(na, 0, 0; 0, 0, 0) \cos nka, \quad -\frac{\pi}{a} \leq k < \frac{\pi}{a}. \end{aligned} \tag{11}$$

Therefore, the inverse matrix $[Q(\lambda) + bI]^{-1}$ is also Töplitz with inputs

$$r_{n,n'} = r_{n-n'} = \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{1}{D(k, \lambda)} e^{i(n-n')ka} dk, \quad -\infty < n, n' < \infty, \tag{12}$$

and the symbol $D(k, \lambda)^{-1}$. Put

$$f_\lambda(k, \mathbf{r}) = \sum_{-\infty}^{\infty} G_\lambda(x, y, z; na, 0, 0) e^{ikna}. \tag{13}$$

We see that in the case of x-independent potential $W(\mathfrak{r})$ for the class of self-adjoint extensions A_b under study, the Krein formula (6) for the corresponding Green functions $G_\lambda^b(\mathbf{r}, \mathbf{r}')$ takes the form

$$G_\lambda^b(\mathbf{r}, \mathbf{r}') = G_\lambda(\mathbf{r}, \mathbf{r}') - \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{1}{D(k, \lambda)} f_\lambda(k, \mathbf{r}) \overline{f_{\bar{\lambda}}(k, \mathbf{r}')} dk. \tag{14}$$

Remind that irrelatively to a specific problem under study, the matrix function $Q(\lambda)$ in the Krein resolvent formula is holomorphic in the upper and the lower half-planes, and it has the following property

$$\frac{1}{2i}\left[Q(\lambda) - Q(\lambda)^*\right] \geq 0, \quad \Im\lambda > 0.$$

Matrix function $Q(\xi)$ is also holomorphic at real regular points ξ of A and hereat $Q(\xi)^* = Q(\xi)$. The same is true for $Q(\lambda) + b \cdot I$ with real b and, consequently, for the symbol $D(k,\lambda)$. From this, we conclude that $D(k,\lambda)$, $-\frac{\pi}{a} \leq k < \frac{\pi}{a}$, is real at real regular points ξ of A and, moreover, at those points, the following inequality takes place

$$\frac{d}{d\lambda}D(k,\lambda)_{|_{\lambda=\xi}} > 0.$$

Let $\varrho_{\Re}(A)$ be the set of real regular points of the initial operator A. By (14), the part of the spectrum $\sigma(A_b)$ of an extension A_b on $\varrho_{\Re}(A)$ can consist only of real λ, $\lambda \in \varrho_{\Re}(A)$, for which there is k, $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, such that

$$D(k,\lambda) = 0. \tag{15}$$

Let us assume that (15) has only one root $E(k)$ for each $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, and that $E(k)$ is a continuous function on $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$. Note that by (11), $D(k,\lambda) = D(-k,\lambda)$. As follows, $E(-k) = E(k)$. Evidently, that for any root $E(k)$ of (15), function $f_{E(k)}(k,\mathbf{r})$ defined by (13) satisfies the Schrödinger equation on $\mathbb{R}_3 \setminus \cup_n\{n\mathbf{a}\}$:

$$-\Delta f(\mathbf{r}) + W(\mathbf{r})f(\mathbf{r}) = E(k)f(\mathbf{r}), \tag{16}$$

and the boundary conditions (8).

Let $[E_{min}, E_{max}]$ be the maximal interval, which is covered by the values of $E(k)$ in $\varrho_{\Re}(A)$ and let $\mathcal{E}_b(s)$, $-\infty < s < \infty$, be the spectral function of the self-adjoint extension A_b. Taking any segment $[E_1, E_2] \subset [E_{\min}, E_{\max}]$ and applying to any smooth function $u \in L^2(\mathbb{R}^3)$ the general relation

$$(\mathcal{E}_b([E_1, E_2])u, u)_{L^2} = \lim_{\varepsilon\downarrow 0}\frac{1}{\pi}\int\limits_{E_1}^{E_2}\Im\mathfrak{m}\left(R_{E+i\varepsilon}\left(A_b\right)u, u\right)dE, \tag{17}$$

one can deduce from (14)that $\mathcal{E}_b([E_1, E_2])$ is the integral operator in $L^2(\mathbb{R}^3)$ with kernel

$$\mathcal{E}_b([E_1, E_2])(\mathbf{r}, \mathbf{r}') = \frac{a}{2\pi}\int\limits_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\chi_{[E_1, E_2]}(k)\psi(k,\mathbf{r})\overline{\psi(k,\mathbf{r}')}dk, \tag{18}$$

where

$$\chi_{[E_1, E_2]}(k) = \begin{cases} 1, & E(k) \in [E_1, E_2], \\ 0, & E(k) \notin [E_1, E_2], \end{cases}$$

and

$$\psi(k,\mathbf{r}) = \left[\frac{\partial D(\lambda,k)}{\partial \lambda}\Big|_{\lambda=E(k)}\right]^{-\frac{1}{2}} f_{E(k)}(k,\mathbf{r}). \tag{19}$$

