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# Properties of Electron Bubbles in Liquid Helium

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*We present calculations of a number of properties of electron bubbles in liquid helium. The size and shape of bubbles containing electrons in different quantum states is determined based on a simplified model. We then find how the geometry of these bubbles changes with the applied pressure. The radiative lifetime of bubbles with electrons in excited states is calculated. Finally, we use a quantum Monte Carlo method to determine the properties of a bubble containing two electrons. We show that this object is unstable against fission.*

***KEY WORDS*:** Electron bubbles; liquid helium; radiative decay.

## 1. INTRODUCTION

When an electron is injected into liquid helium, it forces open a cavity free of helium atoms, referred to as an electron bubble. In a recent paper[1] (referred to as I), we considered what happens when an electron bubble is illuminated by light. If the electron is excited from the lowest energy 1S state of the initially spherical bubble to the 1P state,[2] the bubble shape will change. At high temperatures, the liquid contains many thermal excitations (phonons and rotons) and the damping of the motion of the bubble wall is large. One can therefore expect that the bubble will slowly relax to a new equilibrium shape. It was shown that this equilibrium shape resembles a peanut. However, at lower temperatures, the liquid contains few excitations and so the damping of the bubble wall becomes small. As a result, the bubble will change shape rapidly and after the equilibrium shape has been reached, the liquid surrounding the bubble will still be in rapid motion. The inertia associated with the liquid may then be sufficiently large to cause the waist of the peanut to shrink to zero, thus dividing the bubble into two parts. What happens after this point was not definitely established, and is under experimental investigation. Elser[3] has argued that before the division



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of the bubbles takes place the wave function of the electron will cease to deform adiabatically as the bubble shape develops and that, as a result, all of the wave function will end up in one of the parts. This part would then expand and become a conventional 1S electron bubble and the other part, containing no wave function, would collapse. A different argument has been presented by Rae and Vinen.[4] They claim that if the bubble divides into two baby bubbles each containing half of the wave function, this state would quickly collapse into an incoherent quantum superposition of two separated ground-state bubbles which would have properties no different from ordinary 1S bubbles.

When electron bubbles are introduced into helium, a space charge field is set up which drives the bubbles out of the liquid. This limits the number density of the bubbles. As a result, conventional optical studies of the bubbles are extremely difficult.[5,6] Several experiments have shown that the absorption of light results in a change in the mobility of the bubbles;[7–9] the origin of this change in mobility is not clearly established. Very recently, a new experimental method for the study of the bubbles has been developed.[10] In this experiment, a negative pressure is applied to the liquid. If the pressure is negative with respect to a critical pressure $P_c$, an electron bubble in the liquid will become unstable and explode. The explosion pressure $P_c$ is different for each quantum state. Thus, a measurement of the pressure required to make a bubble explode provides a means to identify the quantum state. This provides the basis for a new method to study the properties of electron bubbles in excited states.

In this paper, we present calculations of various properties of electron bubbles. In Sec. 2, we describe the model that we use for the calculations and estimate the cross-section for light absorption from the ground state of the bubble. In Sec. 3 we calculate the equilibrium shapes of the bubble for several different quantum states of the electron and in 4 consider the radiative lifetime of the 1P, 2P, 2S, and 1D states. Finally, in Sec. 5, we consider the ground state properties of the two electron bubble.

## 2. OPTICAL ABSORPTION

In I, the calculations were performed using a simplified version of a model first used by Grimes and Adams.[6,9] The energy of the electron bubble is approximated by the expression

$$E = E_{el} + \alpha A + PV, \tag{1}$$

where $E_{el}$ is the energy of the electron, $\alpha$ is the surface tension of helium, $A$ is the surface area of the bubble, $P$ is the pressure and $V$ is the bubble volume. The penetration of the wave function of the electron into the liquid is neglected. Thus, for example, for a spherical bubble of radius $R$, the electron energy is $h^2/8mR^2$, where $m$ is the electron mass. The surface tension was taken to have the value 0.341 erg $\cdot$ cm $^{-2}$, and to be independent of the pressure. In I, the energies of the optical transitions 1S → 1P and 1S → 2P were calculated as a function of pressure. The results were in excellent agreement with experimental data.[5–9]

For completeness, we include here a calculation of the cross-section for optical absorption from the ground state within the model that we are using. For light of frequency $\omega$ that is polarized along the $z$-axis, the cross section for a transition from the ground state to a state $n$ is

$$\sigma(\omega) = \frac{4\pi^2 e^2}{c} \omega \, |z_{0n}|^2 \, \delta(E_0 + \hbar\omega - E_n), \tag{2}$$

where $z_{0n}$ is the matrix element of $z$ between the ground state 0 and the state $n$, and $E_0$ and $E_n$ are the energies of these states. Evaluation of the matrix element leads to the result that the oscillator strength for the 1S to 1P and 1S to 2P transitions are 0.967 and 0.0254. These values are in close agreement with the results obtained previously by Fowler and Dexter,[11] Duvall and Celli,[12] and Miyakawa and Dexter.[13] In the earlier calculations, allowance was made for the penetration of the wave function into the liquid. It appears, therefore, that this penetration does not have a significant effect on the oscillator strength.

