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Surface-state energies and wave functions in layered organic conductors

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Abstract: We have calculated and analyzed the surface-state energies and wave functions in quasi-two dimensional (Q2D) organic conductors in a magnetic field parallel to the surface. Two different forms for the electron energy spectrum are used in order to obtain more information on the elementary properties of surface states in these conductors. In addition, two mathematical approaches are implemented that include the eigenvalue and eigenstate problem as well as the quantization rule. We find significant differences in calculations of the surface-state energies arising from the specific form of the energy dispersion law. This is correlated with the different conditions needed to calculate the surface-state energies, magnetic field resonant values and the surface wave functions. The calculations reveal that the value of the coordinate of the electron orbit must be different for each state in order to numerically calculate the surface energies for one energy dispersion law, but it has the same value for each state for the other energy dispersion law. This allows to determine more accurately the geometric characteristics of the electron skipping trajectories in Q2D organic conductors. The possible reasons for differences associated with implementation of two distinct energy spectra are discussed. By comparing and analyzing the results we find that, when the energy dispersion law obtained within the tight-binding approximation is used the results are more relevant and reflect the Q2D nature of the organic conductors. This might be very important for studying the unique properties of these conductors and their wider application in organic electronics.

Keywords: magnetic field resonant values; quantization; quasi-two dimensional organic conductors; skipping electrons; surface states.

1 Introduction

Surface states are important class of quantum states localized near the surface of a solid. These states are not present in the bulk, and their presence is correlated to the change in periodicity of the crystal lattice near the surface. The presence of a boundary significantly changes the character of the motion of the conduction electrons and leads to the appearance of a discrete spectrum of surface states if the electrons are almost specularly reflected from the surface of the sample [1–6]. These states have properties which are quite different from the bulk electronic structure of the material. The quantum mechanical surface states are formed by the surface electrons that move along the surface on skipping trajectories by periodic specular reflection. In the presence of a magnetic field, due to action of the Lorentz force, the electrons are impelled toward the surface and hence are bound to the surface region. The oscillations of the surface impedance of metals in weak fields, discovered by M. Khaikin [7], occur due to resonant transitions between discrete magnetic surface levels of skipping electrons. Nee and Prange [1–3] have made use of the surface levels, by quantizing the periodic motion of the skipping electrons specularly reflected from the surface of the metal, to explain the oscillations of the impedance and shown that they can be treated as a cyclotron resonance due to the transitions between different magnetic surface levels. In contrast to the Landau levels that represent the electrons in the cyclotron electron orbits, the surface energy levels that represent the surface skipping electrons depend on the coordinate of the rotation center since the period of the skipping electrons depend on the coordinate of the center of rotation. The experimental studies of the surface impedance oscillations in metals [8–11] have shown that there is a group of surface electrons that makes a significant contribution to the oscillations of the metal as a function of the magnetic field. Moreover, all the metals in which this effect is observed have almost cylindrical Fermi surface parts. Therefore, knowing the local geometry of the

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Fermi surface is important for studying the surface states and phenomena related to them.

Layered organic conductors are very attractive for researchers due to their unique properties including a sensitive response to weak structural changes and a large number of phase transformations under an external magnetic field [12]. A characteristic feature of the electronic properties of organic metals is a pronounced quasi-one (Q1D) or quasi-two (Q2D) anisotropy arising due to their crystal structure. The Fermi surface of most of the layered organic conductors is known as obtained from the transport experiments and has a form of slightly corrugated sheets for the Q1D and slightly corrugated cylinders for the Q2D organic conductors. On the other hand, high-frequency phenomena strongly suggest that in some families of organic conductors the Fermi surface is a union of Q2D cylinders and quasi-one dimensional sheets. All these properties make layered organic conductors excellent candidates for studding the surface states properties and the effects that occur as a result of the electronic transitions between the discrete surface levels.

In a previous work on the elementary properties of magnetic surface levels in layered organic conductors, the studies were conducted in the simplest case with respect to the geometry of the problem and the form of the energy spectrum [13]. However, due to the simplifications made for the electron energy spectrum, some of the characteristics of the Fermi surface concerning the number of electron orbits involved in the formation of the surface states are disregarded. Therefore, it is recommended that the surface states are also studied using the most general assumptions concerning the form of Q2D electron energy spectrum derived within the tight-binding approximation which is usually used for theoretical studies of the electron properties of organic conductors [12].

As a continuation of the previous work, in the present paper, we consider the surface states and their properties in organic conductors under the most general assumptions concerning the form of Q2D electron energy spectrum obtained in the frame of the tight-binding theory which assumes a weak coupling within the plane of the layers and a strong coupling approximation for the electrons belonging to adjacent layers. In addition, we are also considering the surface-state energies and wave functions obtained by using another form for the Q2D electron energy spectrum, previously used to investigate the nonmagneto-oscillatory surface effects in these conductors in order to reveal the differences that arise by implementation of different forms of the electron energy spectrum and how it reflects on the elementary properties of the surface states in organic conductors.

2 Formulation of the problem: numerical calculation of the magnetic surface levels

The usual approach in theoretical studies of the electronic properties of layered organic conductors is by using the energy spectrum of the form

$$\varepsilon(\mathbf{p}) = \sum_{n=0}^{\infty} \varepsilon_n(p_x, p_y) \cos\left(\frac{anp_z}{\hbar}\right) \quad (1)$$

or if the anisotropy of the energy spectrum in the plane of the layers is neglected, then it is given by the equation

$$\varepsilon(\mathbf{p}) = \frac{p_x^2 + p_y^2}{2m^*} + \sum_{n=1}^{\infty} \varepsilon_n(p_x, p_y) \cos\left(\frac{anp_z}{\hbar}\right) \quad (2)$$

A simplified form of the above equation obtained within the tight-binding approximation when only the first term in the sum over n is taken into account is widely used to describe the transport properties of layered organic conductors.

$$\varepsilon(\mathbf{p}) = \frac{p_x^2 + p_y^2}{2m^*} - t_c \cos\left(\frac{p_z}{p_0}\right) \quad (3)$$

Here p_x and p_y are the in-plane momentum of the electron, m^* is the electron effective mass in the plane of the layers, $t_c = \eta\varepsilon_F$ is the interlayer transfer integral, η is the parameter of quasi-two dimensionality, ε_F is the Fermi energy, $p_0 = \hbar/c$, c is the distance between the layers, and $\hbar$ is the Planck constant divided by 2π .

Previously, the non magneto-oscillatory surface resistance in Q2D organic conductors was studied by applying a different approach which involves a simpler form for the electron energy spectrum which corresponds to a corrugated Fermi surface with different profiles [14]. Here, we shall also consider this form for the electron energy spectrum in order to calculate the magnetic surface levels and compare them with those obtained by using the more general form of the energy spectrum derived within the tight-binding approximation. For the purpose of the investigation of the magnetic surface-state energies, we represent it in the following form

$$\varepsilon(\mathbf{p}) = \frac{p_x^2 + p_y^2}{2m^*} + \frac{t_c}{4} \left(1 + \left(\frac{p_z}{p_0} \right)^2 \right)^2. \quad (4)$$

The above equation corresponds to a Fermi surface with a slightly corrugated cylinder open along the p_z axis similar to that represented by Eq. (3).

