

Study of the Properties of an Excess Electron in Liquid Helium. I. The Nature of the Electron–Helium Interactions

JOSHUA JORTNER, NEIL R. KESTNER,* STUART A. RICE, AND MORREL H. COHEN

Departments of Chemistry and Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

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In this paper we present a theoretical study of the free and localized states of an excess electron in liquid helium. Electron–helium interactions are treated by the pseudopotential method, while multiple scattering effects on the properties of a quasifree electron in the dense fluid are treated using the Wigner–Seitz model. It is demonstrated that the plane-wave state is not the lowest energy state for an excess electron in liquid helium and that fluid deformation leads to a localized state of lower energy. The large, repulsive helium-atom pseudopotential coupled with the small helium polarization potential lead to electron localization which may be attributed entirely to short-range repulsions. The following experimental observations are adequately interpreted by these results: (a) The energy barrier of liquid helium for electrons, (b) the density-dependent transition from a delocalized state to a localized state of the excess electron, (c) the mobility of an excess electron in normal ^4He and in ^3He . Pressure and temperature effects on the electron bubble are also discussed. It is concluded that a pressure-induced transition from the localized to the delocalized state of the excess electron will not occur in the fluid domain even at high pressures. Finally, we present some speculations concerning the optical properties of the excess-electron center.

I. INTRODUCTION

THE use of slow electrons, generated *in situ*, as a probe for the study of superfluid helium was introduced by Williams,^{1a} by Careri,^{1b} and by Meyer and Reif.² It is interesting that several phenomena can be elucidated without knowledge of the details of the nature of the interaction between the electron and the fluid. Thus, the temperature dependence of the ion mobility in liquid ^4He at temperatures below the lambda point may be successfully interpreted in terms of ion–roton scattering.² Also, Rayfield and Reif³ have successfully used electrons to characterize the behavior of quantized vortex rings in the superfluid, and magnetic deflection experiments by Meyer⁴ have shown that the effective mass of the electron in superfluid helium is large.

Now, unlike the experiments cited, an understanding of the magnitude of the mobility of the electron in liquid He requires a detailed study of the nature of the scattering mechanism as well as a quantitative description of the changes in the structure of the liquid caused by the excess electron. It is just this problem which we attack in this paper, focusing attention on the electron mobility in liquid ^4He and ^3He above 2.2°K, where there is no superfluid behavior. The electron–liquid–He system under these conditions is of interest for two reasons:

(a) The electron–helium–atom interaction is easier to calculate from first principles than that corresponding

to the interaction of an electron with larger atoms. For this reason, and because of the strength of the electron–He-atom pseudopotential,⁵ this system is an interesting prototype with which to understand the properties of isolated electrons in simple, nonpolar liquids.

(b) Sanders and Levine⁶ have demonstrated that, as the density of He is increased in the gas phase at 4°K, a critical density is reached at which the mobility of the electron drops a factor of 10^3 to 10^4 . These observations have been interpreted as indicating that the electron in He undergoes a transition from a delocalized state to a localized state as the He is compressed from gaseous densities to liquid densities. An understanding of this behavior may lead to valuable insights into the nature of the transition between delocalized and localized states in other systems.

To date, three models have been proposed to explain the properties of excess electrons in liquid He:

(a) The electron is localized within a cluster of He atoms which, because of the effects of electrostriction, are at a higher density than the surrounding fluid.⁷ The size of the cluster is determined by assuming that the macroscopic equation of state may be extended to provide a valid density–pressure relationship (and hence phase–equilibrium line) at the molecular level. Since it is unlikely that any complex of the form He_n^- is stable, this model is not considered further.

(b) The electron is localized in a cavity in the

* Present address: Department of Chemistry, Stanford University, Palo Alto, California.

¹ (a) R. L. Williams, *Can. J. Phys.* **35**, 135 (1957); (b) G. Careri, F. Scaramuzi, and J. O. Thomson, *Nuovo Cimento* **13**, 186 (1959).

² L. Meyer and F. Reif, *Phys. Rev.* **119**, 1164 (1960).

³ G. S. Rayfield and F. Reif, *Phys. Rev. Letters* **11**, 305 (1963).

⁴ L. Meyer, *Proc. Intern. Conf. Low Temp. Phys.* 9th, Columbus, Ohio, 1964 (to be published).

⁵ (a) N. R. Kestner, J. Jortner, M. H. Cohen, and S. A. Rice, "Low Energy Elastic Scattering of Electrons and Positrons by Helium Atoms" (to be published); (b) J. Jortner, N. R. Kestner, M. H. Cohen, and S. A. Rice, "The Electron Helium Atom Pseudopotential," in *New Developments in Quantum Chemistry—Isianbul Lectures* (Academic Press Inc., New York, to be published).

⁶ J. Levine and T. M. Sanders, *Phys. Rev. Letters* **8**, 159 (1962).

⁷ K. R. Atkins, *Phys. Rev.* **116**, 1339 (1959).

liquid.^{6,8-11} If the electron-atom repulsion is sufficiently strong, this state of local fluid dilation may lead to a stable state despite the large increase in the kinetic energy of the electron which accompanies the localization in the bubble. Hydrodynamic motion of the bubble and enclosed electron is characterized by a large electron effective mass.

(c) The electron is a quasifree particle, basically in a plane-wave state, and scattered by the atoms constituting the dense fluid.¹² When the electron-atom interaction is small, or is attractive because of a long-range polarization interaction, this description will be accurate.

Davis, Rice, and Meyer¹² have treated the electron as a quasifree particle scattered from the atoms in the liquid, with coherence between single scattering from separate centers being accounted for in terms of the radial distribution function of the liquid. It is now known that the electron-He-atom pseudopotential is large and positive.⁵ Experimental confirmation of this conclusion is provided by Sommers' experiment,¹³ which demonstrates that liquid helium (both above and below the lambda point) acts as an energy barrier of magnitude 1.3 eV for electrons. Because of the very large electron-helium-atom interaction, the local structure of the liquid may be changed, and a substantially lower energy state is accessible to the electron if there can be created a cavity in the liquid sufficiently large to reduce the zero-point energy of the localized electron, without costing too much pressure-volume or surface-tension work. This is the factor that leads to the failure of the quasifree-electron model for an electron in liquid helium. On the other hand, the interaction between an electron and an argon atom is strong and attractive, but of long range. Because of the sign and the range of the potential, no cavity formation is expected, and the quasifree-electron state should be energetically favored. Schnyders, Meyer, and Rice¹⁴ have recently obtained preliminary data on the mobility of excess electrons in liquid argon. The magnitude of the field-independent mobility ($500 \text{ cm}^2 \text{ V}^{-1} \cdot \text{sec}^{-1}$ at $T=90^\circ\text{K}$) and its temperature dependence ($T^{-3/2}$) are consistent with the predictions of the single scattering model.¹⁵

⁸ R. P. Feynman, quoted in Ref. 9.

⁹ C. G. Kuper, Phys. Rev. **122**, 1007 (1961).

¹⁰ R. A. Ferrel, Phys. Rev. **108**, 167 (1957).

¹¹ L. Onsager, in *New Developments in Quantum Chemistry—Instanbul Lectures* (Academic Press Inc., New York, to be published).

¹² (a) H. T. Davis, S. A. Rice, and L. Meyer, Phys. Rev. Letters **9**, 81 (1962); (b) H. T. Davis, S. A. Rice, and L. Meyer, J. Chem. Phys. **37**, 947, 2470 (1962).

¹³ W. T. Sommer, Phys. Rev. Letters **12**, 271 (1964).

¹⁴ H. Schnyders, L. Meyer, and S. A. Rice, Phys. Rev. Letters **15**, 187 (1965).

¹⁵ The original analysis presented by Davis, Rice, and Meyer¹² has been modified to include a more general pseudopotential (expressed in terms of the scattering length), and an omitted numerical factor of 4π in the density of states (which was overlooked in the original work) has been included.