In particular, if the spectrum of A_b has not empty intersection with $\varrho_{\mathfrak{R}}(A)$, then the orthogonal projector $\mathcal{P}_{\mathbb{W}}$ onto the spectral subspace $\mathbb{W}$ associated with the spectrum of A_b on $\varrho_{\mathfrak{R}}(A)$ can be written as the integral operator with kernel

$$\mathcal{P}_{\mathbb{W}}(\mathbf{r},\mathbf{r}') = \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \psi(k,\mathbf{r})\overline{\psi(k,\mathbf{r}')}dk. \tag{20}$$

The wave functions from $\mathbb{W}$ conform the states of a particle in which it being in the unrestricted motion along the chain of impurities cannot move far away from the latter, that is the states from $\mathbb{W}$ form the so called waveguide band. According to the definitions (19) and (13) $\psi(k,\mathbf{r})$ is a generalized eigenvector of A_b corresponding to the point of spectrum $E(k) \in \varrho_{\mathfrak{R}}(A)$, which is normalized so that the following relation holds:

$$\int_{\mathbb{R}_3} \psi(k,\mathbf{r})\overline{\psi(k',\mathbf{r})}d\mathbf{r} = \delta(k-k'), \quad -\frac{\pi}{a} \le k, k' < \frac{\pi}{a}. \tag{21}$$

In addition, it has the property

$$\psi(k,\mathbf{r}+\mathbf{a}) = e^{ika}\psi(k,\mathbf{r}), \tag{22}$$

owing to which, it is so called Bloch function.

The obtained results can be used for modelling of impurity waveguide bands, which can appear due to regular chains of dopant atoms on the surface of semiconducting crystal. As an example, let us consider the case of crystal occupying the half-space $z < 0$ in $\mathbb{R}$ while the half-plane $z > 0$ is empty. For simplicity, we will assume also that the effective mass m of electron in the crystal is the same as that in vacuum. Without significant loss of generality, in this case, we can take, as unperturbed self-adjoint operator A, the Schrödinger operator

$$-\Delta + W(\mathbf{r})$$

with the domain $H^2(\mathbb{R}_3)$ and the potential

$$W(\mathbf{r}) = \begin{cases} -W_0, & z < 0, \\ 0, & z > 0, \end{cases} \tag{23}$$

where $W_0 > 0$ is related with the work function E_w for electrons at the bottom of the conductivity band in the crystal by the relation

$$W_0 = \frac{2m}{\hbar^2}E_w.$$

The Green function $G_\lambda\left(\mathbf{r}_{\shortparallel}, z; \mathbf{r}'_{\shortparallel}, z'\right)$, $\mathbf{r}_{\shortparallel} = (x, y)$, of A for regular λ can be written in the form

$$G_\lambda\left(\mathbf{r}_{\shortparallel}, z; \mathbf{r}'_{\shortparallel}, z'\right) = \frac{1}{(2\pi)^2} \int_{\mathbb{R}_2} e^{i\mathbf{p}\cdot(\mathbf{r}_{\shortparallel} - \mathbf{r}'_{\shortparallel})} g_\lambda(z, z'; p) d\mathbf{p}, \quad p = |\mathbf{p}|, \tag{24}$$

where $g_\lambda(z, z'; p)$ for $z < 0$ and $z \le z'$ has the form

$$
\begin{aligned}
g_\lambda(z, z'; p) = {} & \frac{i}{\sqrt{\lambda + W_0 - p^2} + \sqrt{\lambda - p^2}} e^{-i\sqrt{\lambda + W_0 - p^2} z} \\
& \times \left\{ \cos\sqrt{\lambda + W_0 - p^2} z' + i\frac{\sqrt{\lambda - p^2}}{\sqrt{\lambda + W_0 - p^2}} \sin\sqrt{\lambda + W_0 - p^2} z' \right\},
\end{aligned}
\tag{25}
$$

and $g_\lambda(z, z'; p)$ for $z' \le z < 0$ can be obtained from (25) by permutation of z and z'. The corresponding expressions for $z > 0$ can be found is one replaces z, z' in those for $z < 0$ by $-z, -z'$ and transposes $\sqrt{\lambda + W_0 - p^2}$ and $\sqrt{\lambda - p^2}$.

