

which is always negative for $\nu \rightarrow \infty$. Hence the minimum found by Huang in the plot of $P^{(1)}$ versus ν is spurious.

²⁰The coefficient B_k in Eq. (6.39) of Ref. 17 is actually $(4\pi a/\nu)n_0$, where n_0 is the condensate density in the interacting system. The function $f(\xi, x)$ in (Eq. 6.42) of Ref. 17 is, however, not the same as n_0 . The discrepancy arises due to the neglect of the term

$$\frac{1}{N} \sum_{k < k_0} a_k^\dagger a_k$$

in (6.36) while a term of the same order viz.,

$$\frac{1}{N} \sum_{k < k_0} m_k$$

has been retained. Since the appropriate definition of the line of condensation should be $n_0=0$, the replacement of n_0 by $f(\xi, x)$ in the neighborhood of the line of condensation is unjustified, as is also the definition $\xi=0$ of the line of condensation.

Interpretation of Photoejection Experiments and the Well Depth of Electronic Bubbles in Liquid Helium[†]

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A calculation of the optical-absorption cross section of electronic bubbles in liquid helium is presented as a function of energy and pressure for various assumed values of the zero-pressure well depth $V_0(0)$. It is shown that a simple interpretation of the Northby-Zipfel-Sanders experiments on "photoejection" can be based on a value of $V_0(0)$ of 0.95 eV, varying with pressure (i.e., density) according to either the optical or the Wigner-Seitz approximation. We suggest an interpretation in which the electron is not necessarily released from the bubble, and predict that these experiments performed at 12 μ (zero pressure) to 25 μ (15 atm) would show a 10^2 -larger effect.

I. INTRODUCTION

Electronic bubbles in liquid helium have been widely studied in recent years.¹⁻¹¹ A bubble is now generally believed to consist of a cavity in the liquid containing one electron only, the surrounding fluid being expelled by the Pauli-Principle repulsion between the electron and the helium atoms. It has appeared that a satisfactory theoretical model for the bubble is a spherical square-well potential of depth $V_0 \sim 1$ eV and radius $R_0 \sim 30a_0$. (Here $a_0 = \hbar^2/me^2$ is the Bohr radius.)

Several elements of theoretical work support this model. The optical approximation, applied with the observed low-energy electron-scattering length (1.2 a_0) and the density of liquid helium at the equilibrium vapor pressure (~ 0) at 1.25°K, leads to a well depth $V_0(0)$ of 0.66 eV.⁵ (Since this method neglects the increase in electronic kinetic energy, this value should be considered to be a lower limit.) Estimates based on the Wigner-Seitz (WS) approximation, or modifications of it, lead to values about 1.0 to 1.2 eV.^{8,12,13} By minimization of the total energy with respect to bubble radius, as described below, and making use of the observed

bulk surface tension, one is led to an equilibrium radius of about 33 a_0 (with either 0.66 or 1.2 eV well depth).

Several experiments have also confirmed this model. Liquid helium has a negative-electron affinity (i.e., a barrier) of about 1.1 eV, as measured by electron-injection experiments.^{6,7} The trapping of electronic bubbles at vortex lines indicates a bubble radius of about 30 a_0 .^{9,14} Early photoejection experiments,^{15,16} along with photoionization cross sections calculated for various well depths and bubble radii,¹⁷ suggested a well depth of 1.02 eV and radius 40 a_0 .

The interpretation of this last experiment, which at first sight appeared to be simply the photoionization of an electron which contributed a high mobility component to the photocurrent, evidently is more complex. It has been suggested that the action of the light is to free an electron from a bubble, which is itself trapped in turbulence; the electron then rapidly creates another untrapped bubble, which can contribute to the photocurrent.^{16,18}

Because of problems associated with the infrared cutoff in the optical system, the photoejection experiment has recently been repeated,^{18,19} to lar-

ger wavelengths and as a function of pressure. A new lower energy and much larger peak in the photoexcitation spectrum has been observed. This has led to revised values for the radius, $30a_0$, and the well depth, 0.55 eV at zero pressure, in substantial disagreement with the above values for $V_0(0)$.

