Structure of O_2^- in dense helium gas

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The structure and mobility of O_2^- ions in dense helium gas was analyzed theoretically by taking into account the repulsive interaction of the outer electron of the ion with the surrounding helium atoms. It was found that at sufficiently high densities the ion resides in an empty void (bubble) as in the case of excess electrons. Available experimental data by Bartels [Appl. Phys. **8**, 59 (1975)] on O_2^- mobility at a temperature of 77.6 K are in good agreement with the present estimate. At densities of $(2.5-7.5)\times 10^{21}$ cm^{-3}, realized in the experiment, the radius of the bubble with the localized ion was found to be nearly independent of density and the mobility varied with N^{-1}.

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The investigations of the transport properties of excess electrons and positive ions injected in dense gases and liquids have received a great deal of attention [1,2]. It is well known that clusters consisting of several tens of atoms are created around positive ions in rare gases, while electrons in He and Ne are localized at low enough temperature and high densities with the formation of spherical bubbles having radii of 10–20 Å. Much less is known about the properties of negative ions in these systems. Only in a few works was the mobility of O_2^- investigated (particularly in dense supercritical He [3] and Ne [4] and in liquid Ar, Kr [5], and Xe [5,6]). Bartels [3] tried unsuccessfully to explain the anomalous values of the mobility and its temperature dependence by assuming the existence of O_n^- complexes. Borghesani, Neri, and Santini [4] suggested that, as a result of electrostriction, a cluster of Ne atoms is created around O_2^-. They also took into account the influence of the increase of density near the ion on the local viscosity. In all these works the quantum nature of the electron-atom interaction was not taken into account.

In this work it will be shown that the exchange repulsion of the outer, weakly bound electron of O_2^- with the electrons of the surrounding helium atoms results in the formation of an empty void around O_2^- rather than of a cluster.

The electron affinity of O_2 is small, $\varepsilon=0.46$ eV; therefore, the orbit of the outer electron of O_2^- is extended in space with the radius of the orbit given approximately as $R_i \sim \hbar/\sqrt{2m\varepsilon} \cong 4.2a_0$ (a_0 is the Bohr radius). The interaction of the electron with the helium atoms is attractive only at large distances. At short distances the repulsive exchange interaction between the outer electron and the atomic electrons prevails. The repulsion favors the creation of a void around O_2^- in dense He. The situation is very similar to the case of electron and positronium bubbles in gaseous and liquid He [1,7], as well to the case of bubbles that are created around excited atoms [8] and positive alkaline-earth-metal ions [9]. In both of the latter cases the valence electrons have also extended orbits.

Generally, the main properties of a negative ion can be described by the simple model potential shown in Fig. 1,

$$V(r)=\begin{cases} -\dfrac{\alpha e^2}{2r^4} & \text{for } r>R \\ \infty & \text{for } r\le R\ , \end{cases} \tag{1}$$

where R is the radius of the short-range core of the potential and α is the polarizability of the atom or molecule of the medium. This potential has the correct long-range asymptote. It takes into account short-range exchange repulsion. For large enough values of the parameter α/a_0R^2, it has discrete levels with negative energy. As shown in [10], the energy spectrum of an electron in the potential given by Eq. (1) can be determined with good accuracy by joining at $r=R_1$ the short-distance asymptote of the radial wave function

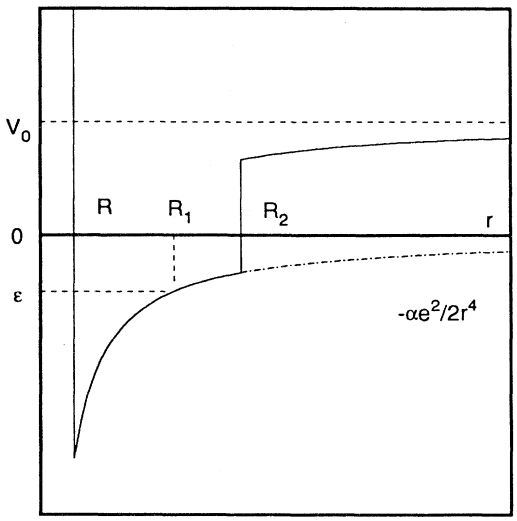

FIG. 1. Model potential for the external electron in a negative ion placed in a dense gas or a liquid.