In particular, for $z = z' = 0$ we get from (24, 25):

$$G_\lambda\left(\mathbf{r}_{\shortparallel}, 0; \mathbf{r}'_{\shortparallel}, 0\right) = \frac{1}{(2\pi)^2} \int_{\mathbb{R}_2} e^{i\mathbf{p}\cdot(\mathbf{r}_{\shortparallel} - \mathbf{r}'_{\shortparallel})} \frac{i}{\sqrt{\lambda + W_0 - p^2} + \sqrt{\lambda - p^2}} d\mathbf{p}. \tag{26}$$

Since

$$\frac{1}{\sqrt{\lambda + W_0 - p^2} + \sqrt{\lambda - p^2}} = \frac{1}{W_0}\left(\sqrt{\lambda + W_0 - p^2} - \sqrt{\lambda - p^2}\right)$$

$$= \frac{1}{W_0} \int_0^{W_0} \frac{1}{2\sqrt{\lambda + s - p^2}} ds$$

and

$$\frac{i}{2\sqrt{\lambda + s - p^2}} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{dq}{q^2 + p^2 - \lambda - s},$$

it follows from (26) that

$$G_\lambda\left(\mathbf{r}_{\shortparallel}, 0; \mathbf{r}'_{\shortparallel}, 0\right) = G_\lambda\left(\mathbf{r}_{\shortparallel} - \mathbf{r}'_{\shortparallel}, 0; \mathbf{0}, 0\right) = \frac{1}{W_0} \int_0^{W_0} \frac{e^{i\sqrt{\lambda + s}|\mathbf{r}_{\shortparallel} - \mathbf{r}'_{\shortparallel}|}}{4\pi|\mathbf{r}_{\shortparallel} - \mathbf{r}'_{\shortparallel}|} ds. \tag{27}$$

In the case under consideration, one has

$$\xi_0(\lambda) = \lim_{r \to 0} \frac{d}{dr} r G_\lambda(\mathbf{r}, \mathbf{0}) = \frac{i}{6\pi W_0}\left[(\lambda + W_0)^{\frac{3}{2}} - \lambda^{\frac{3}{2}}\right]. \tag{28}$$

and

$$Q_{n,n'}(\lambda) = \lim_{\rho_n \to 0} \frac{d}{d\rho_n} r G_\lambda(\mathbf{r}, n'\mathbf{a}) = \frac{1}{4\pi W_0} \int_0^{W_0} \frac{e^{i\sqrt{\lambda + s}|n - n'|a}}{|n - n'|a} ds \tag{29}$$

The self-adjoint operator A_b was defined above by the set of boundary conditions (9) at the points of impurities location. For this operator, the corresponding function $D(k, \lambda)$ in the Krein formula (14) has the form

$$D(k, \lambda) = \frac{1}{4\pi W_0 a} \int_0^{W_0} ds \cdot \ln\frac{\Theta}{\cos\sqrt{\lambda + s}\, a - \cos ka}, \quad \Theta = \frac{1}{2} e^{4\pi ba}. \tag{30}$$

To explain how to choose the parameter b of extension A_b for given semiconducting crystal and impurity atoms, let us consider the simplest case of single donor dopant at $\mathbf{r} = 0$ on the interface $z = 0$. The effect of the latter on electrons near the bottom of the conductivity band of given semiconductor can be modelled by using (instead of A) of the self-adjoint extension A_b^1 with the Green function

$$G_\lambda^{1,b}(\mathbf{r}, \mathbf{r}') = G_\lambda(\mathbf{r}, \mathbf{r}') - \frac{1}{D^{1,b}(\lambda)} G_\lambda(\mathbf{r}, \mathbf{0}) G_\lambda(\mathbf{0}, \mathbf{r}),$$
$$D^{1,b}(\lambda) = \frac{i}{6\pi W_0} \left[(\lambda + W_0)^{\frac{3}{2}} - \lambda^{\frac{3}{2}} \right] + b, \tag{31}$$

that is the extension, which plays the role of the "perturbation" of A by the single zero-range potential at $\mathbf{r} = 0$. It is equivalent to the restriction imposed on the involved wave functions $\psi(\mathbf{r})$ in the form of the following boundary condition

$$\lim_{r \to 0} \left\{ \frac{d}{dr} r\psi(\mathbf{r}) + 4\pi b \cdot r\psi(\mathbf{r}) \right\} = 0, \tag{32}$$

For $b > 0$ the zero-range potential results in the isolated eigenvalue $\lambda_0 < -W_0$ below the bottom of the conductivity band. It is a donor level with minimal energy

$$E_{ion} = -\frac{\hbar^2 (\lambda_0 + W_0)}{2m}$$

required to remove an electron from this level to the conductivity band. If for certain semiconductor and donor dopant E_{ion} is known , then, according to (31), the natural way to model the effect of donor impurities by the zero-range potential (32) is to take

$$b = \frac{1}{6\pi W_0} \left[(\epsilon_{ion} + W_0)^{\frac{3}{2}} - \epsilon_{ion}^{\frac{3}{2}} \right], \quad \epsilon_{ion} = \frac{2m}{\hbar^2} E_{ion}. \tag{33}$$

