

# Exotic Ions in Superfluid Helium

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**Abstract** Exotic ions are negatively charged objects which have been detected in superfluid helium-4 at temperatures in the vicinity of 1 K. Mobility experiments in several different labs have revealed the existence of at least 18 such objects. These ions have a higher mobility than the normal negative ion and appear to be singly charged and smaller. We summarize the experimental situation, the possible structure of these objects, and how these objects might be formed.

**Keywords** Ions · Helium · Superfluid

## 1 Introduction

Positively and negatively charged ions in superfluid helium have been studied in many experiments. The positive ion is a dense cluster of helium atoms [1]. Recent calculations by Mateo and Eloranta [2] indicate that the positive charge is in the form of a triatomic  $\text{He}_3^+$  ion at the center of the cluster. The negative ion is an electron confined in a cavity in the liquid (“electron bubble”) that, at least at low temperatures, is free of helium atoms. This structure was first proposed by Careri et al. [3,4] based on earlier ideas of Ferrell [5], concerning the structure of positronium in liquid helium. The energy of the electron bubble is the sum of the zero-point energy of the electron, the surface energy, and, if the liquid is under pressure, the work done against the pressure in creating the bubble. To a good approximation, the energy of the electron bubble can be taken to be

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$$E = \frac{h^2}{8mR^2} + 4\pi R^2\alpha + \frac{4\pi R^3}{3}P, \quad (1)$$

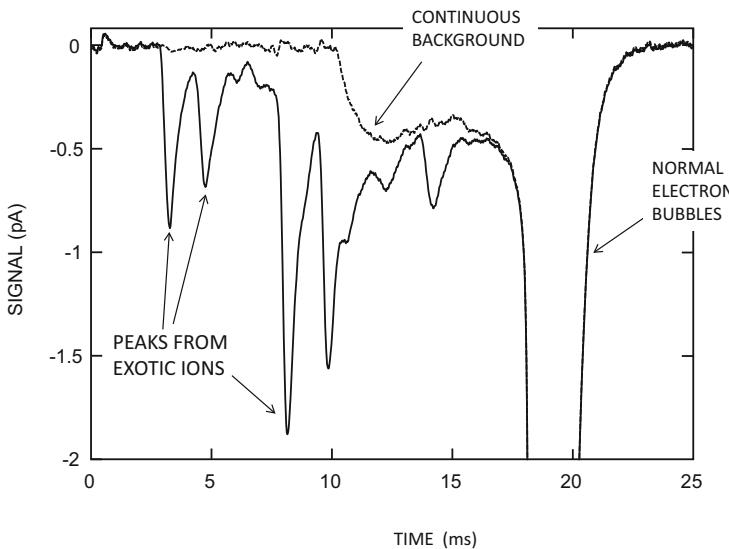
where  $R$  is the radius,  $\alpha$  is the surface tension,  $m$  is the mass of the electron, and  $P$  is the applied pressure. Using the measured value of  $\alpha$ , [6] the energy of the bubble when  $P = 0$  is found to be a minimum when  $R = 19$  Å. This estimate of the bubble size has been confirmed by experimental measurements of the photon energies required to excite the electron to a higher energy state (1P or 2P) [7, 8]. More detailed calculations of the energy of the electron bubble have been made using density functional methods [9], and these give a result for the radius differing only slightly from that obtained from Eq. 1. Measurements have also been made of the effective mass [10–13], again giving results consistent with the size of the bubble as estimated from Eq. 1. The energy of the bubble state as given by Eq. 1 when the pressure is zero is

$$E_0 = \sqrt{\frac{2\pi\alpha h^2}{m}} = 0.2 \text{ eV}, \quad (2)$$

whereas the energy of an electron moving through bulk liquid with uniform density is 1 eV [14].

