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The effect of electron–electron interactions on the conditions of existence of a surface state

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Electronic surface states in one-dimensional two-band tight-binding approximation model are studied using the Green function method. The local density of states at successive atoms in a semi-infinite chain, even in the case of atoms distant from the surface, is found to be clearly different from that observed in an unperturbed (infinite) chain. The surface atom occupancy is calculated self-consistently, with the effect of electron–electron interactions taken into account. The electron–electron interactions are shown to have a significant impact on the conditions of existence of surface states.

Key words: *electron–electron interactions; surface state; Green function*

1. Introduction

The presence of electronic surface states has a substantial effect on the properties of solids. Many apparently surprising features of mesoscopic and nanoscopic systems in which surface effects are particularly conspicuous, the surface representing a significant part of the whole, can be elucidated by the conditions of existence of surface states.

One of the basic models used for description of electronic properties of solids is the tight binding approximation (TBA) model. The pioneering studies on the conditions of existence of an electronic surface state, based on a single-band model of a finite crystal, were reported by Goodwin [1]. The single-band model was then generalized by Artman [2], who introduced a double-band model to investigate the existence of two types of surface states: Shockley states which are induced only by breaking the translational symmetry of a crystal, and Tamm states, generated as a result of introducing an additional perturbation [3]. A breakthrough was marked by the paper by Kalkstein and Soven [4], in which Green's function formalism was used for the

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determination of properties of surface and bulk states in a semi-infinite crystal with a perturbed surface.

The problem of multi-electron effects and their impact on conditions of existence of a surface state has not yet been exhaustively discussed. Papers on chemisorption which is a related issue, are available, though [5, 6]. As in the case of chemisorption, the simplest way of including the impact of the multi-electron effects on the conditions of surface state existence consists in incorporating interaction of electron with charge density into the Coulomb model. Introducing the Hartree potential into the TBA model of a semi-infinite crystal amounts (in the simplest case) to surface atom site energy renormalization.

This study is focused on surface states in a 1 D semi-infinite atom chain being a model of an ionic crystal with two atoms in the unit cell [7, 8]. Multi-electron effects are taken into account only in the Hartree approximation. The surface atom occupancy and site energy values are found through self-consistent calculations using Green's function formalism [4].

2. Model

The model assumes non-zero resonance integral values only for neighbouring sites. Orbitals s and p are alternately attributed to successive chain sites. Hence, resonance integrals for successive site pairs alternate in sign, taking values site energies associated with s or p orbitals denoted α_e or α_0, respectively (Fig. 1).

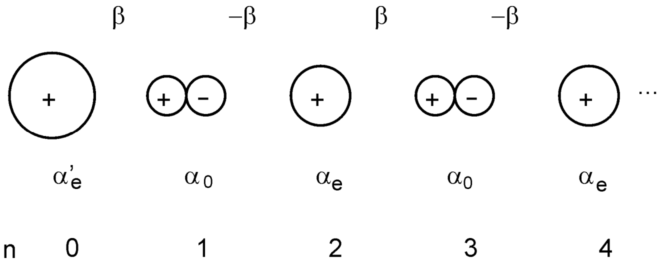

Fig. 1. The model of a semi-infinite 1 D crystal with two-atom unit cell. The surface site ($n = 0$) is occupied by an adatom with the site energy α'_e. The alternating resonance integral sign is a consequence of interaction between s and p orbitals

The wave function in the TBA model is assumed to be a linear combination of atomic functions:

$$|k\rangle = \sum_{n}^{N} \left(c_{2n} |2n\rangle + c_{2n+1} |2n+1\rangle \right) \tag{1}$$

the sum involving all the two-atom unit cells. Expressed in the atomic function basis, the Hamiltonian of an infinite (unperturbed) chain has the following form:

$$\hat{H}_0 = \sum_n \left(\alpha_e |2n\rangle\langle 2n| + \alpha_0 |2n+1\rangle\langle 2n+1| + \beta |2n\rangle\langle 2n+1| - \beta |2n+1\rangle\langle 2n| \right) \tag{2}$$

A surface introduced into the system is regarded as a perturbation breaking the infinite chain into two separate semi-infinite ones [6]:

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{3}$$

$$\hat{V} = (\alpha_e' - \alpha_e)\left(|-1\rangle\langle -1| + |0\rangle\langle 0|\right) + \beta\left(|-1\rangle\langle 0| + |0\rangle\langle -1|\right) \tag{4}$$

The non-zero values of elements *V*(0,0) and *V*(1,1) allow adsorption of atoms of various types.