Let us denote, as above, by $E(k)$ the wave guide band energy defined from the equation $D(k, \lambda) = 0$, $k \in [-\pi/a, \pi/a)$, $\lambda < 0$, with $D(k, \lambda)$ defined by (30). The generalized Bloch eigenfunction $\psi(k, \mathbf{r})$ corresponding to the quasi-momentum k and the energy $E(k)$ is given according to (13, 19) by the expression

$$\psi(k, \mathbf{r}) = \mathcal{N}(k) e^{ikx} \sum_{s=-\infty}^{\infty} e^{i\frac{2\pi}{a} sx} \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} dq e^{iqy}$$
$$\times \left[\theta(-z) g_{E(k)}^- \left(z; \sqrt{(k + 2\pi s/a)^2 + q^2} \right) + \theta(z) g_{E(k)}^+ \left(z; \sqrt{(k + 2\pi s/a)^2 + q^2} \right) \right],$$
$$g_\lambda^- (z; p) = \frac{i}{\sqrt{\lambda + W_0 - p^2} + \sqrt{\lambda - p^2}} e^{-i\sqrt{\lambda + W_0 - p^2} z}, \quad z < 0;$$
$$g_\lambda^- (z; p) = \frac{i}{\sqrt{\lambda - p^2} + \sqrt{\lambda - p^2}} e^{i\sqrt{\lambda - p^2} z}, \quad z < 0, \tag{34}$$

where

$$\mathcal{N}(k) = \left[\frac{\partial D(\lambda, k)}{\partial \lambda}_{|\lambda = E(k)} \right]^{-\frac{1}{2}}$$

and $\theta(z)$ is the Heaviside function.

In the simplest case $W_{)0}$ the waveguide band can be described in more details due to the elementary expression for $D(k, s)$:

$$D(k, s) = \frac{1}{a} \ln \frac{d}{\cos(as) - \cos(ak)}, \tag{35}$$

where $d = \exp(-ba)/2$. For $d \leq 2$, the waveguide band is overlapped with the conductivity band (for $E > 0$) and for $d \ll 2$ it disappears. Formation of the band corresponds to existence of roots of (35) of the form $s = i\chi$, $\chi > 0$. The dispersion law for the waveguide band is given by the expression

$$E = -\frac{h^2 \chi^2}{2\mu}, \tag{36}$$

where χ is related with k by the following manner

$$ch(\chi a) = d + \cos(ka). \tag{37}$$

As a result,

$$E(k) = -\frac{h^2}{2\mu a^2} \left\{ \ln\left[d + \cos(ak) + \sqrt{(d + \cos(ak))^2 - 1}\right] \right\}^2 \; (1.17) \tag{38}$$

The sign of the square root in (38) is determined by the condition $\chi \geq 0$. The band edges are determined by the relation $|\cos(ka)| = 1$

$$E_{\min} = -\frac{h^2}{2\mu a^2} \left\{ \ln\left[d + 1 + \sqrt{(d+1)^2 - 1}\right] \right\}^2, \tag{39}$$

$$E_{\max} = -\frac{h^2}{2\mu a^2} \left\{ \ln\left[d - 1 + \sqrt{(d-1)^2 - 1}\right] \right\}^2, \tag{40}$$

Let us determine the effective masses of electron near the bottom and near the top of the waveguide band. Consider the difference

$$E(k) - E_{\min} =$$

$$\frac{h^2}{2\mu a^2} \left\{ \ln^2\left[d + 1 + \sqrt{d^2 + 2d}\right] - \ln^2\left[d + \cos(ak) + \sqrt{(d + \cos(ak))^2 - 1}\right] \right\}$$

$$\simeq_{k \to 0} \frac{h^2 k^2}{2\mu} \frac{\ln\left[d + 1 + \sqrt{d^2 + 2d}\right]}{d^2 + 2d}.$$

One can see that near the bottom of the waveguide band, one has

$$m_{eff} = \mu \frac{\sqrt{d^2 + 2d}}{\ln\left[d + 1 + \sqrt{d^2 + 2d}\right]}. \tag{41}$$

Analogously, near the top of the waveguide band, one has

$$m_{eff} = \frac{\sqrt{d^2 - 2d}}{\ln\left[d - 1 + \sqrt{d^2 - 2d}\right]}. \tag{42}$$

