Effect of thermal fluctuations of the surface of a liquid on the energy spectrum of electrons localized above liquid helium

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It is shown that the thermal fluctuations of the surface of liquid helium leads to a shift in the hydrogen-like levels in the transverse motion of electrons located above the helium. The corresponding rise of the resonance-transition frequencies at $T \sim 1$ K is ≈ 1.5 GHz for ^{4}He and ≈ 300 MHz for ^{3}He. The dependence of the effect on the temperature uncovers the possibility of experimental observation.

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1. The possibility of localization of electrons over the surface of liquid helium was predicted more than ten years ago.[1,2] Subsequent intense study of localized electrons (a detailed bibliography is contained in Ref. 3) revealed the basic features of its dynamics and kinetics. Nevertheless, in the problem of the localization of electrons over a dielectric with relative permittivity ε close to unity, there still remains a number of unsolved questions. One of them, which has a fundamental nature, is the question of the energy spectrum of the localized electrons.

The motion of an electron along the normal to the surface and near it takes place in the potential of electrostatic image forces, which has an attracting character, while the penetration of the electron inside the dielectric is prevented by the high potential barrier at the surface (1.2 eV for ^{4}He and 0.9 eV for ^{3}He). In the one-dimensional potential well that is formed, a discrete set of stationary states is generated. Since the mean distance $\langle z\rangle_n$ of the electron from the surface (the z axis is directed normal to the surface, the liquid fills the half-space $z<0$, and n is the number of the level) significantly exceeds the interatomic distance under these conditions, which is a consequence of the closeness of ε to unity ($\varepsilon_4 = 1.0572$ for ^{4}He and $\varepsilon_3 = 1.04276$ for ^{3}He), the microscopic structure of the liquid surface has little effect on the spectrum. In particular, in the description of the motion of the electron we can use the macroscopic expression for the potential energy of an electron in the field of image forces.[4]

$$U_0(z) = -e^2(\varepsilon-1)/4(\varepsilon+1)z \equiv -Qe^2/z, \qquad (1)$$

and the motion of the electron in the plane of the boundary can be considered to be free. Such a simple model, with infinitely high walls at $z\leqslant 0$, gives the following well-known hydrogen-like spectrum for motion along the normal:[3]

$$E_n = -Q^2me^4/2\hbar^2n^2 \qquad (2)$$

(m and e are the mass and charge of the electron) with effective Bohr radius $\gamma^{-1} = \hbar^2/me^2Q$. For ^{4}He $\gamma^{-1} = 76$ Å, $E_1 = -0.003$ eV, while $\langle z\rangle_{1,2,3}$ are equal to 114, 456 and 1026 Å, respectively; for ^{3}He the characteristic distance is increased by $Q_4/Q_3 = 1.33$ while the energy is decreased by a factor $(Q_4/Q_3)^2 = 1.78$.

The actually observed transition frequencies between the stationary levels,[5,6] while close to those predicted on the basis of (2), do differ significantly from these theoretical values. For example, for the frequencies of transitions from the ground state with $n = 1$ to excited states with $n = 2$, 3, the calculation by Eq. (2) yields for ^{4}He $\nu_{12} = 119.7$, $\nu_{13} = 141.8$ GHz while direct measurement[5] gives $\nu_{12} = 125.9 \pm 0.2$ and $\nu_{13} = 148.6 \pm 0.3$ GHz. For ^{3}He, the calculated values amount to 67.6 and 80.1 GHz, and the measured,[6,7] 69.8 ± 0.15 and 82.55 ± 0.2 GHz.

Divergences of this sort cannot of course be regarded as surprising if we consider that in such an idealized picture many factors, although secondary, have still not been taken into account. The essential problem from this viewpoint is the character of the transition layer between the liquid and the vapor, which determines the change in the potential (1) over short distances from the surface. Unfortunately, no definite data on the structure of the liquid-vapor boundary have yet been obtained. Therefore, a number of authors[5,7–9] have attempted to make the spectrum (2) more precise by choosing some modification or another of the polarization potential (1), with a more realistic behavior near the surface. With a suitable choice of matching parameters, it is possible to reach an excellent agreement of the transition frequencies with the experimental values.