We have alluded to structural changes in liquid helium near an electron. A model in which the electron is localized in a bubble has been proposed by Ferrel,¹⁰ Feynman,⁸ and Kuper.⁹ In liquid helium, it appears that the electron-atom repulsion is so large that a local fluid dilation does lead to a state of lower free energy than the quasifree-electron state. The basic idea is, of course, that a stable configuration of the system is achieved by a balance between the electron-atom repulsions (summed over all surrounding atoms), the increased kinetic energy of the electron due to localization in the bubble, the contractible force on the bubble resulting from surface tension, and the pressure-volume work of creation of the bubble. To date only simple model calculations have been published in which the nature of the electron-helium-atom interaction is not considered, and simple particle-in-a-box models have been used. In these considerations the bubble boundary was taken as an infinitely steep potential wall, whereupon the bubble boundary becomes infinitely sharp. In addition, macroscopic parameters were used to describe the bubble. In the present work, we used the physical ideas already inherent in the Kuper-Sanders model, but discuss a number of the features of the electron-atom interaction that have up to now been ignored.

II. ELECTRON-HELIUM-ATOM INTERACTION

The first step in developing a quantitative description of the system electron plus liquid He is the determination of the electron-He-atom interaction. Recent work in this laboratory has been concerned with the calculation of the electron-He-atom pseudopotential,^{16,5} and, from that pseudopotential, the cross section for low-energy scattering of electrons from He atoms. The agreement between experiment and theory is good, thereby indicating that the pseudopotential provides an accurate and physically incisive description of the electron-He-atom interaction. Since this calculation is described in detail elsewhere,⁵ here we merely note that the calculated pseudopotential is based on the following:

(i) The pseudopotential V_{ps} is defined by¹⁶

$$V_{ps} = V + V_R,$$

$$V_R \phi = - \sum_c \chi_c \langle \chi_c | V | \phi \rangle, \quad (1)$$

where ϕ is a pseudowavefunction which is equal to the one-electron self-consistent-field wavefunction ψ at large distances from the atom, but inside the core has the oscillations of ψ removed. The functions χ_c are core orbitals. The wavefunction ψ satisfies the one-electron

¹⁶ (a) J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959); (b) M. H. Cohen and V. Heine, *ibid.* **122**, 1821 (1961); (c) B. Austin, V. Heine, and L. J. Sham, *ibid.* **127**, 276 (1962).

self-consistent-field eigenvalue equation

$$(T+V)\psi=\epsilon\psi. \quad (2)$$

(ii) In Eq. (1), V_R is a nonlocal repulsive potential defined by the transformation of (1) to read

$$(T+V+V_R)\phi=\epsilon\phi, \quad (3)$$

and the condition that the eigenvalues of Eqs. (2) and (3) are the same. When, of the possible transformations, that one is chosen which leads to the smoothest orbitals (in the sense of having the lowest kinetic energy), the second of Eqs. (1) is obtained.

(iii) The effective core potential V is constructed from the sum of the nuclear, Coulomb, and exchange potentials, plus the polarization potential arising from the small distortion of the atom by the electronic charge.

(iv) The numerical calculation of the pseudopotential is, finally, based on the use of the Bagus-Gilbert nominal set¹⁷

$$\chi_c=0.18159\varphi_{1s}(2.906)+0.84289\varphi_{1s}(1.453) \quad (4)$$

for the Hartree-Fock orbitals of He. In Eq. (4), $\varphi_{1s}(z)$ is a normalized Slater $1s$ function with orbital exponent z . In Fig. 1 is displayed the total potential for the scattering of an electron in a quasifree plane-wave state [$\phi = \exp(ik \cdot R)$] by He atoms, calculated in the manner outlined for the limiting case $\mathbf{k} \rightarrow 0$. As mentioned, there is good agreement between the observed and computed scattering lengths using this pseudopotential.

III. ESTIMATE OF THE BARRIER TO PENETRATION OF LIQUID He BY AN ELECTRON

It has already been mentioned that a plane-wave state for the electron in liquid He lies at positive energy relative to the vacuum level, which implies that the liquid acts as a barrier to the passage of electrons from vacuum into the liquid. Now, under the conditions of Sommer's experiment,¹³ the electrons move rapidly relative to the He atoms, and it may be assumed that the He atoms do not rearrange in the process of electron injection. In the adiabatic limit just described, it is easy to obtain several complementary estimates of the energy of interaction of the electron and the liquid He.

Consider first a first-order perturbation calculation which gives a rough estimate of the electron-helium interaction. The wavefunction for the electron in a plane-wave state is taken to be

$$|k\rangle = \Omega^{-1/2} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (5)$$

where Ω is the volume. The electron-helium interaction (to first order) is then

$$E(k) = \langle k | T + \sum_{i=1}^N (V + V_R)_i | k \rangle, \quad (6)$$

$$E(k) = (\hbar^2 k^2 / 2m) + \rho \langle k | V + V_R | k \rangle, \quad (7)$$

¹⁷ P. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. Cohen (to be published).

where T is the kinetic energy, V is the atomic SCF potential plus polarization, V_R is the nonlocal repulsive potential for the plane-wave state,⁵ the sum is over all atoms in the liquid, and the density $\rho = N/\Omega$, where N is the number of helium atoms. For $\mathbf{k} = 0$

$$E(0) = 4\pi\rho \int (V + V_R) r^2 dr. \quad (8)$$

The Fourier transform of the pseudopotential is almost energy independent in the region 0 to 0.5 eV, and leads to $E(0) = 1.26$ eV.

The first-order perturbation treatment sketched above is equivalent to the application of the Born approximation. However, at low energies the pseudopotential is obviously too large for the Born approximation to be applicable (see Fig. 1). The proper approach would be to rewrite the electron-helium interaction in terms of the t matrix^{18a} rather than the pseudopotential and to use the experimental value of t for low-energy scattering, so that

$$\int (V + V_R) r^2 dr \rightarrow \langle 0 | t | 0 \rangle = (\hbar^2 / 2m) a, \quad (9)$$

where $|0\rangle$ is the exact wavefunction of the electron for $\mathbf{k} = 0$ and a is the scattering length. This leads to the familiar result

$$E(0) = (2\pi\hbar^2/m)\rho a. \quad (10)$$

From Eq. (10) we get $E(0) = 0.6$ eV. Equation (10) represents an optical approximation which underesti-

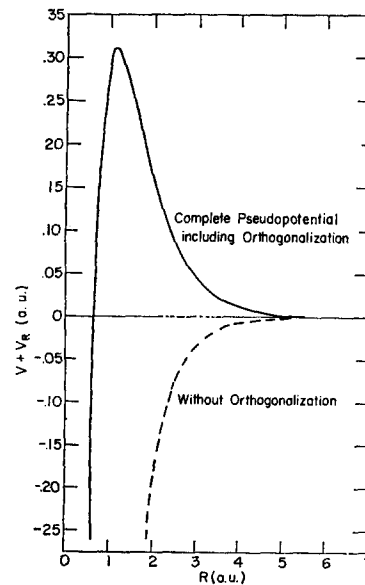


FIG. 1. The electron-helium-atom pseudopotential as a function of the electron-atom separation. The pseudopotential was calculated for a plane-wave state in the limit $k \rightarrow 0$.

¹⁸ (a) See, for example, A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1962), Vol. 2, p. 806; (b) see, for example, F. Seitz, *Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

mates the value of $E(0)$ because the increase of the electronic kinetic energy associated with multiple scattering is not taken into account. To obtain an estimate of the multiple scattering effects, we apply the Wigner-Seitz model^{18b} to an electron in a helium crystal.