In order to compare the energies of the surface levels obtained using the two different forms for the electron

energy spectrum as well as to emphasize the differences due to applying a different approach in the calculations of the magnetic surface levels in organic conductors, we shall consider the simplest geometry for the problem that includes a magnetic field applied strictly parallel to the surface of the conductor along the y -axis, $\mathbf{B} \parallel y$, and a smooth surface parallel to the conducting layer planes. Since in layered organic conductors, the ratio of the velocity along the least conducting axis z of the conductor and the Fermi velocity, v_z/v_F , is small and of order of the parameter of two-dimensionality $\eta \sim 10^{-2}$, we can limit ourselves to a specular reflection of the electrons from the conductor's surface. The z -axis is along the interior normal to the surface $z = 0$ of the organic conductor which occupies the half-space $z > 0$.

2.1 The eigenvalue and eigenstate problem

To determine the surface-state energies and the corresponding wave functions, the Schrödinger equation for the problem must be solved. This involves the following Hamiltonian

$$\mathcal{H} = \frac{(p_x - eBz)^2}{2m^*} + \frac{p_y^2}{2m^*} - t_c \cos\left(\frac{p_z}{p_0}\right) + V(z), \quad (5)$$

where the potential $V(z)$ is zero in the region $z > 0$ and an infinite surface potential barrier for $z < 0$. Using the Landau

gauge, the magnetic field is described by the vector potential $A = (Bz, 0, 0)$. The surface-state wave function in the Landau gauge has the form

$$\Psi(x, y, z) = \frac{1}{(2\pi\hbar)} \exp \frac{i}{\hbar} (p_x x + p_y y) \Phi(z), \quad (6)$$

and vanishes for $z = 0, \infty$; $\Psi(0) = \Psi(\infty) = 0$. The corresponding Schrödinger equation is taking the following form

$$\left[\frac{d^2}{dz^2} + \frac{1}{c^2} \text{Arccos} \left(-\frac{1}{t_c} \left(\varepsilon - \frac{(p_x - eBz)^2}{2m^*} - \frac{p_y^2}{2m^*} \right) \right)^2 \right] \Phi(z) = 0. \quad (7)$$

We consider the most important group among the surface electrons, the skipping electrons, in which the center of the classical orbit is located outside the conductor at a distance approximately equal to the radius of the electron trajectory $r_L = p_F/eB$. In momentum space, these are the electrons that move along closed orbits in the vicinity of the Fermi surface that are extremal cross-sections of the Fermi surface by the plane $\varepsilon(\mathbf{p}) = \varepsilon_F$, $p_y = \text{const}$ is shown in Figure 1a. The transitions of the skipping electrons between these closed orbits account for observation of the magnetic quantum oscillations of the surface resistance in a similar way as the transitions of

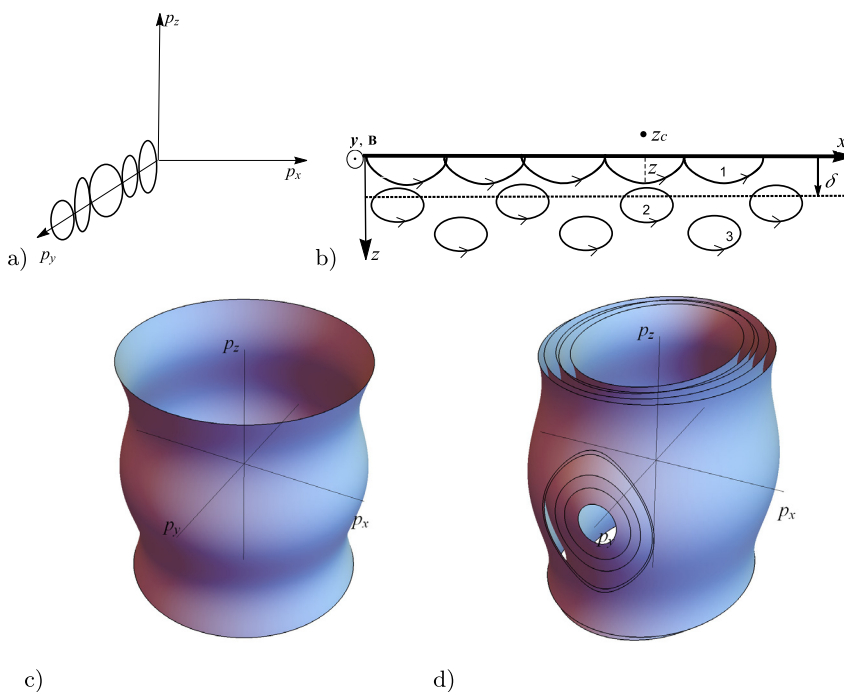


Figure 1: a) The closed orbits in the momentum space. The electrons on these orbits contribute to the surface states in the Q2D organic conductors. They are always perpendicular to the magnetic field, i.e., in our case to the p_y axis as $B \parallel p_y$. When they are rotated for 90° clockwise, one obtains the electron trajectory in the coordinate space, i.e., the skipping electron trajectory. b) The open skipping electron orbit (1) in the surface region with a depth δ and the closed cyclotron orbits (2 and 3) into the depth of the conductor. c) The Fermi surface of a Q2D organic conductor. d) Possible electron orbits for magnetic field along the y -axis obtained as cross-sections by the plane $\varepsilon(\mathbf{p}) = \varepsilon_F$, $p_y = \text{const}$ at the belly of the Fermi surface.

electrons belonging to cyclotron orbits between the Landau levels, leading to magnetic quantum oscillations of the bulk resistance [15]. In the coordinate space, the corresponding orbit is obtained with rotation of the orbit in momentum space by $\pi/2$. Thus, in coordinate space, these electrons are moving along trajectories that are bound to the surface region by periodic specular reflection known as skipping trajectories. Due to the multiple reflections from the surface, the trajectories are open and electrons drift in the x direction along orbit 1 in Figure 1b. The electron motion is confined in the surface skin layer with a depth δ . The corresponding closed cyclotron orbits for the bulk electrons are also shown in Figure 1b for comparison (orbits 2 and 3). Orbits 2 are known as skimming cyclotron orbits due to their proximity to the conductor's surface.

To better understand what orbits are involved in formation of the magnetic surface levels, we present in Figure 1 the Fermi surface of a Q2D organic conductor and the possible electron orbits when the magnetic field is along the y direction. The Fermi surface is an open and slightly corrugated along the p_z -axis cylinder (Figure 1c) and the closed orbits which are cross-sections of the Fermi surface by the plane $\varepsilon(\mathbf{p}) = \varepsilon_F$, $p_y = \text{const}$ are located on the sides or at the belly of the Fermi surface perpendicularly to the magnetic field as show in Figure 1d. The previous work on magnetic surface levels in Q2D organic conductors [13] considers the contributions of the electrons that belong to the closed orbits for which $p_z \ll p_0$, i.e., only the electrons on small closed orbits located in the most inner part of the Fermi surface belly contribute in the surface states. However, the energy spectra given by Eqs. (3) and (4) allow existence of closed orbits for p_z in the interval $-p_0 \leq p_z \leq p_0$, meaning that a larger number of closed orbits on sides of the Fermi surface and consequently larger number of conduction electrons are involved in the formation of the surface states.

