ENERGY SPECTRUM IN THE FORCE FIELD OF AN ELECTROSTATIC IMAGE

O. F. Dorofeev, B. A. Lysov, O. S. Pavlova,
and I. M. Ternov

A new model is proposed for describing localized electron states near the
surface of liquid helium. It uses the ambiguity of the self-adjoint
extension of the Hamiltonian of the problem of the motion of an electron
in the force field of an electrostatic image at a flat insulator—vacuum
interface. In contrast to the well-known model of Grimes, the model
contains a single phenomenological parameter — a mixing angle. It is
shown that the necessary choice of the mixing angle makes it possible
to explain completely the spectroscopic data on electric dipole
transitions between single-particle electron states localized on a
^{4}He or ^{3}He surface.

The localization of electrons above the surface of cryogenized insulators, first
predicted by Cole and Cohen [1] and independently by Shikin [2], is the subject of intense
experimental and theoretical study [3]. Physically, localization of electrons occurs
through the competing effect of long-range electrostatic-image forces and short-range
exchange forces, which prevent penetration of electrons into the region filled with the
insulator.

This phenomenon is most clearly noted in the direct spectroscopic observation of the
discrete electron spectrum. Such observations have been made for liquid ^{4}He [4] and ^{3}He
[5] and, recently, for solid hydrogen [6]. Similar observations are currently being made
for cryogenized deuterium and neon [6].

As is well known [3], the simplest quasihydrogen phenomenological model with potential

$$V(x) = \begin{cases} -\dfrac{Q}{x}, & x>0, \\ \infty, & x \leqslant \infty, \end{cases} \tag{1}$$

already describes to 5% accuracy the observed energy spectrum of electrons localized above
the surface of liquid helium. For better agreement between theory and experiment the
Coulomb divergence in (1) is cut off in some manner, and a potential step of finite height
V_0 is introduced to describe the short-range exchange forces. The most successful model
potential of such kind was introduced by Grimes and collaborators [7]:

$$V(x) = \begin{cases} -\dfrac{Q}{x+x_0}, & x>0, \\ V_0, & x \leqslant 0, \end{cases} \tag{2}$$

where V_0 and x_0 are adjustable parameters of the theory.

The method of eliminating the Coulomb singularity used in (2) can be justified by
taking into account the spatial dispersion of the permittivity in the transition region
between the liquid helium and the vapor of the liquid helium [8]. With regard to the
jump of the potential V_0 at the insulator—vacuum boundary, numerous theoretical and
experimental studies have been devoted to its determination (see, for example, [9] and
the extensive literature quoted there). Depending on the employed model, the calculated
values of V_0 vary from 0.5 eV to 1.5 eV, so that the currently adopted value $V_0 = 1$ eV for
^{4}He is actually based on the very good agreement of this value with the experimental data
on the spectroscopy of resonance transitions between the lowest energy levels of electrons
localized above liquid ^{4}He under the condition that the frequencies of the resonance

---

transitions are calculated by means of the model potential (2).

Although the potential (2) is more realistic than the potential (1), Grimes's model, as a phenomenological model, is not entirely satisfactory, since it contains excess information. The point is that the experimentalists (see, for example, [6]) are now convinced that the observed energy spectrum can be described by a formula that contains just one phenomenological parameter — a Rydberg correction to the Balmer levels with, moreover, this Rydberg correction for liquid ^{4}He and ^{3}He and solid hydrogen being independent of the level number.

It is therefore very natural to look for a phenomenological model that describes the physical situation reasonably well and contains just a single free phenomenological parameter and leads directly to the experimentally observed energy spectrum. As will be shown below, such a model can be obtained mathematically in a natural manner if one treats accurately the quantization of the energy in the force field of an electrostatic image without invoking extraneous information about the magnitude of the repulsive exchange forces that act on the insulator–vacuum boundary.