If the waveguide band is inside the gap for the crystal and the number of free electrons corresponding to a single atom, equals one then the band is half-filled (up to the Fermi energy E_F which corresponds to $ka = \pm\pi/2$:

$$E_F = -\frac{h^2}{2\mu a^2} \ln^2 \left[d + \sqrt{d^2 - 1} \right]). \tag{43}$$

One can obtain the electron wave function for the waveguide band:

$$\Psi_k(\mathbf{r}) = \frac{\sqrt{\chi d}}{4\pi\sqrt{\sqrt{(d + \cos(ka))^2 - 1}}} \sum_{n=-\infty}^{+\infty} \frac{\exp\left[-\chi |\mathbf{r} - \mathbf{n}a| - ikna\right]}{|\mathbf{r} - \mathbf{n}a|}. \tag{44}$$

Here the quasimomentum k and the energy parameter $\chi = \sqrt{2\mu |E|}$ are related by (37). When obtaining expression (44), one use the expansion of $D(k, s)$ near its roots (poles of the Green function).

Consider the asymptotic behavior of the wave function 44) for $p = (x^2 + y^2)^{1/2} \to \infty$, i.e. far from the chain axis. Let us deal with the general case without limitation $d > 2$ as in (44) and correspondingly, not only for $E < 0$). We will show that there is a localization near the chain axis. Moreover, this property preserves if the energy belongs to the conductivity band of the crystal. We start from the general expression for the wave function:

$$\Psi_k(\mathbf{r}) = \frac{C_k}{4\pi} \sum_{n=-\infty}^{+\infty} \frac{\exp\left[is |\mathbf{r} - \mathbf{n}a| - ikna\right]}{|\mathbf{r} - \mathbf{n}a|}. \tag{45}$$

Here C_k is the normalizing factor (for $E > 0$, the parameter s is real, for $E < 0$, one has the expansion (44)). Using the Poisson summation formula, after integration in the cylindrical coordinates system (related to the chain) one represents (45) in the form

$$\Psi_k(\mathbf{r}) = \frac{C_k \exp(kx)}{2\pi a} \sum_{l=-\infty}^{+\infty} \exp\left[\frac{2\pi ilx}{a}\right] K_0\left(p\sqrt{\left(k + \frac{2\pi l}{a}\right)^2 - s^2}\right), \tag{46}$$

where $K_0(z)$ is the McDonald function. The decreasing of $\Psi_k(\mathbf{r})$ is predetermined by the asymptotics of the main term (for $l = 0$)

$$\Psi_k(\mathbf{r}) \simeq_{p\to\infty} \frac{C_k}{2\pi a} \sqrt{\frac{\pi}{2p}} \exp\left[-p\sqrt{k^2 - s^2}\right] \exp(ikx). \tag{47}$$

One can check it by consideration of the average density for the state (46):

$$\left\langle |\Psi_k(\mathbf{r})|^2 \right\rangle = \frac{1}{a} \int_0^a dx \int_{-\infty}^{+\infty} dydz |\Psi_k(\mathbf{r})|^2 =$$

$$\frac{|C_k|^2}{4\pi^2 a^2} \sum_{l=-\infty}^{+\infty} \int_{-\infty}^{+\infty} dydz K_0\left(p\sqrt{\left(k + \frac{2\pi l}{a}\right)^2 - s^2}\right),$$

with using of the known asymptotics of the McDonald function for great argument values.
Parameters k and s are related by (compare with (37)

$$\cos\left(as\right) = d + \cos\left(ak\right). \tag{48}$$

Here $|ak| \leq \pi$, s is found for $d + \cos\left(ak\right) < 1$, $s = i\chi$, $\chi > 0$ for $d + \cos\left(ak\right) > 1$. The
values of the power of the exponentially decaying factor from (47) are equal (due to (48)
to

$$f\left(ka, d\right) = \{. \begin{array}{l} \left[k^2 a^2 - \arccos^2\left(d + \cos\left(ka\right)\right)\right]^{1/2}, \, d + \cos\left(ka\right) \leq 1, \\ \left[k^2 a^2 + Arcch^2\left(d + \cos\left(ka\right)\right)\right]^{1/2}, \, d + \cos\left(ka\right) > 1, \end{array} \tag{49}$$

for the Fermi level $(k = k_F = \pi/2a)$.

2.2   Waveguide Band of Infinite Ideal Surface Chain. Double-band Approximation for Crystal

Consider the case of deep energy level of the impurity chain. We will confine our attention
by two energy domains: near the bottom of the conductivity band and near the top of
the valence band. In this section we will deal with the simplest case of constant crystal
potential W as at the end of the previous section.