Another factor correcting the spectrum (2) is the presence of the vapor of the liquid over the liquid surface. Detailed consideration of this question has been given in a work recently published.[10] Two corrections appear in the spectrum (2) for motion of the electron along the normal. One of these is connected with the polarizability of the vapor and, as could be expected, lowers the energy levels and the transition frequencies. A second correction is connected with the effect of quantum refraction of the electrons by the atoms of the vapor and gives a uniform upward shift for all the hydrogen-like levels. The predicted transition-frequency shifts become significant in certain temperature ranges (rather narrow in view of the strong dependence of the vapor concentration N on the temperature), when the mean distance between the molecules of the vapor falls between the values of the characteristic distances of the electron from the surface in those states between which there occurs the transition $\langle z\rangle_n \ll N^{-1/3} \ll \langle z\rangle_m$. Thus, for ^{4}He at $N = 10^{18}$ cm^{-3}, calculation gives $\nu_{12} = 126.9$ and $\nu_{13} = 148.9$ GHz. Upon decrease in the temperature, the effect rapidly disappears.

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Finally, the liquid surface is by no means a plane. In addition to the quantum fluctuations, which are less important in view of their small amplitude (of the order of interatomic distances), the boundary of the liquid is continually undergoing thermal fluctuations. These latter are not at all small (at not too low temperatures) and, as has previously been noted by Widom,[11] lead to logarithmic divergences, both for short and long wavelengths, in the calculation of the mean square deviation of the surface from its equilibrium form $\overline{\zeta^2}$. On the short wavelength side, cutoff of the logarithm takes place, obviously, at atomic distances. The divergence on the longwave end, as has been shown in Ref. 12, is eliminated when account is taken of the force of gravitation; in this case the logarithm is cut off at the capillary constant.

The effect of the fluctuating distortion of the shape of the liquid surface on the behavior of electrons localized over it has been considered previously in a number of papers, principally from the point of view of scattering of electrons by ripplons—elementary excitations of the liquid surface.[3] This effect determines the imaginary increment of the energy spectrum of the electrons and, together with the scattering of them by the atoms of the vapor, is the reason for the broadening of the transition lines of the hydrogen-like spectrum.[8,13,14] As for the level shift under the action of interaction of the electrons with the curved and vibrating surface, there is only one reliable result here,[13] which pertains to the effect of the electron-ripplon interaction on the motion of the electron along the surface in the presence of the applied electric field. In a long paper,[8] along with other questions, the actual corrections to the energy spectrum of the electron under the action of fluctuation deformations of the surface were calculated. However, as has been noted in Ref. 13, in the analysis of the polarization interaction with the curved surface contains an error due to not taking the perturbations in the boundary condition into account. Moreover, the role of short-wave surface oscillations was not analyzed in proper fashion. For these oscillations $k\gamma^{-1} \gg 1$ (k is the wave number of the ripplon), and it is in just this case that one should expect the greatest effect.[13]

In the present paper we shall show that the fluctuations of the liquid surface produce a shift in the hydrogen-like levels of the transverse motion (2), the magnitude of which falls off slowly with decrease in temperature (proportional to T) and depends on the number of the quantum level n. The corresponding increase in the frequencies of the transitions between them, although it does not allow us to correct the spectrum (2) to the degree that the calculated values coincide with the experimental observations, turns out to be not small and, most importantly, to depend on the temperature, which makes its experimental observation a possibility.

2. Let us recall briefly the character of thermal fluctuations of the liquid surface (the question is discussed in detail in Ref. 12). The shape of the surface can be specified by the function $\zeta(\boldsymbol{\rho})$, which represents the height of its rise above the equilibrium level (the plane $z = 0$) at the point $\boldsymbol{\rho} = (x, y)$. The probability of the fluctuation of the surface with a given flexure is determined by the minimum amount of work necessary to create the given configuration $\zeta(\boldsymbol{\rho})$:[15]

$$w[\zeta(\rho)] \sim \exp(-R_{min}/T).$$

In turn, $R_{\min}$ is equal to the increase in the mechanical (potential) energy ΔE_{mech} of the curved surface relative to its equilibrium value. The excess mechanical energy, expanded in terms of the quantity ζ to second order, is equal to the sum of two contributions:

$$R_{min} = \Delta E_{\text{mech}} = \frac{\alpha}{2}\int d^2\rho\left[\left(\frac{\partial\zeta}{\partial x}\right)^2 + \left(\frac{\partial\zeta}{\partial y}\right)^2\right] + \frac{\rho g}{2}\int d^2\rho\,\zeta^2$$

due to capillary and gravitational forces, respectively.