Suppose that a homogeneous insulator occupies the entire half-space x ≤ 0. If a charge is in the region x > 0, then, as is well known [10], it is subject to electrostatic-image forces, which are attractive; but if it is in the region x < 0, the electrostatic-image forces are repulsive, and the potential energy of the charge can be expressed in the form

$$V(x) = \begin{cases} -\dfrac{\varepsilon-1}{4(\varepsilon+1)}\dfrac{e^2}{x}, & x>0, \\ -\dfrac{\varepsilon-1}{4\varepsilon(\varepsilon+1)}\dfrac{e^2}{x} & x<0. \end{cases} \tag{3}$$

Here, ε is the permittivity, and e is the magnitude of the charge (in what follows we shall take e to be the electron charge).

We propose to use the potential (3) as a model phenomenological potential to describe electron states localized at the surface of cryogenized insulators. In this connection we shall assume that $\varepsilon \simeq 1$, and we divide the Hamiltonian of the transverse motion of electron into two parts:

$$\hat{H}^{(0)} = \frac{\hat{p}_x^2}{2m} - \frac{e^2(\varepsilon-1)}{8\varepsilon}\frac{1}{x}, \tag{4}$$

$$\hat{H}^{(1)} = -\frac{e^2(\varepsilon-1)^2}{8\varepsilon(\varepsilon+1)}\frac{1}{|x|}. \tag{5}$$

We shall regard $\hat{H}^{(0)}$ as an unperturbed Hamiltonian, and $\hat{H}^{(1)}$ as a perturbation.

In the coordinate representation the unperturbed Schrödinger equation is

$$\frac{\hbar^2}{2m}\frac{d^2\Phi}{dx^2} + \left(\frac{Ze^2}{x} + E^{(0)}\right)\Phi = 0, \quad Z = \frac{\varepsilon-1}{8\varepsilon}, \tag{6}$$

an ordinary differential equation for which the point x = 0 is a regular singular point of the type of a limit circle, and the minimal symmetric operator generated by the formal differential operator $\hat{H}^{(0)}$ has deficiency indices (1.1) and, therefore, by von Neumann's well-known theorem [11], admits a single-parameter family of self-adjoint extensions. We note that Eq. (6) is identical to the radial Schrödinger equation in the nonrelativistic problem of the s states of the hydrogen atom though in that case the "redundant" extensions are filtered out by requiring the total three-dimensional Hamiltonian to be self-adjoint [11]. It is obvious that in the considered case this argument is invalid.

We obtain one of the possible self-adjoint extensions of $\hat{H}^{(0)}$ by requiring that at the singular point x = 0 the boundary condition $\Phi(0) = 0$ hold. For such a boundary condition the solution of Eq. (6) that belongs to $L_2(R)$ vanishes in the region x ≤ 0, this being equivalent to the simple quasihydrogen model with potential (1).

Our basic idea is very simple — instead of reconciling the theory with experiment by changing the form of the potential (3), replacing it, for example, by a potential of the form (2), we achieve agreement by the choice of a suitable self-adjoint extension of the formal Hamiltonian $\hat{H}^{(0)}$.

To parametrize the family of self-adjoint extensions in which we are interested, it is convenient to introduce the mixing angle [12,13] α, augmenting Eq. (6) with an additional boundary condition at the singular point x = 0:

$$\Phi'(+0) - \Phi'(-0) = \frac{2\pi m Z e^2}{\hbar^2} \operatorname{ctg} \alpha \Phi(0). \tag{7}$$

Going over to the dimensionless variables

$$E^{(0)} = -\frac{Z^2 e^4 m}{2\hbar^2 \varkappa^2}, \quad \xi = \frac{2}{\varkappa} \frac{x}{x_0}, \quad x_0 = \frac{\hbar^2}{Ze^2 m}, \tag{8}$$

we write Eq. (6) in the form

$$\frac{d^2\Phi}{d\xi^2} + \left(\frac{1}{4} - \frac{\varkappa}{\xi}\right)\Phi = 0. \tag{9}$$