Derived from the secular equation for Hamiltonian $\hat{H}_0$, the expansion coefficients c_n and the dispersion relation read as follows:

$$\begin{cases} c_{2m} = Ae^{im\theta/2} \\ c_{2m+1} = ABe^{im\theta/2} \end{cases} \tag{5}$$

$$X = \pm\sqrt{\tau^2 + 2 - 2\cos\theta} \tag{6}$$

where

$$A = \sqrt{\frac{X+\tau}{2N\xi}}, \quad B = \frac{2i\sin(\theta/2)}{X+\tau} \tag{7}$$

and

$$\xi = \begin{cases} X, & |X| > \tau \\ \tau, & |X| < \tau \end{cases} \tag{8}$$

Parameters *X* and θ represent the dimensionless energy and wave vector, respectively:

$$X = \frac{E - \bar{\alpha}}{\beta}, \quad \theta = \frac{2\pi k}{N} \tag{9}$$

$\bar{\alpha}$ and τ are defined as follows:

$$\bar{\alpha} = \frac{\alpha_e + \alpha_o}{2}, \quad \tau = \frac{\alpha_e - \alpha_o}{2\beta} \tag{10}$$

The Greenian matrix elements:

$$\hat{G}_0(k) = \sum_k \frac{|k\rangle\langle k|}{E - E(k)} \tag{11}$$

expressed in the atomic function basis, read within the energy bands:

$$G_0\left(2m,2n\right)=-\frac{X+\tau}{\beta}\frac{t_<^{n-m}}{t_<-t_>} \tag{12}$$

$$G_0\left(2m+1,2n+1\right)=-\frac{X-\tau}{\beta}\frac{t_<^{n-m}}{t_<-t_>} \tag{13}$$

$$G_0\left(2m,2n+1\right)=\frac{1-t_<}{\beta}\frac{t_<^{n-m}}{t_<-t_>} \tag{14}$$

$$G_0\left(2m+1,2n\right)=\frac{1-t_<^{-1}}{\beta}\frac{t_<^{n-m}}{t_<-t_>} \tag{15}$$

where

$$t_>=Z+\operatorname{sign}\left(X\right)i\sqrt{Z^2-1},\qquad t_<=Z-\operatorname{sign}\left(X\right)i\sqrt{Z^2-1} \tag{16}$$

and

$$Z=\frac{\tau^2+2-X^2}{2}=\cos\theta \tag{17}$$

Selected Greenian matrix elements for perturbed (semi-infinite) crystal can be found from the Dyson equation:

$$\hat{G}=\hat{G}_0+\hat{G}_0\hat{V}\hat{G} \tag{18}$$

The diagonal elements read:

$$G\left(m,m\right)=G_0\left(m,m\right)+\frac{G_0\left(0,m\right)\left(G_0\left(m,0\right)V\left(0,0\right)+G_0\left(m,-1\right)V\left(-1,0\right)\right)}{1-G_0\left(0,0\right)V\left(0,0\right)-G_0\left(0,-1\right)V\left(-1,0\right)} \tag{19}$$

This allows the determination of the local density of states (LDOS):

$$\rho\left(X,m\right)=-\pi\operatorname{Im}\left[\beta G\left(m,m\right)\right] \tag{20}$$

and the surface state occupancy in successive chain sites:

$$\left\langle n\left(m\right)\right\rangle=\operatorname{Res}\left[G\left(m,m\right),X_s\right] \tag{21}$$

where X_s is the surface state energy determined from the condition of $G(m,m)$ zeroing.

Self-consistent renormalization of the site energy at successive sites is necessary for electron–electron interactions to be taken into account. By defining

$$\tau_m = \frac{\alpha_m - \bar{\alpha}}{\beta}, \quad \alpha_m = \alpha'_e, \alpha_o, \alpha_e, \alpha_o, \alpha_e, \ldots \tag{22}$$

we get:

$$\tau'_m = \tau_m + U\left\langle n(m)\right\rangle \tag{23}$$

where U is a parameter defining interaction of electron with charge density. Surface state localization is equivalent to state occupancy fading inward the crystal. Therefore, the highest site energy gradient is expected at the surface. In the first approximation, site energy modification can concern only the surface atom.

