Variational approach to the problem of energy spectrum of surface electrons over liquid-helium film

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The energies of first two subbands are calculated, within a variational approach, for electrons localized over the surface of a liquid-helium film covering a solid substrate. The results are obtained for arbitrary value of the dielectric constant of the solid substrate, covering both the limit of a substrate with a dielectric constant close to unity (such as a rare gas solid) and a metal. The results for the subband energies for a metallic substrate are compared with those obtained previously by a different method by Gabovich, Ilchenko, and Pashitskii. The agreement is rather good supporting the applicability of the variational method for calculating the energy spectrum of surface electrons in a wide range of substrate parameters.

1. Introduction

The properties of surface electrons (SE) localized over liquid-helium film are essentially more complicated than those over bulk helium. As is known the potential energy of SE in the point z over bulk liquid occupying the semispace with $z \le 0$ can be written as [1]

$$U_b(z) = -\frac{\Lambda_0}{z + z_0} + eE_\perp z \qquad (1)$$

where $\Lambda_0 = e^2(\varepsilon_{\mathrm{He}} - 1)/[4(\varepsilon_{\mathrm{He}} + 1)]$, $E_\perp$ is the holding electric field oriented normally to helium surface, e is the electron charge, and $\varepsilon_{\mathrm{He}} \simeq 1.0572$ is the dielectric constant of liquid helium. The parameter $z_0 \simeq 1.01$ Å is introduced in Eq. (1) to account the finiteness of the potential barrier $V_0 \simeq 1$ eV on the liquid helium surface, which is an obstacle to electron penetration inside the liquid phase, and to avoid divergence of the first term of Eq. (1) at $z \to 0$. The value of z_0 is estimated by comparison of the experimental data on the frequencies of spectroscopic transitions between the SE surface states and theoretical calculation based on Eq. (1) in the limit of small holding field. One should note that the approach $V_0 \to \infty$ ($z_0 = 0$) gives a SE energy spectrum very close to that really observed [2], and for this reason it is widely used in calculations. The applicability of the approach $V_0 \to \infty$ is based on the strong inequality $|\Delta_l| \ll V_0$ where Δ_l is the energy of SE states numbered by $l = 1, 2, \ldots$

For a liquid-helium film located at $-d < z < 0$ over a solid substrate with dielectric constant ε_s the SE potential energy can be written as [3]

$$U_f(z) = U_b(z) + U_s(z) \qquad (2)$$

where

$$U_s(z) = -\Lambda_1 \sum_{n=1}^{\infty} \frac{(-a)^{n-1}}{z + nd},$$

$\Lambda_1 = e^2\varepsilon_{\mathrm{He}}(\varepsilon_s - \varepsilon_{\mathrm{He}})/[(\varepsilon_{\mathrm{He}} + 1)^2(\varepsilon_s + \varepsilon_{\mathrm{He}})]$, and $a = (\varepsilon_{\mathrm{He}} - 1)(\varepsilon_s - \varepsilon_{\mathrm{He}})/(\varepsilon_{\mathrm{He}} + 1)(\varepsilon_s + \varepsilon_{\mathrm{He}})]$. Due to small difference between $\varepsilon_{\mathrm{He}}$ and unity one can disregard, in the sum of $U_s(z)$, the terms with $n \ge 2$ and write, to a very good accuracy, $U_s(z) = -\Lambda_1/(z + d)$.

The additional contribution $U_s(z)$ to the equation for SE potential energy, in comparison with that over bulk liquid, is connected with polarization interaction between SE and image forces in the solid substrate at $z < -d$. This energy influences strongly the properties of SEs over film changing not only the structure of the SE energy states, which were first considered by Shikin and Monarkha [3], but also the Hamiltonian of electron−ripplon scattering, which determines the

kinetic properties of the SEs under their motion in the plane of the vapor−liquid phase boundary [3]. Furthermore, one more scattering mechanism by substrate surface defects can appear contributing to the SE transport properties [4].