Using the calculated oscillator strengths, we find that the integral $\int \sigma(\omega)\, d(\hbar\omega)$ of the cross-section over the line width has the values $1.06 \times 10^{-16}$ and $2.79 \times 10^{-18}$ cm$^2 \cdot$ eV for the 1S → 1P and 1S → 2P transitions, respectively. For electron bubbles in helium, the line width is broadened because of thermal fluctuations in the size and shape of the bubble. The theory of the width of the absorption line has been discussed by Lerner *et al.*[14] From the measurements of Grimes and Adams,[6,9] the line width for the 1S → 1P transition at zero pressure is about 0.017 eV. Hence the peak value of the cross section for this transition is of the order of $\sim 6 \times 10^{-15}$ cm$^2$. Note that within the present approximation, these cross-sections are independent of pressure.

## 3. VARIATION OF BUBBLE GEOMETRY WITH PRESSURE

After the electron has been raised to the 1P state, the outward pressure exerted by the electron on the bubble wall will vary around the bubble surface. As a result, this pressure will no longer be balanced by the sum of the surface tension force and the pressure in the surrounding liquid. Hence, the bubble will begin to change its shape. The motion of the bubble occurs on a time scale $\tau$ which is of the order of 10 to 100 psecs.[15] Provided that

$$\hbar/\tau \ll \Delta E, \tag{3}$$

where $\Delta E$ is the spacing between electronic energy levels, the wave function of the electron will adiabatically deform as the shape of the bubble changes.[16] Since the spacing of the energy levels of the electron is generally of the order of 0.1 eV, the adiabatic condition is well satisfied unless a special situation arises that leads to a degeneracy. One way in which a degeneracy can arise is if the waist of the bubble becomes very small. Another mechanism is discussed in more detail below in relation to the stability of the 2P state. We assume in this section that the damping provided by the rotons and phonons is sufficiently large that the bubble relaxes smoothly to an equilibrium shape that minimizes the total energy. In a previous conference paper,[17] we have presented the results of calculations of equilibrium bubble shapes as cross sectional views of the bubbles. It was found that the 1P state, for example, evolved into a shape resembling a peanut. Here, we present the results in more quantitative detail and in the next section use these shapes to find the radiative lifetime. Note that throughout this paper when we refer to a quantum state as 1P, for example, we mean a state with a wave function that would be deformed back into the 1P state if the shape of the bubble were slowly changed back to spherical. When the bubble state is distorted from spherical, the wave function for the "1P state" contains components that do not have $l = 1$.

Before presenting the results of these calculations, we want to remark that as far as we are aware, there are no general theorems applicable to the problem of the shape determination.[18] For example, we have to assume without proof in the following that for each quantum state there is at most one shape of minimum energy. In addition, there are interesting questions concerning what happens to a bubble which is initially spherical and in which the angular momentum $l$ of the electron is non-zero. The $(2l+1)$-fold degeneracy of these states is removed as soon as the bubble ceases to be spherical. Consider, for example, $l = 1$. If the bubble is slightly non-spherical, the degeneracy will be lifted by a small amount and the eigenstates will be of the form

$$\psi_x = \frac{x'}{r} j_1(kr), \qquad \psi_y = \frac{y'}{r} j_1(kr), \qquad \psi_z = \frac{z'}{r} j_1(kr), \tag{4}$$

where $x'$, $y'$, $z'$ are coordinates along three mutually orthogonal directions with orientation determined by the detailed form of the non-sphericity of the bubble. If the electron is in the first of these states, the pressure exerted by the electron will be large along the positive and negative $x'$ axis, and so the bubble will elongate along this axis. The equilibrium shape will be of the form of a peanut aligned along $x'$. In similar fashion, bubbles in which the wave function is $\psi_y$ or $\psi_z$ will elongate along $y'$ and $z'$, respectively. Thus, it appears that the three 1P states will each evolve into an equilibrium configuration of the same size and shape but with a different orientation. The bubble will have axial symmetry, and the wave function will be independent of the azimuthal angle around the bubble axis. However, as already mentioned, we are unable to prove that there are no other equilibrium states.

To find the shape of the bubble for a particular electronic state, we write the distance $r$ to the bubble surface in the direction $\theta$ relative to the bubble axis as an expansion in Legendre polynomials of even order

$$r(\theta) = \sum_{L=0,2,\ldots,L_{\max}} a_L P_L(\theta). \tag{5}$$

We use $L_{\max} = 6$, and solve Schrödinger's equation for the wave function using the partial wave expansion method described in I. The $\{a_L\}$ coefficients are then adjusted to minimize the sum of the electronic, surface and volume energy.