We now choose a rectangle $0 \leqslant x \leqslant L_x$, $0 \leqslant y \leqslant L_y$ in the plane of the unperturbed boundary $z = 0$ and expand the function $\zeta(\boldsymbol{\rho})$ on it is a Fourier series. Since ζ is real, we write

$$\zeta(\rho) = \frac{1}{2}\sum_{\mathbf{k}}(\zeta_{\mathbf{k}} e^{i\mathbf{k}\rho} + \zeta_{\mathbf{k}}^{*} e^{-i\mathbf{k}\rho}), \tag{3}$$

while $k_{x,y} = 2\pi n_{x,y}/L_{x,y}$, $n_{x,y}$ are integers, $\zeta_{\mathbf{k}}^{*} = \zeta_{-\mathbf{k}}$. Substituting (3) in the expression for ΔE_{mech} and taking into account the periodicity of the individual harmonics in the chosen rectangle with area $S = L_x L_y$, we find

$$\Delta E_{\text{mech}} = \frac{\alpha S}{2}\sum_{\mathbf{k}} k^2|\zeta_{\mathbf{k}}|^2 + \frac{\rho g S}{2}\sum_{\mathbf{k}}|\zeta_{\mathbf{k}}|^2 = \frac{\alpha S}{2}\sum_{\mathbf{k}}(k^2+\varkappa^2)|\zeta_{\mathbf{k}}|^2,$$

where $k = |\mathbf{k}|$, $\varkappa^2 = 2/d^2 = \rho g/\alpha$, d is the capillary constant. Obviously, fluctuations with different **k** are statistically independent. The probability of the fluctuation $\zeta_{\mathbf{k}}$ is

$$w(\zeta_{\mathbf{k}}) \sim \exp\left[-\frac{\alpha S}{T}(k^2+\varkappa^2)|\zeta_{\mathbf{k}}|^2\right].$$

The doubling of the exponent is connected with the equal probability of fluctuations with wave vectors **k** and $-$**k**. With account of the real and imaginary parts of $\zeta_{\mathbf{k}}$, we find the mean square of the fluctuations with wave vector k in the form

$$\overline{|\zeta_{\mathbf{k}}|^2} = T/\alpha S(k^2+\varkappa^2). \tag{4}$$

Squaring (3), averaging, and transforming from summation to integration, it is not difficult to perceive the logarithmic singularity of $\overline{[\zeta(\boldsymbol{\rho})]^2}$ noted above. Actually,

$$\overline{[\zeta(\rho)]^2} = \sum_{\mathbf{k}}\overline{|\zeta_{\mathbf{k}}|^2} = \frac{T}{2\pi\alpha}\int_0^\infty \frac{k\,dk}{k^2+\varkappa^2}.$$

As $k \to \infty$, the cutoff must be made at the reciprocal interatomic distance, a^{-1}. The divergence due to failure to take into account gravitational forces (i.e., at $\varkappa = 0$) as $k \to 0$ is now absent. The role of the smallest k is played by the reciprocal of the capillary length $\varkappa$. Thus, we verify that

$$\overline{[\zeta(\rho)]^2} = \frac{T}{2\pi\alpha}\ln\left(\frac{1}{\varkappa a}\right), \quad \varkappa a \ll 1.$$

3. We now find the change, due to the curvature of the liquid surface, in the electrical energy of interaction of an electron, with the polarization charges on the surface. First of all, we note that the rate of formation of the image field significantly exceeds the characteristic velocities of the electron in a potential well near the surface. For the frequencies, this means satisfaction of the inequality $\omega_e = Q^2\omega_e^{\text{at}} \ll \omega_e^{\text{at}}$. Thus, we do not have to take into account beforehand the retardation of the polarization and the dispersion of ε ($Q^2 \sim 10^{-4}$). On the other hand, the characteristic frequency of the electron in the well, $\omega_e = Q^2me^4/\hbar^3 \sim 10^{12}$ GHz, significantly exceeds the capillary-wave frequencies $\omega_{\text{cap}}^2 = (\alpha/\rho)k^3$, which determine the rates of surface deformation: $\omega_e \gg \omega_{\text{cap}}$. The inequality is weakened only in the immediate vicinity of the maximum surface-oscillation frequency corresponding to the wave number $k_{\max} \sim a^{-1} \sim 10^8$ cm^{-1} and amounting, in order of magnitude, to 10^{12} Hz for He at $T \sim 1$ K. This face, however, is not so important, since the final answer for the shift in the levels will be obtained with logarithmic accuracy.