Certain difficulties exist in the interpretation of this experiment, as discussed in Ref. 18. One relates to the rapid variation of well depth with pressure, $V_0(P)$. Another is the unexpected invariance of spectral shape to pressure, which changes the well depth by a factor of 2 and the radius by 0.6 over the range studied. Still another is the shape of the photoexcitation spectrum. We shall comment below on possible explanations of these effects.

In view of the rather different picture of the bubble which has emerged from these latest photoejection experiments, we undertook a calculation of the spectroscopy of the *discrete* transitions, hoping thereby to encourage experimental studies which might determine the potential more precisely. (It is possible, for example, that a square-well potential is adequate to treat bound states, but not the continuum states reached in photoionization.) In the process of these computations we found that an interpretation can be given which avoids the difficulties referred to above, and which is reasonably consistent with other experiments and theory.

II. CALCULATIONS

We deal with a Hamiltonian that includes E_e , the electronic energy of an electron in a square well of depth $V_0(P)$ and radius $R(P)$; the PV term, being the work against the external pressure required to form the bubble; the surface energy; and a polarization energy in the surrounding liquid arising from the charge in the cavity.²⁰ Thus, the total energy in electronic state j is given by

$$E_j = E_{e,j} + \frac{4}{3}\pi R^3 P + 4\pi R^2 \sigma - \frac{1}{2}[(\kappa - 1)/\kappa]e^2/R, \quad (1)$$

where σ is the surface tension and κ is the dielectric constant of liquid He at pressure P . To a very good approximation $(\kappa - 1)/\kappa$ is given by $4\pi n\alpha$, where n is the number density of He atoms in the liquid at pressure P , and α is the atomic polarizability of a free He atom, 2.0×10^{-25} cm³.

All calculations were made for a system at 1.25 °K, at which temperature the equilibrium vapor pressure is essentially zero. Added external pressure affects each term in Eq. (1). It changes the well depth, through its dependence on n , and hence changes $E_{e,j}$; it appears explicitly in the next term; it changes n in the last term; and it modifies σ in the surface energy. We have used theory to scale σ according to²¹

$$\sigma(P) = \sigma(0)[n(P)c(P)/n(0)c(0)], \quad (2)$$

where we use measured densities and velocities of sound c at the various pressures up to 25 atm, and the measured bulk surface tension at zero pressure.²² The parameters employed are shown in Table I.

Two common methods have been used to compute V_0 as a function of atomic density. In one, the liquid is treated as if it were a crystal of the same density as the liquid, and the WS method is applied; the other is the so-called optical approximation.^{5,8,20} For each of several assumed well depths $V_0(0)$ at zero pressure we computed by each method, through the density dependence, what the well depth would be at pressure P . The results are shown in Fig. 1, along with those determined experimentally in Ref. 18. The main features are that the well depth varies with pressure rather similarly for the WS and optical approximations, and that the "experimental" variation is much more rapid than either. It has been suggested¹⁸ that an increased ordering of the liquid occurs upon application of pressure; the addition of long-range effects could increase the importance of multiple scattering, and although the optical approximation might be reasonably valid at low pressure, the WS model becomes better at high pressure. Certainly one would have to conclude that a major change is occurring in the liquid as pressure is applied, if the bubble model and the "experimental" well depths are to be believed.

With these well depths for the calculation of $E_{e,j}$ as a function of R , and knowledge of the other terms in Eq. (1) at each pressure, we computed the total energy of Eq. (1) for numerous values of R near the minimum energy for the ground electronic (1s) state. (That is, we computed a "configuration-coordinate" curve²³ for the ground electronic state in the radial mode of vibration for each potential at each pressure.) At the minimum energy for each configuration-coordinate diagram we noted the value of the radius $R_0(P)$. These equilibrium radii are shown in Fig. 2, along with the experimentally determined radii of Ref. 18, as a function of pressure. We exhibit here and in the following only the results from the WS calculation for the sake of clarity. The

TABLE I. Parameters for the evaluation of Eq. (1), at $T = 1.25$ °K.