The results for the $a_L$ coefficients for the 1P state are shown in Fig. 1. In this plot the coefficient $a_6$ has not been included because of its small

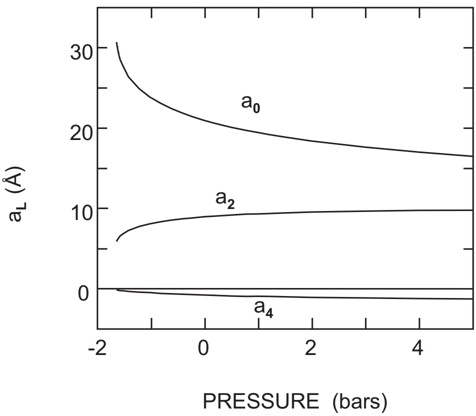


Fig. 1. Parameters $a_0$, $a_2$, and $a_4$ describing the shape of the 1P bubble as a function of pressure.

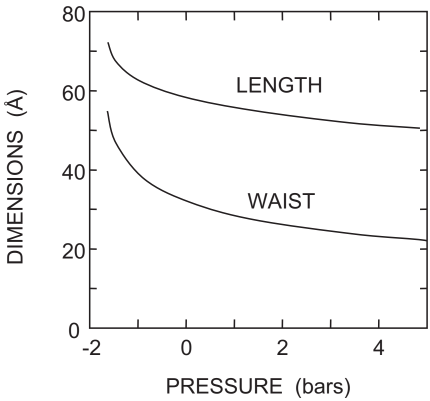


Fig. 2. Length and waist diameter of the 1P bubble as a function of pressure.

magnitude (less than 0.3 Å). The length and the waist diameter are shown in Fig. 2. At a pressure of $-1.63$ bars, the bubble becomes unstable against unlimited expansion; this is the explosion pressure of the bubble. From Fig. 1, it can be seen that as this pressure is approached, the $a_0$ coefficient grows rapidly while the $a_2$ coefficient decreases. Thus, the bubble is expanding in a way such that it becomes more spherical. For positive pressure, the 1P bubble takes on a shape like a peanut with a waist that steadily shrinks as the pressure is increased. The bubble has a waist because the wave function vanishes in the $xy$-plane and so the electron exerts no outward pressure. For large pressures, the bubble has a shape that is approximated by two spheres that overlap by a small amount. For pressures above about 5 bars, the radius of the waist becomes comparable to atomic dimensions, and our calculation of the equilibrium shape becomes unreliable.

Results for the 2P state are shown in Figs. 3 and 4. The explosion pressure is found to be $-1.22$ bars. One can compare the results for the explosion pressures with what is obtained from a simplified model in which the bubble is taken to be spherical. The spherical model gives pressures of $-1.58$ and $-1.21$ bars for the 1P and 2P states, respectively, compared with $-1.63$ and $-1.22$ bars from the more general theory. The difference between the spherical and general calculation is less for the 2P state because close to explosion this state is nearer to being spherical (see Figs. 2 and 4).

The behavior of the 2P state at positive pressures is more complex and unexpected. Using $L_{max} = 6$, we find that when the pressure exceeds 1.53 bars, it is not possible to find a stable equilibrium state. We have

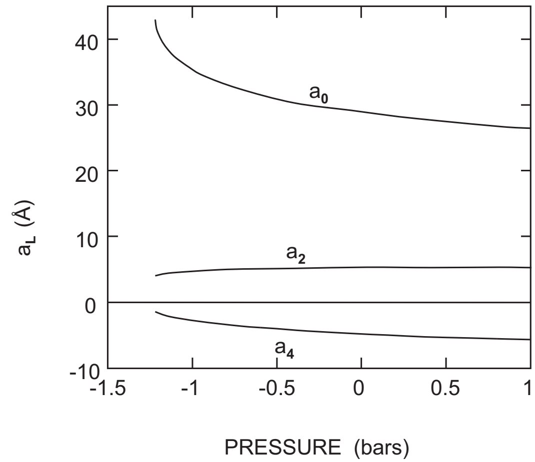


Fig. 3. Parameters $a_0$, $a_2$, and $a_4$ describing the shape of the 2P bubble as a function of pressure.

investigated this surprising result and find that the lack of stability is connected to the existence of a degeneracy between the 2P and 1F states, as we now explain. In a spherical bubble, these states are, of course, non-degenerate, and the energies of all states vary as the inverse square of the bubble radius $a_0$. We next consider a bubble which has a shape specified by the parameters $a_0$ and $a_2$. In this case, it is convenient to consider the energy as a function of the parameters $a_0$ and $a_2/a_0$. Clearly, a degeneracy can arise

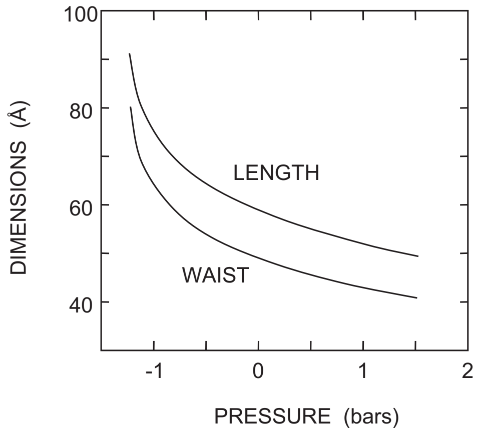


Fig. 4. Length and waist diameter of the 2P bubble as a function of pressure.