The neglect of all temporal effects, which is possible under the given conditions, allows us to solve a purely static problem. Using the coordinates mentioned above, we assume that the electron is located in a vacuum at the point $z = h$, $\boldsymbol{\rho} = 0$ and we expand the potential in the vacuum (index 1) and in the liquid (index 2) to terms of second order in the displacement of the surface:

$$\begin{aligned}\varphi_1(\mathbf{r}) &= \varphi_0 + \varphi_1^{(0)} + \varphi_1^{(1)} + \varphi_1^{(2)} \\ &= \frac{e}{|\mathbf{r}-\mathbf{h}|} - \frac{\varepsilon-1}{\varepsilon+1}\frac{e}{|\mathbf{r}+\mathbf{h}|} + \varphi_1^{(1)} + \varphi_1^{(2)},\end{aligned} \tag{5}$$

$$\varphi_2(\mathbf{r}) = \varphi_2^{(0)} + \varphi_2^{(1)} + \varphi_2^{(2)} = \frac{2e}{(\varepsilon+1)|\mathbf{r}-\mathbf{h}|} + \varphi_2^{(1)} + \varphi_2^{(2)}, \quad \mathbf{h} = \hat{\mathbf{z}}h.$$

Here we have substituted the well-known solution[4] for a charge above a plane surface.

The corrections $\varphi_{1,2}^{(1,2)}$ in both media satisfy Laplace's equation and the standard boundary conditions of continuity of the potential and of the normal component of the induction vector:

$$\Delta\varphi(\mathbf{r}) = 0, \tag{6a}$$

$$\varphi_1 = \varphi_2, \quad \frac{\partial\varphi_1}{\partial n} = \varepsilon\frac{\partial\varphi_2}{\partial n}, \quad \mathbf{r} = \mathbf{r}_{\text{bound}} = \boldsymbol{\rho} + \boldsymbol{\zeta}(\boldsymbol{\rho}), \quad \boldsymbol{\zeta} = \hat{\mathbf{z}}\zeta. \tag{6b}$$

We expand the desired potentials $\varphi_{1,2}^{(1,2)}(z, \boldsymbol{\rho})$ similar to (3), in a two-dimensional Fourier series in the x-y plane. The expansion, for example, of the potential $\varphi_1^{(1,2)}$ which satisfies (6a) (and falls off as $z \to +\infty$), has the form

$$\begin{aligned}\varphi_1^{(1,2)}(z, \boldsymbol{\rho}) &= \frac{1}{2}\sum_{\mathbf{k}} e^{-kz}[\varphi_{\mathbf{k}}^{(1,2)} e^{i\mathbf{k}\boldsymbol{\rho}} + \varphi_{\mathbf{k}}^{(1,2)*} e^{-i\mathbf{k}\boldsymbol{\rho}}], \\ \varphi_{\mathbf{k}} &= \frac{1}{S}\int d^2\rho\, e^{-i\mathbf{k}\boldsymbol{\rho}}\varphi(z, \boldsymbol{\rho}).\end{aligned} \tag{7}$$

Further, after obtaining the expansion of the boundary conditions (6b) on the curved surface up to terms of second order in $\zeta(\boldsymbol{\rho})$ (we do not write them out here because of their cumbersome form), we transform in them to the Fourier components with the help of (7) and (3) and with the use of the potentials (5) of the unperturbed problem. The resultant boundary conditions allow us easily to find the Fourier components of the potentials themselves. For the potential in a vacuum, in first order, we obtain

$$\varphi_{\mathbf{k}}^{(1)} = -\frac{4Qe}{(\varepsilon+1)\hbar^2 S}\int\frac{d^2\rho\, e^{-i\mathbf{k}\boldsymbol{\rho}}}{(1+\rho_1^2)^{3/2}}\sum_{\mathbf{k}_1}\left\{(\zeta_{\mathbf{k}_1}e^{i\mathbf{k}_1\boldsymbol{\rho}} + \zeta_{\mathbf{k}_1}^* e^{-i\mathbf{k}_1\boldsymbol{\rho}})\left[\varepsilon + \frac{2-\rho_1^2}{kh(1+\rho_1^2)}\right] + i(\mathbf{k}_1\boldsymbol{\rho})(\zeta_{\mathbf{k}_1}e^{i\mathbf{k}_1\boldsymbol{\rho}} - \zeta_{\mathbf{k}_1}^* e^{-i\mathbf{k}_1\boldsymbol{\rho}})\right\},$$