The surface perturbation parameter can be expressed as follows:

$$\Delta_e = \frac{\alpha'_e - \alpha_e}{\beta} = \tau_0 - \tau_{2m}, \quad m = 1, 2, 3, \ldots \tag{24}$$

When interaction of electron with charge density is taken into account:

$$\Delta'_e = \tau'_0 - \tau_{2m}, \quad m = 1, 2, 3, \ldots \tag{25}$$

In the case considered here ($\tau = 1$), the surface state energy is expressed by the following formula:

$$X_{s\pm} = \frac{1 + \Delta'_e \pm \sqrt{1 - 4\Delta'_e + 6\Delta'^2_e + 4\Delta'^3_e + \Delta'^6_e}}{2\Delta'^2_e} \tag{26}$$

X_{s+} and X_{s-} being the solutions valid for $\left|\Delta'_e + 1/2\right| > \sqrt{5}/2$ and $\Delta'_e < 0$ respectively.

3. Results

Computations were performed at $\tau = 1$ ($\alpha_e - \alpha_0 = 2\beta$). Figure 2 shows the surface state energy, X_s, plotted versus the surface perturbation. No Shockley states are found to exist in the model discussed [5], as no surface states are found in the absence of perturbation. Tamm states, induced through modifying the surface atom site energy, are found to emerge from the upper energy band (associated with α_e).

The surface states emerging from the bottom edge of the band are induced by an arbitrarily small perturbation value. For surface states to be induced above the upper band, however, the perturbation value must be positive and fulfil the condition $\Delta'_e > 1/2(\sqrt{5} - 1)$. Perturbation values from the interval $0 < \Delta'_e < 1/2(\sqrt{5} - 1)$ correspond to the non-existence of surface states. The solid and dotted lines in Fig. 2 represent surface state levels found with or without the electron–electron interactions taken into account, respectively. Clearly, the multi-electron effects (in the Hartree approximation) boost the surface state energy levels, resulting in weakened or strengthened localization of surface states below or above the upper band, respectively. However, the electron–electron interactions have no effect on the interval of surface perturbation parameter values at which surface states are found to exist.

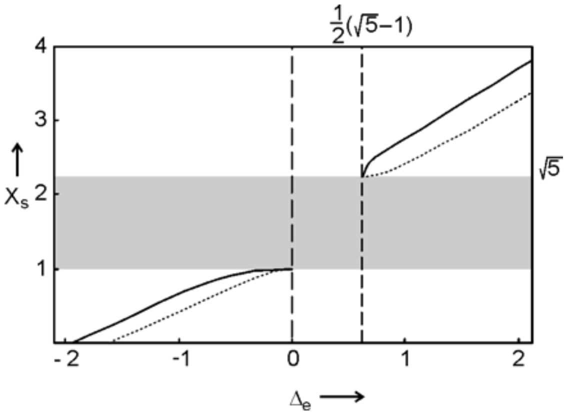

Fig. 2. Surface state levels around the upper band (gray area). The solid and dotted lines represent the state levels found with and without the electron–electron interactions taken into account, respectively. The dashed lines delimit the region in which no surface states exist

The effect of the surface on the electronic states in the considered chain is the most evident in the LDOS spectrum. Figure 3 shows the LDOS plots obtained for the four sites closest to the surface: $n = 0, 1, 2, 3$. Three different perturbation values are assumed, corresponding to surface state appearing below the upper band ($\Delta_e = -0.75$), not induced at all ($\Delta_e = 0.5$), and induced above the upper band ($\Delta_e = 1$). The solid and dotted lines represent the LDOS calculated with multi-electron effects taken into account or neglected, respectively. As a result of including the multi-electron effects, the LDOS in the upper band is increased; at the same time, the occupancy of the surface state below the band decreases, and the state moves towards the band edge. An opposite effect is found to occur for the surface state above the upper band: the LDOS in the band is found to decrease, while the surface state occupancy increases and the state moves inwards the gap. Comparing relative occupancy changes at successive sites, one notes a stronger localization in states closer to the band edge. Because of band asymmetry, the surface state occupancy should be compared between either even or odd sites. With multi-electron effects taken into account, the occupancy ratio of site ($n = 0$) (the surface atom) to site $n = 2$ is found to increase or decrease for states above or below the upper band, respectively. Note that even in the absence of surface states, the presence of the surface still affects the LDOS spectrum. The van Hove singularities at the band edges are eliminated, and LDOS minima appear inside the bands.

