Contribution to the theory of the states of electrons injected into a dense gas

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The localization of electrons injected into dense nonpolar gases is investigated. It is shown that, along with the localization of electrons in "bubbles" in gases with low polarizabilities (He, H_2), the localization of electrons in "clusters" in high-polarization gases (e.g., Xe) is possible. Methods for the experimental detection of the clusters are proposed.

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The problem of the electron in a dense disordered medium simulates quite a number of phenomena connected with the behavior of electrons in nonpolar liquids[1], dense gases[2], strongly doped semiconductors[3,4], metal vapors[5,6], and other systems[7,8]. The formation of electron bound states in a medium is the most interesting effect. The best studied effect is the localization of electrons in cavities in liquid helium ("bubbles").

In investigating the behavior of an electron in a dense gas, it is necessary to know the potential for its interaction with the atoms. The He atom is an exception when its interaction with an electron is described with the aid of only one quantity—the scattering length a. Other atoms (molecules) possess appreciable polarizabilities α. It is shown below that allowance for the long-range interaction can lead to qualitatively new results.

Allowance for polarization involves well-known difficulties: the divergence of the polarization potential ($\alpha e^2/2r^4$) and, as a result, the necessity for its truncation at small r. However, at the long-wave limit (at low temperatures), the information that a and α contain about the electron-atom interaction is sufficient. Then it turns out that, despite the notion that no bound states exist in the heavy inert gases[1] (we have, as always, bubbles in mind), bound states are possible. They are, however, realized in density condensations, i.e., in clusters, which is connected in the final analysis with the prevalence at large α of the attractive forces. The theory is equally applicable at small α, when $a > 0$. It then describes the influence of polarization on the bubbles.

First, using the optimal-fluctuation method[8,9], we derive general expressions in which proper allowance is made for both the polarization and short-range interactions. Further, the properties of the clusters in Xe are considered, and methods for their experimental investigation are proposed. A rough allowance is made for the interatomic interaction. Finally, the theory is applied to bubbles in He and H_2. In the last case the allowance for polarization proves to be important.

ELECTRON BOUND STATES IN A DENSE GAS. THE OPTIMAL-FLUCTUATION METHOD

The use of the optimal-fluctuation method allows us to describe the various fluctuonic states—both bubbles and clusters—from a single position. The expressions obtained below contain only the scattering length a for scattering of an electron by an atom and the polarizability α, and do not depend on the specific (and usually unknown) form of the electron-atom interaction potential V(r) at small interparticle distances.

If we neglect the interatomic interaction, then the formation of a bound state causes the free energy of the system to decrease by an amount equal to the binding energy ϵ of the electron and to increase by the amount $T\Delta S$ (ΔS is the change in entropy and T is the temperature):

$$\begin{gathered}\varepsilon=-(K+U),\\ K=\langle\psi|p^2/2m|\psi\rangle,\qquad U=\left\langle\psi\left|\sum_i V(\mathbf{r}-\mathbf{R}_i)-N\overline{V}\right|\psi\right\rangle,\end{gathered}\tag{1}$$

where K and U are the mean values of the kinetic and potential energies; ψ and p are the electron wave function and electron momentum; and N is the mean atom density. Using the Poisson distribution for the atom concentration, we can easily determine the quantity ΔS.

Introducing the relative change $c(r) = [N(r) - N]/N$ in the atom concentration, we have for the free-energy change arising as a result of the electron localization the expression

$$\begin{gathered}\Delta F=\frac{1}{2}\int|\nabla\psi|^2\,d\mathbf{r}+N\int d\mathbf{r}\,d\mathbf{r}'\,V(\mathbf{r}-\mathbf{r}')\,c(r')\,|\psi(r)|^2\\ +NT\int d\mathbf{r}\{[c(r)+1]\ln[c(r)+1]-c(r)\}.\end{gathered}\tag{2}$$

From the condition for a minimum of $\Delta F(\psi, c)$ with respect to c(r) we find a relation between c(r) and the electron wave function $\psi(r)$:

$$c(r)=\exp\left\{-\beta\int d\mathbf{r}'\,V(\mathbf{r}-\mathbf{r}')\,|\psi(r')|^2\right\}-1.\tag{3}$$