where $\boldsymbol{\rho}_1 = \boldsymbol{\rho}/h$. Using the potentials $\varphi_{\mathbf{k}}^{(1)}$ in the vacuum and in the liquid, we find the second-order corrections by an analogous method. We note that, in view of the proportionality of these quantities to the small factor Q, additional account of the departure of ε from unity in the corresponding expressions would lie beyond the accuracy of the work. The correction $\varphi_{\mathbf{k}}^{(2)}$ in the vacuum, which is of interest to us, is equal to

$$\begin{aligned}\varphi_{\mathbf{k}}^{(2)} = -\frac{Qe}{h^3 S}\int\frac{d^2\boldsymbol{\rho}\, e^{-i\mathbf{k}\boldsymbol{\rho}}}{(1+\rho_1^2)^{3/2}}\sum_{\mathbf{k}_1,\mathbf{k}_2}&\{[\zeta_{\mathbf{k}_1}\zeta_{\mathbf{k}_2}e^{i(\mathbf{k}_1+\mathbf{k}_2)\boldsymbol{\rho}} + \zeta_{\mathbf{k}_1}\zeta_{\mathbf{k}_2}^* e^{i(\mathbf{k}_1-\mathbf{k}_2)\boldsymbol{\rho}}] \\ \times F(\boldsymbol{\rho}, \mathbf{k}, \mathbf{k}_1) &+ [\zeta_{\mathbf{k}_1}^*\zeta_{\mathbf{k}_2}e^{i(\mathbf{k}_2-\mathbf{k}_1)\boldsymbol{\rho}} + \zeta_{\mathbf{k}_1}^*\zeta_{\mathbf{k}_2}^* e^{-i(\mathbf{k}_1+\mathbf{k}_2)\boldsymbol{\rho}}]F(\boldsymbol{\rho}, \mathbf{k}, -\mathbf{k}_1)\},\end{aligned} \tag{8}$$

where

$$F(\boldsymbol{\rho}, \mathbf{k}, \mathbf{k}_1) = \frac{2-\rho_1^2}{1+\rho_1^2} + hk\left[1 - \frac{(\mathbf{k}_1\mathbf{k})}{k^2}\right] + i(\mathbf{k}_1\boldsymbol{\rho}).$$

The energy of interaction of the electron with the polarization charges on the surface of the liquid can be found from the general formula for the total energy of the field,[4] after subtracting the characteristic energy of the electron

$$U = \frac{e}{2}\varphi_1(h, \rho=0) = -\frac{Qe^2}{h} + \frac{e}{2}[\varphi_1^{(1)} + \varphi_1^{(2)}]_{\substack{z=h\\ \rho=0}} = U_0 + \Delta U.$$

We now assume, and this is confirmed by the calculation, that the principal contribution to ΔU is made by the surface oscillations with large k: $kh \gg 1$. This assumption corresponds to the fact that[13] the distortions of the shape of the surface manifest themselves to the greatest degree in the short-wave range $k\gamma^{-1} \gg 1$ (see above). (The absence of a contribution from the long-wave oscillations with $kh \ll 1$ is explained by the fact that the inertia-free electron is simply moved adiabatically along with the surface, the portion of which under it can be regarded in this case as locally plane.) The wavelengths of such oscillations are much shorter than the characteristic distance of the electron from the surface; therefore, the electron senses them as a fine ripple. Desiring to isolate only the principal effect, we can average the expression for ΔU over the spatial oscillations of the surface. Such space averaging, as is not difficult to see, is equivalent in the given case to a statistical averaging over the statistically independent $\zeta_{\mathbf{k}}$ because within a distance along the surface, equal in order of magnitude ot the quantity h, a distance that is characteristic for the considered problem, we can place a large number of intervals, within which oscillations take place with given but arbitrarily differing, wavelengths ($\lambda \ll h$). In the averaging of ΔU the correction of first order in ζ vanishes and there remains

$$\overline{\Delta U}=\frac{e}{2}\overline{\varphi_1^{(2)}}(h,\rho=0)=\frac{e}{4}\sum_{\mathbf{k}}e^{-kh}[\overline{\varphi_{\mathbf{k}}^{(2)}}+\overline{\varphi_{\mathbf{k}}^{(2)*}}]. \qquad (9)$$