The mobility of an electron bubble can be determined by introducing electrons into the liquid helium at the top of a cell in which there is a uniform drift field. The time taken for these charges to reach a collector electrode at the bottom of the cell is measured. In the superfluid phase, the mobility of an electron bubble is limited by the drag exerted on the bubble by thermal excitations, i.e., by phonons and rotons [15–18]. The measured temperature dependence of the mobility is in agreement with this assumption. In several of these mobility measurements, other negative ions which arrive at the collector before the normal electron bubbles (NEB) have been detected. The first such ion was seen in an experiment performed by Doake and Gribbon in 1969 [19]. This ion has become known as the “fast ion” and has a mobility about six times higher than the normal electron bubble. Shortly after this, Ihas and Sanders [20–22] detected several ions with a mobility intermediate between the mobility of the fast ion and the mobility of the normal electron bubble. These “exotic ions” have since been studied in more detail [23–30], and in a recent experiment [30], it has been shown that there are at least 18 such objects. These measurements have been performed at temperatures in the vicinity of 1 K, where the mobility is primarily limited by collisions of rotons with the ions. Since at this temperature the rotons have a mean free path through the liquid which is larger than the dimensions of the bubble, the drag force should be proportional to  $R^2$  and the mobility proportional to  $R^{-2}$ . From this, it follows that the fast ion has a radius of around 8 Å, and the exotic ions have a radius between this and the radius of the NEB.

Each of the 18 exotic ions just mentioned gives rise to a sharp peak in the collector current at a time determined by their mobility. Thus, each peak comes from the simultaneous arrival of some number of ions all of the same size. However, it has been discovered that in addition to these signals, there is a background signal coming from ions with a continuous distribution of mobility. This is a remarkable result since this



**Fig. 1** Solid curve shows the current arriving at the collector as a function of time. The temperature is 0.991 K, the drift field is  $82.1 \text{ V cm}^{-1}$ , and the length of the drift cell is 6.15 cm. The dashed curve shows the same data with the peaks removed

background signal must come from ions which have a continuous distribution of size. For a more detailed discussion of this background, see Ref. [30].

In Fig. 1 we show an example of the signal reaching the collector as a function of the time after ions leave the top of the cell. Each peak in the signal arises from one of the exotic ions. By removing the contribution to the signal from each of the peaks, the continuous background mentioned above is revealed (dashed curve).

## 2 Origin of the Exotic Ions

Despite considerable effort, it has not so far been possible to find a plausible explanation of the structure of the exotic ions [30]. Consider first the possibility that the ions are impurities. An impurity atom which has an extra electron will form a bubble which, if the electron affinity has a suitable value, will have a size in the size range of the exotic ions. The dependence of the bubble size on electron affinity has been calculated [30, 31]. The calculations show that in order for impurities to be the explanation of the exotic ions, the impurities have to have a low electron affinity, i.e., less than  $\sim 1 \text{ eV}$ . A serious difficulty with the impurity model is that the number density of impurities in liquid helium is expected to be very small. Furthermore, it is hard to believe that the liquid can contain 18 different impurities in sufficient number and with electron affinity in the required range. Since each impurity will give rise to an ion of a particular definite size, it is also obviously impossible for impurities to be the explanation of the continuous background.

As a second approach suppose that the exotic ions are negative helium ions. Ions of both the helium atom [32–36] and the helium dimer have been studied [37–39]. However, these ions have a lifetime much shorter than the time for an ion to pass through the mobility cell. In mobility experiments performed so far, this time has been as large as 100 ms. In addition to this problem, helium ions cannot provide an explanation of the continuous background. In a recent paper, Elser [40] has proposed that the exotic ions may be an electron bound to a small vortex ring. But it is not yet clear how this approach can be developed to explain the existence of 18 exotic ions together with the a continuous background.

To overcome these problems, it has been proposed in the “fission model” [41] that the exotic ions are bubbles which contain only a fraction of the total wave function of an electron. An electron entering the liquid will lose energy by collisions with helium atoms and will have a complicated wave function. Can part of this wave function sometimes be trapped in one bubble and the remaining part in another? As discussed in more detail below, a bubble containing only a fraction of the wave function would be smaller than a normal electron bubble. Let  $F$  be the integral of  $|\psi|^2$  over the volume of a bubble. If  $F$  can have a continuous range of values, this will lead to a continuous size distribution of bubbles and provide a simple explanation of the experimentally observed continuous background. In addition, there is a mechanism (see detailed description in Ref. [30]), which leads to the formation of bubbles with particular values of  $F$ , thereby providing a possible explanation of the exotic ions with many particular discrete sizes.