In the following, we shall make some justified assumption in an attempt to find the eigenvalues and eigenstates, i.e., the surface-state levels and wave functions of the problem. First, since the motion of skipping electrons is in the proximity of the surface, in the skin layer with a depth δ , their z coordinate is small ($z \ll \delta$), and therefore, it is enough to take into account only the linear in z term in the argument of Arccos . Thus the Schrödinger equation assumes the following form

$$\left[\frac{d^2}{dz^2} + \frac{1}{c^2} \text{Arccos} \left(- \left(q - \frac{\hbar \Omega z_c}{t_c l_B} z \right) \right) \right] \Phi(z) = 0, \quad (8)$$

where $z_c = |Z|/l_B$, $|Z| = \frac{p_x}{eB}$ is the coordinate of the center of

electron rotation which is negative, $|Z| = -Z$, because the center of orbit is outside the conductor, $q = \frac{1}{t_c} \left(\varepsilon - \frac{p_x^2}{2m^*} - \frac{p_y^2}{2m^*} \right)$, $\Omega = \frac{eB}{m^*}$ is the cyclotron frequency and $l_B = \sqrt{\frac{\hbar}{eB}}$ is the magnetic length.

Second, an expansion in power series of $\text{Arccos} \left(- \left(q - \frac{\hbar \Omega z_c}{t_c l_B} z \right) \right)^2$ up to the linear in z term transforms Eq. (8) into the final form suitable for obtaining the surface-state energies and wave functions of Q2D organic conductors

$$\left[\frac{d^2}{dz^2} + \frac{1}{c^2} \left(\pi - (\text{Arccos}(q))^2 - \frac{2\hbar \Omega z_c (\pi - \text{Arccos}(q))}{t_c l_B \sqrt{1-q^2}} z \right) \right] \Phi(z) = 0. \quad (9)$$

The solution of Eq. (9) is given by the Airy function [16]

$$\Phi(z) = CAi \left(\left(\frac{2z_c l_B^2 \hbar \Omega_0 B (\pi - \text{Arccos}(q))}{c^2 t_c \sqrt{1-q^2}} \right)^{1/3} \left(\frac{z}{l_B} - \frac{t_c \sqrt{1-q^2} (\pi - \text{Arccos}(q))}{2z_c \hbar \Omega_0 B} \right) \right), \quad (10)$$

where $\Omega_0 = e/m^*$ and the normalization constant C is determined as

$$C = \left(\frac{\left(\frac{2z_c l_B^2 \hbar \Omega_0 B (\pi - \text{Arccos}(q))}{c^2 t_c \sqrt{1-q^2}} \right)^{1/3}}{Ai'^2 \left(- \left(\frac{l_B t_c \sqrt{1-q^2} (\pi - \text{Arccos}(q))^2}{2z_c \hbar \Omega_0 B} \right)^{2/3} \right)} \right)^{1/2}. \quad (11)$$

The surface-state energy levels are obtained from the boundary condition $\Psi(0) = 0$ which reduces to determination of the roots of the following equation

$$Ai \left(- \left(\frac{l_B t_c \sqrt{1-q^2} (\pi - \text{Arccos}(q))^{4/3}}{(2z_c \hbar \Omega_0 B)^{2/3}} \right) \right) = 0. \quad (12)$$

This yields the following relation for the quantity q that allows to calculate the surface-state energies ε_n of the Q2D organic conductors in a magnetic field

$$\left(\frac{l_B t_c \sqrt{1-q^2} (\pi - \text{Arccos}(q))^2}{2z_c \hbar \Omega_0 B} \right)^{2/3} = \left(\frac{3\pi}{2} \left(n - \frac{1}{4} \right) \right)^{2/3}. \quad (13)$$

The above identity does not allow to analytically derive a relation for the surface-state energies, and therefore, they are calculated numerically by evaluating q and then using the expression $\varepsilon_n(p_x, p_y, Z) = \frac{p_x^2}{2m^*} + \frac{p_y^2}{2m^*} + q t_c$. In Q2D organic conductors, the plane of the layers is the most conducting plane where electrons move with average velocities close to the Fermi velocity, $\bar{v}_y \sim v_F$, $\bar{v}_x \sim v_F$, that allows the energy of a surface state with a quantum number n to be expressed in terms of the Fermi momentum p_F , $\varepsilon_n(p_F, Z) = \frac{p_F^2}{m^*} + q t_c$. Hence, the following relation suitable

for numerical calculation of the surface-state energies is obtained

$$\sqrt{1 - \left(\frac{1}{t_c} \left(\varepsilon_n - \frac{p_F^2}{m^*}\right)\right)^2} \left(\pi - \arccos\left(\frac{1}{t_c} \left(\varepsilon_n - \frac{p_F^2}{m^*}\right)\right)\right)^2 = \frac{3\pi z_c \hbar \Omega_0 B c}{l_B t_c} \left(n - \frac{1}{4}\right). \quad (14)$$

In a similar way, by using the energy dispersion law defined by Eq. (4) and keeping only the linear in z term in the expansion in power series of $\left(q - \frac{\hbar \Omega_0 B z_c}{l_B t_c} z\right)^{1/2}$ one obtains the following Schrödinger equation for the problem

$$\left[\frac{d^2}{dz^2} + \frac{1}{c^2} \left(2\sqrt{q} - \frac{\hbar \Omega_0 B z_c}{t_c l_B \sqrt{q}} z - 1\right)\right] \chi(z) = 0, \quad (15)$$

which yields the surface wave functions of the form

$$\chi(z) = C \text{Ai} \left(\left(\frac{z_c l_B^2 \hbar \Omega_0 B}{c^2 t_c \sqrt{q}} \right)^{1/3} \left(\frac{z}{l_B} - \frac{t_c (2q - \sqrt{q})}{z_c \hbar \Omega_0 B} \right) \right), \quad (16)$$

with a normalization constant C

$$C = \left(\frac{\left(\frac{z_c l_B^2 \hbar \Omega_0 B}{c^2 t_c \sqrt{q}} \right)^{1/3}}{\text{Ai}' \left(- \left(\frac{l_B t_c \sqrt{q}}{z_c \hbar \Omega_0 B} \right)^{2/3} (2\sqrt{q} - 1) \right)} \right)^{1/2}. \quad (17)$$

The corresponding magnetic surface levels in terms of the Fermi momentum are determined numerically from the following relation

$$\left(\frac{l_B t_c \sqrt{\frac{1}{t_c} \left(\varepsilon_n - \frac{p_F^2}{m^*}\right)}}{z_c \hbar \Omega_0 B} \right)^{2/3} \left(2\sqrt{\frac{1}{t_c} \left(\varepsilon_n - \frac{p_F^2}{m^*}\right)} - 1 \right) = \left(\frac{3\pi}{2} \left(n - \frac{1}{4}\right) \right)^{2/3}. \quad (18)$$