The role of $U_s(z)$ is especially well pronounced for substrates with $\varepsilon_s \gg 1$, such as, for example, some types of glass, where $\varepsilon_s \gtrsim 7$ to say nothing of metals, where $\varepsilon_s \to \infty$. For a metallic substrate one has $\Lambda_1 = e^2 \varepsilon_{He}/(\varepsilon_{He} + 1)^2 \simeq e^2/4$ and the contribution of $U_s(z)$ dominates in $U_f(z)$ of Eq. (2). The Schrödinger equation for the SE wave functions and energy spectrum has been solved, in that approximation, by Gabovich, Ilchenko, and Pashitskii [5], and the final expression for the spectrum at $E_\perp = 0$, in the limit of $V_0 \to \infty$, can be written as

$$\Delta_l \simeq -\frac{e^2}{32a_0}\left[l - \frac{3}{4} + \frac{1}{\pi}\sqrt{\frac{2d}{a_0}}\right]^{-2} \qquad (3)$$

which differs essentially from the hydrogen-like spectrum $\Delta_l = -\Delta_0/l^2$ of SEs over bulk helium [3]. Here $a_0 = \hbar^2/me^2$ is the Bohr radius, $\Delta_0 = \hbar^2\gamma_0^2/2m$, $\gamma_0 = m\Lambda_0/\hbar^2$, and m is the free electron mass. Equation (3) is valid for $1 \ll (e^2/4\hbar)\sqrt{m/2|\Delta_l|} \ll d/a_0$, which is well satisfied for $d \geq 5 \cdot 10^{-7}$ cm.

For the substrates with relatively small ($\varepsilon_s \gtrsim 1$) or intermediate values of ε_s the contribution of $U_b(z)$ to $U_f(z)$ can be compatible with that of $U_s(z)$. In such a condition the only possible way to estimate analytically the SE spectrum over helium film is to apply the variational approach. The aim of the present work is to obtain the variational solution for the energies of two lowest SE subbands $l = 1$ and $l = 2$. For the sake of generality, the consideration is carried out for the substrate with arbitrary value of ε_s and the effect of holding field is also included. The result for a metallic substrate

is obtained under the limiting transition $\varepsilon_s \to \infty$ and is compared with that given by Eq. (3). Such a comparison can make clearer the possibilities of applying the different approaches in the problem of description of the SE spectrum. In view of the rising interest in investigating both quasi-two-dimensional and quasi-one-dimensional SE properties over helium film in recent years, the present study seems timely [7−13].

2. Main relations

To calculate the energies Δ_1 and Δ_2 one applies the orthonormalized trial wave functions [14,15]

$$f_1(z) = 2\gamma_1^{3/2}z\exp(-\gamma_1 z), \qquad (4)$$

$$f_2 = \frac{2\sqrt{3}\gamma_2^{5/2}z}{(\gamma_1^2 - \gamma_1\gamma_2 + \gamma_2^2)^{1/2}}\left[1 - \left(\frac{\gamma_1 + \gamma_2}{3}\right)z\right]\exp(-\gamma_2 z), \qquad (5)$$

where γ_1 and γ_2 are variational parameters. The energy of lth subband is calculated as

$$\Delta_l = \langle l| -\frac{\hbar^2}{2m}\frac{d}{dz} + U_f(z)|l\rangle.$$

The method of calculation is a generalization of that developed in Ref. 15 for the microstratified liquid solution ${}^3\mathrm{He}-{}^4\mathrm{He}$, and the final expressions for the energies are

$$\Delta_1 = \frac{\hbar^2\gamma_1^2}{2m} - \Lambda_0\gamma_1 - \Lambda_1\gamma_1[1 - 2\gamma_1 d -$$

$$- 4(\gamma_1 d)^2\exp(2\gamma_1 d)Ei(-2\gamma_1 d)] + \frac{3eE_\perp}{2\gamma_1} \qquad (6)$$

and

$$\Delta_2 = \frac{\hbar^2\gamma_1^2}{6m}\left(\frac{\gamma_1^2 - \gamma_1\gamma_2 + 7\gamma_2^2}{\gamma_1^2 - \gamma_1\gamma_2 + \gamma_2^2}\right) - \frac{\Lambda_0\gamma_2}{2}\left(\frac{\gamma_1^2 - 2\gamma_1\gamma_2 + 3\gamma_2^2}{\gamma_1^2 - \gamma_1\gamma_2 + \gamma_2^2}\right) - \frac{\Lambda_1\gamma_2}{2(\gamma_1^2 - \gamma_1\gamma_2 + \gamma_2^2)} \times$$