P (atm)	$n \times 10^{-22}$ cm ⁻³	σ (erg/cm ²)
0	2.193	0.3600
5	2.292	0.4335
10	2.386	0.4958
15	2.463	0.5530
20	2.532	0.6068
25	2.593	0.6557

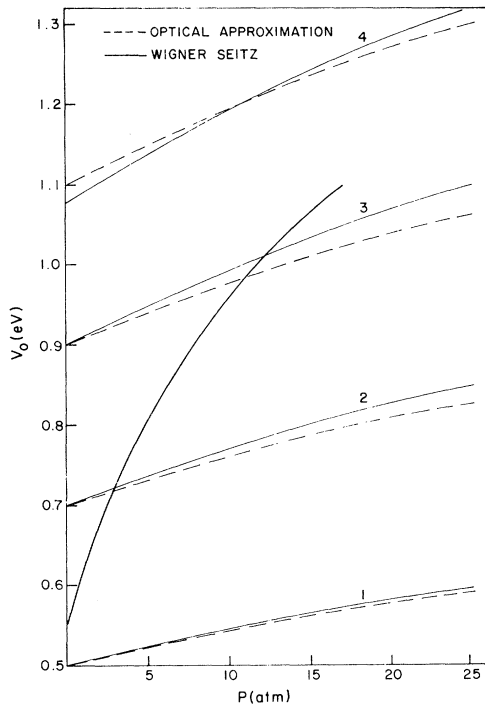


FIG. 1. Computed well depths $V_0(P)$ as a function of pressure for several assumed values $V_0(0)$ of the well depth at zero pressure. The dashed curves are based on computations with the optical approximation, and the solid curves are based on a WS model. Shown in the heavy solid curve are the experimental values taken from Fig. 26 of Ref. 18.

optical approximation gives very similar results.²⁴ It is apparent that although the radius varies appreciably with pressure, it is not at all sensitive to well depth in this range. Since the $1s$ state is tightly bound in a well of depth as small as 0.5 eV, any increase of well depth makes little difference.

For each set of parameters, and for the value of $R_0(P)$ at each calculated minimum, we computed the energy of the lowest state allowed in an optical transition, the $1p$ electronic state. The energy difference $E_{1p} - E_{1s}$ is extremely close to the center of the vibrationally broadened band of the lowest-energy optical transition of the electronic bubble. This transition has approximately 0.97 of all the oscillator strength associated with the bubble, and has a band width of approximately 0.01 eV.²³ It is the relatively huge absorption cross section associated with this transition which makes it appear so attractive for experimental spectroscopy.

The excitation energies $\Delta E_{1p} \equiv E_{1p} - E_{1s}$ are also plotted as a function of P , for the various choices of $V_0(0)$, in Fig. 2. As would be expected from the weak dependence of R_0 on $V_0(0)$, ΔE is rather weakly dependent on $V_0(0)$ particularly at low pressure. At 20 atm, however, determination of ΔE_{1p} to an

accuracy of $\frac{1}{4}$ its expected linewidth could determine $V_0(0)$ to within about 0.1 eV.

III. INTERPRETATION

One would expect the higher excited p states to be much more sensitive to the well depth, and this was found to be the case. For example, no bound $3p$ state was found at the equilibrium radius $R_0(P)$ at any pressure for $V_0(0) \leq 1.1$ eV, and the bound $2p$ state disappeared at various pressures for $V_0 < 1.1$ eV. The results for $\Delta E_{2p} \equiv E_{2p} - E_{1s}$ are exhibited in Fig. 3. The termination of each line occurs at or slightly below the pressure at which the $2p$ state merges with the continuum. In the case of $V_0(0) = 0.7$ eV, the $2p$ state is (barely) bound at zero pressure, but not at 5 atm. For $V_0(0) = 0.948$ atm, it is bound at 17 but not at 20 atm. Also shown are the positions of the lowest-energy peaks of the experimental photoexcitation spectrum.