2.2 The quantization condition

For the purpose of this study as well as for comparison, we shall explore all the possible ways available for determination of the surface-state energies in Q2D organic conductors. The motion of the skipping electrons along the z direction is periodic and therefore quantized. This allows us to determine the surface energy levels from the Bohr–Sommerfeld quantization condition by taking into account

that in a magnetic field the quantities p_z and Z are canonically conjugate variables. The quantization rule reads as

$$S(\varepsilon, p_y, z_c) \equiv \int p_z dp_x = 2\pi(n - \gamma)\hbar eB, \quad (19)$$

and can be applied within the quasi-classical approximation, which for the Q2D organic conductors is applicable when the condition $\hbar\Omega \ll t_c$ is satisfied. The quantization rule for closed orbits is also valid for open periodic skipping orbits [17]. In the case of energy spectrum defined by Eq. (3), it can be written as

$$S(\varepsilon, p_y, z_c) \equiv p_0 \int \arccos \left(-\frac{1}{t_c} \left(\varepsilon - \frac{(p_x - eBz)^2}{2m^*} - \frac{p_y^2}{2m^*} \right) \right) dz = 2\pi\hbar(n - \gamma). \quad (20)$$

The value of γ is determined by the boundary conditions. For a complete cyclotron orbit, $\gamma = 1/2$ and for skipping orbit is $\gamma = 1/2$ if $\text{Ai}(0) = 0$ [1] or $\gamma = 3/4$ if $\text{Ai}'(0) = 0$ [6]. $S(\varepsilon, p_y, z_c)$ is the area bounded by the curve $\varepsilon(\mathbf{p}) = \varepsilon_F$, $p_y = \text{const}$, $Z = \text{const}$ in momentum space between two neighboring turning points. In an unbounded metal, the area S does not depend on Z and equals the area bounded by the entire curve $\varepsilon(\mathbf{p}) = \varepsilon_F$, $p_y = \text{const}$. For the electrons that collide with the surface, such as the skipping surface electrons, the area S depends on Z .

Here, we make use of the boundary condition $\Psi(0) = 0$ or $\text{Ai}(0) = 0$, and therefore, $\gamma = 1/4$. We will integrate Eq. (17) in z while keeping only the term proportional to z in the expansion in power series of $\arccos(- (q - \frac{\hbar \Omega_0 B z_c}{t_c l_B} z))$. This yields the following integral

$$\frac{2\hbar \Omega_0 B z_c}{t_c l_B c \sqrt{1 - q^2}} \int_0^{z_n} (z_n - z) dz = 2\pi \left(n - \frac{1}{4}\right). \quad (21)$$

where $z_n = \frac{t_c l_B \sqrt{1 - q^2}}{\hbar \Omega_0 B z_c} (\pi - \arccos(q))$ is the maximum distance of electrons from the surface. By solving it, one obtains the following relation to calculate the surface-state energies ε_n

$$\sqrt{1 - \left(\frac{1}{t_c} \left(\varepsilon_n - \frac{p_F^2}{m^*}\right)\right)^2} \left(\pi - \arccos\left(\frac{1}{t_c} \left(\varepsilon_n - \frac{p_F^2}{m^*}\right)\right)\right)^2 = \frac{2\pi z_c \hbar \Omega_0 B c}{l_B t_c} \left(n - \frac{1}{4}\right). \quad (22)$$

Evidently, Eq. (22) is similar to the one that we derived from solving the eigenvalue and eigenstate problem (Eq. (14)).

Hence, it is reasonable to expect similar values for the magnetic surface-state energies.

Similarly, applying the quantization rule in the case of energy spectrum defined by Eq. (4), the surface-state energies are obtained from the relation

$$\left(2\sqrt{\frac{1}{t_c}\left(\varepsilon_n - \frac{p_F^2}{m^*}\right)} - 1\right)^2 \sqrt{\frac{1}{t_c}\left(\varepsilon_n - \frac{p_F^2}{m^*}\right)} = \frac{2\pi z_c \hbar \Omega_0 B c}{l_B t_c} \left(n - \frac{1}{4}\right). \quad (23)$$

The equations derived in this section for the surface-state energies and wave functions are valid in the limiting case $q < 1$ or equivalently $\varepsilon_n < t_c + 2\varepsilon_F$.

3 Discussion

In the following, we shall present the surface-state energies evaluated by implementing different energy dispersion law in a magnetic field parallel to the surface. In addition, we shall also calculate the resonance values of the magnetic field at which the surface electron excitation occurs. Due to the resonance transitions between the surface states, there appear peaks in the quantum oscillations of surface resistance at certain magnetic field values $B = B_{mn}$. It is important to obtain these values for the magnetic field for the purpose of fitting with the ones experimentally determined. This will allow to evaluate accurately the resonance magnetic field values from experimental curves. To determine the surface-state energy levels and wave functions, we are using the following values for the characteristic parameters [18]: $m^* = 4.2m_e$ (m_e is the free electron mass), $v_F = 1.5 \times 10^5$ m/s, $t_c = 0.35$ meV, $\Omega_0 = 0.042 \times 10^{12}$ Hz, $l_B = 2 \times 10^{-8}$ m and $c = 1.5$ nm.

Table 1: Surface-state energies for $n = 1$ to $n = 6$ in quasi-two dimensional (Q2D) organic conductors as obtained by applying different models for the energy dispersion law and different mathematical approach involving the eigenvalue problem and quantization rule.

n	$\varepsilon_n(\text{eV})$ Eq. (14)	$\varepsilon_n(\text{eV})$ Eq. (18)	$\varepsilon_n(\text{eV})$ Eq. (22)	$\varepsilon_n(\text{eV})$ Eq. (23)
1	0.53679	0.53691	0.53679	0.53695
2	0.53683	0.53695	0.53684	0.53700
3	0.53686	0.53699	0.53688	0.53703
4	0.53688	0.53702	0.53690	0.53706
5	0.53690	0.53704	0.53693	0.53709
6	0.53692	0.53707	0.53695	0.53711

3.1 The surface-state energies

In Table 1, we present the surface-state energies for $n = 1$ to $n = 6$ calculated for $B = 3$ T from the corresponding equations derived in the previous section. We shall analyze and compare the results in order to obtain information about the elementary properties of the magnetic surface states that can be of great significance for accurate experimental estimation of the values of the relevant quantities for the magnetic surface oscillations.

We find that there is a slight difference in the values of the surface-state energies obtained by applying different energy dispersion law and different approach in the calculations. Comparing the surface-state energies from the eigenvalue and eigenstate problem, we find that Eq. (18) yields slightly larger values than Eq. (14). The difference between them is of order of 10^{-4} eV and is slightly increasing while going from lower to higher surface states from 1.2×10^{-4} eV for $n = 1$ to 1.5×10^{-4} eV for $n = 6$. On the other hand, the quantization rule yields slightly higher values for the surface-state energies for both energy dispersion laws than those obtained by solving the Schrödinger equation. Apart from that, in this case, the difference in energy of a surface state with a quantum number n , obtained from Eqs. (22) and (23), is constant of order of 1.6×10^{-4} eV. The increasing difference in the surface-state energies obtained from the eigenvalue problem is correlated with the change of the value of the coordinate of the electron orbit in case when calculations are performed by using the energy dispersion law (3). Indeed, the energies are calculated numerically with each mathematical approach used but under different conditions. These conditions involve different allowed values for the coordinate of the electron orbit from the surface when using Eq. (14), i.e., in order to obtain the energies from Eq. (14) one has to apply different values for z_c . The values for z_c are the highest for the lowest state and decrease for higher states. The allowed skipping trajectories are determined from the expression

$$z_n = \frac{t_c l_B}{\hbar \Omega_0 B z_c} \sqrt{1 - \left(\frac{1}{t_c}(\varepsilon_n - 2\varepsilon_F)\right)^2} \left(\pi - \arccos\left(\frac{1}{t_c}(\varepsilon_n - 2\varepsilon_F)\right)\right).$$