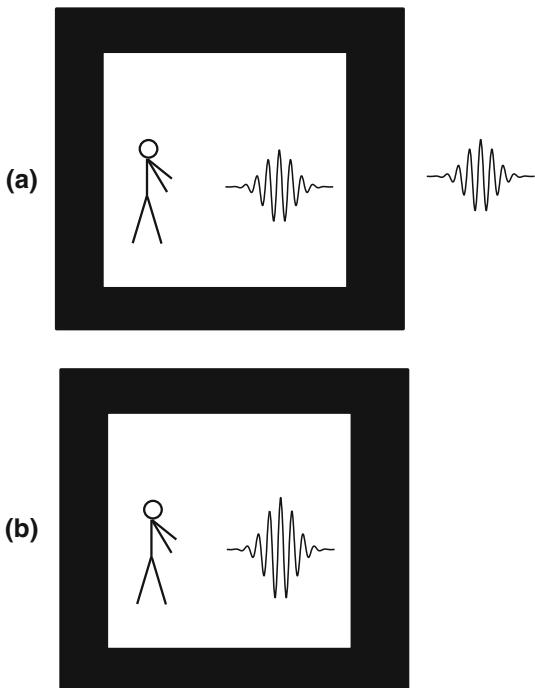
### 3 Quantum Mechanics and the Exotic Ions

According to quantum mechanics, the state of a system is completely described by the wave function  $\Psi$ . As has been pointed out many times, the theory is remarkable in that the wave function changes with time by two apparently distinct mechanisms. The time-dependent Schrödinger equation gives  $d\Psi/dt$  in terms of the Hamiltonian and the instantaneous form of the wave function. But in addition, according to the Copenhagen interpretation, measurements also result in changes in  $\Psi$ . If a quantity  $g$  is measured, the result of the measurement must be one of the eigenvalues  $\{g_n\}$  of the operator  $\hat{g}$ . If the result of the measurement is  $g_n$ , then the wave function immediately changes to equal the eigenfunction  $\xi_n$  corresponding to this eigenvalue.

This leads to a number of unresolved issues. The first problem is that there is no agreement as to what constitutes a measurement. Does a measurement automatically result from an interaction between the system of interest and any other large complicated system? Or does a person (“consciousness”) have to be involved? These questions were presented long ago in a series of papers by Putnam [42, 43], by Margenau and Wigner [44–46], and by Cooper and Van Vechten [47–49].

A second and equally obvious question concerns relativity [50]. Suppose that at time  $t$  a measurement is made at a point  $\vec{r}$  to look for a particle, and the particle is found to be there. Then the wave function is supposed to immediately collapse and become zero everywhere except at  $\vec{r}$ . This requires that news of the measurement travel faster than the speed of light. A related question concerns the effect of a barrier on collapse.

**Fig. 2** **a** Initial condition with part of the wave function *inside* a box and with the remainder outside. **b** Final condition after a measurement has found the particle *inside* the box



Suppose that we make a box with thick walls providing a very large potential barrier preventing passage of the wave function. Then consider an initial condition in which a part of the wave function of a particle is inside the box and a part outside (Fig. 2a). An observer inside the box performs an experiment to look for the particle. If the result of the experiment is that the particle is found, then all of the wave function has to be inside the box as in Fig. 2b. But how does the part of the wave function that was out of the box get inside? This question arises in the discussion below of the fission model as a possible explanation of the exotic ions.

