Pis'ma v ZhETF, vol.65, iss.6, pp.454 - 458

NEGATIVE IONS IN LIQUID HELIUM: EXISTENCE OF NEW BOUND STATES

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Submitted 10 December 1996
Resubmitted 11 February 1997

It is shown that fundamentally new bound states can be formed when a foreign negative ion is embedded in liquid helium. For such states the excess electron forms a bubble with a radius $R_0 \simeq 17-18$Å and a foreign neutral atom is trapped inside this bubble because of the polarization interaction with the electric field of the excess electron, which has a maximum at a point $r \simeq R_0/2$. The main properties of such structures are considered.

PACS: 39.60.+f, 67.55.Lf

It is well known that an excess electron embedded in liquid helium-4 pushes away the helium atoms and resides in a bubble with the radius of $17-18$Å at zero pressure [1]. This occurs because the repulsive interaction of an excess electron with helium atoms at typical interatomic distances is strong (the barrier for a free electron to penetrate into liquid helium U_0 is 1.02 eV [2]) and the surface tension of helium is small. Various properties of such bubbles are now rather well studied both experimentally and theoretically (see, e. g., Refs. [1-4] and references cited therein).

Relatively recently spectral and other characteristics of neutral atoms and positive ions embedded in liquid helium have also become a rather popular object of study, and a number of experimental [5-7] and theoretical [8-11] investigations in the field have been carried out. It has been shown that the main properties of such atoms and positive ions are reasonably well characterized by the model of a spherical bubblelike state, analogous to the free electron case: foreign atoms and ions embedded in liquid helium create bubbles with radii $R \sim 8-13$Å through the repulsive interaction of the helium atoms with the outer valence electron of the foreign atom or ion.

In this letter we would like to point out the fact that bound states of a fundamentally new type can be formed in the case of *negative* ions implanted in liquid helium. For these states a quasifree excess electron creates a bubble with a radius R_0 and a foreign neutral atom is localized *inside* this bubble through the polarization interaction with the electric field of the excess electron, which has a maximum at $r \simeq R_0/2$. In this case the excess electron can be regarded as the "nucleus" and a neutral atom can be regarded as the "electron" of a new type atom.

The wave function $\psi(r)$ of an electron in the bubble with a raduis R_0 can be written as [3, 12]:

$$\psi(r) = \frac{A}{r}\sin(k_0 r) \text{ for } r \leq R_0, \qquad (1)$$

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$$\psi(r) = \frac{B}{r}\exp(-kr) \text{ for } r \geq R_0, \tag{2}$$

where

$$k = \sqrt{2U_0 - k_0^2}. \tag{3}$$

(Here and below, unless specifically stated to the contrary, the system of atomic units with $m = e = \hbar = 1$ will be used.) k_0 value can be found from the condition of matching the ratio ψ'/ψ for (1) and (2) at the point $r = R_0$:

$$\tan(k_0 R_0) = -\frac{k_0}{k}, \tag{4}$$

and A and B are normalization constants which can be found from the usual relation $\int \psi^2 r^2 dr = 1$. In the case of the simplest model of an impenetrable spherical square well potential barrier at $r = R_0$ the relation (4) is replaced by the condition $\psi(R_0) = 0$, which for the $1s$ ground state of the electron in a bubble gives $k_0 = \pi/R_0$. For the subsequent discussion we shall use for the R_0 value the experimental data of Grimes and Adams [4], who found for the case of zero external pressure that $R_0 = 17.2$ Å $= 32.5$ atomic units. Using this value and the barrier height $U_0 = 1.02$ eV $= 0.0375$ one easily finds that $k_0 = 0.084$, $k = 0.26$, $A = 0.231$ and thus for $r \leq R_0$:

$$\psi(r) = \frac{0.231}{r}\sin(0.084r). \tag{5}$$

Let us define $q(r)$ as the total electric charge contained in the region $0 \leq r_1 \leq r$ ($r \leq R_0$); then

$$q(r) = \int_0^r \psi^2(r_1) r_1^2 dr_1 = \frac{A^2}{2}\left(r - \frac{\sin(2k_0 r)}{2k_0}\right). \tag{6}$$