We obtain the following values: $z_c = 21, 10, 7, 5.3, 4.5, 3.8$ for $n = 1$ to $n = 6$, respectively. This signifies that the trajectories of the skipping electrons that take place in the formation of quantum surface states differ in their dimensions depending on the number of the state. In comparison, by using the quantization rule, we obtain higher values for z_c : $z_c = 32, 16, 11, 8.5, 7, 6$ for $n = 1$ to $n = 6$. Since z_c decreases with increasing n it follows that the trajectories of the electrons in the higher quantum surface states have correspondingly larger dimensions. This allows to

numerically calculate the electron trajectories for each surface state. For example, we find the following values for the first to sixth surface state: $z_1 = 6.5$ nm, $z_2 = 14$ nm, $z_3 = 21$ nm, $z_4 = 28$ nm, $z_5 = 34$ nm and $z_6 = 40$ nm, respectively.

On the other hand, this is not the case when the other energy dispersion law (Eq. (4)) is used. On contrary, here the surface-state energies might be calculated by using one value for $z_c = 1.5$ for both the eigenvalue problem and quantization rule. However, the expression $z_n = \frac{t_c l_B}{\hbar \Omega_0 B z_c} \sqrt{\frac{1}{t_c} (\epsilon_n - 2\epsilon_F)} (2\sqrt{\frac{1}{t_c} (\epsilon_n - 2\epsilon_F)} - 1)$ for the allowed electron trajectories also yields larger trajectories with increasing number of the surface state. In comparison, the following values are obtained: $z_1 = 9.3$ nm, $z_2 = 17$ nm, $z_3 = 26$ nm, $z_4 = 32$ nm, $z_5 = 37$ nm and $z_6 = 44$ nm, respectively. In this case, the maximum distance of electrons from the surface z_n is slightly larger due to the larger surface-state energies. We find that the reason for the observed differences between the values for the surface-state energies obtained from Eqs. (14) and (18) arises from the different velocity of periodic motion of electrons along the z direction. This, in turn, gives a different $v_z^{\max}/v_F$ ratio, signifying that the conditions for specular reflection of the electrons from the surface are not the same in both cases. The specular electron reflection is necessary for the formation of surface states and this implies that they are not obtained under same conditions. While the electron velocity along the x direction is close to the Fermi velocity v_F , $v_x \sim v_F$ due to the isotropic nature of the energy dispersion laws in the plane of the layers, the electron velocity along the periodic z direction is much less than the Fermi velocity due to the strong anisotropy along this direction. It is evident that Eqs. (3) and (4) yield different maximum electron velocity along z , $v_z^{\max} = \eta v_F$ and $v_z^{\max} = 2\eta v_F$, respectively. Obviously, the latter is twice larger than the former meaning that one obtains larger $v_z^{\max}/v_F$ ratio in case of the energy dispersion law (4). The lower $v_z^{\max}/v_F$ ratio provides better specular reflection of the electrons from the surface and hence, more favorable conditions for formation of the surface states in Q2D organic conductors. Thus, we find the surface-state energies calculated from Eq. (14) are more reliable compared to those obtained from Eq. (18), although they differ only in order of 10^{-4} eV.

Using the values for the surface-state energies given in the second and third column in Table 1, we present the magnetic surface levels in Figure 2 for $B = 3$ T with the possible transitions between them indicated by arrows. It is evident by comparison of Figures 2a and 2b that there are apparent differences in the ordering of the magnetic surface levels in the Q2D organic conductors

obtained with different models for the energy dispersion law. We find that the surface quantum levels of the skipping electrons are not equidistant as expected.

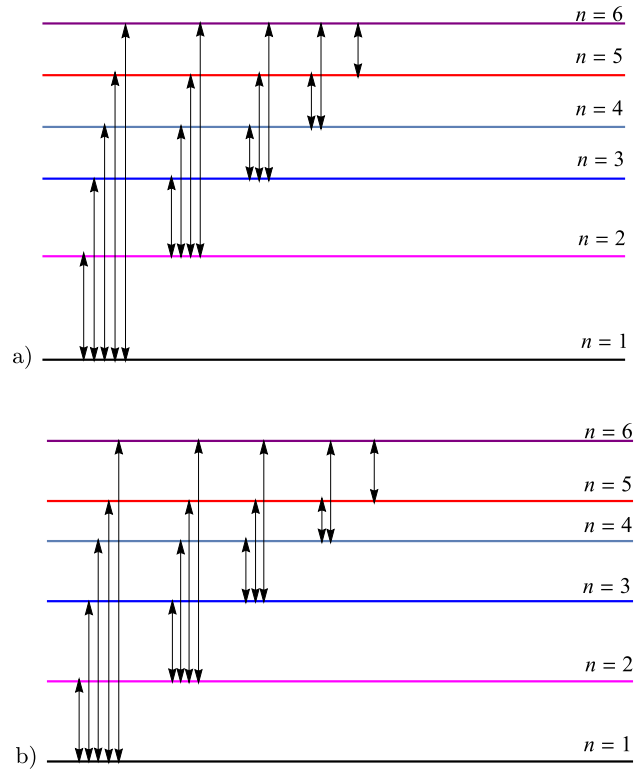


Figure 2: Schematic representation of the magnetic surface energy levels ($n = 1$ to $n = 6$) with the resonant transitions between them indicated by arrows obtained by using the a) Eq. (14) and b) Eq. (18). The different ordering of the magnetic surface levels is evident.

Table 2: Magnetic field resonant values for the transitions between the surface states obtained from the eigenvalue problem (ep) and the quantization rule (qr) for both energy dispersion laws.

n	m	$B_{mn}^{*ep}(\text{T})$	$B_{mn}^{*qr}(\text{T})$	$B_{mn}^{**ep}(\text{T})$	$B_{mn}^{**qr}(\text{T})$
1	2	0.3	0.3	1.4	1.6
1	3	0.15	0.15	0.7	0.8
1	4	0.1	0.1	0.5	0.5
1	5	0.07	0.07	0.4	0.4
1	6	0.06	0.06	0.3	0.3
2	3	0.6	0.6	1.4	1.6
2	4	0.3	0.3	0.7	0.8
2	5	0.2	0.2	0.5	0.6
2	6	0.16	0.15	0.4	0.4
3	4	0.9	0.85	1.4	1.6
3	5	0.4	0.4	0.7	0.8
3	6	0.3	0.3	0.5	0.6
4	5	1.2	1.1	1.4	1.6
4	6	0.6	0.6	0.7	0.8
5	6	1.4	1.3	1.4	1.6

Consequently, the distance between the neighboring surface levels $\Delta\varepsilon = \varepsilon_n - \varepsilon_m$ is not the same. The general trend is that it is larger between the states with small n and smaller for the states with higher n . The different values for $\Delta\varepsilon$ are affecting the resonant transitions between the surface levels and the magnetic field at which those transitions occur. The resonant transitions between the surface levels are observed at certain magnetic fields known as resonant magnetic fields that can be determined from $\Delta\varepsilon = \hbar\omega_{nm}$ at fixed transition frequency $\omega_{nm} = \omega$. At these fields, the peaks in the surface resistance magnetic oscillations are observed. The resonant magnetic fields are also determined numerically since we can not obtain an explicit expression for $\Delta\varepsilon$. Although for the magnetic surface levels presented in Figures 2a and 2b, $\Delta\varepsilon$ is similar in value, we find a significant discrepancy in the magnetic

field resonant values. They are shown in Table 2 and represent guiding values that can help in accurate estimation of the corresponding resonant values from the experimental measurements of surface oscillations as well as to calibrate the obtained experimental curves.