With allowance for (3), ΔF becomes a functional of only the function $\psi(r)$:

$$\beta\Delta F=\frac{1}{2T}\int|\nabla\psi(r)|^2\,d\mathbf{r}-N\int d\mathbf{r}[\exp(-\beta\tilde{V}(r))+\beta\tilde{V}(r)-1],\tag{4}$$

$$\tilde{V}(r)=\int d\mathbf{r}'\,V(\mathbf{r}-\mathbf{r}')\,|\psi(r')|^2.\tag{5}$$

To compute the pseudopotential $\tilde{V}(r)$, let us split V(r) up into two components:

$$V_1(r)=\begin{cases}V(r) & (r<r_1)\\ 0 & (r>r_1)\end{cases},\qquad V_2(r)=\begin{cases}0 & (r<r_1)\\ V(r) & (r>r_1)\end{cases},\tag{6}$$

the distance r_1 being chosen to be large enough to allow the assumption to be made that the potential $V_2(r)$ is a polarization potential, i.e., that $V_2(r) = \alpha e^2/2r^4$ for $r > r_1$. Further, let us require that the condition of applicability of the Born approximation be fulfilled in the scattering by the potential $V_2(r)$, i.e., that $r_1^2 \gg \alpha/a_0$.

On the other hand, let us assume that the electron wavelength $\lambda \gg r_1$. Then the scattering of an electron by the potential $V_1(r)$ is completely described by the scattering length a_1 for scattering of an electron by this potential. It is not difficult to show1) that under the indicated assumptions, i.e., for

$$\lambda^2 \gg \alpha/a_0, \quad \lambda \gg |a| \tag{7}$$

the scattering length a for scattering of an electron by the potential $V(r)$ is connected with a_1 by the relation

$$a = a_1 + \frac{m}{2\pi\hbar^2}\int V_2(r)\,d\mathbf{r}. \tag{8}$$

Let us substitute (6) into (5) and then use (8) to transform $\tilde{V}(r)$ into the form

$$\tilde{V}(\mathbf{r}) = 4\pi\frac{\hbar^2 a_1}{2m}|\psi(r)|^2 + \int\limits_{|\mathbf{r}-\mathbf{r}'|>r_1} d\mathbf{r}'\, V(\mathbf{r}-\mathbf{r}')\,|\psi(r')|^2. \tag{9}$$

Adding to the first term and subtracting from the second the expression $|\psi(r)|^2 \int V_2(r')\,dr'$, we obtain

$$\tilde{V}(r) = 4\pi\frac{\hbar^2 a}{2m}|\psi(r)|^2 - \frac{\alpha e^2}{2}\int\limits_{|\mathbf{r}-\mathbf{r}'|>r_1} d\mathbf{r}'\,\frac{|\psi(r')|^2 - |\psi(r)|^2}{(\mathbf{r}-\mathbf{r}')^4}. \tag{10}$$

In the last integral we can remove the restriction $|r - r'| > r_1$, and extend the integration over the entire volume. In doing this, we assume that $r_1 \ll \lambda$ and take only the first nonvanishing terms of the power-series expansion in r_1/λ into account. Thus,

$$\tilde{V}(r) = 4\pi\frac{\hbar^2 a}{2m}|\psi(r)|^2 - \frac{\alpha e^2}{2}\int d\mathbf{r}'\,\frac{|\psi(r')|^2 - |\psi(r)|^2}{(\mathbf{r}-\mathbf{r}')^4}. \tag{11}$$

This expression for $\tilde{V}(r)$ already does not contain the auxiliary cutoff radius r_1, all the information about $V(r)$ being contained in its characteristics a and α. This fact is directly connected with the theory of slow-electron scattering by atoms[10,11], a theory which expresses the scattering amplitude in terms of only a and α.

Besides the inequalities (7), which limit the region of applicability in the two-particle electron-atom problem, there arises the inequality $N|a_1^3| \ll 1$. As is usual in the Fermi pseudopotential theory, it requires that the short-range components of the potential $V(r)$ should not overlap in the medium. In a gas this inequality is fulfilled, since $|a_1|$ is close to atomic dimensions. As to the long-range polarization component of $V(r)$, a component which makes a large contribution to a, it is additive and allows the overlapping of the potentials.