only as a result of the variation of the parameter $a_2/a_0$. However, it is found that regardless of the value of this parameter, the 2P and 1F states never become degenerate. This is in agreement with the analysis of Von Neumann and Wigner[19] who showed that the variation of one parameter in a Hamiltonian is normally insufficient to lead to a degeneracy. Variation of a single parameter may cause states to approach each other but, unless some special situation exists, level repulsion will occur and the levels will never meet. However, when *two or more* parameters are varied, a degeneracy is possible. For a further discussion of this interesting topic, see the papers by Longuet-Higgins,[20] Berry and Wilkinson,[21] and Yarkony.[22] The locations in parameter space at which degeneracies occur have been given the name "diabolical points" for the following reason. If the energy is plotted as a function of two parameters, then it is found that the energy surfaces in the vicinity of the degeneracy have the form of the two sheets of a double cone (diabolo). The two cones touch at the degeneracy point.

In the present context, this means that a degeneracy can occur when the bubble shape is specified by three or more parameters. As $a_2$ is varied at fixed $a_0$, two states can approach, and for a special value of the ratio of $a_4$ to $a_0$, the matrix element that normally prevents the levels meeting will vanish and a degeneracy can occur. We have found that when the bubble is described by the three parameters $a_0$, $a_2$, and $a_4$, there is indeed a degeneracy if $a_2/a_0 = 0.202$ and $a_4/a_0 = -0.259$. Thus, the 2P and 1F levels are degenerate along a line in $a_0$, $a_2$, $a_4$ space that passes through the origin. With $L_{\max} = 6$, the degeneracy exists on a surface in the $a_0$, $a_2$, $a_4$, $a_6$ parameter space. We have investigated the energy as a function of the parameters $a_2/a_0$ and $a_4/a_0$ (with $a_6$ and all higher order coefficients zero) and confirmed that the energy surfaces do indeed have this form.

To describe what happens near to the critical pressure 1.53 bars in more detail, it is convenient to discuss how the total energy of the bubble (not just the energy of the electron) varies as a function of the parameters $a_2/a_0$ and $a_4/a_0$ when for given values of these two parameters, the value of $a_0$ is always adjusted to give a minimum energy. For pressures less than 1.53 bars, we find that in $a_2/a_0$–$a_4/a_0$ space, there are two minima of the total energy. For one of these (the "normal minimum"), the energy varies quadratically in the parameters $a_2/a_0$ and $a_4/a_0$ in the region around the minimum. The other minimum is located at the degeneracy point. Near to this point the energy varies linearly with distance in parameter space from the minimum. This is because the surface for the electron energy in the 2P state is conical, whereas the other contributions to the energy coming from the bubble volume and surface area vary smoothly with $a_2/a_0$ and $a_4/a_0$. At pressures less than 1.53 bars there is a saddle point lying between these two minima. When 1.53 bars is reached, the saddle point disappears and the only minimum becomes the one at the diabolical point. Thus, as the pressure is increased towards 1.53 bars, the parameters $a_2/a_0$ and $a_4/a_0$ do not continuously vary until they reach their values at the diabolical point, but instead jump discontinuously to the diabolical point from some distance away in $a_2/a_0-a_4/a_0$ space. For pressures close to 1.53 bars, the energy at the normal minimum is higher than the energy at the diabolical point, and so the normal minimum is metastable.

Once the bubble jumps to the diabolical point, the bubble can make a radiationless transition from 2P to 1F.[22] With the electron in the 1F state, the energy of the bubble can be lowered further by reducing the radius of the waist towards zero,[23] effectively forming two "baby bubbles." At this point each baby bubble contains one half of $|\psi|^2$ and the wave function inside each has a form similar to that of a 1P state. Of course, we have not proven that when pressure above 1.53 bars is applied to a 2P bubble the end result will be two bubbles; the calculation simply shows that a two-bubble state can be reached via a path along which the energy continuously decreases.

For the S states, it is reasonable to assume that the bubbles are spherical. The radius of the 1S and 2S bubbles as a function of pressure is shown in Fig. 5. The explosion pressures are −1.89 and −1.33 bars, respectively. The radius of the 1S and 2S states decreases monotonically as the pressure is increased. Within the current model in which no penetration

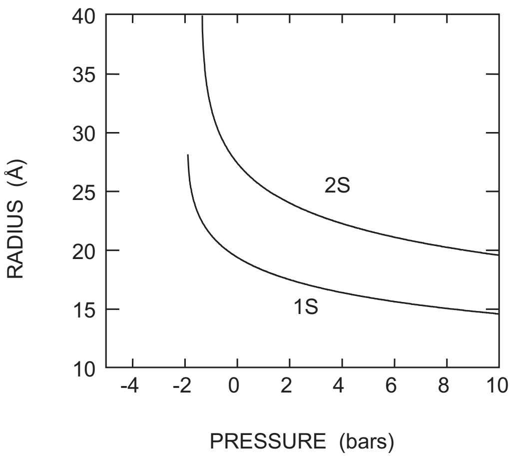


Fig. 5. Radius of the 1S and 2S bubbles as a function of pressure. The 1S and 2S bubbles become unstable at −1.89 and −1.33 bars, respectively.