The resonant magnetic fields are obtained for a fixed frequency $\omega = 60$ GHz that corresponds to the transition between the second and first magnetic surface level, $2 \rightarrow 1$, for which the difference between the corresponding levels is the same and of order of $\Delta\varepsilon = 4 \times 10^{-4}$ eV in each case. It follows that, in Q2D organic conductors, the surface quantum oscillations should be observed in the millimeter frequency range. We note that the fields B_{mn}^* are obtained by using the corresponding z_c value for each state and the fields B_{mn}^{**} are obtained for $z_c = 1.5$.

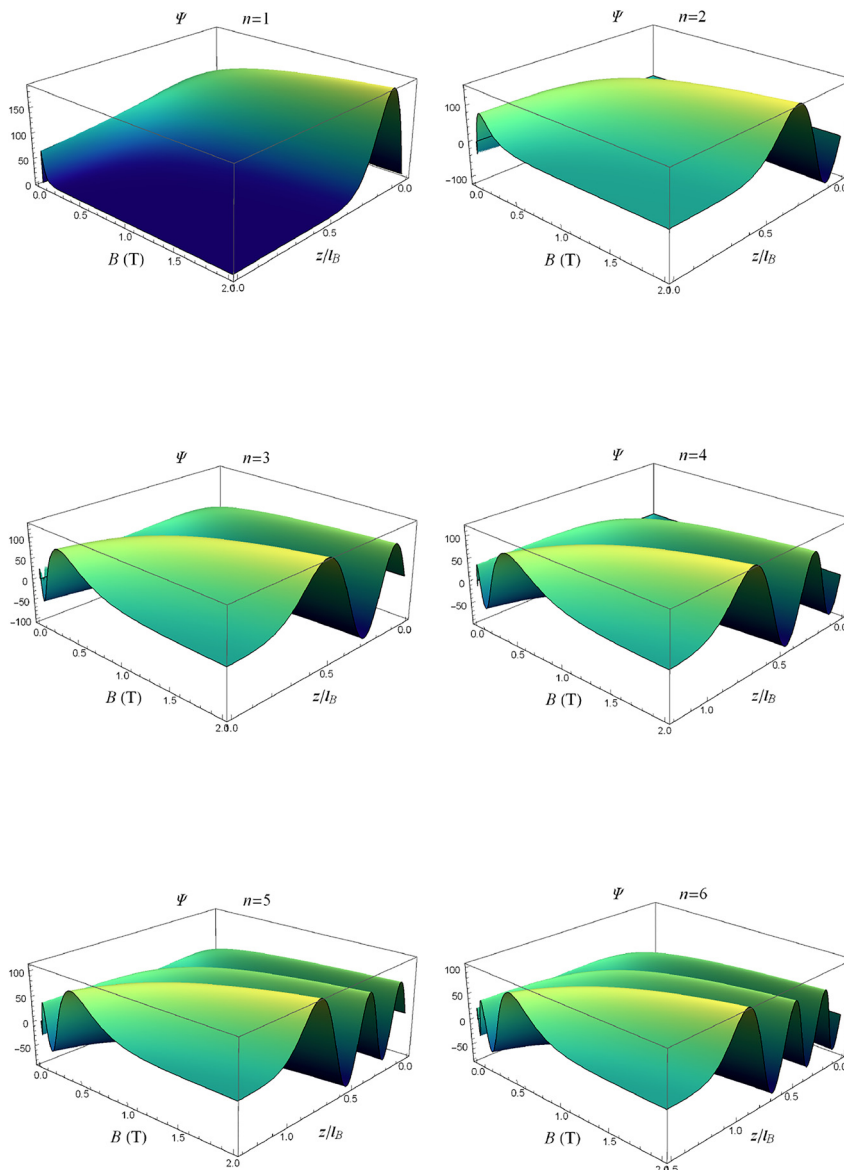


Figure 3: The dependence of the wave functions of the surface states of skipping electrons $\Psi_n(x, y, z) = \frac{1}{(2\pi\hbar)} \exp \frac{i}{\hbar} (p_x x + p_y y) \Phi_n(z)$ with a quantum number n on the distance from the surface z/l_B and the magnetic field B obtained by using the corresponding value of z_c for each state.

