Electron Clusters in Inert Gases

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This Letter addresses the counterintuitive behavior of electrons injected into dense cryogenic media with negative scattering length L. Instead of strongly reduced mobility at all but the lowest densities due to the polaronic effect involving the formation of density enhancement clusters (expected in the theory with a simple gas-electron interaction successfully applied earlier to electrons in helium where $L > 0$) which should substantially decrease the electron mobility, an opposite picture is observed: with increasing $|L|$ (the trend taking place for inert gases with the growth of atomic number) and the gas density, the electrons remain practically free. An explanation of this behavior is provided based on consistent accounting for the nonlinearity of the electron interaction with the gaseous medium in the gas atom number density.

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One of the most interesting and still important issues in physics of cryogenic media is the problem of electron clusters which emerged almost simultaneously with that of electron bubbles. However, it is much less transparent (compared to the case of electron bubbles) from the experimental side. Although there are some indications of the existence of electron clusters in xenon [1], they are not observed on the expected scale in media with comparatively high atomic polarizabilities (krypton, xenon) which are presumably likely to develop various electron autolocalization phenomena. On the contrary, the data on electron mobility in Ar, Kr, and Xe [2–8] reveal that electrons remain practically free (compared to mobility of positive ions possessing the structure of massive polaronic-type formations) in their motion, at least in the vicinity of the characteristic electron mobility peak which is observed for all heavy inert gases.

The existing description [9–11] of electron clusters in cryogenic media with negative scattering lengths L employs the well-known approximation [12,13] for the electron-medium interaction energy, which is linear in the gas density n. Within this approximation, the minimal energy V_0 of delocalized electron injected into the gaseous media is calculated as

$$V_0 = \frac{2\pi\hbar^2 L}{m} n, \tag{1}$$

where m is the free electron mass. In terms of electron energy bands in solids, V_0 is the conduction band bottom energy. The case of $L > 0$ corresponds to formation a single-electron bubble. On the other hand, a density enhancement domain with higher gas atom concentration (i.e., a cluster) may develop around the electron if $L < 0$. The authors of Refs. [9–11] made every effort to provide a quantitatively accurate description of the gas density around the localized electron in the linear approximation. In addition to (1), they also introduced a nonlocal electron-gas interaction of the type

$$E_{\text{int}} = \iint d^3 r' d^3 r n(r) v(r - r') \psi^2(r') \tag{2}$$

where $\psi(r)$ is the electron wave function, took into account the deviation of the gas entropy contribution to the total free energy from the ideal gas, etc. Their final conclusions [9–11] practically coincide with the intuitively expected picture: the electron cluster should exist, and the electron localization degree as well as the cluster mass should monotonically grow with the density media and polarizability demonstrating exponential sensitivity to the temperature. The outlined approach [9–11] reveals no hints of electron mobility growth with the medium density [2–8].

In the present Letter we show that in gaseous media with negative values of L it is possible for an electron, in a certain range of gas densities and temperatures, to form an autolocalized state involving the formation of a cluster with the characteristic length $\lambda \gg a_B$ (where a_B is the Bohr radius) if the electron-gas interaction $V_0(n)$ is treated beyond the linear approximation in n (1). The Letter is organized as follows. First, the formal grounds for considering the nonlinear behavior of $V_0(n)$. Then the electron cluster structure is calculated within the nonlinear approach. Finally, the nature of deviations from nonlinearity at small n is discussed.