of the wave function into the liquid is allowed, these states continue to exist for all positive pressures. However, if a finite height $V_0$ of the potential barrier is used, then clearly at some pressure $P_{\text{collapse}}$ the energy of the electron $E_{el}$ will become greater than the barrier height and the bubble will collapse. For the 1S and 2S states, the calculated values of $E_{el}$ at 25 bars are 0.24 and 0.54 eV, respectively, and thus these states will exist up to the pressure at which solidification occurs.

## 4. RADIATIVE DECAY OF EXCITED STATES

For an electron in the 1P state, the electron can radiate a photon and return to the ground state 1S. After this emission has taken place, the shape of the bubble will begin to change and it will eventually become spherical with a radius that minimizes the energy of the 1S state. The radiative lifetime $\tau$ of a state $\alpha$ decaying to $\beta$ is given by

$$\tau = \frac{3\hbar c^3}{4e^2\omega^3} \frac{1}{|\langle\alpha| x |\beta\rangle|^2 + |\langle\alpha| y |\beta\rangle|^2 + |\langle\alpha| z |\beta\rangle|^2}, \tag{6}$$

where $\omega$ is the frequency of the radiation emitted. For the 1P (with $m = 0$) to 1S transition, this expression reduces to

$$\tau = \frac{3\hbar c^3}{4e^2\omega^3} \frac{1}{|\langle 1\text{P}| z |1\text{S}\rangle|^2}, \tag{7}$$

where $|\langle 1\text{P}| z |1\text{S}\rangle|$ is the matrix element of the coordinate $z$ between the 1P and 1S states. Note that since the Franck–Condon principle applies, the wave functions of both the 1P and the 1S states are to be calculated for a bubble having the equilibrium 1P shape. The energy of the photon that is emitted will be the difference in the energy of these two wave functions. The radiative lifetime has been considered previously in a paper by Fowler and Dexter.[11] They obtained a lifetime of 13 μs from a simplified model in which the 1P bubble shape was taken as spherical. They recognized that a more accurate calculation in which allowance was made for the non-sphericity of the bubble would give a significantly smaller transition energy $\hbar\omega$, and hence a longer lifetime.

The calculation of the equilibrium shape was performed using the method already described. The wave functions $\psi_{1\text{S}}$ and $\psi_{1\text{P}}$ were then found, and the matrix element calculated. Results for the transition energy

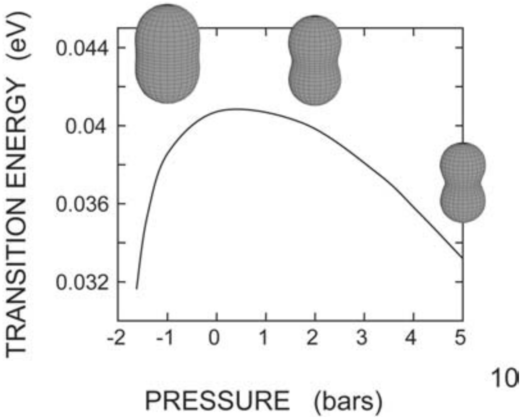


Fig. 6. Energy of the 1P → 1S transition as a function of pressure. The shapes of the 1P bubble at −1, 2, and 5 bars are indicated.

$\hbar\omega$ are shown in Fig. 6. When the pressure is increased starting from a negative value, $\hbar\omega$ at first increases. In this range of pressure, the bubble is nearly spherical (see Fig. 6). The transition energy in this range varies as the inverse square of the bubble radius, and hence increases with increasing pressure. For positive pressures, the bubble begins to develop a pronounced waist (Fig. 6). This decreases the energy difference between the 1P and 1S states; the states would become degenerate in the limit that the radius of the waist goes to zero. The calculation of $\hbar\omega$ becomes increasingly difficult as the radius of the waist decreases, and for this reason we have not included results for pressures above 5 bars. Over the pressure range from the explosion pressure to 5 bars, the matrix element is almost independent of pressure. The results for the lifetime are shown in Fig. 7. At zero pressure our result for the lifetime is 44 μs, i.e., about three times larger than the prediction of Fowler and Dexter.[11] It is important to note that the lifetime of the 1P state may be reduced as a result of non-radiative processes. We have not attempted to make a calculation of these processes.