We now consider the general features of the quantum state that is produced when an electron enters helium, and two bubbles are formed with part of the wave function in each. The size of each of these bubbles is determined by the outward pressure exerted by the electron balanced against the surface tension force; this force arises because of the repulsion between the electron and helium atoms. Rae and Vinen [51] have argued that, despite this repulsion, when two bubbles are formed one of them will always collapse. As a particular case, they consider two bubbles each of radius  $R_{1/2}$ ; for each bubble, the integral of  $|\Psi|^2$  over the bubble volume is  $1/2$ . They emphasize that a many-body wave function is needed to describe the electron and the helium. They then propose that this wave function is of the form (their Eq.5)

$$\Psi = \chi(R_{1/2}, R_{1/2}) [c_1 \psi_1 + c_2 \psi_2, ] \quad (3)$$

where  $\chi(R_{1/2}, R_{1/2})$  describes the helium containing the two holes, and  $\psi_1$  and  $\psi_2$  are wave functions of the electron confined within these holes. They then argue that such a state would be unstable and would lead to one of the holes in the helium collapsing and the wave function of the system ending up as a linear combination of two states, each with only one bubble containing an electron. Unfortunately, it is easy to see that this choice of wave function is inadequate. The wave function in Eq. 3 is the product of a function  $f_{hel}$  involving only helium coordinates with a function  $g_{el}$  of the electron coordinates. Let us write the Hamiltonian of the entire system as

$$\hat{H} = \hat{H}_{hel} + \hat{H}_{el} + V_{int}, \quad (4)$$

where  $\hat{H}_{hel}$  involves only helium coordinates,  $\hat{H}_{el}$  involves only electron coordinates, and  $V_{int}$  is the potential of interaction between the helium and the electron. Then the Schrödinger equation  $\hat{H}\Psi = E\Psi$  becomes

$$(\hat{H}_{hel} + \hat{H}_{el} + V_{int}) f_{hel} g_{el} = E f_{hel} g_{el}. \quad (5)$$

Then taking note of the variables on which the different components of the Hamiltonian act,

$$(\hat{H}_{hel} f_{hel}) g_{el} + f_{hel} (\hat{H}_{el} g_{el}) + V_{int} f_{hel} g_{el} = E f_{hel} g_{el}, \quad (6)$$

and so after dividing by  $f_{hel} g_{el}$ , we obtain

$$\frac{(\hat{H}_{hel} f_{hel})}{f_{hel}} + \frac{(\hat{H}_{el} g_{el})}{g_{el}} + V_{int} = E. \quad (7)$$

The first term on the left hand-side contains only helium coordinates and the second term only electron coordinates. It follows that  $V_{int}$  has to be the sum of a function of helium coordinates and a function of electron coordinates, and so, in fact, there is no interaction between the electron and the helium. Given this, it is not surprising that the presence of an electron does not prevent holes in the helium from collapsing.

We therefore need a more realistic model that includes the interaction between the electron and a helium atom and also the interaction between helium atoms. The simplest approach is to treat the helium–helium interactions in the Hartree approximation. This leads to the Gross–Pitaevskii (GP) equation [52–55]. After inclusion of the interaction between the helium and an electron [55, 56], the GP equation takes the form of two coupled differential equations:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2M} \nabla^2 \psi + (U_0 |\phi|^2 + V_0 |\psi|^2) \psi, \quad (8)$$

$$i\hbar \frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \phi + U_0 |\psi|^2 \phi, \quad (9)$$

where  $\psi$  describes the state of the helium ( $|\psi(\vec{r})|^2$  is the number density of helium atoms at position  $\vec{r}$ ),  $\phi$  gives the state of the electron,  $M$  is the mass of a helium atom,  $V_0$  gives the strength of the potential between two helium atoms, and  $U_0$  sets the strength

of the potential between an electron and the helium. In this simplest version of the GP equation, both the helium–helium interaction and the electron–helium interaction are taken to be of short range. An electron at rest in liquid helium with uniform number density  $2.2 \times 10^{22} \text{ cm}^{-3}$  is known to have an energy of approximately 1 eV. This sets the value of  $U_0$  as  $7.3 \times 10^{-35}$  in cgs units.

It is well known that, as they stand, these equations do not give quantitatively correct values for properties of liquid helium. For example, since the helium–helium interaction in Eq. 8 is entirely repulsive the system has to be under a positive pressure in order for the equilibrium number density  $N/V$  to equal the number density in liquid helium at zero pressure ( $2.2 \times 10^{22} \text{ cm}^{-3}$ ). As a second example, if  $V_0$  is chosen to give the correct sound velocity, the surface tension  $\alpha$  does not have the value found experimentally. These problems can be fixed through the use of more complicated models [57–59], for example, models in which the interaction potentials have finite range. There have been a large number of computer simulations performed using the GP equation. These include studies of vortex dynamics, the attachment of electron bubbles to vortices [60], and the changes in shape of electron bubbles due to motion through the superfluid [59, 61] and due to optical excitation [62, 63]. In the present context, since we are just trying to give a qualitative discussion of the physics of the exotic ions, there is no need to use one of these more improved models.