$$\times \{\gamma_1^2 - 2\gamma_1\gamma_2 + 3\gamma_2^2 - \frac{2}{3}(\gamma_2 d)(\gamma_1 + \gamma_2)^2 + \frac{2}{3}\gamma_2^2[3 + (\gamma_1 + \gamma_2)d]^2[1 - 2\gamma_2 d - 4(\gamma_2 d)^2\exp(2\gamma_2 d)Ei(-2\gamma_2 d)]\} +$$

$$+ \frac{eE_\perp}{2\gamma_2}\left(\frac{5\gamma_1^2 - 2\gamma_1\gamma_2 + 2\gamma_2^2}{\gamma_1^2 - \gamma_1\gamma_2 + \gamma_2^2}\right) \qquad (7)$$

where $Ei(x)$ is the exponential integral. In the limiting case $d \to \infty$ the terms depending on d in Eqs. (6) and (7) disappear, and we reproduce the values of γ_l obtained in Refs. 14,15 for the bulk liquid. It is interesting to note that for $d \to 0$ the terms depending on

d also disappear in Eqs. (6) and (7), which are formally the same as those for $d \to \infty$ but now depend on $\Lambda_0^* = \Lambda_0 + \Lambda_1$. One can easily see that we obtain in this limit, replacing ε_{He} by unity in Λ_0, the energies of an electron localized over a semi-infinite medium

at $z \leq 0$ with a dielectric constant ε_s and without a helium blanket.

The values of γ_1 and γ_2 are calculated numerically by cumbersome transcedental equations $\partial \Delta_1 / \partial \gamma_1 = 0$ and $\partial \Delta_2 / \partial \gamma_2 = 0$. By determining the roots of these equations and replacing the values of γ_1 and γ_2 in Eqs. (6) and (7) by them one calculates the energies Δ_1 and Δ_2.

3. Results and discussion

Here we restrict ourselves to the limit of zero holding field $E_\perp = 0$, where the influence of film effects on the SE energy spectrum is especially pronounced. The corrections due to finite value of $E_\perp$ can be included in a straightforward way [5,6].

We start our consideration by calculating the mean electron distance from the helium surface. Based on the SE wave functions of Eqs. (4) and (5) one can easily obtain

$$\langle z \rangle_1 = \frac{3}{2} \gamma_1^{-1} \quad \text{and} \quad \langle z \rangle_2 = \frac{5\gamma_1^2 - 2\gamma_1\gamma_2 + 2\gamma_2^2}{2\gamma_2(\gamma_1^2 - \gamma_1\gamma_2 + \gamma_2^2)}. \quad (8)$$

The dependences of $\langle z \rangle_1$ and $\langle z \rangle_2$ on d are plotted in Fig. 1 for metallic substrate. As is seen from Fig. 1 the values of $\langle z \rangle_l$ increase with d. For a small film thickness of $5 \cdot 10^{-7}$ cm one has $\langle z \rangle_1 \simeq 29$ Å and $\langle z \rangle_2 \simeq 72.5$ Å. At smaller values of d the mean electron distance, calculated by Eq. (8), tends to the microscopic range, where the applicability of the above-mentioned approach to the description of the SE states over helium film vanishes. Note that, for the same d, the values of $\langle z \rangle_1$ and $\langle z \rangle_2$ are substantially larger for the substrate with $\varepsilon_s \gtrsim 1$. For example, for solid neon ($\varepsilon_s \gtrsim 1.20$) we estimate $\langle z \rangle_1 \simeq 89$ Å and $\langle z \rangle_2 \simeq 288$ Å (for comparison, $\langle z \rangle_1 \simeq 144$ 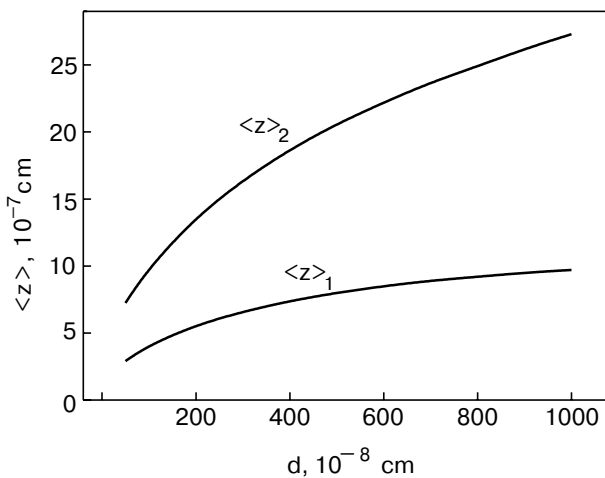Å and $\langle z \rangle_2 \simeq 456$ Å for SE over bulk helium [3]). One concludes that the characteristic values of the mean electron distance from the liquid surface satisfy the inequality $\langle z \rangle_l \gg z_0$, being substantially larger than atomic scale $\sim 10^{-8}$ cm. For this reason the microscopic nature of the helium surface, leading, in particular, to a small incertainty of the position of the potential barrier V_0, cannot influence appreciably the SE energy properties; this supports the applicability of the approach $V_0 \to \infty$ with the boundary condition for the SE wave function $f_l(z) = 0$ at $z = 0$ [3].