The decay of the 2P state is much more complex and we have made calculations only for zero pressure. Decay can occur to the 1S, 2S, and 1D states. Calculation of the decay rate to the S states is straightforward since a formula similar to Eq. (6) is applicable. The lifetimes for decay to 1S and 2S are 54 and 219 μs, respectively and the energies of the emitted photons are 0.191 and 0.040 eV. The decay to the 1D state is more complex. For a spherical bubble this energy level is 5-fold degenerate. However, since the bubble has the 2P equilibrium shape, these levels will be split. The bubble

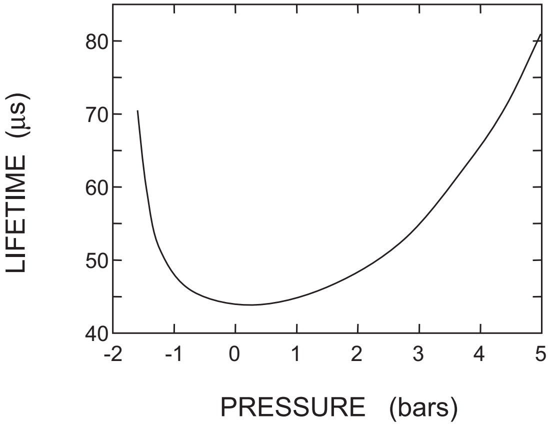


Fig. 7. Lifetime for radiative decay of the 1P state as a function of pressure.

has axial symmetry and the level is split into a singlet $m = 0$, and two doublets $m = \pm 1$ and $m = \pm 2$. We find that the energies of the electrons in these three levels are $E_0 = 0.140$, $E_{\pm 1} = 0.137$, and $E_{\pm 2} = 0.173$ eV. In the $m = \pm 2$ state, the electron spends most of its time near to the plane $z = 0$. Hence the energy of this state is increased relative to the other states because the diameter of the waist of the bubble is less than the length of the bubble. If we ignore the splitting of the 1D levels, it follows that the total decay rate to the multiplet is simply 5 times the rate from the 2P level to the 1D state with $m = 0$.[24] The lifetime for decay into the group of 1D states is found to be 2.6 μs, and the decay energy averaged over the levels is 0.085 eV. The decays are summarized in Fig. 8. The lifetime of the 2P state, counting all decay processes, is 2.5 μs, and is dominated by the decay into 1D states. The decay to 1D is much faster than to 1S even though the energy of the photon emitted in the 2P → 1S transition is larger than for the 2P → 1D. This is because the matrix element of $z$ between the 2P and the 1D states is small due to a near-cancellation of contributions from different ranges of the integral.[25] The same cancellation occurs in the matrix element between the 2P and 1D states of the hydrogen atom.[26]

We have also calculated the lifetime of the 2S state for decay into the 1P manifold. The result, summed over the three 1P states, is 4.1 μs. Finally, we considered the decay of the relaxed 1D state into the 1P manifold. For this process we simplified the analysis by first calculating the rate for the transition to the 1P state with $m = 0$, and then multiplying by 3 to allow for the other states. The result for the lifetime is 8 μs.

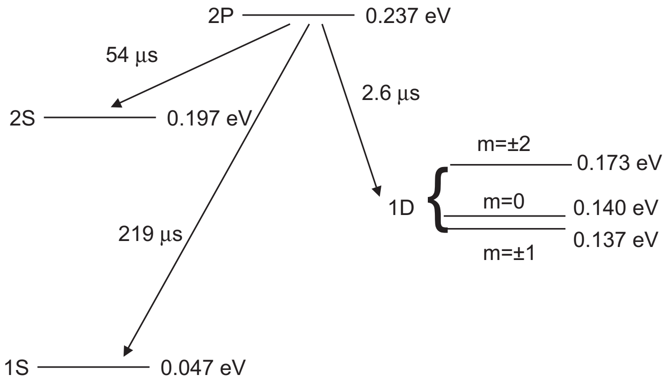


Fig. 8. Summary of the decay of the 2P bubble at zero pressure. The lifetime of the different decay channels and the energy of the different electron states inside the equilibrium 2P bubble shape are indicated.

## 5. BUBBLES CONTAINING TWO ELECTRONS

For a bubble containing two electrons, Dexter and Fowler[27] have obtained an approximate value for the electron energy using a variational method with a simple trial wave function. Their calculation assumes a spatial component of the wave function that is symmetric with respect to the interchange of the coordinates $\vec{r}_1$ and $\vec{r}_2$ of the electrons and so implicitly assumes that that the spins are anti-parallel. They found that at zero applied pressure the equilibrium radius was 33.9 Å, with the electron energy and total energy of the bubble at this radius being 0.56 eV and 0.88 eV, respectively.[28] Later, Shikin[29] gave a general discussion of the properties of bubbles containing 2 or more electrons. In the calculation of the energy of two electrons inside a spherical cavity with a hard wall, the key role is played by the relative magnitudes of the energy of Coulomb repulsion between the electrons and the quantum zero point energy. For very large bubbles, the Coulomb energy will dominate and the electrons will avoid each other by staying on opposite sides of the bubble and remaining near to the bubble wall. Thus, in the limit of large $R$ the electron energy is simply $e^2/2R$. Shikin then included the electron zero point energy in an approximate way. He noted that, providing the electrons remain near the wall, each electron experiences an electric field of strength $\approx e/(2R)^2$ due to the other. Then each electron moves in a potential of the form

$$\begin{aligned} V(r) &\approx \text{constant} + \frac{e^2}{4R^2}\,z \qquad & z > 0 \\ &= \infty & z < 0, \end{aligned} \tag{8}$$

where $z$ is the distance from the wall measured inwards. The wave function in a potential of this form is expressible in terms of the Airy function, and each electron has a zero-point energy of

$$2.33810\cdot\left(\frac{\hbar^2}{2m}\right)^{1/3}\left(\frac{e^2}{4R^2}\right)^{2/3}. \tag{9}$$