We shall carry out the subsequent analysis, using the variational method under the natural assumption that the fluctuations are spherically symmetric. As the trial wave function of the ground state, let us take the one-parameter function

$$\psi(r) = \left(\frac{2}{\pi\lambda^2}\right)^{3/4}\exp\left(-\frac{r^2}{\lambda^2}\right). \tag{12}$$

It is convenient to introduce new dimensionless variables expressing all the system's characteristics whose dimension is length in terms of the thermal wavelength $\lambda_\beta = \hbar(2mT)^{-1/2}$ of the electron:

$$z = \frac{\lambda_\beta}{\lambda}, \quad z_N = \lambda_\beta\left(\frac{4\pi}{3}N\right)^{1/3}, \quad z_\alpha = \lambda_\beta\left(\frac{a_0}{\alpha}\right)^{1/2}, \quad z_a = \frac{\lambda_\beta}{a}. \tag{13}$$

Integrating (5) with the use of $\psi(r)$ from (12), we obtain

$$\beta\tilde{V}(x) = -8\left(\frac{2}{\pi}\right)^{1/2}\frac{z^3}{z_a}e^{-x^2} - 8\frac{z^4}{z_\alpha^2}f(x), \quad x = \frac{\sqrt{2}\,r}{\lambda}, \tag{14}$$

$$f(x) = 1 - \left(x^2 - \frac{1}{2}\right)e^{-x^2}\int_0^1 \frac{dy}{\sqrt{y}}e^{yx^2} = \sum_{k=0}^{\infty}(-1)^k\frac{2^{k+1}(k+1)x^{2k}}{(2k+1)!!}. \tag{15}$$

The function $f(x)$ changes its sign when $x \approx 1$, and has the asymptotic form

$$f(x) = \begin{cases} 2, & x \ll 1, \\ -1/2x^4, & x \gg 1. \end{cases} \tag{16}$$

The behavior of $f(x)$ at large x is easy to understand. At $x \gg 1$ $(r \gg \lambda)$ the quantum effects are negligibly small, and the effective potential $\tilde{V}(r)$ goes over into $V(r) = -\alpha e^2/2r^4$. Furthermore, $f(x)$ satisfies the condition

$$\int_0^\infty x^2 f(x)\,dx = 0. \tag{17}$$

Thus, using (13) and (14), we can rewrite the expression (4) for $\beta\Delta F$ in the form

$$\beta\Delta F = 3z^2\left\{1 - \frac{z_N^3}{2^{1/2}z^5}\int_0^\infty dx\,x^2[\exp(-\beta\tilde{V}) + \beta\tilde{V} - 1]\right\}. \tag{18}$$

As $\lambda \to 0$, this expression goes over into the classical expression (since $\tilde{V}(x) \to V(x)$):

$$\Delta F = \frac{p^2}{2m} - NT\int d\mathbf{r}[e^{-\beta V(r)} + \beta V(r) - 1]. \tag{19}$$

ON THE POSSIBILITY OF THE EXISTENCE OF ELECTRON CLUSTERS IN THE HEAVY INERT GASES

Let us assume for simplicity that the appearance of clusters is due to localization in small fluctuations, when ΔF, given by (18), assumes the form:

$$\beta\Delta F = \beta K - \beta^2\overline{U^2}/2, \quad \overline{U^2} = N\int d\mathbf{r}\,\tilde{V}^2(r). \tag{20}$$

Let us first analyze the quantity $\overline{U^2}$, the stray-field variance, in its general form after expressing it in terms of the Fourier transforms

$$V(q) = \int V(r)e^{i\mathbf{qr}}\,d\mathbf{r}, \quad \varphi(q) = \int |\psi(r)|^2 e^{i\mathbf{qr}}\,d\mathbf{r}.$$

Then

$$\overline{U^2} = N(2\pi)^{-3}\int V^2(q)\varphi^2(q)\,d\mathbf{q}. \tag{21}$$

It is clear that for localization to be possible, the small fluctuation should be sufficiently extended and the wavelength λ of the ground state of the electron should be long. If it exceeds the range of the potential $V(r)$, then only small $q \lesssim \lambda^{-1}$ are important in (21). Further, let us take into account the fact that when the conditions (7) are fulfilled the effective-radius theory[10] directly relates $V(q)$ to the amplitude of slow-electron scattering by atoms: $V(q) = 2\pi\hbar^2 m^{-1} f(q)$. Therefore,

$$\overline{U^2} \approx Nf^2(\lambda^{-1})/\lambda^3, \tag{22}$$

$$\beta\Delta F \approx \frac{\lambda_\beta^2}{\lambda}[1 - N\lambda_\beta^2\lambda^{-1}f^2(\lambda^{-1})]. \tag{23}$$

Since $f(q)$ is well known from experiment, (23) already allows us to carry out the entire qualitative analysis.