$$\chi(r)=Ar\sin[\sqrt{\alpha/a_0}(r^{-1}-R^{-1})]\ , \tag{2}$$

and its long-distance asymptote

$$\chi(r)=Be^{-\gamma_1 r}\ ,\quad \gamma_1^2=\frac{2m\varepsilon}{\hbar^2}=\frac{\alpha}{a_0R_1^4}\ . \tag{3}$$

A and B are numerical constants and ε is the electron affinity of the atom or molecule (we assume that $\varepsilon \ll \alpha e^2/2R^4$). The relation between R, α, and ε is given by

$$\cot[\sqrt{\alpha/a_0}(R_1^{-1}-R^{-1})]-R_1\sqrt{a_0/\alpha}=1\ ,\quad \varepsilon=\frac{\alpha e^2}{2R_1^4}\ . \tag{4}$$

In the case of the ion O_2^-, the electron affinity is $\varepsilon=0.46$ eV. The polarizability of the molecule O_2 is $\alpha=10.6a_0^3$ and with help of (4) we obtain $R\cong 0.93a_0$. Note that an exact numerical solution of the Schrödinger equation with the potential given by Eq. (1) with the same ε and α gives approximately the same value $R=0.92a_0$ [10].

The interaction of the outer electron of O_2^- with rare gas atoms can be treated in analogy to the case of excess electrons. The strong exchange repulsion in He and Ne leads to a shift of the energy of the electronic conduction band V_0 to a positive value with respect to the vacuum level, i.e., $V_0>0$ [7]. The density fluctuations lead to fluctuations of V_0. Decompressions present potential wells capable of the capture of electron. In the case of the outer electron of O_2^-, the energy of the system of ion and atoms is reduced if the work necessary for the creation of the fluctuation does not exceed the increase of the electron binding energy.

Let us consider an ion O_2^- placed in an empty spherical void of radius R_2. Then, in accordance with Fig. 1, the model potential for the outer electron can be represented by

$$V(r)=\begin{cases} V_0-\dfrac{\alpha e^2}{2r^4} & \text{for } r>R_2 \\ -\dfrac{\alpha e^2}{2r^4} & \text{for } R<r\le R_2 \\ \infty & \text{for } r\le R\ . \end{cases} \tag{5}$$

Near the solid core the wave function of the external electron $\chi(r)$ still coincides with (2). Far away from the molecule ($r\gg R_2$), $\chi(r)$ practically coincides with (3), except that γ_1 is to be replaced by γ_2, where

$$\gamma_2^2=\gamma_1^2+\frac{2mV_0}{\hbar^2}\ . \tag{6}$$

In the intermediate region $R_1<r<R_2$, the wave function is given as

$$\chi(r)\cong C_1e^{\gamma_1 r}+C_2e^{-\gamma_1 r}\ . \tag{7}$$

Joining the logarithmic derivatives of the wave function at the points $r=R_1$ and $r=R_2$, one obtains the equation for the dependence of the electron binding energy of the negative ion on the bubble radius R_2

$$\cot[\sqrt{\alpha/a_0}(R_1^{-1}-R^{-1})]-R_1\sqrt{a_0/\alpha}=\frac{\left[1+\dfrac{\gamma_2}{\gamma_1}\right]e^{-\gamma_1(R_1-R_2)}-\left[1-\dfrac{\gamma_2}{\gamma_1}\right]e^{\gamma_1(R_1-R_2)}}{\left[1+\dfrac{\gamma_2}{\gamma_1}\right]e^{-\gamma_1(R_1-R_2)}+\left[1-\dfrac{\gamma_2}{\gamma_1}\right]e^{\gamma_1(R_1-R_2)}}\ . \tag{8}$$

For $V_0=0$ or $R_2\to\infty$, Eq. (8) naturally coincides with Eq. (4).