We represent each helium atom by an equivalent hard sphere of radius a , the scattering length. The electron wavefunction is then

$$\psi = [\sin k(r-a)/r], \quad (11)$$

while the equivalent sphere size r_s is related to the density by

$$1/\rho = \frac{4}{3}\pi r_s^3.$$

The boundary conditions on ψ_0 , the electron wavefunction of lowest energy, require the vanishing of $d\psi_0/dr$ at the boundary of the equivalent sphere. This leads to

$$\tan k_0(r_s - a) = k_0 r \quad (12)$$

for the determination of the wavenumber, k_0 , characteristic of the lowest energy state, whose energy is

$$E_0 = \hbar^2 k_0^2 / 2m. \quad (13)$$

In the limiting case $k_0(r_s - a) \ll 1$, Eq. (13) takes the form

$$E_0 = \frac{2\pi\rho a}{[1 - (a/r)]^2} \frac{\hbar^2}{m}, \quad (14)$$

which provides a correction term to the result obtained from Eq. (10), arising from the exclusion of the electron from the region occupied by the hard spheres. Since in almost all cases $k_0 r_s$ is of order unity, the condition for the applicability of Eq. (14) is that $a \approx r_s$, which is not correct for liquid helium. A direct solution of Eq. (12) for k_0 leads to the results presented in Table I for a quasifree-electron interacting with helium fluid at several densities. The calculated energy of an excess electron in a hypothetical helium lattice characterized by the liquid density is found to be $E_0 = 1.04$ eV.

Recent experimental work¹⁸ has shown the potential barrier of liquid helium to electrons to be 1.3 ± 0.3 eV, in good agreement with the 1.04 eV calculated here,¹⁹ especially since a barrier experiment of this form must determine an upper limit to the barrier.

IV. SOME ELEMENTARY ESTIMATES OF THE PROPERTIES OF AN ELECTRON IN A CAVITY

The pseudopotential formalism may also be used conveniently in the study of the localized state of the

¹⁹ Recently, a calculation of the energy of an electron interacting with a periodic lattice of helium atoms was performed. The quasifree-electron-helium interaction was represented by the experimental scattering length [B. Burdick, Phys. Rev. Letters 14, 11 (1965); L. Onsager, Ref. 11]. This treatment leads to an interaction energy of 1.09 eV at liquid-helium density, in excellent agreement with the results of the Wigner-Seitz model.

TABLE I. Energy calculations for plane-wave electrons in helium.

Density (a.u.)	Wave vector k_0 [Eq. (12)] (a.u.)	Energy (a.u.)		
		Born ap- proximation (first-order perturbation theory)	Exact single scattering result	Wigner- Seitz model
0.2813×10^{-2} (liquid density) 4.2°K	0.277	0.0463	0.0221	0.0384
0.2813×10^{-3}	0.072	0.00463	0.00221	0.00259
0.1407×10^{-3}	0.051	0.00232	0.00111	0.00130

excess electron. A direct solution of this problem in the SCF scheme is obviously impossible at present, while the pseudopotential formalism makes the problem tractable.

We start with the assumption that the electron is in a localized state, and therefore require that the electron wavefunctions tend to zero for large distances from the center of localization. For convenience, a simple one-parameter smooth wavefunction of the form

$$\phi_\xi(\mathbf{r}) = (\xi^3/\pi)^{1/2} \exp(-\xi |\mathbf{r} - \mathbf{r}_0|) \quad (15)$$

is used to describe the excess electron.²⁰ Note that this wavefunction is referred to a coordinate system centered at \mathbf{r}_0 , which is also taken to be the center of the cavity in the liquid. As usual, ξ is a variational parameter to be used in the minimization of the energy.

The electronic energy is written in the form

$$E_e(\xi) = \langle \phi_\xi | -(\hbar^2/2m)\nabla^2 + V_{ps}(\xi) | \phi_\xi \rangle \quad (16)$$

and is stationary with respect to the variation of ξ , i.e.,

$$\partial E_e(\xi) / \partial \xi = 0.$$

The electronic energy of the system, for a constant fluid configuration, can now be displayed in the form

$$E_e(\xi) = \frac{\hbar^2 \xi^2}{2m} + \int v_\xi(\mathbf{r}) \rho(\mathbf{r}) d^3r, \quad (16')$$

²⁰ This 1s hydrogenic-type variational wavefunction is not entirely satisfactory for small values of $|\mathbf{r} - \mathbf{r}_0|$ since there is a cusp in the center, introduced only by Coulomb interaction. However, the variational calculations of the energy of interaction of the excess electron with helium atoms at distances larger than 10 a.u. should not be affected by the presence of this cusp. An alternative choice for a variational wavefunction would be that corresponding to a particle in a box with finite walls, $\phi(\mathbf{r}) = (\sin k |\mathbf{r} - \mathbf{r}_0| / |\mathbf{r} - \mathbf{r}_0|)$ for $|\mathbf{r} - \mathbf{r}_0| < R_0$ and $\phi(\mathbf{r}) = \exp(-\xi |\mathbf{r} - \mathbf{r}_0|) / |\mathbf{r} - \mathbf{r}_0|$ for $|\mathbf{r} - \mathbf{r}_0| > R_0$. Still another different function might be considered: $\phi(\mathbf{r}) = \exp(-\beta |\mathbf{r} - \mathbf{r}_0|^2)$. In the variational treatment of strongly coupled polaron states [S. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akademie-Verlag, Berlin, 1954)] where the interaction potential between the electron and the medium is finite (and not Coulombic) at small distances, the hydrogenic 1s-type wavefunction and the Gaussian wavefunction lead to practically identical results.

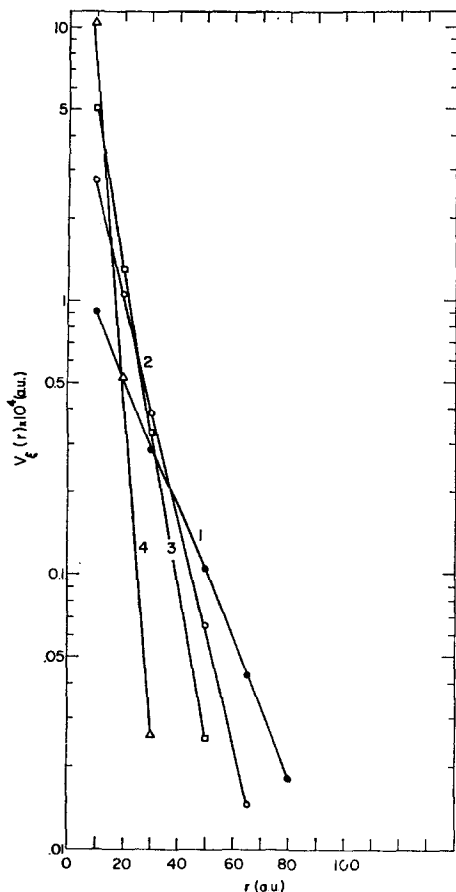


FIG. 2. The electron-helium-atom diagonal matrix element of the pseudopotential for a localized $1s$ state. (1) ●, $\xi=0.03$ a.u., (2) ○, $\xi=0.05$ a.u., (3) □, $\xi=0.07$ a.u., (4) △, $\xi=0.15$ a.u.

where

$$v_{\xi}(r) = \langle \phi_{\xi} | V + V_R | \phi_{\xi} \rangle \quad (17)$$

and $\rho(r)$ is the density of He atoms a distance r from the center of the cavity.