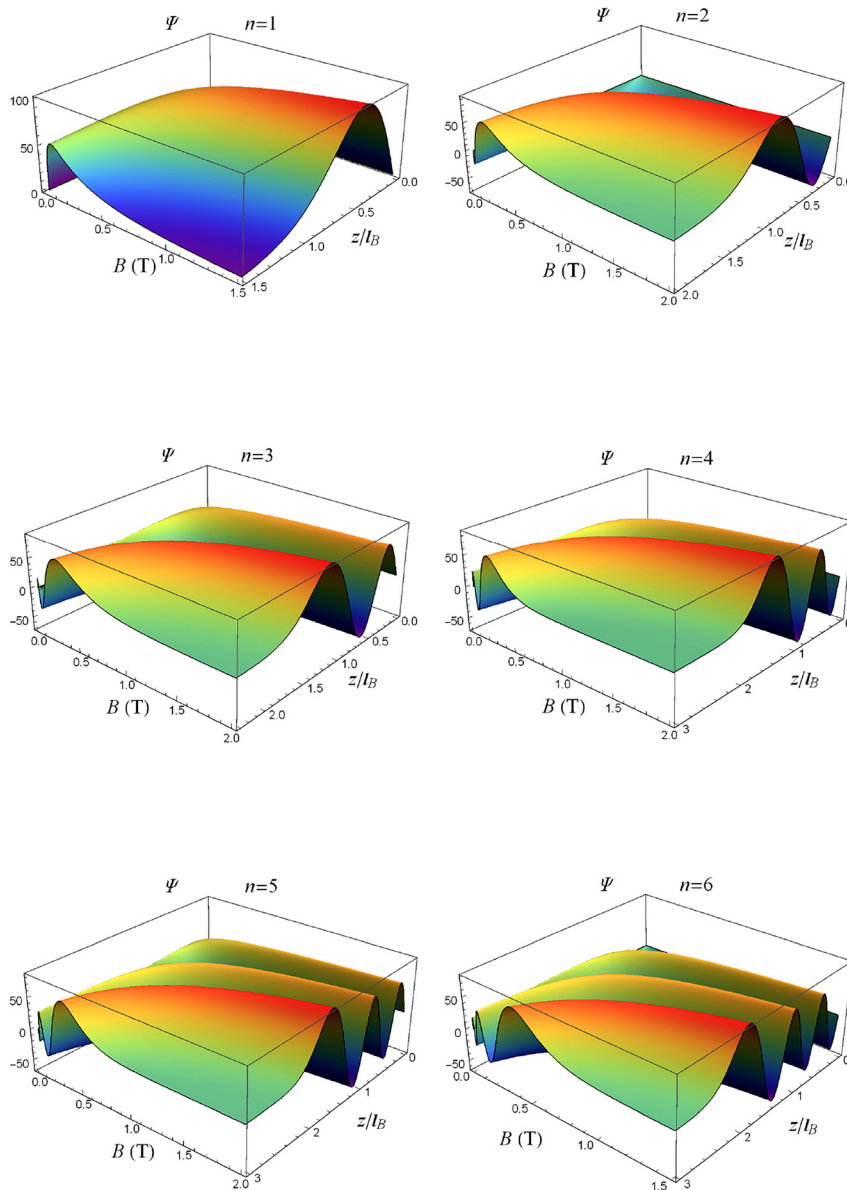


Figure 4: The dependence of the wave functions of the surface states of skipping electrons $\Psi_n(x, y, z) = \frac{1}{(2\pi\hbar)} \exp \frac{i}{\hbar} (p_x x + p_y y) \chi_n(z)$ with a quantum number n on the distance from the surface z/l_B and the magnetic field B for $z_c = 1.5$.

It is evident that the resonant magnetic fields obtained in the frame of a given energy dispersion law are similarly calculated by both the eigenvalue problem and quantization rule (the first and second column are obtained by using Eqs. (14) and (22) (B_{mn}^*) while the third and fourth column are obtained from Eqs. (18) and (23)) (B_{mn}^{**}). In comparison, we find that the resonant magnetic fields B_{mn}^{**} are far larger than B_{mn}^* for the transitions that take place to lower surface states whereas for the transitions between the higher states we observe similar resonant magnetic fields values. As the resonant values in Table 2 were calculated for same fixed transition frequency, we ascribe this difference to the specific characteristics of the electron skipping trajectories obtained from Eqs. (14) and (22), i.e., it is correlated to the change of z_c with the

quantum surface state. As discussed above, these equations yield larger z_c for lower surface states and smaller z_c for higher surface states. The larger z_c yields smaller resonant magnetic field B_{mn}^* . On the other hand, the magnetic field resonant values B_{mn}^{**} determined from Eqs. (18) and (23) are larger as they are obtained by using only one value for z_c that is much smaller than those used for calculating B_{mn}^* . The smaller z_c for the higher surface states leads to increasing values for B_{mn}^{**} , and therefore, for higher states, the resonant fields B_{mn}^* and B_{mn}^{**} are similar. As suggested above, the surface-state energies obtained from Eq. (14) are more relevant results than those obtained from Eq. (18). Consequently, the values obtained for B_{mn}^* are more valid magnetic field resonant values than those obtained for B_{mn}^{**} .

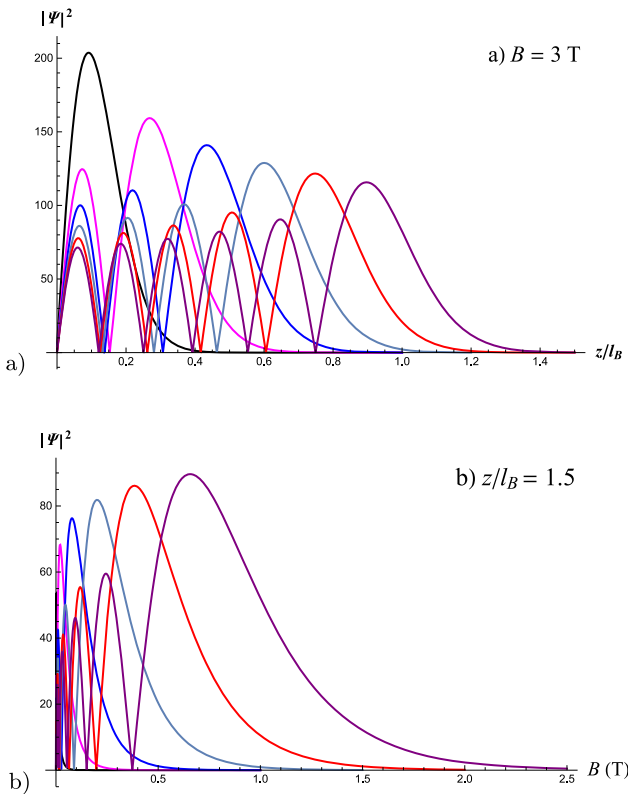


Figure 5: The probability density for electrons in the n -th state ($n = 1$ to $n = 6$) as a function of the a) distance from the surface z/l_B at $B = 3$ T and b) the magnetic field B at $z/l_B = 1.5$. The same color is used to represent the probability density for a given state as used for the energy levels in Figure 2a.

3.2 The surface-state wave functions

The corresponding wave functions for the surface states, $\Psi_n(z, B)$, are obtained by solving the Schrödinger equation for the problem. They are defined by the Airy functions (Eqs. (11) and (16)) and depend on the distance from the surface, the magnetic field magnitude as well as on the characteristic parameters of the Q2D organic conductor. The corresponding normalized surface-state wave functions, $\Psi_n(x, y, z) = \frac{1}{(2\pi\hbar)} \exp\left(\frac{i}{\hbar}(p_x x + p_y y)\right) \Phi_n(z)$ and $\Psi_n(x, y, z) = \frac{1}{(2\pi\hbar)} \exp\left(\frac{i}{\hbar}(p_x x + p_y y)\right) \chi_n(z)$, as a function of both the distance from the surface z/l_B and the magnetic field B are presented in Figure 3 and Figure 4, respectively. The wave functions in Figure 3 are obtained by using the corresponding value of z_c for each state while those in Figure 4 are obtained for $z_c = 1.5$. This allows to follow the evolution of the wave function of each surface state with a quantum number n . Obviously, they are satisfying the corresponding boundary conditions (Eq. (7)) and are oscillatory functions of both z/l_B and B . Figures 3 and 4 allow to determine the distance from the surface and

magnetic field where the wave functions are attenuated, which in turn enables to obtain additional information on the surface states properties. The general trend is that the wave functions of higher surface states are attenuated at larger distance from the surface and at higher magnetic field. From Figure 3, we find that the wave function for $n = 1$ is attenuated at $z \sim 0.5 l_B \sim 0.5 \times 10^{-8}$ m whereas for $n = 6$ it attenuates at $z \sim 1.5 l_B \sim 1.5 \times 10^{-8}$ m. The magnetic field interval where the surface-state wave functions are attenuated is $B \sim 0.1$ – 2 T. On the other hand, the wave functions shown in Figure 4 are attenuated in the intervals $z \sim 1.5$ – $3 l_B \sim 1.5$ – 3×10^{-8} m and $B \sim 1$ – 2 T for the distance from the surface and the magnetic field, respectively.