The remarkable agreement of the latter with the energies of the $1s-2p$ transition for $V_0(0) = 0.95$ eV led us to a calculation of the $1s$ -continuum cross sections¹⁷ as well, for several values of $V_0(0)$, and the associated values of $V_0(P)$, at the predicted equilibrium radius $R_0(P)$. Figure 4 shows some of the results for $V_0(0) = 0.948$ eV at pressures of 0, 10,

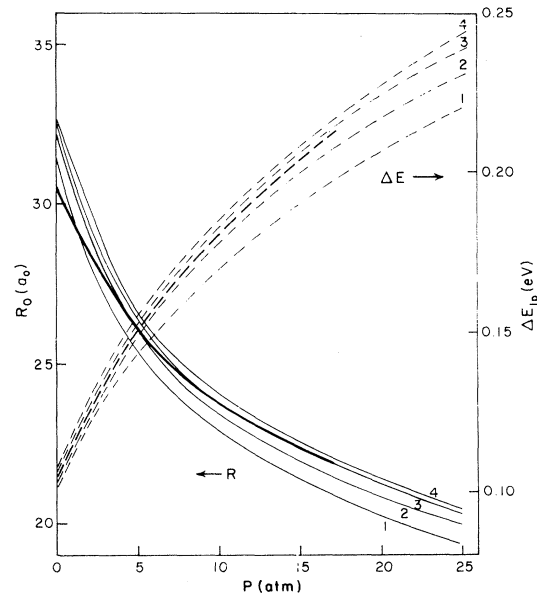


FIG. 2. Equilibrium bubble radii R_0 and $1s-2p$ excitation energies ΔE_{1p} as a function of pressure. The light lines are computed on the basis of the WS approximation for various well depths $V_0(0)$. Curves 1-4 are for $V_0(0) = 0.50, 0.70, 0.90,$ and 1.076 , respectively. The heavy solid line for R_0 is taken from the dashed curve of Fig. 25 of Ref. 18, and the heavy dashed line is the value of ΔE_{1p} computed from the well depth $V_0(P)$ of Fig. 26 in Ref. 18.

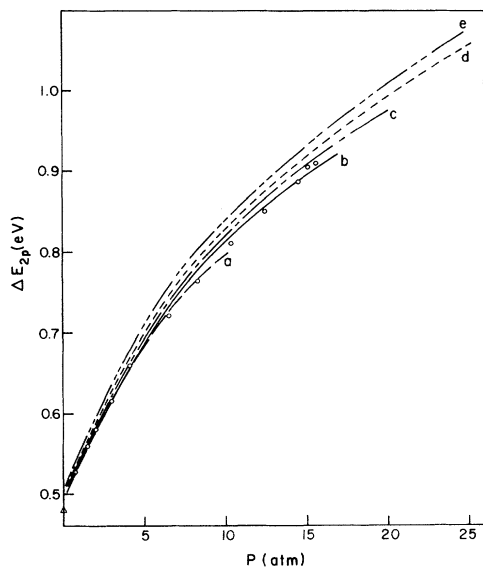


FIG. 3. Computed excitation energies for the $1s-2p$ transition as a function of pressure for various values of $V_0(0)$, in the WS approximation. Curves a, b, c, d, and e correspond to values of $V_0(0)$ equal to 0.90, 0.948, 1.002, 1.049, and 1.076 eV, respectively. The triangle at $P=0$ is for $V_0(0)=0.7$ eV. The experimental values for the first peak in the photoexcitation spectrum, shown in open circles, are taken from Fig. 19 of Ref. 18.

and 20 atm. The peak heights for the discrete transitions are based on calculated oscillator strengths and widths of the $1s-1p$ and $1s-2p$ lines. The widths were taken to be 0.01 and 0.02 eV, respectively.²³ It is evidently unnecessary for our pur-

poses to consider vibrational broadening of the transitions to the continuum. The general similarity to the observed photoexcitation spectra is clear, particularly when due account is taken of the wide slits employed in the experiments.¹⁸ At nonzero low pressures there exists a small peak in the cross section just above threshold for photoionization. For example, at $P=10$ atm, this bump, which below we shall refer to as b , appears at 0.9 eV.