The pseudopotential (1) for the localized state is displayed in the form

$$V_{ps}(\xi)\phi_{\xi} = (V_{\text{coul}} + V_{\text{nuc}} + V_{\text{exc}})\phi_{\xi} - \langle \chi_c | V_{\text{coul}} + V_{\text{nuc}} + V_{\text{exc}} | \phi_{\xi} \rangle | \chi_c \rangle, \quad (18)$$

where V_{coul} , V_{nuc} , and V_{exc} are the Coulomb, nuclear, and exchange interaction potentials of the excess electron with the helium core. A straightforward calculation leads to the result

$$\begin{aligned} v_{\xi}(r) &= \langle \phi_{\xi} | V_{ps}(\xi) | \phi_{\xi} \rangle \\ &= 2 \langle \phi_{\xi}(1)\phi_{\xi}(1) | 1/r_{12} | \chi_c(2)\chi_c(2) \rangle \\ &\quad - 2 \langle \phi_{\xi} | 1/r_1 | \phi_{\xi} \rangle - \langle \chi_c(1)\phi_{\xi}(1) | 1/r_{12} | \chi_c(2)\phi_{\xi}(2) \rangle \\ &\quad - \langle \phi_{\xi} | \chi_c \rangle \langle \chi_c(1)\phi_{\xi}(1) | 1/r_{12} | \chi_c(2)\chi_c(2) \rangle \\ &\quad + 2 \langle \phi_{\xi} | \chi_c \rangle \langle \chi_c | 1/r_1 | \phi_{\xi} \rangle. \quad (19) \end{aligned}$$

In contrast to our previous treatment of quasifree-electron scattering by He atoms,⁶ in the present case two-center interactions between the localized excess electron and the helium atoms must be considered. These two-center integrals were calculated on an IBM 7094 using the molecular integrals programs written by A. C. Wahl and P. Cade at the Laboratory of Molecular Structure and Spectra, the University of Chicago.

To evaluate $E_e(\xi)$, it is necessary to specify the form of the density distribution $\rho(r)$. We have used the simple distribution

$$\begin{aligned} \rho(r) &= 0, & r < R_0, \\ \rho(r) &= \rho \{ 1 - [1 + \alpha(r - R_0)] \exp[-\alpha(r - R_0)] \}, & r > R_0, \quad (20) \end{aligned}$$

where α and R_0 are variational parameters, R_0 corresponding to the cavity radius, and α^{-1} measuring the thickness of the boundary layer. When $\alpha \rightarrow \infty$, the density distribution reduces to the step-function form

$$\begin{aligned} \rho(r) &= 0, & r < R_0, \\ \lim_{\alpha \rightarrow \infty} \rho(r) &= \rho, & r > R_0. \quad (20') \end{aligned}$$

It should be noted that

$$\lim_{R_0 \rightarrow 0, \xi \rightarrow 0} E_e = 4\pi\rho \int v_0(r)r^2 dr$$

which is just the Fourier transform, evaluated at $k=0$, of the pseudopotential for an electron in a plane-wave state in interaction with an He atom (see Fig. 1). Thus, in the limit cited, the energy E_e is identical to the energy computed from first-order perturbation theory in the quasifree-electron model.

In Fig. 2 is displayed the diagonal matrix element of the pseudopotential for the range of values of ξ of interest. Of course, since the pseudopotential depends on the pseudowavefunction used, the pseudopotential for the localized state differs from that for the plane-wave state.

We now examine the electronic energies corresponding to bubble sizes and boundary widths and for different fluid densities. The orbital exponents corresponding to the density distribution of Eq. (20'), the infinitely thin boundary layer, for several different densities are displayed in Fig. 3. In Fig. 4 is shown the electronic energy obtained for two fluid densities, again for the density distribution defined in Eq. (20').

It is instructive at this point to compare the results of the present calculation with calculations based on the electron in a box model. For the case of a spherical box with infinite walls, $E_e = \pi^2/2R_0^2$ a.u. As is apparent

from Fig. 4, at the normal density of liquid He, the results of our calculation are not appreciably different from those of the simple box model. However, at the lower fluid densities and small R_0 , the box model is inadequate because it cannot account for the substantial charge leakage to the region outside the bubble.

Before closing this discussion we should point out that in the present calculations for the localized state the effect of electronic polarization of the medium by the excess electron has not been included. We consider an excess-electron trapping center which nearly preserves the charge distribution of the atoms constituting the fluid. In view of the low polarizability of the helium atom it appears that core polarization effects due to the excess electron are small. For the energy of a quasi-free-electron in a plane-wave state in liquid helium, we obtain from first-order perturbation theory 4.85×10^{-2} a.u. when polarization effects are included, and 5.38×10^{-2} a.u. when polarization effects are neglected. In the localized state of the excess electron, the contribution of the electronic polarization also appears to be small. The contribution of the polarization energy in the localized state of an electron in a bubble of radius R_0 , neglecting penetration effects, can be expressed as $E_p = 2\pi\rho\alpha e^2/R_0$, where α is the atomic polarizability.

For the case of liquid helium, setting $R_0 = 40$ a.u., we obtain $E_p = 0.60 \times 10^{-3}$ a.u. to be compared with the electronic energy $E_e = 0.61 \times 10^{-2}$ a.u. calculated neglecting polarization effects. Hence, the error involved in neglecting polarization effects does not exceed 10%.

V. TOTAL ENERGY OF THE SYSTEM—THE BUBBLE MODEL

We have as yet not calculated the total energy of the system under investigation, nor have we examined the nature of the configuration determined by minimizing the free energy of the system. It is this task to which we now turn.

The total energy of the system, E_t , is, in our approximation, simply the sum of the electronic energy and

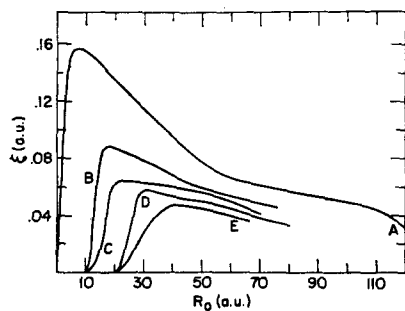


FIG. 3. The dependence of the excess-electron 1s-wavefunction orbital exponent on the cavity size and on the fluid density. A, $\rho = 1.9 \times 10^{21}$; B, $\rho = 3.8 \times 10^{20}$; C, $\rho = 1.9 \times 10^{20}$; D, $\rho = 1.6 \times 10^{20}$; and E, $\rho = 3.5 \times 10^{19}$ atom/cc.

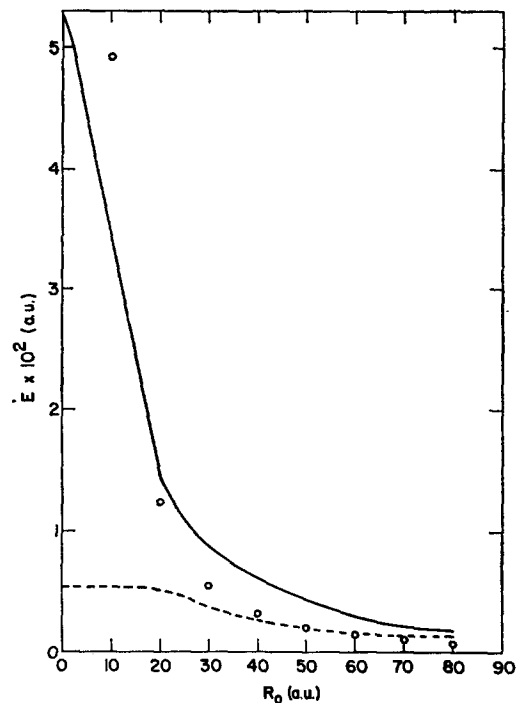


FIG. 4. The dependence of the electronic energy of a localized state of the excess electron on the cavity size. These results were obtained by the variation method using the pseudopotential approximation and the density distribution. —, liquid helium density at 4.2°K and 1 atm ($\rho_0 = 1.9 \times 10^{22}$ atom/cc); - - -, gas density at 4.2°K and 0.85 atm ($\rho = 1.9 \times 10^{21}$ atom/cc). Open circles represent the electron in the box model.