The dependences of the SE energies Δ_1 and Δ_2 on d for a solid neon substrate, calculated numerically by Eqs. (6) and (7), are presented in Fig. 2. One observes the increase of the energies with d (the decrease of absolute values of Δ_1 and Δ_2), which is a natural consequence of the decreasing contribution of $-\Lambda_1 / (z + d)$ with increasing d. As a result, the absolute values of surface level energies decrease, and the distance between them also decreases, tending, for zero holding field, to the hydrogen-like values of SE energies over bulk helium, $\Delta_l = -\Delta_0 / l^2$, whereas the roots of the minimization equations $\partial \Delta_1 / \partial \gamma_1$ and $\partial \Delta_2 / \partial \gamma_2$ tend to the values $\gamma_1 = \gamma_0$ and $\gamma_2 = \gamma_0 / 2$, coinciding with the exact result of solving the Schrödinger equation in the limit $d \to \infty$ and $E_\perp = 0$ [3]. For solid neon this asymptotic limit is achieved for $d \gtrsim 10^{-5}$ cm. At the same time, for a metallic substrate, where the value of Λ_1 is much larger than that over solid neon, Δ_1 and Δ_2 start to practically coincide with those of the hydrogen-like spectrum at significantly larger values $d \gtrsim 10^{-4}$ cm.

In Fig. 3 the dependences of Δ_1 and Δ_2 on d are depicted for a metallic substrate (solid lines). For comparison the values of the level energies calculated by Eq. (3) are also plotted by the dashed lines. It is seen that the agreement between the energies calculated in
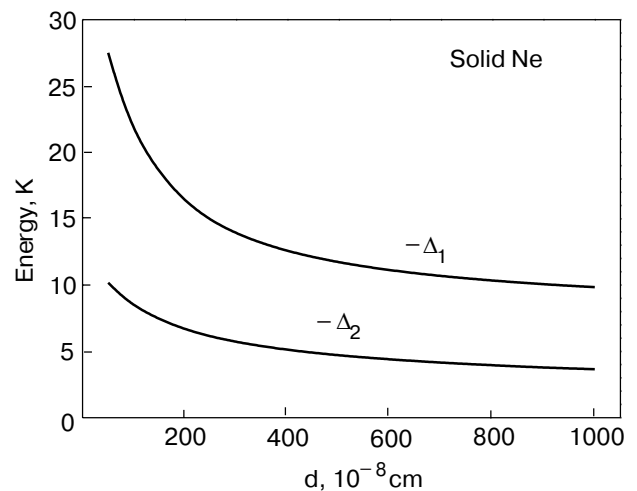

Fig. 1. The mean electron distance from the helium surface for the subbands 1 and 2 as a function of film thickness d for metallic substrate.