Equation (9) is a special case of Whittaker's equation, and its solutions that vanish at plus and minus infinity (we are interested only in the discrete spectrum) are the Whittaker functions $W_{\varkappa, \frac{1}{2}}(\xi)$ and $W_{-\varkappa, \frac{1}{2}}(|\xi|)$, respectively. A wave function possessing the necessary behavior at infinity and continuous at the origin can be written in the form

$$\Phi(x) = B \begin{cases} \dfrac{1}{\Gamma(1+\varkappa)} W_{\varkappa, \frac{1}{2}}\left(\dfrac{2}{\varkappa}\dfrac{x}{x_0}\right), & x \geq 0, \\[3mm] \dfrac{1}{\Gamma(1-\varkappa)} W_{-\varkappa, \frac{1}{2}}\left(\dfrac{2|x|}{\varkappa x_0}\right), & x \leq 0, \end{cases} \tag{10}$$

where B is a normalization constant. This function belongs to the space $L_2(R)$ for all negative values of E (all positive values of $\varkappa$). Requiring further that the wave function (10) satisfy the boundary condition (7), we can readily obtain the relation

$$\cos\left(\frac{\pi Z e^2}{2\hbar}\sqrt{\frac{2m}{|E|}}\right) + \operatorname{ctg}\alpha \sin\left(\frac{\pi Z e^2}{2\hbar}\sqrt{\frac{2m}{|E|}}\right) = 0. \tag{11}$$

For the energy levels of the transverse motion of the electron in the field of the electrostatic-image forces we obtain

$$E_n = -\frac{Z^2 e^4 m}{2\hbar^2 (n - \alpha/\pi)^2}, \quad n = 1, 2, \ldots, \quad 0 < \alpha < \pi. \tag{12}$$

We see that the mixing angle determines a Rydberg correction to Balmer levels of electron states localized over the surface of liquid helium.

The question of the choice of a definite value of the mixing angle, in other words, the question of the choice of a particular self-adjoint extension of the formal Hamiltonian, is of course not a mathematical but a physical question, and the answer to it must be given by the microscopic theory of the interaction of the electron with the atoms of the insulator. Since we do not dispose of an exhaustive quantitative theory of such an interaction, we are forced to regard the mixing angle α as a macroscopic phenomenological parameter and determine its value from experimental data.

To clarify the physical meaning of the mixing angle α, we note that the additional boundary condition (7), which fixes a definite self-adjoint extension of the operator $\hat{H}^{(0)}$, is actually equivalent to the fact that the initially existing, so to speak unrenormalized potential of the electrostatic-image forces is augmented with a δ-function potential barrier (or well, if $\alpha > \pi/2$). Indeed, with allowance for the boundary condition (7) Eq. (6) can be written in the form [14]

$$-\frac{\hbar^2}{2m}\frac{d^2\Phi}{dx^2} + \left[-Ze^2 \mathscr{P}\left(\frac{1}{x}\right) + \pi Z e^2 \operatorname{ctg}\alpha\,\delta(x)\right]\Phi = E\Phi, \tag{13}$$

where $\mathscr{P}$ is the principal value symbol. Thus, cot α determines the penetrability of the induced δ-function potential.

In the above we took into account only some of the electrostatic-image forces, ignoring entirely the contribution to the spectrum from the operator $\hat{H}^{(1)}$. It is readily seen that standard perturbation theory already leads to a divergence in the first order. This is because we must here deal with a singular perturbation of a singular potential [12,15].

The contribution to the spectrum from the singular perturbation could be calculated by means of regularized perturbation theory, as is done in quantum field theory [16] and was done, for example, in [12] for the exactly solvable model problem considered there. However, in our case it is simpler to go over to the momentum representation, bearing in mind that in the sense of generalized functions the Fourier transform of the function $|x|^{-1}$ is given by [17]

$$F[|x|^{-1}] = -2(\gamma + \ln|t|), \tag{14}$$

where γ is Euler's constant.