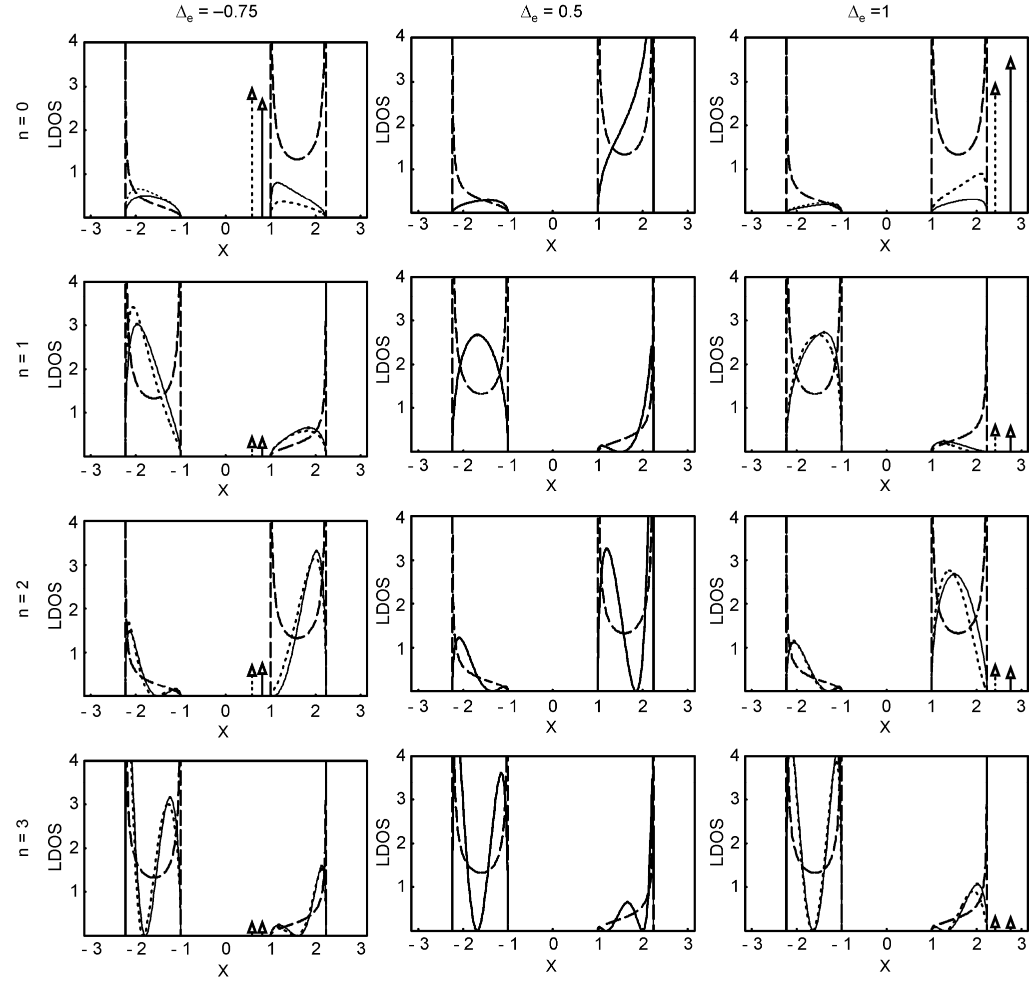

Fig. 3. The local densities of states, $(\pi\rho(X))$ at successive chain sites starting from the surface ($n = 0, 1, 2, 3$). Results obtained at three different perturbation values, Δ_e, are grouped into columns. The dashed line represents the LDOS for infinite chain. The dotted and solid lines represent the LDOS found for semi-infinite chain with electron–electron interactions neglected or taken into account, respectively. The arrows indicate the surface state occupancy

4. Conclusions

Focused on the effect of electron–electron interactions on the conditions of surface state existence (in the Hartree approximation), the study presented above shows that the localization of surface states generated above or below the upper energy band can be increased or decreased, respectively, by the electron–electron interactions in the considered model. However, the interval of perturbation of the values of surface parameters corresponding to surface state existence is found to remain unaffected by taking these interactions into account in the calculations.

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