the energy required for bubble formation, E_b ,

$$E_t = E_e + E_b, \quad (21)$$

and the energy, E_t , is to be minimized with respect to the parameters determining the bubble size and boundary-layer thickness,

$$\partial E_t / \partial R_0 = 0, \quad \partial E_t / \partial \alpha = 0. \quad (22)$$

Consider first the simple classical expression

$$E_b = 4\pi R_0^2 \gamma(R_0) + \frac{4}{3}\pi p R_0^3, \quad (23)$$

which represents the work of formation of the bubble, at constant pressure, as the sum of surface work and volume work terms. Note that in Eq. (23) p is the pressure, $\gamma(R_0)$ is a size-dependent surface tension, and the relation displayed is written for the limit $\alpha \rightarrow \infty$. The surface tension $\gamma(R_0)$ may be taken, in two different approximations, as either the (size-independent) surface tension at the liquid-vapor interface, or the energy expended on introduction of a spherical cavity in a classical rigid-sphere fluid. In the latter case, the interfacial tension between the rigid-sphere fluid and

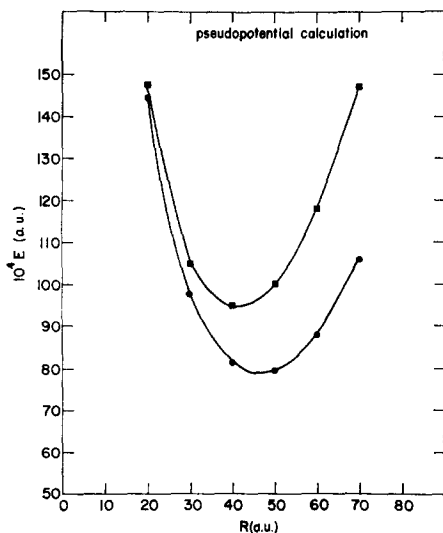


FIG. 5. The ground-state energy of a localized excess electron in liquid helium at 4.2°K and 1 atm. Calculations for $\gamma=0.098$ dyn/cm (experimental surface tension) and for $\gamma=0.22$ dyn/cm are indicated, respectively, by circles and squares (for the statistical model of Reiss *et al.*).

a perfect rigid wall can be expressed as²¹

$$\gamma(R_0) = \gamma_0 [1 - (2\delta/R_0)], \quad (24)$$

where

$$\begin{aligned} \gamma_0 &= (kT/4\pi\sigma^2)(x+18x^2) - \frac{1}{2}p\sigma, \\ \delta &= \frac{1}{4}\sigma \left[\frac{6x+18x^2 - \pi p\sigma^3/kT}{6x+9x^2 - \pi p\sigma^3/kT} \right], \\ x &= \frac{(\pi\rho\sigma^3/6)}{1 - (\pi\rho\sigma^3/6)}, \end{aligned} \quad (25)$$

and σ is the diameter of the rigid-sphere molecule. For He, $\sigma=2.56$ Å, and Eqs. (24) and (25) lead to the prediction²¹ that $\gamma_0=0.22$ dyn/cm at 4.2°K, which should be compared with the experimental liquid-vapor surface tension²² of $\gamma_0=0.096$ dyn/cm. Only at liquid densities is the surface work an important contribution to E_b ; at lower densities (say the saturated vapor density at 4.2°K and 1 atm) the surface contribution to E_b is wholly negligible.

In Fig. 5 we display the results of the calculations for the total ground-state energy of a localized excess electron in liquid He. The calculations shown are for the density distribution (20') and used the two different approximations to the surface work mentioned above. The results are also summarized in Table II. At high densities, as already noted, the penetration of the surrounding medium by the excess electron is extremely

²¹ H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.* **32**, 119 (1960).

²² G. A. Cook, *Argon, Helium and the Rare Gases* (Interscience Publishers, Inc., New York, 1962).

small. For liquid He at 4.2°K, and $p=1$ atm, $\zeta=0.09$ a.u., whereupon about 98% of the excess-electron charge density is localized within the bubble of radius 40 a.u.

The temperature dependence of the bubble size is relevant for the interpretation of the temperature dependence of the mobility of negative ions in normal liquid helium.²³ It should also be noted that the bubble size in superfluid helium is of considerable interest with relation to the interpretation of the cross sections for the interaction of the negative ion and quantized vortex rings in rotating He II.²⁴ In Table II we display the calculated temperature dependence of R_0 , obtained using only the surface term to define the configuration changes of the fluid. It is seen that the bubble size decreases by 20% as T decreases from 4.2°K to the lambda point. Below the lambda point the temperature effect is smaller because of the slow change of the surface tension with temperature in that region.

In contrast with the preceding, when the He density is low and the surface work negligibly small,

$$E_b = p \int \left(1 - \frac{\rho(r)}{\rho} \right) d^3r, \quad (26)$$

so that

$$E_b = \frac{4\pi}{3} p R_0^3 \left[1 + \frac{6}{\alpha R_0} + \frac{18}{(\alpha R_0)^2} + \frac{24}{(\alpha R_0)^3} \right] \quad (26')$$

using the density distribution (20). In Fig. 6 and Table III is displayed the total ground-state energy of an excess electron in He in the density range $0.01 \leq \rho/\rho_0 \leq 0.1$, with ρ_0 the liquid density at 4.2°K. From these results it becomes apparent that for large R_0 (~ 40 a.u.; where the minimum energy is attained) the values of α which minimize the energy are large. Since α^{-1} measures the thickness of the boundary layer, this result supports the use of the simple density distribution (20')

TABLE II. The ground-state energy of an excess electron in liquid helium calculated for the steep bubble approximation.

Model	T (°K)	γ (dyn/cm)	R_0 (a.u.)	E (a.u.)	ζ (a.u.)
a	4.2	0.098	46	7.9×10^{-3}	0.084
a	4.2	0.223	40	9.5×10^{-3}	0.095
b	4.2	0.098	42	5.1×10^{-3}	...
b	4.2	0.223	41	6.5×10^{-3}	...
a	2.2	0.29	38	10.6×10^{-3}	0.10
a	0.5	0.37	36	11.5×10^{-3}	0.103

^a Pseudopotential variational calculation.

^b Particle in box model.

²³ L. Meyer, H. T. Davis, S. A. Rice, and R. J. Donnelly, *Phys. Rev.* **126**, 1927 (1962).

²⁴ R. J. Donnelly, *Phys. Rev. Letters* **14**, 39 (1965).

in the high density limit. This result derives from the fact that the electron-He-atom interaction is so strongly repulsive that leakage of the He atoms into the cavity, where the electron density is high, greatly increases the energy of the system. When R_0 is small, smaller values of α lead to the minimum energy, so that there is a possible continuous distribution of boundary widths coupled with bubble sizes.

Having estimated the energies of both the localized state and the quasiparticle-wave state, can we determine which is lowest in energy? In Fig. 7 these energies are compared over a range of fluid density. Since the cal-

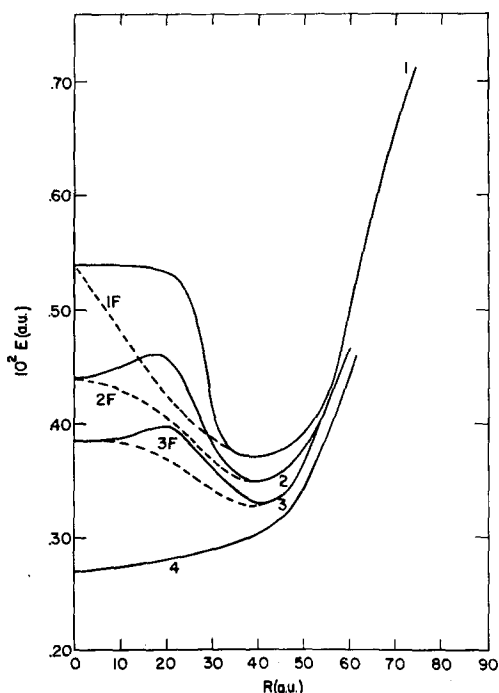


FIG. 6. The energy of a localized electron in helium at low densities. The calculations were performed for isobaric energy curves at 1 atm. The solid curves represent results for the sharp bubble, while the dashed curves represent the data for the fuzzy bubble. (1) $\rho/\rho_0=0.1$, (2) $\rho/\rho_0=1/12$, (3) $\rho/\rho_0=1/14$, (4) $\rho/\rho_0=1/20$.

culations in each case were made using the variational method, the separate energies represent upper limits to the energies of the states considered. Hence, the lower of the two energies at each density is expected to represent the more stable of two configurations.²⁵ Examination of Fig. 7 leads to the conclusion that the localized state is stable relative to the plane-wave state at high He densities. It should be stressed, again, that the electron localization in liquid He arises from strong short-range electron-atom repulsion, and is basically different from the trapping of electrons in liquid NH_3

²⁵ This is correct only if the uncertainties in the two variational calculations are smaller than the energy separation between the two states.