Finally, we exhibit in Fig. 5 the energies of various low-energy peaks of the calculated cross section for $V_0(0)=0.948$ eV as a function of pressure. The $1s-2p$ transition energy is plotted as ΔE_{2p} , and the lowest-energy-continuum bump as b . These join at about 17 atm, where the $2p$ state merges with the continuum. At this pressure, much of the $1s-2p$ oscillator strength (~ 0.023) becomes available to b , so that it grows markedly. (cf. the peak at ~ 0.95 eV in Fig. 4 at $P=20$ atm). The position of the maximum of the next wide band, which moves continuously to higher energy as pressure is increased, is labeled w . Also included in Fig. 5 are the positions of the first two experimental peaks, called ϵ_1 and ϵ_2 in Ref. 18. (No measurements were made below about 0.5 eV, and we omit the $1s-1p$ transitions accordingly.) The similarity of these calculated and experimental energies strongly suggests that the experimental peak ϵ_1 be interpreted as the energy of the $1s-2p$ transition, and ϵ_2 be interpreted as w , the wide continuously shifting band in the continuum. (The numerical difference in the peak energies for ϵ_2 could easily be attributed to difficulties in reading the position of the broad experimental peak with small signal-noise ratios.) The small bump b , which should grow abruptly at about 17 atm, and become ϵ_1 , is

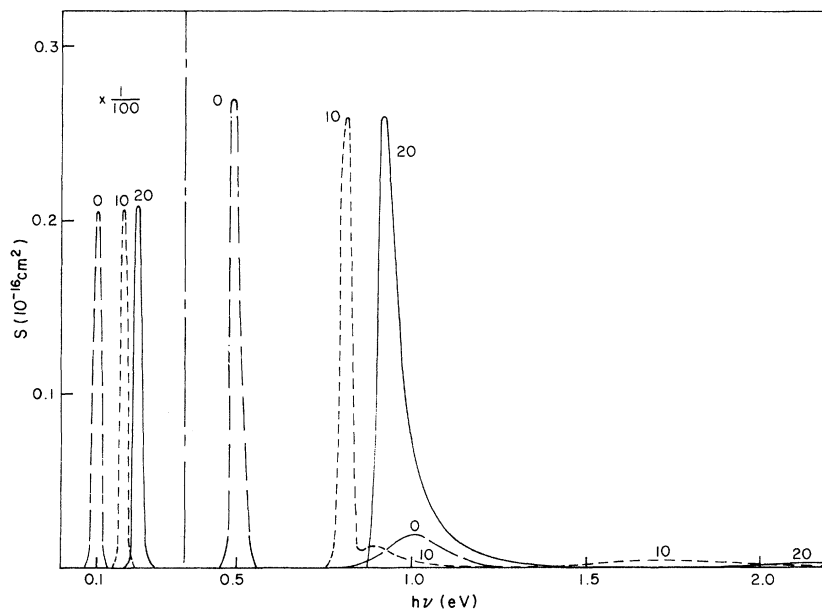


FIG. 4. Computed absorption cross section of a bubble of well depth $V_0(0)=0.948$ eV for pressures of 0, 10, and 20 atm, as labeled. The low-energy peaks for the $1s-1p$ transition have been multiplied by 10^{-2} before plotting.