As already mentioned earlier, the existing theory of autolocalized electrons in cryogenic media employs the electron-gas interaction (1). However, the true minimal energy of an electron injected in inert gases with negative scattering length (Ar, Kr, Xe) is substantially nonlinear. Direct experiments [14,15] reveal that the energy $V_0(n)$ is only approximately linear at very small n following Eq. (1). With further growth of n, the energy V_0 reaches some minimal value $V_{\min}$ at a certain density $n_{\min}$ after which it grows again (see Fig. 1; for Ar $n_{\min} = 13 \times 10^{21}$ cm^{-3}, $V_{\min} = -0.3$ eV, for Kr $n_{\min} = 14 \times 10^{21}$ cm^{-3}, $V_{\min} = -0.66$ eV, for Xe $n_{\min} = 11 \times 10^{21}$ cm^{-3}, $V_{\min} = -0.83$ eV). Most important in our problem of cluster formation is the range of n near $n_{\min}$
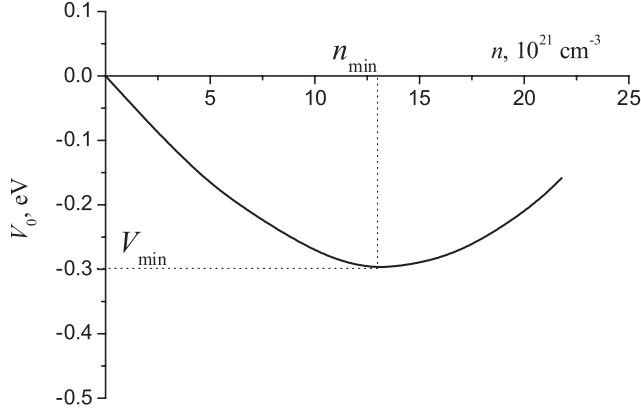
FIG. 1. Minimal energy of delocalized electron injected in argon as a function of gas atom number density as a typical example of the behavior of $V_0(n)$ for heavy inert gases with negative scattering length.

where the derivative $\partial V_0/\partial n$ changes its sign. Indeed, it is natural to assume that dominating in the problem of self-consistent calculation of the gas atom number density $n(r)$ will be the densities minimizing the electron-gas interaction energy. Hopefully, the quantitative analysis can be based on any reasonable interpolation of the true $V_0(n)$ reproducing the correct minimum depth and position. In fact, we used the simplest polynomial approximation yielding in addition the correct slope of $V_0(n)$ at small n:

$$V_0(n) = \frac{2\pi\hbar^2 L}{m} n(1 + An + Bn^2). \tag{3}$$

The parameters A and B were chosen for each inert gas in such a way that the correct values [14,15] of the minimum depth V_{min} and position n_{min} were reproduced.

Formally, the problem of finding the ground state of a single electron in the gaseous media reduces to minimizing the free energy F of the entire "electron + gas" system with respect to variations of the (spherically symmetric) electron wave function $\psi(r)$ and gas atom number density $n(r)$ [16,17],

$$F = \int d^3 r \tilde{F}(r), \qquad \tilde{F} = \frac{|\nabla\psi|^2}{2m} + nT\ln(nB) + \tilde{F}_{int},$$

$$\tilde{F}_{int} = V_0(n(r))\psi^2(r), \tag{4}$$

where $B(T)$ is a function of temperature which does not affect final results and therefore is not specified here. This procedure results in a set of two coupled equations for $n(r)$ and $\psi(r)$:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi, \qquad V(r) = V_0(n(r)), \tag{5}$$

$$4\pi \int_0^\infty \psi^2(r)r^2 dr = 1, \tag{6}$$

$$n(r) = n_g \exp\left[-\frac{|\psi|^2 \partial V_0/\partial n}{T}\right], \tag{7}$$

where n_g is the gas atom number density at infinity, $n(r)$ is

the local atom number density, $\psi(r)$ is the electron wave function normalized to unity, and T is the temperature.

To solve the equation set (5)–(7) we employed (just as in Refs. [16,17]) the variational approach with $\psi(r)$ selected in the form