TABLE III. Variational calculations of the total energy for the rigid and the fuzzy electron bubble models.

Density (a.u.)	R_0	Rigid bubble $10^8 E_t$ (a.u.)	Fuzzy bubble	
			α (a.u.)	$10^8 E_t$ (a.u.)
0.281×10^{-3}	0	0.538	...	0.538
	10	0.536	0.1	0.480
	20	0.530	0.133	0.424
	30	0.411	0.2	0.386
	40	0.370	1.0	0.369
	50	0.390	3.0	0.390
	60	0.495	3.0	0.495
0.233×10^{-3}	0	0.448	...	0.448
	10	0.450	0.22	0.425
	20	0.458	0.4	0.403
	30	0.382	1.0	0.364
	40	0.349	2.0	0.349
	50	0.373	3.0	0.373
	60	0.469	3.0	0.469
0.200×10^{-3}	0	0.384	...	0.384
	10	0.386	0.2	0.375
	20	0.397	0.25	0.368
	30	0.359	0.35	0.340
	40	0.327	2.0	0.330
	50	0.365	2.0	0.365
	60	0.461	2.0	0.461

or from polaron formation which is due to long-range interactions.²⁶

VI. TRANSITION FROM THE DELOCALIZED STATE TO THE LOCALIZED STATE

The experimental work of Sanders and Levine⁶ provides unambiguous experimental evidence for the fact

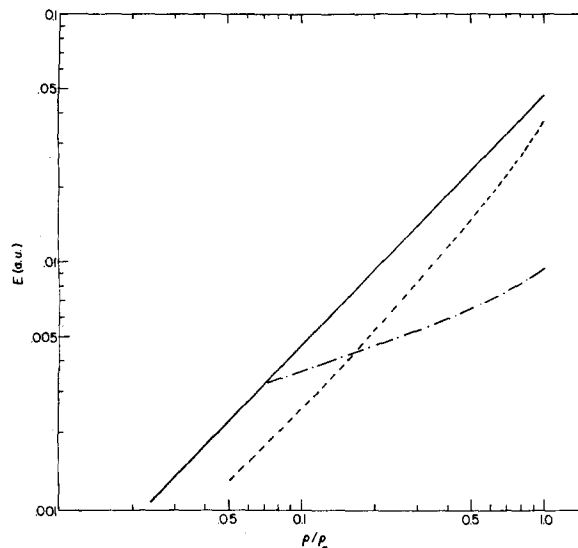


FIG. 7. The density dependence of the energy of the localized and the quasifree-electron states in helium. (—) quasifree electron: first-order perturbation theory; (---) quasifree electron: Wigner-Seitz model; (-·-) localized electron (1 atm) (ρ_0 normal helium density).

²⁶ J. Jortner, S. A. Rice, and E. G. Wilson, *Proceedings of the Weyl Conference on Metal Ammonia Solutions* (W. A. Benjamin, Inc., New York, 1964).

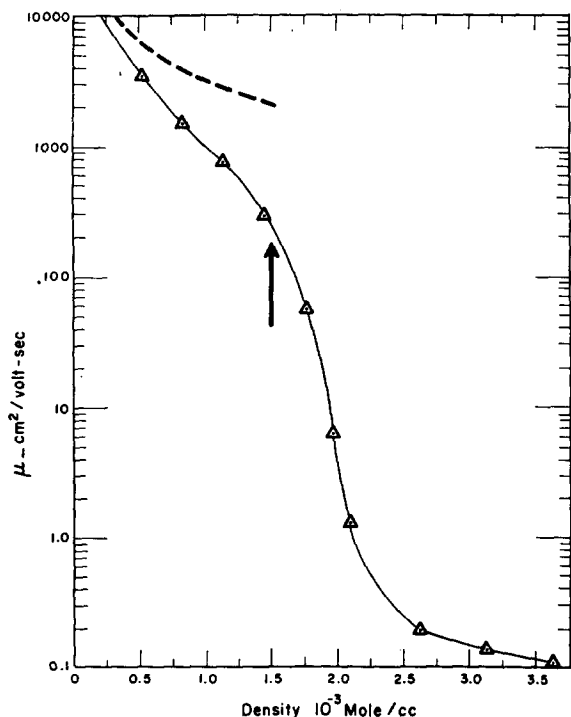


FIG. 8. Mobility data for electrons in helium gas at 4.2°K. The experimental data (solid curve) are taken from Ref. 6. The dashed curve represents the calculated free-electron mobility using a single scattering model. The arrow shows the calculated critical density for the transition from the delocalized to a localized state.

that the localized state of an electron in a bubble is not the configuration of lowest free energy at low densities. In the density region 0.6×10^{21} to 1.2×10^{21} atom/cc at 4°K, a critical density is reached at which the electron

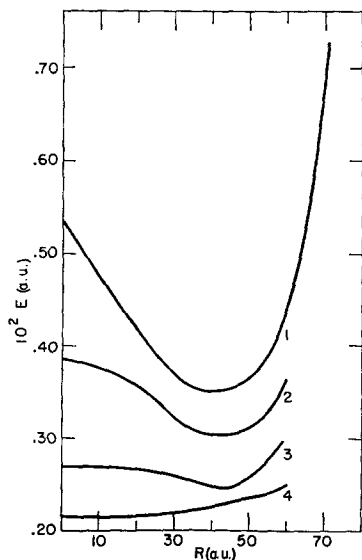


FIG. 9. The transition from the localized to the delocalized state of an excess electron in helium at 4.2°K (isothermal energy curves). (1) $\rho/\rho_0=0.1$, (2) $\rho/\rho_0=1/14$, (3) $\rho/\rho_0=1/20$, (4) $\rho/\rho_0=1/25$.

mobility drops by three to four orders of magnitude and a transition from the delocalized state to a localized state of the electron is observed (Fig. 8). In Table IV and Fig. 9 we present the isothermal energy curves for the density dependence of an excess electron in helium. In Table V we display the density dependence of the well depth for the localized state, defined as $\Delta\epsilon = E_{\text{free}} - E_l$. The occurrence of a transition from the free state to a localized state is manifested by the disappearance of the minimum corresponding to a bound state (i.e., $\Delta\epsilon \rightarrow 0$) at $\rho/\rho_0=0.045$, (i.e., at the density 0.9×10^{21} atom/cc). These results are summarized in Table VI. The calculated transition density is in good agreement with the experimental value derived from the mobility data of Sanders and Levine. This result

TABLE IV. Dependence of the energy of an excess electron in helium on the bubble diameter.