In the experiments of Bartels [3] on the mobility of O_2^- in dense gaseous He the temperature was 77.6 K, the gas density changed from 2.5×10^{21} to 7.5×10^{21} cm^{-3}, and V_0 varied from 0.08 to 0.24 eV [11]. For these conditions Eq. (8) gives a radius of the void $R_2\cong 9a_0$, which is almost independent of the density. The electron binding energy in O_2^- increases from 0.53 to 0.72 eV. The mean free path of helium atoms exceeds the bubble radius and for a rough estimation of the bubble mobility it is possible to use the solution of the Boltzmann equation for a heavy particle moving in an ideal gas. The scattering cross section of helium atoms on the void is approximately πR_2^2 and the mobility in this so-called Knudsen regime coincides with the mobility of a heavy ion in a gas of light particles. It is given as

$$\mu=\frac{3e}{8NR_2^2\sqrt{2\pi MT}}\ , \tag{9}$$

where M is the mass of the atoms and N is the number density of the gas. The results of the calculation with this formula are shown in Fig. 2. They are in good agreement with the results of Bartels [3] for the absolute value as well as for the density dependence of the mobility. It should be noted that with decreasing temperature, the size of the void increases significantly. For example, in

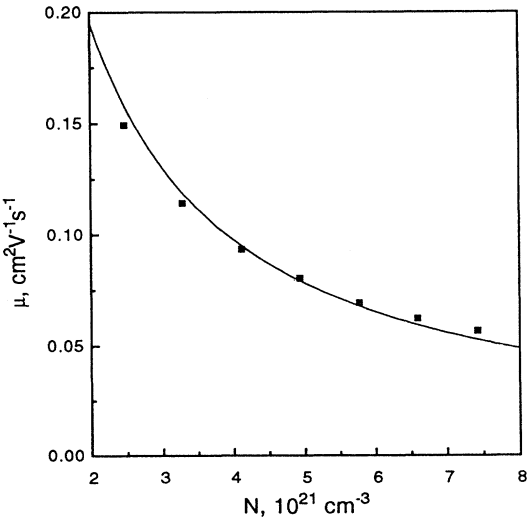

FIG. 2. Mobility of O_2^- in dense helium gas at $T=77.6$ K. Experimental points are the data of Bartels [3]. The line was calculated by means of Eq. (9).

the saturated vapor of He at $T=4.2$ K the bubble radius is about $R_2 \cong 20a_0$.

An extension of the foregoing discussion to the mobility of negative ions in other rare gases requires a careful analysis of three effects: (i) exchange repulsion, (ii) attraction due to long range polarization, and (iii) an increase of density around the ion due to electrostriction. The electron-atom scattering length L is a suitable measure of the relative importance of the exchange repulsion and polarization attraction. Large positive values of L indicate the predominance of the repulsion, while large negative values describe the influence of the attraction. In helium, the exchange repulsion is the dominant factor, while the attraction by polarization can be neglected. The scattering length $L=1.16a_0$ is positive. In neon, the exchange repulsion is almost completely compensated by the attraction due to polarization. The electron-atom scattering length is $L=0.45a_0$. In the heavier rare gases, the polarization dominates and the scattering length is negative; $L=-1.63a_0$ for argon [7], for example. In the case of helium we used the experimental dependence of V_0 on the atomic density N [11] to describe the local potential acting on the outer electron of the negative ion. In the case of neon, the polarization potential given approximately as $-2\pi N\alpha e^2/R_2$ must be included. The effect of electrostriction is described by the pressure produced $p \sim \alpha/R_2^4$. Since it is proportional to the polarizability of the atom it becomes more important in the heavier rare gases. Electrostriction leads to an increase of the local density around the ion and thus to an increase of the viscosity. It is important to note that in the case of a negative ion, as result of the quantum nature of the outer electron, the effect of the electrostriction will be smaller than in the case of a positive ion. The properties of O_2^- in neon and other rare gases will be analyzed in a future presentation.

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