The independence of the fluctuations with different **k**, expressed by the equations

$$\overline{\zeta_{\mathbf{k}_1}\zeta_{\mathbf{k}_2}}=\overline{\zeta_{\mathbf{k}_1}{}^*\zeta_{\mathbf{k}_2}{}^*}=\overline{|\zeta_{\mathbf{k}_1}|^2}\delta_{\mathbf{k}_2,\,-\mathbf{k}_1},$$
$$\overline{\zeta_{\mathbf{k}_1}{}^*\zeta_{\mathbf{k}_2}}=\overline{\zeta_{\mathbf{k}_1}\zeta_{\mathbf{k}_2}{}^*}=\overline{|\zeta_{\mathbf{k}_1}|^2}\delta_{\mathbf{k}_2,\,\mathbf{k}_1},$$

allows us to carry out the summation over $\mathbf{k}_2$ in (8) without difficulty. Then, transforming in (8) and (9) from summation over the wave vectors to integration, we get for the energy $\overline{\Delta U}$, averaged over the fluctuations,

$$\overline{\Delta U}=-\frac{Qe^2T}{4\pi^3\alpha h^3}\int\frac{d^2\rho}{(1+\rho_1^2)^{3/2}}\int d^2ke^{-kh}\cos(\mathbf{k}\boldsymbol{\rho})\left(\frac{2-\rho_1^2}{1+\rho_1^2}+kh\right)$$
$$\times\int\limits_{k_{1min}}^{k_{1max}}\frac{k_1\,dk_1}{k_1^2+\varkappa^2}.$$

Integration over k_1 is carried out over the region of significant wave numbers $k_1h\gg1$, i.e., limited by the values $k_{1\,\min}\sim h^{-1}$ and $k_{1\,\max}\sim a^{-1}$; hence $\varkappa^2$ can be omitted in the denominator. Integrating over the angle φ between **k** and **ρ**,[16] we find

$$\overline{\Delta U}=-\frac{Qe^2T\ln(h/a)}{\pi\alpha h}$$
$$\times\int\limits_0^\infty\frac{\rho_1\,d\rho_1}{(1+\rho_1^2)^{3/2}}\int\limits_0^\infty k\,dke^{-kh}J_0(k\rho)\left(\frac{2-\rho_1^2}{1+\rho_1^2}+kh\right),$$

where $J_0(x)$ is a Bessel function of zero order. Then integrating over k (Ref. 16) and then over ρ_1, we finally obtain

$$\overline{\Delta U}=-\frac{Qe^2T}{2\pi\alpha h^3}\ln\left(\frac{h}{a}\right). \qquad (10)$$

4. Finally, we consider the quantum mechanical part of the problem. The presence of the small parameter $\gamma\zeta\ll1$ allows us to make use of perturbation theory for the calculation of the shift in the levels. The Schrödinger equation with the boundary conditions has the form

$$\frac{\hbar^2}{2m}\Delta\Psi(z,\rho)+[E-(U_0+\Delta U^{(1)}+\Delta U^{(2)})]\Psi(z,\rho)=0, \qquad (11a)$$

$$\Psi(z=\zeta(\rho),\rho)=0,\quad \Psi(z\to\infty,\rho)\to0. \qquad (11b)$$

The electrostatic energy of interaction of the electron with the deformed surface of the liquid in (11a) is expanded in powers of ζ up to terms of second order: U_0 is defined in (1); $\Delta U^{(1)}$ is explicitly written out in Ref. 13 and is a correction that is linear in ζ; the value of the second correction $\overline{\Delta U^{(2)}}$, averaged over the fluctuations of the surface, is found above (10) (in place of the value of the z-th coordinate of the electron h used above, we now write simply z).