R_0 (a.u.)	$10^3 E$ (a.u.)			
	(a) Isobaric curves, $p=1$ atm			
	$\rho/\rho_0=0.050$	$\rho/\rho_0=0.071$	$\rho/\rho_0=0.083$	$\rho/\rho_0=0.100$
0	2.69	3.84	4.38	5.38
10	2.72	3.79	4.26	4.80
20	2.81	3.68	4.03	4.24
30	2.90	3.40	3.64	3.86
40	3.02	3.27	3.49	3.70
50	3.44	3.65	3.73	3.90
60	4.45	4.61	4.69	4.95
	(b) Isothermal curves, $T=4.2^\circ\text{K}$			
	$\rho/\rho_0=0.40$	$\rho/\rho_0=0.050$	$\rho/\rho_0=0.071$	$\rho/\rho_0=0.100$
0	2.14	2.68	3.85	5.38
10	...	2.67	3.74	4.69
20	2.14	2.65	3.57	4.20
30	...	2.58	3.20	3.70
40	2.26	2.48	3.04	3.53
50	...	2.57	3.10	3.66
60	2.50	3.02	3.64	4.47

may be readily rationalized by noting that at low densities the bubble is not the configuration of lowest energy since the volume work expended in creating a void is still relatively large, while lowering of the energy of the localized state relative to the energy of the plane-wave state is small at low densities. The agreement between the calculated and observed transition can be considered to represent a significant confirmation of the bubble model.

It is interesting to speculate about the possibility of a pressure-induced transition from the localized state to a delocalized state, since an increase in pressure should increase the volume work expended in creating the void and thereby tend to make the localized state unstable. For a rough estimate of the magnitude of the pressure required, we use the particle in a box model, a good approximation in the case of the dense fluid. When the energy expended in creating the void

is determined by the pressure [this is the case at high pressures when $(\frac{4}{3}\pi R_0^3) \rho \gg 4\pi R_0^2 \gamma$], the total energy is approximated by

$$E = (\pi^2 \hbar^2 / 2m R_0^2) + (4/3) \pi \rho R_0^3, \quad (27)$$

leading to

$$R_0 = (\pi \hbar^2 / 4m \rho)^{1/3} = 46.94 (\rho / \text{atm})^{-1/3} \text{a.u.}, \quad (28)$$

so that

$$E = 0.00372 (\rho / \text{atm})^{1/3} \text{a.u.} \quad (29)$$

Correspondingly, the delocalized plane-wave state energy is approximated by the results of first-order perturbation theory,

$$E_{\text{free}} = 0.0482 (\rho / \rho_0) \text{a.u.}, \quad (30)$$

where ρ_0 is the density of liquid helium at 4.2°K and at 1 atm. Unfortunately, as is evident from Table VII, the pressure necessary to induce the transition from the localized state to a delocalized state is always higher than the melting pressure of He: Along the fusion curve

TABLE V. The density dependence of the well depth for the localized state of an electron in helium.

ρ / ρ_0	$\Delta \epsilon \times 10^4$ (a.u.)	
	Isothermal 4.2°K	Isobaric $p = 1$ atm
0.050	2.0	...
0.071	8.0	5.7
0.083	12.4	9.9
0.100	18.4	15.0

of helium in the temperature region 4° to 40°K, $E < E_{\text{free}}$, so that the expected transition will not occur in the fluid domain.

VII. COMMENTS ON THE MOBILITY DATA

An *a priori* calculation of the mobility of an electron trapped in a bubble in liquid helium is fraught with difficulty. Clearly, since the penetration of the fluid by the charge distribution of the excess electron is small at high density, no bubble-to-bubble tunneling is expected. It might be argued that the bubble moves by expanding in one direction and contracting in another direction. This "amoeba motion" is improbable because too much energy is expended in moving a helium atom into the cavity, i.e., the bubble is essentially nondeformable on the thermal energy scale. Consider now the possibility that the motion of the charged bubble can be adequately described by classical hydrodynamics, at least above the lambda point. This is not unreasonable, as the calculated bubble radius is much larger than the interatomic separation. The bubble is then considered to be a rigid sphere moving through the liquid. The boundary conditions at the surface should be near-to-zero transverse velocity, i.e., both the radial

TABLE VI. Calculated critical densities for the transition from the delocalized to the localized state of an excess electron in helium.

Model for free-electron state	Experimental conditions	$(\rho / \rho_0)^c$	
		calc.	exptl.
a	Isobaric $p = 1$ atm	0.070	...
b	Isobaric $p = 1$ atm	0.17	...
a	Isothermal 4.2°K	0.045	0.035–0.070

^a First-order perturbation theory.

^b Wigner-Seitz model.

^c $\rho_0 = 1.92 \times 10^{22}$ atom/cc = 0.281×10^{-2} a.u. (density of normal ⁴He at 4.2°K and 1 atm).

velocity and the transverse velocity vanish at the surface. There should be no internal excitation due to flow since there can be no exchange of energy between the helium atom and the electron (the lowest electronic excitation energy is too high).

Since at the densities characteristic of liquid helium the particle in a box model provides a good approximation to the electronic energy, the ground-state energy at low pressure and high density can be roughly represented in the form

$$E = (\pi^2 \hbar^2 / 2m R_0^2) + 4\pi R_0^2 \gamma, \quad (31)$$

where

$$R_0 = (\pi \hbar^2 / 8m \gamma)^{1/2}. \quad (32)$$

The Stokes law mobility μ_- is then given by

$$\mu_- = \frac{e}{6\pi} \left(\frac{8m}{\pi \hbar^2} \right)^{1/2} \frac{\gamma^{1/2}}{\eta}, \quad (33)$$

where η is the fluid viscosity. In Table VIII we have displayed the relevant mobility data for electrons in ⁴He and ³He using the results of Meyer, Davis, Rice, and Donnelly.²³ It is apparent that the temperature dependence of the product $\mu_- \eta$ is almost exactly counterbalanced by the temperature dependence of the surface tension. These results provide support for the conjecture that the mechanism of negative charge transport in liquid helium involves the gross motion through the liquid of the bubble plus the trapped electron.

The calculated Stokes law mobility $\mu_- = e / 6\pi \eta R_0$ for a negative ion in liquid helium at 4.2°K and 1 atm is

TABLE VII. Bound- and free-electron energies in helium at the melting (fusion) pressure.

T_m^a (°K)	p_m^a (atm)	ρ (a.u.)	E (a.u.)	E_{free} (a.u.)
4	128.6	5.16×10^{-3}	2.57×10^{-2}	8.85×10^{-2}
10	580	6.61×10^{-3}	5.05×10^{-2}	11.3×10^{-2}
20	1740	8.0×10^{-3}	7.40×10^{-2}	13.7×10^{-2}
30	3280	8.8×10^{-3}	9.25×10^{-2}	14.6×10^{-2}
42	5600	11×10^{-3}	11.8×10^{-2}	18.9×10^{-2}

^a The melting temperature T_m and the melting pressure p_m from Cook, Helium, Argon and the Rare Gases (Ref. 22).

TABLE VIII. Mobility of electrons in liquid He I and ⁴He.

	Temperature (°K)	$\mu\eta$		$\gamma^{1/4}$	
		absolute	ratio	absolute	ratio
⁴ He	4.2	0.79	1.00	0.557	1.00
	3.0	0.94	1.19	0.682	1.22
	2.0	1.08	1.37	0.735	1.32
³ He	3.2	0.6	1.00	0.38	1.00
	1.2	1.0	1.67	0.604	1.60

0.0135 cm²/V·sec, which is somewhat lower than the experimental value. We conclude that the treatment described in this paper overestimates the bubble size.²⁷

VIII. SPECULATIONS ON THE OPTICAL SPECTRUM OF THE LOCALIZED ELECTRON IN HELIUM

At present there are no experimental data defining the energy-level distribution of an excess electron in liquid helium. An application of the pulse radiolysis technique,²⁸ recently developed for the study of bound electron states in polar solvents (i.e., H₂O and aliphatic alcohols), should make the localized states of an excess electron amenable to spectroscopic study.