There is also a much smaller contribution to the zero point energy coming from the motion of the electrons parallel to the wall. Neglecting this latter contribution, the total energy of the electrons can be written as

$$E_{el}\approx\frac{e^2}{2R}+4.77620\cdot\left(\frac{\hbar^2}{2m}\right)^{1/3}\left(\frac{e^2}{4R^2}\right)^{2/3} \tag{10}$$

For a bubble of radius 30 Å, the two contributions have magnitude 0.24 and 0.19 eV and so $E_{el}\approx 0.43$ eV. Other approximation methods for the calculation of the properties of bubbles have been presented and discussed by Salomaa and Williams[30] and Shung and Lin.[31]

Here we calculate the energy of the two electron system exactly using a simple diffusion algorithm. We want to solve the Schrödinger equation for two particles of position $\vec{r}_1$ and $\vec{r}_2$ with potential $V(\vec{r}_1,\vec{r}_2)=e^2/r_{12}$ when both particles are inside the bubble of radius $R$ and with infinite potential outside. We first replace the time in the time-dependent Schrödinger equation by $-i\tau$. The equation then has the form

$$\frac{\partial\psi}{\partial\tau}=D\,\nabla^2\psi-K\psi, \tag{11}$$

where $\nabla^2=\nabla_1^2+\nabla_2^2$, $D=\hbar/2m$ and $K=V/\hbar$. Suppose that at time $t=0$ we start with an arbitrary initial $\psi$. We can write this as a linear combination $\sum_n A_n\psi_n$ of energy eigenfunctions $\psi_n$. After a sufficiently long time, $\psi$ will be approximately given by

$$\psi\approx A_0\psi_0\exp(-E_0\tau/\hbar), \tag{12}$$

where $E_0$ is the ground state energy. To perform this time development of $\psi$, we note that Eq. (10) is of the same form as the diffusion equation in 6 dimensions with the addition of the term $-K\psi$. We introduce $N$ "walkers" which are initially placed at random positions in $\vec{r}_1$, $\vec{r}_2$ space but with both $\vec{r}_1$ and $\vec{r}_2$ inside the bubble. At each time step of magnitude $\delta\tau$ in the time development, each walker is given a random step in 6-space of magnitude consistent with the value of the diffusion coefficient $D$. In addition, there is a probability $\exp(-K\,\delta\tau)=\exp[-V(\vec{r}_1,\vec{r}_2)\,\delta\tau/\hbar]$ that the walker will disappear. Thus, walkers that pass out of the region of the bubble are immediately annihilated. To keep the total number of walkers constant, new walkers are introduced at the locations of randomly chosen existing walkers. It can be seen from these rules that after a long time the average number density of the walkers must have the same spatial form as $\psi_0$. In addition, the average rate at which it is necessary to introduce new walkers to keep the number of walkers constant gives the ground state energy.

Using this method, we find the results for the ground state energy as a function of bubble radius that are shown in Fig. 9. For a radius of 33.9 Å, we find an energy of 0.49 eV, compared to the variational result of 0.56 eV obtained by Dexter and Fowler. It can be seen that in the radius range up to 60 Å, the approximation of Eq. (9) is not in good agreement with the exact result. However, for larger R we have confirmed that Eq. (9) does become a good approximation. For a radius of 500 Å, for example, Eq. (8) gives an energy that is only 7% less than the exact value. From the calculated two-electron wave function, we can also calculate the single-electron probability distribution per unit volume $P(r)$. This is shown in Fig. 10 for bubbles of radius 30, 40, 50, and 60 Å. This has been normalized so that the integral of $4\pi r^2 P(r)$ is unity. One can see that in agreement with the ideas outlined above, as the radius of the bubble increases the electrons become more localized in the region near to the bubble wall and the probability density in the center of the bubble becomes very small.

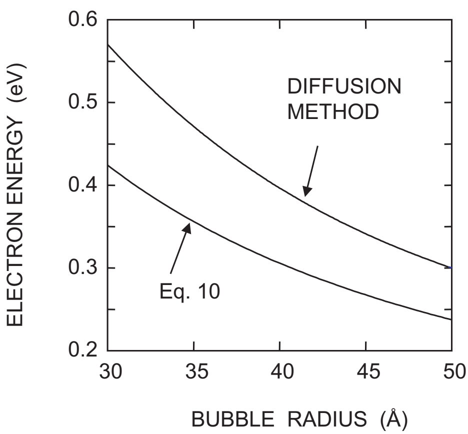


Fig. 9. Energy of two electrons inside a spherical bubble as a function of the bubble radius.