$$\psi(r, k) = \left(\frac{k^3}{\pi}\right)^{1/2} e^{-kr}. \tag{8}$$

Here the variational parameter k measures the electron localization. By substituting Eq. (8) into Eq. (7) and finding $n(r, k)$ one can calculate the free energy of the system $F(k)$ (4). To study the possibility of electron auto-localization at given n_g and T one should then plot the curve $\delta F(k) = F(k) - F_{deloc}$ [where $F_{deloc} = V_0(n_g) + NT\ln(n_g B(T))$ is the total free energy of system consisting of a uniform gas and delocalized electron described by the wave function $\psi(r) = $ const, N being the total number of gas atoms in the system] and check if this curve has a minimum which is sufficiently deep compared to the temperature. For single-electron bubbles, where $L > 0$, this program was realized in [16,17] where the linear approximation for V_0 was employed. The single-electron bubble formation proves energetically favorable at sufficiently low temperatures and sufficiently high densities (threshold values of temperature and density follow the relation $n \sim T^{2/3}$), and all the parameters of the arising bubble well satisfy the adopted assumptions: the bubble size is much larger than the interatomic distance, the free energy minimum depth substantially exceeds temperature, etc. We omit any quantitative details since for $L > 0$ the nonlinearity of $V_0(n)$ does not introduce any qualitative corrections to the bubble parameters and the resulting picture is practically identical to that obtained earlier [16,17].

In the problem with $L < 0$ we first mention that the relation

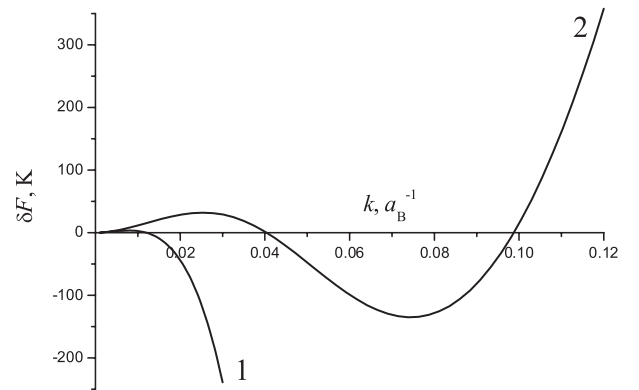$$n(r, k) = n_g \exp\left[+\frac{2\pi\hbar^2 |L\|\psi(r, k)|^2}{mT}\right] \tag{9}$$

FIG. 2. Gain in the free energy due to electron localization in Xe as a function of the variational parameter k in the linear approximation (curve 1) and taking into account the nonlinear behavior of $V_0(n)$ (curve 2) calculated for $n_g = 4 \times 10^{21}$ cm^{-3}, $T = 150$ K.

following from Eqs. (7) and (1) leads in the linear theory to an unavoidable singularity in the density distribution $n(r \to 0)$ (in the adopted model which neglects interatomic repulsion at small distances nothing can prevent the arbitrarily strong shrinking of electron wave function and the corresponding growth of the gas density at the center of the cluster resulting in infinite reduction of the system free energy) as illustrated by variational calculations which yield for $\delta F(k)$ the results plotted in Fig. 2 (curve 1).

By employing a more general expression for $n(r, k)$ with $V_0(n)$ specified by Eq. (3) it is easy to see that the trend towards density enhancement around the localized electron taking place at relatively large distances from the cluster core and correctly described by Eq. (9) is stopped near the cluster center where the derivative $\partial V_0 / \partial n$ changes its sign. It is also qualitatively clear that the halt in the density growth is actually important if the uniform gas density n_g far from the cluster core is not too close to $n_{\min}$. If the inequality $n_g \sim n_{\min}$ is satisfied, the cluster formation mechanism defined by Eqs. (5) and (7) becomes inefficient (no energy gain can be acquired by tuning the gas density to its optimal value in the vicinity of the cluster center), and that is actually why electrons in heavy inert gases behave as practically free particles for gas densities close to $n_{\min}$.