Following [23], one considers (in the framework of the effective mass approximation)
the unperturbed Hamiltonian H_0 in the form:

$$H_0 \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = \begin{pmatrix} -\frac{h^2}{2\mu_1}\Delta + \frac{1}{2}E_g & 0 \\ 0 & \frac{h^2}{2\mu_2}\Delta - \frac{1}{2}E_g \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}. \tag{50}$$

Here μ_1, Ψ_1 and μ_2, Ψ_2 are effective masses and electron wavefunction near the bottom
of the conductivity band and near the top of the valence band, correspondingly, E_g is
the width of gap. Electrons from different bands looks like different one-electron excitations with positive and negative energies (the origin for energies is chosen at the center
of the gap). The Hamiltonian spectrum consists from two disjoint parts: $\left[\frac{1}{2}E_g, +\infty\right)$,
$\left(-\infty, -\frac{1}{2}E_g\right]$.

The construction of the model is the same as in the previous section. For the case of
single impurity atom at point $\mathbf{r} = \mathbf{0}$, the solution of the matrix Schrödinger equation.

$$H_0\Psi = E\Psi$$

has the form

$$\Psi = \begin{pmatrix} \frac{\mu_1}{4\pi\hbar^2}C^{(1)}\exp\left(-\chi_1 r\right)/r \\ \frac{\mu_2}{4\pi\hbar^2}C^{(2)}\exp\left(-\chi_2 r\right)/r \end{pmatrix}, \tag{51}$$

$$\chi_1 = \left[-2\mu_1\left(E - E_g/2\right)/\left(\hbar^2\right)\right]^{1/2},$$

$$\chi_2 = \left[2\mu_2 \left(E + E_g/2 \right) / \left(\hbar^2 \right) \right]^{1/2}$$

To take into account an influence of two crystal bands, we choose a specific form of self-adjoint operator extension, namely, that corresponds to the following "boundary condition" at zero:

$$\lim_{r \to 0} \left[\frac{\partial}{\partial r} - B \right] r \Psi = 0,$$

$$r = |\mathbf{r}|.$$

Here B is a Hermitian matrix,

$$B = \begin{pmatrix} \alpha & \gamma \\ \overline{\gamma} & \beta \end{pmatrix}, \quad \Im \alpha = \Im \beta = 0. \tag{52}$$

In the case of periodic chain, the presentation analogous to (51) has the form

$$\Psi = \sum_{n=-\infty}^{\infty} \begin{pmatrix} \frac{\mu_1}{4\pi\hbar^2} C_n^{(1)} \frac{\exp[-\chi_1 |\mathbf{r} - \mathbf{a}n|]}{|\mathbf{r} - \mathbf{a}n|} \\ \frac{\mu_2}{4\pi\hbar^2} C_n^{(2)} \frac{\exp[-\chi_2 |\mathbf{r} - \mathbf{a}n|]}{|\mathbf{r} - \mathbf{a}n|} \end{pmatrix}, \tag{53}$$

The boundary condition at $n-$th point in this case takes the form

$$\lim_{p_n \to 0} \left[\frac{\partial}{\partial p_n} - B \right] p_n \Psi = 0, \tag{54}$$

$$p_n = |\mathbf{r} - n\mathbf{a}|; \quad n = 0, \pm 1, \ldots$$

Substitution of (53) into (54) gives one the following system for $C_n^{(1)}, C_n^{(2)}$:

$$\begin{aligned} (\chi_1 + \alpha) C_n^{(1)} - \sum_{n' \neq n} C_{n'}^{(1)} \frac{\exp[-\chi_1 a |n-n'|]}{a|n-n'|} + \frac{\mu_2}{\mu_1} \gamma C_n^{(2)} &= 0, \\ \frac{\mu_1}{\mu_2} \overline{\gamma} C_n^{(1)} + (\chi_2 + \beta) C_n^{(2)} - \sum_{n' \neq n} C_{n'}^{(2)} \frac{\exp[-\chi_2 a |n-n'|]}{a|n-n'|} &= 0. \end{aligned} \tag{55}$$

Let us introduce matrix notations in (55):

$$\Delta (k, E) = \begin{pmatrix} D_\alpha & -\overline{\gamma}\frac{\mu_1}{\mu_2} \\ -\gamma\frac{\mu_2}{\mu_1} & D_\beta \end{pmatrix},$$

where

$$D_\alpha (k, \chi_1) = (\chi_1 + \alpha) - \sum_{n \neq 0} \exp\left[-\chi_1 a |n| + ikna \right] / \left(a |n| \right),$$

$$D_\beta (k, \chi_2) = (\chi_2 + \beta) - \sum_{n \neq 0} \exp\left[-\chi_2 a |n| + ikna \right] / \left(a |n| \right).$$

System (55) can be rewritten in the form

$$\Delta\left(k,E\right)\begin{pmatrix} \sum\limits_{n} C_n^{(1)} \exp\left(ikna\right) \\ \sum\limits_{m} C_m^{(2)} \exp\left(ikma\right) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{56}$$