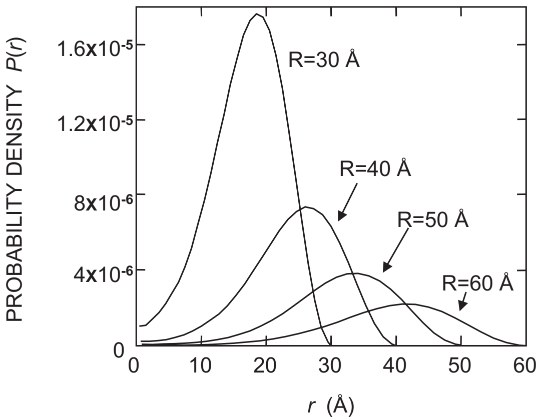


Fig. 10. Electron probability density as a function of distance $r$ from the bubble center for a series of bubble of different radius $R$.

Using the results for the electron energy, we can calculate the total energy of the bubble and find the equilibrium radius as a function of pressure. Results are shown in Fig. 11. As the pressure increases, the electron energy becomes larger and it becomes necessary to allow for the penetration of the wave function into the helium. For this reason, we include in Fig. 11 results up to only 3 bars. We find that the bubble becomes unstable against a uniform expansion at a critical pressure $P_c$ of $-1.00$ bars.

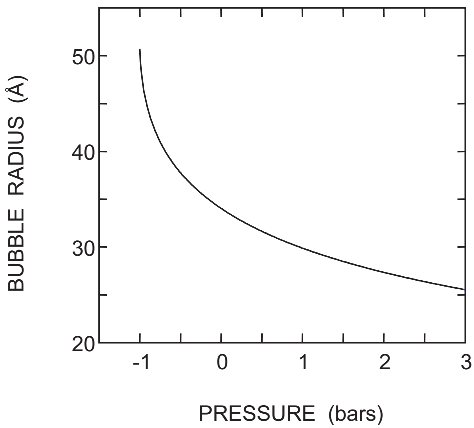


Fig. 11. The radius that minimizes the total energy of a two-electron bubble as a function of the pressure.

There has been considerable discussion about the stability of the two electron bubble. It was pointed out by Dexter and Fowler[27] that its energy is greater than the energy of two single electron bubbles. However, it is important to determine whether the bubble is stable against small perturbations. Since we are able to find a radius at which the total energy is a minimum, it is clear that at all pressures above $P_c$ the bubble is stable against isotropic expansion or contraction, i.e., against perturbations of $l = 0$ symmetry. We have investigated the stability of the bubble against perturbations of $l = 2$ symmetry, i.e., we have considered a bubble in which the distance to the surface in direction $\theta$ was $R + a_2 P_2(\cos\theta)$. For $R = 34$ Å, the energy of the bubble, including surface energy, is plotted as a function of $a_2$ in Fig. 12. It can be seen that the spherical bubble is indeed unstable against the increase of $a_2$. For $R$ fixed at 34 Å, there is a minimum energy when $a_2$ is approximately 16 Å. Calculations show that starting from the configuration with $R = 34$ Å and $a_2 = 16$ Å, the energy of the bubble can be further reduced by decreasing $R$ and increasing $a_2$, and that there is a path along which the energy decreases monotonically to a configuration in which the bubble has split into two single electron bubbles. It seems unlikely that this result will be modified by a more accurate calculation, for example, taking into account the penetration of the wave function into the liquid. Thus, our conclusion is that there is no barrier that prevents the two-electron bubble from decaying.

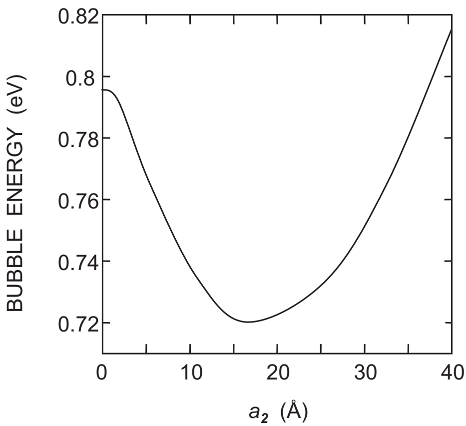


Fig. 12. The total energy of a two-electron bubble as a function of the parameter $a_2$. The distance from the center of the bubble to the surface in direction $\theta$ is $R + a_2 P_2(\cos\theta)$, where $R$ is 34 Å.

The above discussion is entirely concerned with the energetics of a bubble with two electrons with anti-parallel spins. One could also consider parallel spins, but in this case the spatial part of the wave function will change sign when $\vec{r}_1$ and $\vec{r}_2$ are interchanged and the diffusion algorithm that we have used cannot be applied. The ground state energy for $S=1$ will be higher than for $S=0$. In principle, these states will be unstable against reorientation of the spins, but the lifetime for this process is likely to be very long.

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