In the p representation $\hat{H}^{(1)}$ is an integral operator whose kernel can be represented by means of (14) in the form

$$\langle p|\hat{H}^{(1)}|p'\rangle = -\frac{Ze^2}{\pi\hbar}\frac{\varepsilon-1}{\varepsilon+1}\left\{\gamma + \ln\frac{|p-p'|}{p_0}\right\}, \tag{15}$$

where $p_0 = \hbar/x_0$, x_0 is determined in (8).

Thus, in the first order of perturbation theory the correction to the n-th level can be calculated in accordance with the formula

$$\Delta E_n^{(1)} = \frac{Ze^2}{\pi\hbar}\frac{\varepsilon-1}{\varepsilon+1}\left\{\gamma\left|\int\psi_n(p)\,dp\right|^2 + \iint\psi_n^*(p)\psi_n(p')\ln\frac{|p-p'|}{p_0}\,dp\,dp'\right\}, \tag{16}$$

where $\psi_n(p)$ is the unperturbed wave function of the n-th stationary state in the p representation.

Bearing in mind that

$$\psi_n(p) = \sqrt{\frac{2\varkappa_n}{\pi p_0}}\left[1 + \left(\varkappa_n\frac{p}{p_0}\right)^2\right]^{-1}\exp\left[-2i\varkappa_n\,\mathrm{arctg}\left(\varkappa_n\frac{p}{p_0}\right)\right], \quad \varkappa_n = n - \alpha/\pi, \tag{17}$$

we obtain after simple but laborious calculations

$$\Delta E_n^{(1)} = 2\frac{\varepsilon-1}{\varepsilon+1}\frac{Z^2e^4m}{\hbar^2\pi^2}\left[\frac{\sin^2\varkappa_n\pi}{\varkappa_n^3}\left(\gamma + \ln\frac{2}{\varkappa_n}\right) - \frac{\sin^2\varkappa_n\pi}{\varkappa_n}\sum_{k=1}^{\infty}\frac{3k^2-\varkappa_n^2}{k(k^2-\varkappa_n^2)^2}\right]. \tag{18}$$

In (18) for small mixing angles $\alpha \ll 1$ the term with the number $k = n$ is significantly greater than all the remaining terms, and it is therefore expedient to make a certain regrouping of the terms in the sum $E^{(0)}+\Delta E^{(1)}$, expressing for this the charge number Z in terms of the charge number Q defined by

$$Q = \frac{\varepsilon-1}{4(\varepsilon+1)}. \tag{19}$$

We then obtain

$$E_n = \tilde{E}_n^{(0)} + \Delta\tilde{E}_n^{(1)}, \tag{20}$$

where

$$\tilde{E}_n^{(0)} = -\frac{Q^2e^4m}{2\hbar^2(n-\delta)^2}, \quad \delta = \alpha/\pi, \tag{21}$$

$$\Delta\tilde{E}_n^{(1)}/\tilde{E}_n^{(0)} = \frac{(\varepsilon-1)}{4\varepsilon^2}\left\{3\varepsilon+1 + \frac{4(\varepsilon+1)}{\pi^2\varkappa_n}\sin^2\alpha\left[\gamma + \ln 2 - \ln\varkappa_n - \varkappa_n^2\sum_{k=1}^{\infty}\frac{3k^2-\varkappa_n^2}{k(k^2-\varkappa_n^2)^2}\right]\right\}. \tag{22}$$

The expression (21) describes well the experimentally observed energy spectrum for liquid ^{4}He and ^{3}He, and also for solid hydrogen. According to [6], the measured values of the Rydberg correction δ in these cases were found to be 0.022, 0.014, and 0.11. The corrections to the first three energy levels (21), calculated by means of (22), do not exceed hundredths of a percent for ^{4}He and ^{3}He, while for solid hydrogen the expression (21) is valid for the lowest levels with one-percent accuracy.