Impurity waveguide bands appear when there are additional branches of roots $E = E\left(k\right)$ of equation

$$\det \Delta\left(k,E\right) = 0 \tag{57}$$

belonging to the gap. Our model allows one to describe the waveguide bands explicitly due to a possibility to summarize series for matrix inputs $D_\alpha\left(k,\chi_1\right)$ and $D_\beta\left(k,\chi_2\right)$. One has

$$\Delta\left(k,E\right) = \begin{pmatrix} \frac{1}{a}\ln\frac{ch(a\chi_1)-\cos(ak)}{d_1} & -\frac{\mu_2}{\mu_1}\gamma \\ -\frac{\mu_1}{\mu_2}\overline{\gamma} & \frac{1}{a}\ln\frac{ch(a\chi_2)-\cos(ak)}{d_2} \end{pmatrix}, \tag{58}$$

where $d_1 = \exp\left(-\alpha a\right)/2$, $d_2 = \exp\left(-\beta a\right)/2$, and the dispersion law for the waveguide bands is determined by the equation

$$\ln\frac{ch\left(a\chi_1\right)-\cos\left(ak\right)}{d_1}\ln\frac{ch\left(a\chi_2\right)-\cos\left(ak\right)}{d_2} - a^2\left|\gamma\right|^2 = 0. \tag{59}$$

For $d_i \leq 2\exp\left(-\left|\gamma\right|a\right)$, waveguide bands are overlapped with the bands of the continuous spectrum for the crystal. For $d_i \ll 2\exp\left(-\left|\gamma\right|a\right)$ they disappear. For $\gamma = 0$ one has

$$\begin{aligned} E_1^{(0)} &= E_g/2 - h^2\chi_{10}\left(k\right)/\left(2\mu_1\right), \\ E_2^{(0)} &= h^2\chi_{20}\left(k\right)/\left(2\mu_2\right) - E_g/2 \end{aligned} \tag{60}$$

Parameters $\chi_{i0}\left(k\right)$ are determined by the equation

$$\begin{aligned} ch\left(a\chi_{i0}\left(k\right)\right) &= d_i + \cos\left(ak\right), \\ &\left(i = 1,2\right). \end{aligned} \tag{61}$$

For small $\left|\gamma\right|^2$, one can simply find corrections to solutions (60) of equation (59) by the Newton method

$$\begin{aligned} \chi_i\left(k\right) &= \chi_{i0}\left(k\right) + a\left|\gamma\right|^2/R_i\left(k\right), \\ R_i\left(k\right) &= \left[1 + 2\cos\left(ak\right)/d_i - \sin^2\left(ak\right)/d_i^2\right]^{1/2} \end{aligned} \tag{62}$$

Correspondingly, the impurity bands are described more precisely:

$$E_i\left(k\right) = E_i^{(0)}\left(k\right) \mp \frac{h^2 a^2}{\mu_i R_i\left(k\right)}\left|\gamma\right|^2\chi_{i0}\left(k\right). \tag{63}$$

One can see, that for nonzero γ overlapping of the impurity bands is possible. Generally speaking, such overlapping can occur for $\gamma = 0$ also. One can find band edges and effective

masses analogously to the previous section. To determine the explicit expression for the wave function (53) including the determination of the normalizing constants, one should consider the matrix Green function (50):

$$G\left(\mathbf{r},\mathbf{r}',E\right) = G\left(\mathbf{r}-\mathbf{r}',E\right)$$

$$-\frac{h^2}{2}\sum_{n,n'} G_0\left(\mathbf{r}-n\mathbf{a},E\right)\Delta^{-1}\left(k,E\right)\begin{pmatrix} \mu_1^{-1} & 0 \\ 0 & \mu_2^{-1} \end{pmatrix}\times G_0\left(n'\mathbf{a}-r',E\right)\exp\left[ika\left(n-n'\right)\right].$$

(64)

Here $\Delta^{-1}\left(k,E\right)$ is the inverse matrix for $\Delta\left(k,E\right)$, and

$$G_0\left(\mathbf{r},E\right) = \frac{1}{4\pi h^2}\begin{pmatrix} \mu_1\exp\left(-\chi_1 r\right)/r & 0 \\ 0 & \mu_2\exp\left(-\chi_2 r\right)/r \end{pmatrix} \qquad (65)$$

Inversion of matrix $\Delta\left(k,E\right)$ can be performed by the following procedure (see [24]). For any root $E_j\left(k\right)$ of equation (59), there exists a non-zero vector-function

$$t_j\left(k\right) = \begin{pmatrix} t_{j1}\left(k\right) \\ t_{j2}\left(k\right) \end{pmatrix}$$

such that

$$\left[\Delta\left(k,E\right)t_j\left(k\right)\right]_{E=E_j(k)} = 0. \qquad (66)$$