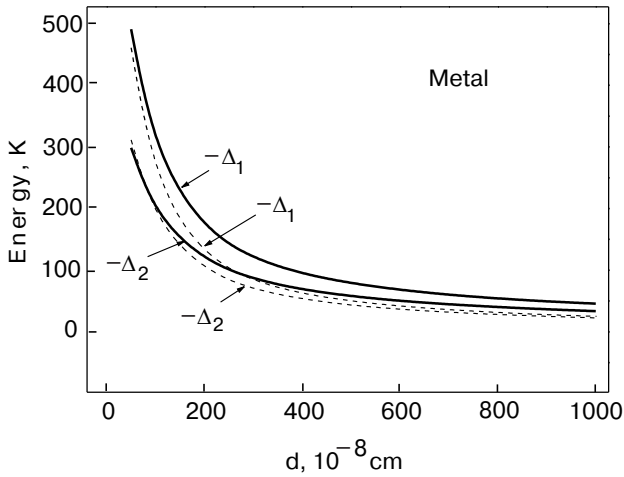*Fig. 2.* The energies of the subbands 1 and 2 vs. film thickness for solid neon substrate.

Fig. 3. The same as in Fig. 2 but for a metallic substrate. Solid lines are the results of the present work, the dashed lines are those of Ref. 5.

different ways is reasonable, especially for relatively small values of d. At the same time, the agreement becomes less satisfactory under increase of d. Note that the contribution $-\Lambda_0/(z+z_0)$ of the polarization of liquid helium to the SE potential energy was omitted in Ref. 5 to derive Eq. (3). Obviously, under increasing d and a decreasing contribution $-\Lambda_1/(z+d)$ of the polarization of the solid substrate to Eq. (2), the role of $-\Lambda_0/z$ becomes more essential which can explain some divergence of the results calculated by Eqs. (3), (6), and (7) at $d > 10^{-6}$ cm. To make this point more clear we have plotted, in Fig. 4, the values of Δ_1 and Δ_2 calculated by Eqs. (6) and (7), where we put $\Lambda_0 = 0$. One can see the substantially better agreement with the results of Eq. (3) than that in Fig. 3, especially for the level $l = 2$ with the larger value of $\langle z \rangle_2$ and, consequently, with the larger distance from the helium free surface, leading to a decreasing a contribution of the SE potential energy, due to media polariza-
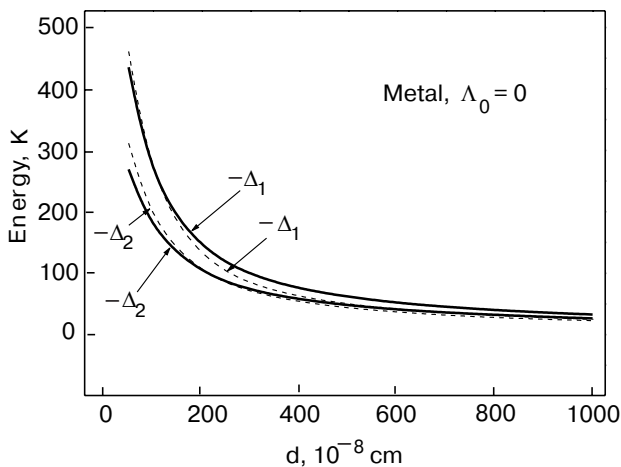
tion, to the structure of subband $l = 2$ in comparison with that to the ground subband. As a result, the choice of approach to describe the SE potential energy becomes less essential for $l = 2$ than for $l = 1$.

4. Conclusions

In the present work the energies of the ground and first excited SE subbands over helium film are estimated within a variational approach. The expressions for the level energies are estimated for arbitrary value of substrate dielectric constant ε_s. The values of the mean electron distance from the helium surface are estimated in the macroscopic range, supporting the applicability of the approach $V_0 \to \infty$ where the potential barrier is supposed to be exactly at the free helium surface. The SE energies are calculated, as functions of film thickness, for substrates of solid neon and a metal. The results for the metallic substrate are compared with those obtained analytically in Ref. 5. The agreement between the results of present work and those of Ref. 5 seems rather good, being especially satisfactory for thin helium films with $d < 10^{-6}$ cm, in spite of the different methods of calculations in the present work and in Ref. 5. One should note the application of variational approach to obtain the energies of subbands with $l > 2$ leads to overcumbersome calculations with practically intractable results. In such a situation the results of Ref. 5 (Eq. (3)) are especially important, giving the only way to describe analytically the energy spectrum for subbands with $l \geq 3$ of SEs localized over a helium film covering a metal.

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Fig. 4. The same as in Fig. 3 but for $\Lambda_0 = 0$.

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