Now that the singularity suppression mechanism is clear, one can apply the outlined variational procedure to quantitatively test the above qualitative picture concerning the possibility of electron cluster formation. Calculations reveal that at not-too-high temperatures T there do exist density ranges where the free energy gain due to electron localization $\delta F(k)$ as a function of k has a minimum with the depth exceeding T (curve 2 in Fig. 2). Numerical results for Xe are shown in Fig. 3 where the free energy gain calculated for electron wave function defined by Eq. (8) and optimized with respect to k is plotted. It is clearly seen that the localized state is only energetically favorable for not-too-low densities outside some interval around $n_{\min}$; the characteristic cluster radii prove to be 10–20 a_B. It should be noted that the structure of an arising localized state proves to be completely different for $n_g < n_{\min}$ and $n_g > n_{\min}$. As already mentioned earlier, the free energy gain in the localized state occurs due to the proximity of the gas atom density around the electron $(r \to 0)$ to the density $n_{\min}$ providing the lowest possible interaction energy between the electron and the gas. Therefore, at $n_g < n_{\min}$ the localized state corresponds to formation of a cluster (i.e., density enhancement in the vicinity of $r = 0$) as shown by curve 1 in Fig. 4, while at $n_g > n_{\min}$ a single-electron bubble is formed with the gas atoms squeezed out of the vicinity of $r = 0$ (curve 2 in Fig. 4).

Hence, the nonlinear corrections to the interaction energy (1) behave in qualitatively different ways for $L > 0$ and $L < 0$. For positive scattering lengths, nonlinear corrections to Eq. (1) only slightly modify the overall picture of electron localization arising in the linear approach. On the contrary, for negative scattering lengths the presence of
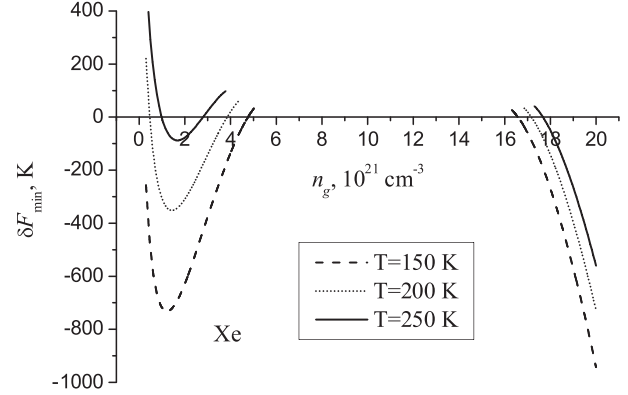

FIG. 3.   Gain in free energy due to electron localization in Xe as a function of gas atom number density at three different temperatures.

nonlinearity in $V_0(n)$ becomes critically important since in the adopted model it is the only factor capable of preventing the cluster from shrinking to the Bohr length scale. Therefore, it is very desirable to study the deviation of $V_0(n)$ from the linear approximation (1), at least for small n. However, in spite of the fact that the problem of calculating $V_0(n)$ has been addressed in many works (e.g., see Refs. [18]), currently available theoretical results are mainly numerical in nature and derived by replacing the disordered medium with an imaginary crystalline solid consisting of the gas atoms with appropriate density after which the conduction band bottom is calculated within the Wigner-Seitz model. Major efforts in these works have been concentrated on choosing the optimal pseudopotential describing the free electron interaction with the inert gas atom closed shell and correct screening of the long-range attracting potential $-\alpha e^2 / 2 r^4$ due to the Coulomb interaction between the electron and polarizable gas atom, α being the atom polarizability. On the other