Consequently, $E = E_j\left(k\right)$ is also a root of function

$$Q_j\left(E\right) = \sum_{i,i'}^{2} \overline{t_{ij}\left(k\right)}\Delta_{ii'}\left(k,E\right)t_{i'j}\left(k\right)$$

where $\left(\overline{t_{1j}\left(k\right)},\overline{t_{2j}\left(k\right)}\right) = t_j^{+}\left(k\right)$ is the vector adjoint to t_j. Definition of function $Q_j\left(E\right)$ leads to $\Im E\Im Q \geq 0$, $\Im E \neq 0$, hence, $Q_j\left(E\right)$ is R-function having only simple roots which belong to real axis. Roots strictly interspersed as poles lying on positive half-axis. Matrix function $\Delta^{-1}\left(k,E\right)$ has simple poles at $E = E_j\left(k\right)$. The following presentation is valid

$$\Delta_{ii'}^{-1}\left(k,E\right) = \left[E - E_j\left(k\right)\right]t_{ij}^{-1}\left(k\right)\overline{t_{i'j}\left(k\right)}/\Gamma_j\left(k\right) + O\left(1\right). \qquad (67)$$

Here

$$\Gamma_j\left(k\right) = \left[\frac{d}{dE}Q_j\left(E\right)\right]_{E=E_j(k)} \neq 0.$$

Comparison of (64) (with substitution (67)) and matrix analog of expansion (44) gives one

$$\Psi_{ij}\left(\mathbf{r},k\right) = \frac{\sqrt{\mu_1}}{4\pi h\sqrt{\Gamma_j\left(k\right)}}\sum_{n=-\infty}^{\infty}\frac{\exp\left[-\chi_{ij}\left|\mathbf{r}-n\mathbf{a}\right|-ikna\right]t_{ij}\left(k\right)}{\left|\mathbf{r}-n\mathbf{a}\right|}, \qquad (68)$$

where $\chi_{ij} = \chi_i \left(E = E_j \right)$ and χ_{ij} is determined by (62) or, in general case, by (59). As for wave functions (68), it is simple to repeat (with the corresponding modifications) the proof of exponential decay far from the chain axis (see the previous section). Thus, if one takes into account two bands of the crystal-matrix, the qualitative result is the same: there is a possibility of appearance of waveguide bands localized in a neighborhood of the chain. It should be noted that appearance of the waveguide band does not related with the effective mass approximation. One can perform the analysis by taking a periodic potential Hamiltonian for the crystal. The impurity influence can be modeled by zero-range potentials as earlier. One chooses the parameters of these potentials in such a way that the impurity level in a band coincides with the experimentally observed ones. As a result, the wave functions for the states corresponding to the waveguide band can be sought in the form

$$\sum_n \widetilde{G} \left(\mathbf{r}, n\mathbf{a}, E \right) \exp \left(-inka \right)$$

where $\widetilde{G} \left(\mathbf{r}, \mathbf{r}', E \right)$. The dispersion equation for the waveguide band is obtained from the boundary condition. Taking into account that the behavior of the Green function $\widetilde{G} \left(\mathbf{r}, \mathbf{r}', E \right) \mathbf{r} \to \mathbf{r}'$ is analogous to the behavior of $\left[-4\pi \left| \mathbf{r} - \mathbf{r}' \right| \right]^{-1}$. The dispersion equation will be as follows:

$$-b + \sum_n \Gamma \left(n \right) e^{ikna} = 0,$$

$$\Gamma \left(n \right) = \lim_{r \to 0} \left[\frac{\partial}{\partial r} \left(r, \widetilde{G} \left(\mathbf{r}, n\mathbf{a}, E \right) \right) \right]$$

3   Conclusion

Effective mathematical model for description and calculation of waveguide bands is suggested. It is based on the theory of self-adjoint extensions of symmetric operators. It is a version of zero-range potential model. Periodic chain of point-like potentials at the surface of nanoparticle, crystal-matrix (in the model - a half-space filled with the crystal). We take into account an influence of one and two bands of the main crystal. For the second case, one use an effective mass approximation. An additional waveguide band appears. The corresponding state is localized near the chain of impurities. It decays exponentially when the distance from the chain axis increases. Correspondingly, the electron density near the nanoparticle surface increases. It leads to the growth of the catalytic activity of the nanocatalyst (in a model, the half-crystal is the nanocatalyst). Thus, we describe a mechanism of increasing of catalytic activity of nanocatalyst. The model allows one to make calculations directly and, correspondingly, to choose proper impurities for nanocatalyst improvement.

Acknowledgments

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