Consider now the application of the GP equations to the exotic ions. Energy eigenstates are to be found from the equations

$$E_{hel}\psi = -\frac{\hbar^2}{2M}\nabla^2\psi + (U_0|\phi|^2 + V_0|\psi|^2)\psi, \quad (10)$$

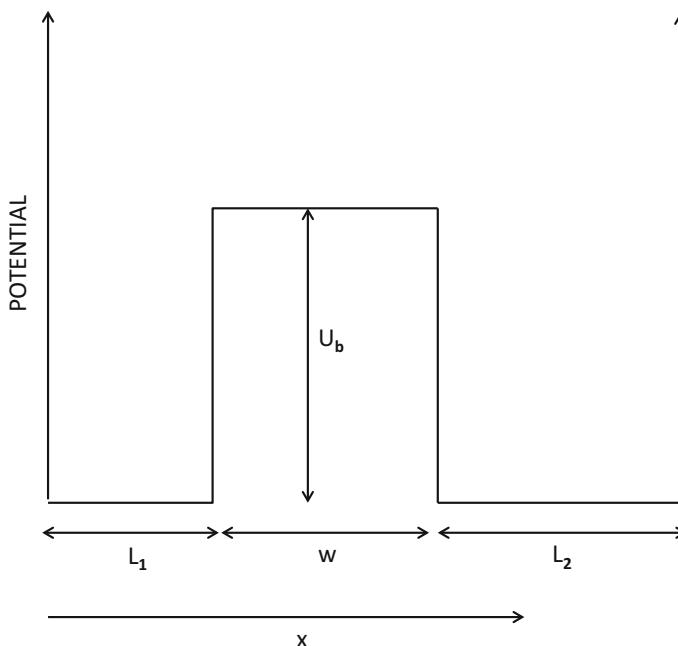
$$E_{el}\phi = -\frac{\hbar^2}{2m}\nabla^2\phi + U_0|\psi|^2\phi. \quad (11)$$

One can see immediately that there are eigenstates in which the density of the helium is uniform ( $\psi = \sqrt{N/V}$ ), and there is uniform probability density for the electron ( $\phi = \exp(ik.r)/\sqrt{V}$ ). However, the lowest energy eigenstates are the “normal electron bubble states,” i.e., states with the electron trapped in a single bubble as already described. The electron wave function and the variation of the helium density around the single bubble have been calculated from Eqs. 10 and 11 a long time ago by Clark [64], and the same type of calculation has been performed for more complicated versions of the Gross–Pitaevski model [9, 65]. Since the energy of any one of these states is independent of the bubble position, these states have a high degeneracy. There must also be a family of eigenstates corresponding to moving bubbles. As far as we know, there has been no study of other families of eigenstates of the Gross–Pitaevskii equation.

Consider now the formation of a bubble or bubbles as a result of an electron entering the liquid. Take the case in which an electron enters the helium and the wave function evolves in a way such that it has high amplitude in two regions containing fractions  $F$  and  $1 - F$  of the integral of  $|\Psi|^2$ . We suppose that these regions do not overlap significantly so that two bubbles will form, bubble A with  $\int |\Psi|^2 dV = F$  and bubble B with  $\int |\Psi|^2 dV = 1 - F$ , with a region of helium of full density lying between