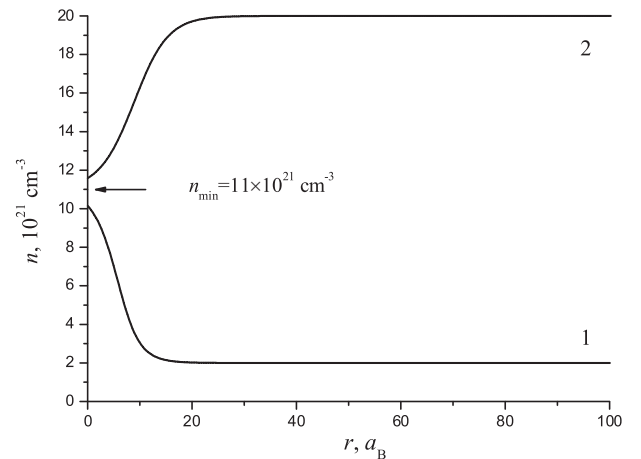FIG. 4.   Gas atom density distribution in the localized state for Xe for $n_g = 2 \times 10^{21}$ cm$^{-3} < n_{\min}$ (curve 1, cluster) and $n_g = 20 \times 10^{21}$ cm$^{-3} > n_{\min}$ (curve 2, bubble) calculated for $T = 150$ K.
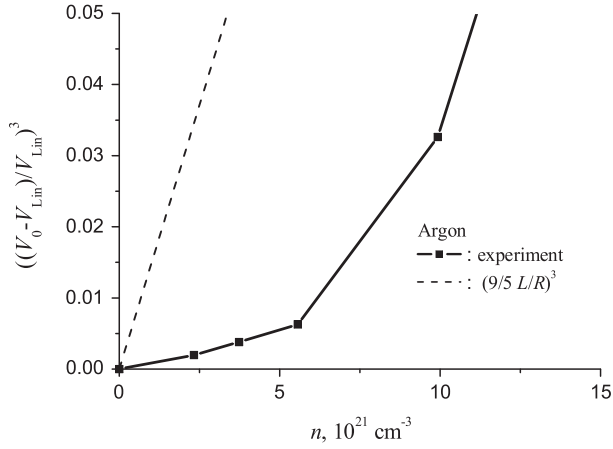
FIG. 5.   Deviations from linear behavior of $V_0(n)$ at small n for Ar. $V_{Lin} = \frac{2\pi\hbar^2 L}{m} n$. Experimental points are taken from Ref. [14].

hand, it is interesting to note that for short-ranged potentials the Wigner-Seitz model allows finding the asymptotic behavior of $V_0(n)$ at small n beyond the linear approximation through the scattering length L. Indeed, in that case the requirement of the vanishing of the wave function first derivative at the spherical cell boundary (whose radius tends to infinity as $n \to 0$) results in the following expression for the conduction band bottom:

$$V_0(n) = \frac{2\pi\hbar^2 L n}{m}\left[1 + \frac{9}{5}\frac{L}{R} + O\left(\frac{L^2}{R^2}\right)\right], \qquad (10)$$

where $R = (\frac{3}{4\pi n})^{1/3}$. It is seen that the relative corrections to the linear approximation (1) are proportional to the small parameter $L/R \ll 1$ which is the prediction that can be tested experimentally. As an example, plotted in Fig. 5 are experimental data on the low density behavior of $V_0(n)$ for argon in the $[(V_0 - V_{Lin})/V_{Lin}]^3, n)$ coordinates, where $V_{Lin} = V_0$ from Eq. (1). It is obvious that $\delta V_0(n)/V_{Lin} \propto L/R$, although the experimental proportionality coefficient is different from that predicted by Eq. (10). The reason for this discrepancy is most likely the long-ranged nature of the effective potential for electron interaction with the gas atom containing the polarization contribution obeying the r^{-4} law.

Thus, by taking into account the nonlinear behavior of $V_0(n)$, it is possible to extend the existing theory of electron autolocalization in dense gases with positive scattering lengths (single-electron bubbles in helium) to electrons in inert gases with negative scattering lengths and describe possible formation of electron clusters in these media. The clusters can arise at gas densities both lower and higher than n_{min}, and are not formed at densities close to n_{min}. The outlined picture is consistent with available data on electron mobility μ in dense cryogenic gases. The point is that with growing n the possibility of interpreting the mobility μ in terms of single-particle collisions between the electrons and gas atoms is gradually lost. However, if under these conditions the electron still remains in an almost free

nonlocalized state as suggested by the above analysis, it is natural to describe its interaction energy with the gaseous media responsible for scattering by the expression [19]

$$\delta V_0 = \frac{\partial V_0(n)}{\partial n}\delta n \qquad (11)$$

where δn is the gas density fluctuation of the thermal origin. It is then obvious that the derivative $\partial V_0(n)/\partial n$ vanishing at $n = n_{min}$ yields a peak in the density dependence of electron mobility. Hence, experimental observation of electron mobility peaks in all three heavy inert gases around the respective values of n_{min} can be considered as a confirmation of the absence of electron localization in the vicinity of the mobility peak.

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