Thus, our model is in excellent agreement with the currently known experimental data on the energy spectrum of electrons localized above the surface of cryogenized insulators. It differs advantageously from the previously proposed models in containing only one free phenomenological parameter. Finally, in our model the exchange forces that act on the insulator-vacuum interface, and have no classical analog, are taken into account purely

quantum mechanically, namely, by means of the choice of a suitable self-adjoint extension of the operator $\hat{H}^{(0)}$, and not by a modification in the Schrödinger equation of the potential of the electrostatic-image forces, as was done earlier.

LITERATURE CITED

1. M. W. Cole and M. H. Cohen, Phys. Rev. Lett., 23, 1238 (1969).
2. V. B. Shikin, Zh. Eksp. Teor. Fiz., 58, 1748 (1970).
3. V. S. Édel'man, Usp. Fiz. Nauk, 130, 675 (1980).
4. C. L. Zipfel, T. R. Brown, and C. C. Grimes, Surface Science, 58, 283 (1976).
5. A. P. Volodin and V. S. Édel'man, Pis'ma Zh. Eksp. Teor. Fiz., 30, 688 (1979).
6. V. V. Zav'yalov and I. I. Smol'nikov, Zh. Eksp. Teor. Fiz., 92, 339 (1987).
7. C. C. Grimes, T. R. Brown, M. L. Burns, and C. L. Zipfel, Phys. Rev. B, 13, 140 (1976).
8. A. M. Gabovich, L. G. Il'chenko, and É. A. Pashinskii, Zh. Eksp. Teor. Fiz., 79, 665 (1980).
9. D. G. Ohn and M. Silver, Phys. Rev., 183, 295 (1969).
10. L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media, Pergamon Press, Oxford (1960).
11. R. D. Richtmyer, Principles of Advanced Mathematical Physics, Springer, New York (1978, 1981).
12. V. B. Gostev, V. S. Mineev, and A. R. Frenkin, Teor. Mat. Fiz., 68, 45 (1986).
13. O. F. Dorofeev, A. N. Vasil'ev, B. A. Lysov, and O. S. Pavlova, Izv. Vyssh. Uchebn. Zaved. Fiz., 30, No. 9, 125 (1987); Paper deposited at VINITI, No. 933-B87, Moscow (1987).
14. S. Flügge, Practical Quantum Mechancis, 2 vols., Springer Verlag, Berlin (1971).
15. M. Reed and B. Simon, Methods of Modern Mathematical Physics, Vol. 4, Academic Press, New York (1978).
16. N. N. Bogolyubov and D. V. Shirkov, Introduction to the Theory of Quantized Fields, 3rd ed., Wiley, New York (1980).
17. Yu. A. Brychkov and A. P. Prudnikov, Integral Transforms of Generalized Functions [in Russian], Nauka, Moscow (1977).

ONE-DIMENSIONAL STEADY MIGRATION OF QUANTUM PARTICLES

A. A. Serikov and V. N. Kharkyanen*

The formalism of nonequilibrium density matrices is used to investigate transmembrane transport of quantum particles along a molecular chain. For a homogeneous chain analytic expressions that describe a steady flux of particles and their distribution are found. The features of the transport are analyzed for the case of a disordered chain.

Introduction

The problem of the transport of particles (or quasiparticles) traditionally occupies one of the central positions in the physics the condensed state. It is sufficient to mention here the motion of charged particles responsible for the conduction of metals and electrolytes, the migration of excitons that determines the heat conduction of crystalline substances and is responsible for processes of sensitized luminescence, electrophoresis in colloidal systems, the transport of reactants in chemical reactions, the migration of radiation defects in crystals and other such phenomena.

In connection with the successes of molecular biology, investigators are now turning their attention to transmembrane transport of particles in natural and synthesized biopolymers. Membranes, which separate regions of space with different physical and

---

*Temporary Scientific Collective Otklik (Response).