A rough estimate of the optical excitation energy can be obtained from the particle in a box model. The $1s \rightarrow 2p$ transition energy, $\Delta E_{1s \rightarrow 2p}$, is given by

$$\Delta E_{1s \rightarrow 2p} = 1.046 E_e = 1.046 \pi^2 / 2 R_0^2 \text{ a.u.}$$

For liquid helium at 4.2°K and 1 atm $\Delta E_{1s \rightarrow 2p} = 0.08$ eV, so that the first optical transition is predicted to lie in the infrared region at about 1000 cm⁻¹. The transition energy should be extremely sensitive to the pressure in view of the pressure dependence of the cavity radius. Thus, at 4.2°K and 100 atm $R_0 = 19$ a.u. and $E_{1s \rightarrow 2p} = 0.37$ eV (i.e., 3000 cm⁻¹), while at $p = 5000$ atm (which can be achieved at 40°K) $R_0 = 9$ a.u. and $E_{1s \rightarrow 2p} = 1.9$ eV (i.e., 15 000 cm⁻¹). It should be stressed that these estimates are reliable only to within a numerical factor of 2 to 3. These transitions should have an oscillator strength of the order of unity. Although the experiments suggested are very difficult, successful completion will lead to valuable information concerning electron-liquid-helium interactions.

IX. DISCUSSION

In this paper an attempt has been made to present a systematic study of free and localized electrons in

liquid helium. The pseudopotential formalism used herein has previously been applied to the study of the electronic states of liquid metals and to scattering problems. The application of these techniques in quantum chemistry, particularly to the study of highly excited electronic states (i.e., Rydberg states) of atomic and molecular systems is obviously of considerable interest. The present application of the pseudopotential formalism to the description of the localized states of an excess electron in a dense fluid is useful for the study of short-range electron-solvent interactions of excess electrons in polar solvents (i.e., NH or H₂O) and for studies of electron trapping centers (i.e., *F* centers) in ionic crystals.

We have demonstrated, in a semiquantitative fashion, that the plane-wave state is not the lowest energy state of an excess electron in liquid helium, and that fluid deformation can lead to the formation of a localized state of the excess electron, where the excess-electron wavefunction tends to zero at large distances from the trapping center. It becomes obvious now that the large repulsive pseudopotential and the small polarization potential of the helium atom lead to the strong short-range repulsion which is responsible for electron localization in this system. In the cases of liquid Ar, Kr, and Xe, the attractive contribution of the polarization potential overwhelms the repulsive part of the Hartree-Fock pseudopotential. This is evident from the observation that the increase of the core polarization effects with increasing atomic number lead to negative scattering lengths for these atoms.²⁹ In these cases, an excess electron is expected to be adequately described by a plane-wave state. It should be noted that in this case we cannot at present exclude the possibility of local fluid-density fluctuation leading to the formation of clusters at higher density than the surrounding fluid, thus increasing the attractive electron-fluid interaction.

The available experimental evidence is in agreement with the results of the present theoretical study. Thus, positron annihilation data in liquid helium,¹⁰ the Sanders-Levine mobility data in the gaseous phase,⁶ and the mobility studies in liquid ⁴He above the lambda point and in ³He, are in agreement with the bubble model. In a recent theoretical study of the interaction of ions and quantized vortices in rotating He II, it was shown by Donnelly²⁴ that the experimental work of Careri *et al.*³⁰ and of Tanner *et al.*³¹ can be adequately interpreted by assuming that the negative ion is characterized by a radius of 12 Å and mass $m_i = 100M$ in qualitative agreement with the localized model for the excess electron. In the present work we have used a simplified phenomenological model to describe the con-

²⁷ It is amusing to note that if there were perfect slip between the bubble and the surrounding fluid the mobility would be $\mu_{-} = e/4\pi R_0 \eta = 0.02$ cm²/V·sec.

²⁸ See, for example, (a) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.* **84**, 4090 (1962); (b) M. Matheson and L. M. Dorfman, *Progr. Reaction Kinetics* (to be published).

²⁹ T. F. O'Malley, *Phys. Rev.* **130**, 1030 (1963).

³⁰ G. Careri, W. D. McCormick, and F. Scaramuzzi, *Phys. Letters* **1**, 61 (1962).

³¹ D. J. Tanner, B. E. Springett, and R. J. Donnelly, *Proc. Intern. Conf. Low Temp. Phys.* 9th, Columbus, Ohio, 1964 (to be published).

figurational changes of the fluid. Indeed, the increase of the kinetic energy of the fluid atoms removed from the bubble region is not properly included in our analysis. This increase in kinetic energy will increase the energy required for bubble formation, leading to smaller values of R_0 . The available mobility data, as well as the cross sections for the interaction of negative ions and quantized vortices in He II, all indicate that the cavity radius calculated herein is too large by about a factor of 2. A much more general treatment of the liquid configuration changes, as described in the following paper, leads to a smaller cavity radius, which is found to be in better agreement with the experimental data.

It would be extremely interesting to obtain direct spectroscopic evidence regarding the energy levels and charge distribution of the excess electron in liquid helium. The first optical transition of this center in liquid helium at 4.2°K and 1 atm should be located at

about 0.1 eV (1000 cm^{-1}) and could be observed by application of the pulse radiolysis technique in conjunction with infrared spectroscopy to liquid helium. Another difficult but interesting experiment would be the study of the electron paramagnetic resonance spectrum of the excess electron in liquid helium. The resonance line corresponding to the localized electron in ^4He is expected to be extremely narrow, but will be broadened in ^3He by hyperfine interactions.

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Study of the Properties of an Excess Electron in Liquid Helium. II. A Refined Description of Configuration Changes in the Liquid

KAZUO HIROIKE,* NEIL R. KESTNER,† STUART A. RICE, AND JOSHUA JORTNER

Department of Chemistry and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

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In this paper we present a study of the structural changes in liquid helium in the vicinity of an excess electron. We have used the formal similarity between the pair distribution function of an N -boson system, with the wavefunction expressed as the product of pair wavefunctions, and the pair distribution function of a classical fluid. The present model leads to an interfacial surface energy term which is in good agreement with the observed surface tension of liquid helium at 0°K. An important contribution to the bubble energy arises from the volume kinetic energy arising from the excess kinetic energy of the fluid atoms removed from the boundary layer. The bubble radius of 12.4 Å calculated herein is found to be in excellent agreement with the available experimental data.

I. INTRODUCTION

IN the preceding paper¹ a bubble model² as a representation of the localized state of an electron in liquid helium was examined. In that paper it was

* Present address: Department of Applied Science, Faculty of Technology, Tohoku University, Sendai, Japan.

† Present address: Department of Chemistry, Stanford University, Palo Alto, California.

¹ J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, *J. Chem. Phys.* **43**, 2614 (1965).

² (a) R. A. Farrel, *Phys. Rev.* **108**, 167 (1957); (b) R. G. Kuper, *ibid.* **122**, 1007 (1961); (c) J. Levine and T. M. Sanders, *Phys. Rev. Letters* **8**, 159 (1962); (d) L. Onsager, *New Developments in Quantum Chemistry—Istanbul Lectures* (Academic Press Inc., New York, to be published); (e) J. Jortner, S. A. Rice, and N. R. Kestner, *ibid.*

demonstrated, through the use of the pseudopotential formalism, that a stable liquid configuration is achieved by a balance between the short-range electron-atom repulsion (summed over all surrounding atoms) and the contractile force acting on the bubble and arising from the surface tension work and the pressure-volume work of bubble creation. When the experimental surface tension is employed in the calculations, the bubble radius is predicted to be of the order of 20 Å.

The analysis just described depends upon the use of very simple models for the change in liquid configuration accompanying the formation of a bubble. In particular, we have not assessed the role played by the transition region between bubble and bulk fluid, nor