The electric field strength accociated with the charge distribution (6) is:

$$E(r) = \frac{q(r)}{r^2} = \frac{A^2}{2}\left(\frac{1}{r} - \frac{\sin(2k_0 r)}{2k_0 r^2}\right) \tag{7}$$

For the subsequent discussion the most important fact is that the electric field strength $E(r)$ (7) has a maximum at $r_0 = \pi/2k_0 = 18.7 = 9.9$Å *inside* the bubble. (For the above-mentioned simplest model of the impenetrable square well barrier, $r_0 = R_0/2 = 8.6$Å.) It means that the energy of interaction between an atom with a polarizability α and the electric field E of the excess electron

$$U = -\frac{1}{2}\alpha E^2 \tag{8}$$

has a minimum at the same radius $r = r_0$, and this atom can be trapped in the vicinity of this point and form a bound system of a new type. The potential energy of this polarization interaction is fairly high, and for many atoms it is much higher than the typical thermal energy of liquid helium. For example, for a lithium atom of polarizability $\alpha = 160$ [13] this energy is equal to $1.6 \cdot 10^{-4} = 51$ K, for a magnesium atom ($\alpha = 74$ [13]) $U \simeq 24$ K, etc. (here the polarizability unit in the Coulomb system $a_0^3 = 1.48 \cdot 10^{-25}$ cm^{-3} is used, a_0 is the Bohr radius). At the same time, the energy of polarization interaction is much smaller than the energy of the $1s$ ground state of an electron in the bubble $E_0 = k_0^2/2 = 7 \cdot 10^{-3} = 0.19$ eV and thus the excess electron can really be treated as a quasifree one for which this interaction has a character of a relatively small correction to its repulsive interaction with liquid helium. We believe that such a relation between the typical energies of interaction between an excess electron and a foreign atom and between an excess electron and liquid helium justify the use of the simple model considered in this paper. A more detailed analysis of energy states for the system considered will be published later elsewhere. For such an analysis it is necessary to take into account some factors which have been neglected here: first of all an additional repulsive interaction of helium atoms with the outer valence electron of a foreign atom inside a bubble [8–11], etc. At the same time, it should be noted that the maximum electric field strength in the case considered is equal to $\simeq 7\cdot 10^6$ V/cm, i. e. exactly of the same order of magnitude (even slightly below) as that available in experiments on the field evaporation of atoms adsorbed on sharp metal tips (see, e. g., [14] and references cited therein). These experiments revealed that the interaction between the electric field and the atom can be satisfactorily described by the simple polarization potential (8), even for such strong fields, which is an additional justification of the model used in the present work.

Note that the values of r_0 and $R_0 - r_0$ are somewhat larger then the typical Hartree radii of light atoms $r_{at} \sim$ 2–4 Å Ref. [13], and the effective mass of the bubble, which is ~ 240 times the mass of a ^{4}He atom [1, 11] is much larger than the mass of a foreign neutral atom. Thus the system considered can really be regarded as a new type atom, where the "light electron" (a neutral atom) is orbiting "in vacuum" (inside a bubble) around a "heavy nucleus" (an excess electron which forms a bubble).

To estimate roughly the total number N of bound states in the system considered we can use the well-known semiclassical result of Pokrovskiĭ: for the case of a spherically-symmetric interaction potential this number can be expressed by the integral [12]

$$N \simeq \frac{M}{4}\int_0^{R_0}(-U)rdr = \frac{M\alpha A^4}{32}\int_0^{R_0}\left(\frac{1}{r} - \frac{\sin(2k_0 r)}{2k_0 r^2}\right)^2 rdr. \qquad (9)$$

For the case of the lithium atom such an estimate gives $N \simeq 200$, and for the magnesium atom, $N \simeq 370$, which are much greater than unity (the value of the last integral in (9) is 1.10).