Thus, in Q2D organic conductors in general, the wave functions oscillate at relatively small distance from the conductor's surface of order of 10^{-8} m and at low magnetic fields up to 2 T. The period of oscillations depends on the organic conductor characteristics, on the magnetic field magnitude and the number of the state. The distance z at which the surface wave functions are attenuated into the conductor is less than the allowed values for the maximal depth of penetration z_n of the electrons and is also much smaller than the corresponding depth of the skin layer δ . In Q2D organic conductors, $\delta \sim 1 \mu\text{m}$ [18], indicating that the oscillations of the wave function are confined only in the proximity of the surface. In addition, the lower values for the magnetic field at which the wave functions decay signify that in Q2D organic conductors a smaller Lorentz force $F_L = ev_x B \sim ev_F B$ is necessary for the electrons to be pulled toward the surface. Hence, their drift velocity along the skipping trajectory (orbit 1 in Figure 1b), $\tilde{v}_x$, is almost constant (the electrons are moving essentially parallel to the surface) and of order of the Fermi velocity v_F . Thus, even a low magnetic field can cause a change in the electron distribution in the conductor's skin layer while leading to an increased specular electron reflection from the surface. All these observations indicate that in Q2D organic conductors there are more favorable conditions for formation of the surface states than in the ordinary metals.

In addition, as the electron motion is restricted in the proximity to the surface, they are less exposed to the influence of the bulk electrons that are situated on the so called skimming cyclotron orbits (orbit 2 in Figure 1b) and therefore are less scattered from them. In that regards, the electronic transitions take place only between the closed electron orbits in the immediate vicinity of the Fermi surface $\varepsilon(\mathbf{p}) = \varepsilon_F$. Consequently, the peaks in the magnetic field dependence of the surface resistance (that correspond to the resonant transitions between the magnetic surface levels) are expected to be observed in

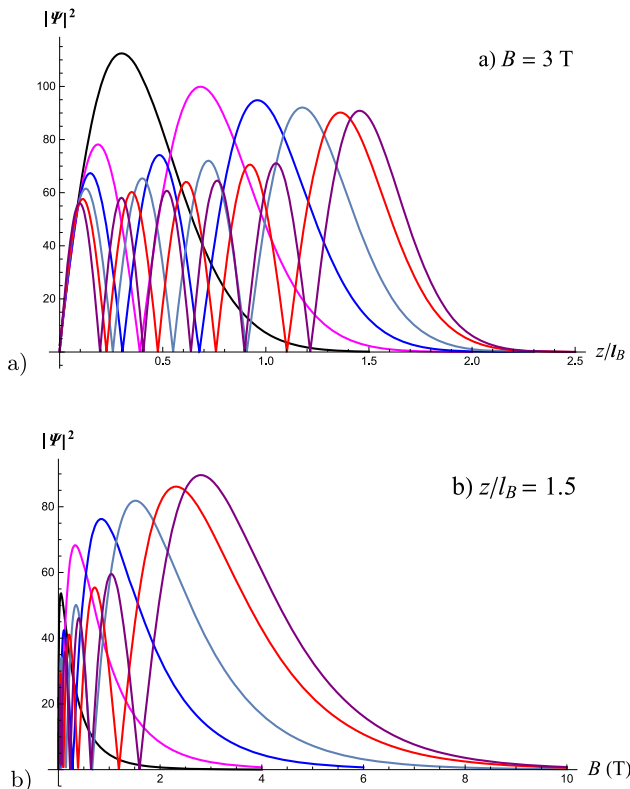


Figure 6: The probability density for electrons in the n -th state ($n = 1$ to $n = 6$) as a function of the a) distance from the surface z/l_B at $B = 3$ T and b) the magnetic field B at $z/l_B = 1.5$. The same color is used to represent the probability density for a given state as used for the energy levels in Figure 2b.

weak magnetic fields in the millimeter range of frequencies at distance of order of $z \sim 0.5\text{--}2 \times 10^{-8}$ m from the surface depending on the number of the quantum surface state n .

A similar trend is also apparent in the corresponding distribution of the probability density for electrons situated in the n -th state with the distance z and the magnetic field B , $|\Psi_n(z, B)|^2$, shown in Figures 5 and 6, respectively. However, some features that distinguish the both distributions have to be addressed. We find that at a fixed magnetic field $B = 3$ T the probability density $|\Psi_n(z, B)|^2$ is higher in Figure 5a, but it attenuates at smaller distance from the surface compared to the one in Figure 6a. On the contrary, the magnetic field dependence of the probability densities obtained at a fixed distance from the surface $z = 1.5$ m reveal that although they are of the same magnitude, the probability densities shown in Figure 6b are attenuated at far larger magnetic fields than those shown in Figure 5b. The values for z/l_B and B at which there are peaks in the probability density correspond to the distance where the skipping electrons are mostly located

from the surface as well as to the field at which resonant electron transitions between the electron orbits near the Fermi surface occur. The smaller values for the distance from the surface and the magnetic field in Figure 5 indicate that in this case the electrons are moving along skipping trajectories that are much closer to the surface and therefore are less exposed to the influence of the bulk electrons situated near the surface especially those on the skimming cyclotron orbits. In that way the conditions for specular reflection of the electrons from the surface are more easily achieved. This, however, confirms the above discussed that the results obtained for the surface-state energies and wave functions would be more reliable if one makes use of the energy dispersion law derived in the frame of the tight-binding theory.

4 Conclusions

The energies and wave functions of the surface states in Q2D organic conductors are obtained by using two different forms for the Q2D electron energy spectrum. The first one derived within the tight-binding theory is usually used in studying the properties of the Q2D organic conductors, and the second one is the form previously used to investigate the surface effects in the Q2D organic conductors. The two different forms are used in order to investigate in detail the surface states in organic conductors and extract more information on their elementary properties. We also make use of both the Schrödinger equation and the quantization rule to calculate and compare the surface-state energies. We find that the energies differ in order of 10^{-4} and more importantly are obtained under different conditions when a different form of the energy dispersion law is used. When the energy dispersion law obtained in the frame of the tight-binding theory is applied, the surface-state energies (Eqs. (14)) and Eqs. (22)) are determined for different values for the coordinate of the electron orbit z_c . On the other hand, with the second form for the energy dispersion law the surface-state energies (Eqs. (18)) and Eqs. (23)) and wave functions are obtained by using only one value for z_c . This, in turn, allows to determine the geometric characteristics of the electron skipping trajectories in Q2D organic conductors. We ascribe the differences in the values for the surface energies to the different maximum electron velocity along the direction of periodic motion of the electrons. The lower ratio of the maximum velocity along the z direction and the Fermi velocity is obtained in the case of the first energy dispersion law, indicating that in this case

the conditions for formation of the surface states in Q2D organic conductors are more favorable and therefore the values for the surface-state energies are more reliable than those obtained with the other form for the energy dispersion law. In this case, the resonant magnetic field values show that the electron transitions in Q2D organic conductors occur at weak magnetic fields. In addition, the analyzes of the corresponding surface wave functions further confirm that the more reliable results should be obtained if one makes use of the energy dispersion law derived in the frame of the tight-binding theory. We expect here presented results and observations to be of great significance for further studies of the surface states properties in Q2D organic conductors. Although by far there is no experimental evidence of the surface quantum oscillations in Q2D organic conductors, yet we believe that our results would provide necessary basics for future experimental studies. This would be very useful as the organic conductors are interesting for applications in the organic electronics.

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