In first-order quantum perturbation theory, the distortion in the boundary condition at the curved surface (11b) and the term linear in ζ of the interaction energy $\Delta U^{(1)}$, as was shown in Ref. 13, do not make a contribution to the shift in the energy levels of the unperturbed problem. On the other hand, the quantum correction $\overline{\Delta U^{(2)}}$ in this approximation leads precisely to a shift in the energy levels which, as will be seen from the calculation carried out below, turns out to be equal in order of magnitude to $(\gamma\zeta)^2\ln^2(\gamma a)$. Estimating the level shift under the action of the first two of the enumerated perturbations in the second approximation, it is not difficult to establish the fact that their contribution turns out to be of the order of $(\gamma\zeta)^2$, i.e., it does not contain the square of a large logarithm. Account of these contributions would actually mean refinement of the constant under the logarithm sign, which would be an exaggeration of the logarithmic accuracy of the given calculation. Thus, in Eq. (11a), it suffices to keep only $\overline{\Delta U^{(2)}}$, and to write out the boundary condition (11b) on the unperturbed plane boundary of the liquid.

After separation of the variables we obtain for the wave function $\Phi_n(z)$ that describes the motion of the electron along the normal to the surface, the equation

$$\frac{\hbar^2}{2m}\Phi_n''(z)+\left[E-\left(\frac{Qe^2}{z}+\frac{Qe^2T}{2\pi\alpha z^3}\ln\frac{z}{a}\right)\right]\Phi_n(z)=0$$

with the usual boundary conditions and normalization

$$\Phi_n(0)=0,\quad \Phi_n(z\to\infty)\to0,\quad \int\limits_0^\infty\Phi_n^2(z)\,dz=1.$$

The wave equation of the unperturbed problem has the form[18]

$$\Phi_n^{(0)}(z)=-\frac{2\gamma^{3/2}z}{n!\,n^{5/2}}e^{-2\gamma z/n}L_n^1\left(\frac{2\gamma z}{n}\right).$$

The shift in the n-th level is given by

$$E_n^{(1)}=\int\limits_0^\infty\overline{\Delta U^{(2)}}[\Phi_n^{(0)}(z)]^2dz$$
$$=-\frac{Qe^2T\gamma^3}{2\pi\alpha}\int\limits_0^\infty\frac{dz}{z}\ln\left(\frac{z}{a}\right)\left(\frac{2}{n!\,n^{5/2}}\right)^2e^{-4\gamma z/n}\Big[L_n^1\ \frac{2\gamma z}{n}\Big)\Big]^2. \qquad (12)$$

As is seen, the principal contribution to the integral is made by the region of small z. In this region, the Laguerre polynomials

$$L_n^1(x)=-\frac{n!}{(n-1)!}\frac{e^x}{x}\frac{d^{n-1}}{dx^{n-1}}(e^{-x}x^n)$$
$$=-nn!\left(1-\frac{n-1}{2}x+\ldots\right)$$

tend toward a constant–nn! Limiting the integration in (12) at small z to the value $z_{\min}\sim a$, and at large z to the characteristic distance of the electron from the surface $z_{\max}\sim\langle z\rangle_n$, we find, with logarithmic accuracy,

$$E_n^{(1)}=-\frac{Qe^2T\gamma^3}{\pi\alpha n^3}\ln^2\left(\frac{\langle z\rangle_n}{a}\right). \qquad (13)$$

The energy of the n-th level is lowered and becomes equal to

$$E_n=\hbar\omega_e\Big\{-\frac{1}{2n^2}-\frac{T\gamma^2}{\pi\alpha n^3}\ln^2\ \frac{\langle z\rangle_n}{a}\Big)\Big)\Big\}. \qquad (14)$$

We estimate the shifts of the transition frequencies $\Delta\nu_{12} = \nu_{12} - \nu_{12}^{(0)}$ and $\Delta\nu_{13} = \nu_{13} - \nu_{13}^{(0)}$. For electrons above ^{4}He at $T = 1.3$ K, which corresponds to the conditions of the experiment of Ref. 5, we find with the aid of (14), $\Delta\nu_{12} = 1.5$ and $\Delta\nu_{13} = 1.64$ GHz. Under the experimental conditions of Ref. 7, we obtain for electrons over ^{3}He, at $T = 0.4$ K, $\Delta\nu_{12} = 276$ and $\Delta\nu_{13} = 302$ Mhz. We note that these values exceed by a wide margin the natural line widths estimated in the first and second cases, respectively, to be < 450 MHz[3] and < 110 MHz.[7] The temperature dependence of the level shift (13), which must manifest itself also in the temperature dependence of the frequencies of the resonant transitions $\nu_{mn}(T)$, allows us to identify the discussed effect uniquely.

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