them. There will then be a large barrier which will prevent wave function passing from one bubble to the other. A barrier of height 1 eV results in the wave function of an electron decaying with distance  $x$  as  $\exp(-x/\zeta)$ , where  $\zeta = 1.95 \text{ \AA}$ . Thus, if we assume an attempt frequency of  $10^{14} \text{ s}^{-1}$ , the time for tunneling through the barrier reaches 1 s when the shortest path through the liquid between bubbles is about  $30 \text{ \AA}$ . In this situation, the amount of  $|\Psi|^2$  inside each bubble cannot change significantly with time, at least not as a result of the change in  $\Psi$  predicted by Schrödinger's equation. However, the form of the wave function can change. As one example, suppose the wave function in A is not the ground state wave function in the potential provided by the wall of bubble A, but an excited state. This wave function can transition to the ground state with emission of a photon; this does not result in a transition of any  $|\Psi|^2$  from A to B. There could also be changes in the wave function resulting from the interaction of the wave function in A with fluctuations of the bubble wall. But again, since these fluctuations are at the frequencies characteristic of thermal vibrations or zero-point vibrations of the liquid ( $f < 10^{11} \text{ Hz}$ ), they cannot excite an electron to a state of high enough energy to pass over the barrier.

It is important to note that the states just considered are not eigenstates satisfying Eqs. 10 and 11. Because the bubbles differ in size, the pieces of electron wave function in each bubble will have different energies and so, as one can see from the GP equation, will oscillate at different frequencies, i.e., the electron wave function will certainly not oscillate in time as it does in an eigenstate. Let us make this explicit by means of a simple example. Consider the potential in one dimension as shown in Fig. 3:



**Fig. 3** Sketch of the potential specified by Eq. 12

$$\begin{aligned}
V(x) &= \infty \quad x < 0 \\
&= 0 \quad 0 < x < L_1 \\
&= U_b \quad L_1 < x < L_1 + w \\
&= 0 \quad L_1 + w < x < L_1 + w + L_2 \\
&= \infty \quad L_1 + w + L_2 < x.
\end{aligned} \tag{12}$$

If the height  $U_b$  of the barrier is very large and the widths of the two wells are not very close to being equal, there are two families of eigenstates and eigenvalues:

$$\psi = \sqrt{\frac{2}{L_1}} \sin\left(\frac{n_1 \pi x}{L_1}\right) \quad 0 < x < L_1 \quad E = \frac{\pi^2 n_1^2 \hbar^2}{2m L_1^2} \tag{13}$$

and

$$\psi = \sqrt{\frac{2}{L_2}} \sin\left(\frac{n_2 \pi x}{L_2}\right) \quad L_1 + w < x < L_1 + w + L_2 \quad E = \frac{\pi^2 n_2^2 \hbar^2}{2m L_2^2}, \tag{14}$$

with  $\psi$  is zero outside of the indicated ranges. These eigenstates are different from the wave functions proposed for the exotic ions. Taking only the lowest state in each well, these wave functions are of the form

$$\begin{aligned}
\psi &= \sqrt{F} \sqrt{\frac{2}{L_1}} \sin\left(\frac{\pi x}{L_1}\right) \exp[-i(\omega_1 t + \phi_1)] \quad 0 < x < L_1 \\
&= \sqrt{1-F} \sqrt{\frac{2}{L_2}} \sin\left(\frac{\pi x}{L_2}\right) \exp[-i(\omega_2 t + \phi_2)] \quad L_1 + w < x < L_1 + w + L_2,
\end{aligned} \tag{15}$$

where  $\omega_1 = \pi^2 \hbar / 2m L_1^2$ ,  $\omega_2 = \pi^2 \hbar / 2m L_2^2$ , and the phases  $\phi_1$  and  $\phi_2$  can have any value.

## 4 Summary

In this paper, we have focused on describing in some detail the type of wave function that is proposed in the fission model. We argue that if the wave function undergoes time-development determined by Schrödinger's equation, then two bubbles separated by a large distance will be stable objects. If, on the other hand, the helium forming the boundary of a bubble performs a measurement to determine whether or not the bubble contains an electron, this measurement will result in "collapse of the wave function" and only one bubble will survive. Thus, if an experiment can be performed to show that the exotic ions are indeed bubbles containing a fraction of  $|\Psi|^2$ , this will provide interesting information about the quantum measurement process.

It is a great pleasure to contribute this article to this special issue of the Journal of Low Temperature Physics in honor of Horst Meyer. We thank him for his contributions to physics, his generous nature, and his great service to the low-temperature physics community over many years.

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