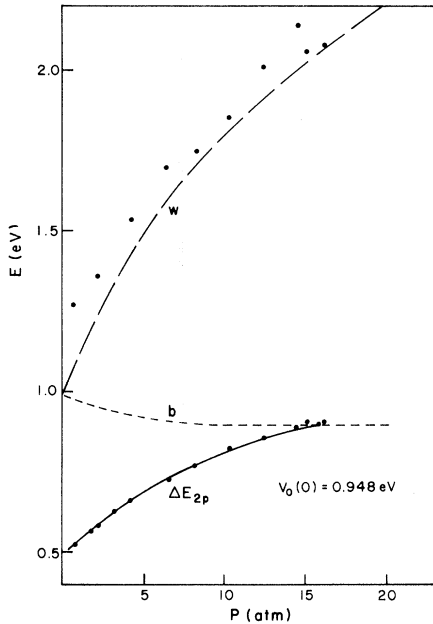


FIG. 5. Calculation of the peak positions of the absorption cross section for a bubble with well depth $V_0(0) = 0.948$ eV, as a function of pressure. The solid circles represent experimental values from Table I of Ref. 18. See text for the meaning of the labels b and w .

very likely associated with the low-energy “anomalies” of Fig. 21 of Ref. 18. (These are slight peaks in the photoexcitation spectrum which find no explanation if ϵ_1 and ϵ_2 are the first two peak energies of the photoionization spectrum. We cannot comment on the high-energy anomalies, if indeed they are real.)

Another question relates to the shape and the relative strengths of the bands labeled ΔE_{2p} and w . The strength of the calculated w varies smoothly with pressure, as observed, as do the peak height and width (which was greater than the slit widths of the equipment of Ref. 18). The total oscillator strength of the band w varies from 4.0×10^{-3} at $P=0$ to 2.4×10^{-3} at $P=15$ atm, and broadens with increasing P . The oscillator strength associated with the $1s-2p$ band ranges from 0.0256 at $P=0$ to 0.0185 at $P=16$ atm, and the strength of the low-energy-continuum band, into which the $1s-2p$ line continuously merges, is 0.021 at 20 atm and 0.020

at 25 atm. The computed f sum was unity to within 0.0003 for an upper limit on the energy of 2.2 eV at $P=0$, and within 0.005 up to 2.37 eV at $P=25$ atm.

The electronic bubble also possesses $1d$ and $1f$ states between the $1p$ and $2p$ states. In particular, under the presence of $l=2$ modes of oscillation of the bubble, a $1s-1f$ transition should be weakly observable at an energy ΔE_{1f} between ΔE_{2s} and ΔE_{2p} , perhaps 0.7 eV at $P=10$ atm. It is possible that this transition is responsible for the apparent signal at energies below ϵ_1 in Figs. 13–17 of Ref. 18.

The major physical question is how the mere excitation, not ionization, of a bubble can affect the current flow. We believe that the answer is to be found in the thermal energy released by a bubble during relaxation after excitation. It was shown in Ref. 23 that ~ 0.05 eV is given up in heat following excitation, during the bubble relaxation to a new configuration characteristic of its changed “ $1p$ ” charge distribution. This thermal energy would raise the local temperature of each surface atom by several degrees for a short time. It was shown in Ref. 18 that the (differential) photoexcitation signal decreases rapidly above 1.3°K, and in Ref. 14 it appeared that bubbles thermally dissociated from vortex lines above 1.34°K. Since the thermal energy released following a $1s \rightarrow 2p$ transition is substantially greater than for a $1s \rightarrow 1p$ transition,²³ it seems reasonable to suppose that the action of the light is to remove bubbles from traps even without photoionization. It also seems probable that excitation of the $1s \rightarrow 1p$ transition would likewise free the bubble. The absorption coefficient for this process would be at least 50 times stronger than that for the ϵ_1 line, and the effort required to work in the 10–25 μ region would seem to be justified.

In summary, it appears possible to interpret the photoexcitation experiments with a well depth $V_0(0) \sim 0.95$, close to that for electron injection, with a variation of V_0 with pressure equal to that predicted in the model. The best test of this interpretation would be study of the optical properties of bubbles at larger wavelength.

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