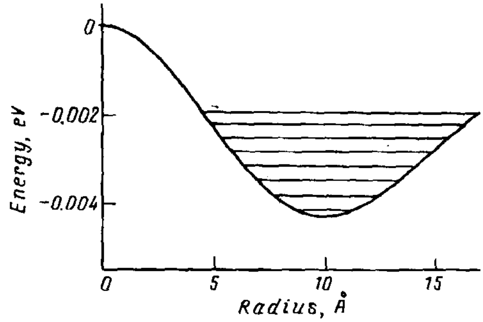
The energy levels $E_{n,l}$ of the system considered can be found from the usual semiclassical quantization condition [12, 15]:

$$\int_{r_1}^{r_2}\sqrt{2M(\frac{\alpha E^2}{2} - \frac{1}{2Mr^2}(l+1/2)^2 + E_{n,l})} = \pi(n+1/2), \qquad (10)$$

where M is the mass of the foreign neutral atom, l is the angular momentum, and n is an integer designating the number of energy states with a given l value. The energy $E(r)$ can be found from relation (7), and r_1, r_2 are the roots of the equation

$$\frac{\alpha E^2}{2} + E_{n,l} - \frac{(l+1/2)^2}{2Mr^2} = 0; \qquad (11)$$

for angular momentum $l = 0$ the term containing $(l+1/2)^2$ in (10) should be omitted. Generally such a semiclassical quantization procedure gives precise results for large n and l values only, but the results of such calculations are frequently used for the qualitative evaluation of the energies of the states even with the smallest n and l [12, 15]. Some of these results for the cases of lithium and magnesium atoms are shown on Figure. It can be seen that the energy difference between different (n, l) and $(n, l+1)$ states with the same principal quantum number n and neighbouring angular momenta l, $l+1$ is very small: this difference is of the order of $\sim 3 \cdot 10^{-5}$ eV for $n=1$ and rapidly decreases with increasing n. Certainly such a small energy difference is due to the large foreign atom mass M: it is easy to see that for not very large l the first term in (10) (polarization attraction) is much larger than the second term (centripetal potential). The sequence of energy levels for the case of lithium atom is as follows: $1s$, $1p$, $1d$, ..., 1 $l=11$, $2s$, $2p$, $2d$, 1 $l=12$, $2f$, $2g$, 1 $l=13$, $2h$, 2 $l=6$, 1 $l=14$, 2 $l=7$, 2 $l=8$, 1 $l=15$, 2 $l=9$, 1 $l=16$, 2 $l=10$, $3s$, etc. Note, that similarly to the free excess electron case, a number of dipole allowed radiative transitions between the considered different states of negative ions in liquid helium should exist.



An interaction potential and energy levels of the bound states of a lithium atom residing inside a bubble created by an excess electron for the case $l=0$

Calculations based on formulas (10) or (9) show that bound states cannot exist for the atoms with very small polarizability. Certainly, such states cannot exist also for atoms for which the electron-atom repulsion dominates (such as helium or neon). In this case the "electron pressure" effect will be the most important: such an embedded atom, which is "impenetrable" to the electron, decreases the volume of the region in which the excess electron is localized, which leads to an increase in the energy of this localized electron. Thus the electron tends to push these atoms out of the bubble; quantitatively this process can be descibed using a concept of a localized electron pressure – see, e. g., [1] and references cited therein.

Thus we have shown that negative ions embedded in liquid helium can form bound states of a fundamentally new type. For atoms which can form free stable negative ions (such as lithium) these states can be regarded as a highly excited metastable states of a different nature from that of the ground state of a free negative ion. For such atoms which cannot form free stable negative ions but at the same time have non-negligible polarizability (such as magnesium) these states are the only possible bound states of the negative ion (which in this case can exist only inside liquid helium). Certainly an experimental study of such states would be very interesting from the viewpoints of the physics of particles embedded in liquid helium as well as the physics of the excess-electron/neutral atom interaction. It seems that such systems (even for the case of atoms which cannot form free stable negative ions) can be prepared using the same technique of laser sputtering of samples embedded in liquid helium, which has been already successfully used for neutral-atom implantation in liquid helium [16]. Analogous energy states can be realized also for negative ions trapped inside of cryodielectrics other than liquid helium with a negative electron affinity (liquid and solid hydrogen, neon, etc. [1]). The case of solid hydrogen is especially interesting because here the dimensions of the trap are not governed by the surface tension and can be arbitrary.

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Edited by J.Anderson.