For small energies the expression $f(q)$ is known in terms of the scattering length a and the atomic polarizability α[10,11]:

$$f(q) = a + \alpha q/4a_0. \tag{24}$$

The cross sections for scattering of an electron by an atom that follow from (24) are in good agreement with the experimental cross sections[10,12].

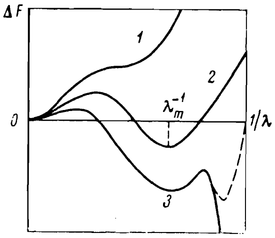

FIG. 1

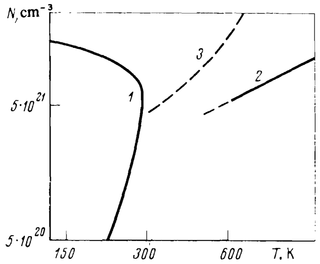

FIG. 2

FIG. 1. Qualitative form of the dependence of the change ΔF in free energy on the electron wavelength λ.

FIG. 2. Curve 2) the density value N_c at which electron localization occurs in Xe; 1) the vapor-liquid phase coexistence curve; 3) curve corresponding to $N|B(T)|=1$.

Figure 1 shows the qualitative form of $\Delta F(\lambda)$ for $a < 0$, i.e., for atoms whose cross sections possess the Ramsauer minimum. For small N/T the quantity ΔF monotonically increases (the curve 1) and localization is unfavorable. As N/T increases, the values of ΔF become negative (the curve 2) and pass through a minimum. The value $\lambda = \lambda_m$ corresponds to the most favorable clusters. The stabilization of the clusters is ensured by the competition between the short-range and polarization interactions. Let us give the formula for λ_m:

$$\lambda_m \approx \frac{16\sqrt{\pi}\,\alpha}{3a_0|a|}\left[1+\left(1-\frac{8\alpha}{3a_0\lambda_\beta{}^2|a|^3N}\right)^{1/2}\right]^{-1}. \tag{25}$$

From the condition $\Delta F(\lambda_m) = 0$, we find the density $N_c(T)$ starting from which bound electrons predominate over the free electrons:

$$N_c(T)\approx 3\alpha/|a|^3\lambda_\beta{}^2a_0. \tag{26}$$

Substituting (26) into (25), we obtain the value λ_m^0 corresponding to the minimum of $\Delta F(\lambda)$ on the $N_c(T)$ curve:

$$\lambda_m{}^0=4\sqrt{\pi}\alpha/a_0|a|. \tag{27}$$

For $N = N_c$ the electron binding energy in a cluster is given by $\epsilon = \hbar/2m(\lambda_m^0)^2$: a cluster contains one energy level.

The numerical factors are accurately retained with the aid of the formulas (18) and (14):

$$\beta\Delta F=3z^2\left[1-z_N{}^3\left(1{,}1\frac{z}{z_a{}^2}+4{,}0\frac{z^2}{z_az_\alpha{}^2}+4{,}2\frac{z^3}{z_\alpha{}^4}\right)\right]. \tag{28}$$

On the basis of (28) we have constructed in Fig. 2, next to the phase-equilibrium diagram (curve 1), the dependence $N_c(T)$ for Xe (curve 2; $a = -7.1a_0$[13], $\alpha = 27.2a_0^3$). For $N > N_c$ the majority of the electrons are localized. For $N \approx N_c$ the cluster dimensions are close to 10–15 Å, and each of the clusters contains about 50 atoms.

With the aid of λ_m^0 from (25) and N_c from (26), let us rewrite the conditions of applicability of the long-wave approximation on the curve $N = N_c(T)$. From the condition of applicability of the Gauss approximation ($|U| \lesssim (\overline{U^2})^{1/2}$), the inequalities (7), and the requirement that $N\lambda^3 \gg 1$, we obtain

$$N_ca^2\lambda_\beta\equiv\xi\geqslant 1,\ |a|\ll\xi\lambda_\beta,\ \alpha\ll\xi^2a_0\lambda_\beta{}^2,\ N_c\lambda_\beta{}^3\xi^3\gg 1. \tag{29}$$

All these inequalities are well fulfilled in Xe on the section of the $N = N_c(T)$ curve shown in Fig. 2. The most important of them—the first inequality—can be rewritten in the form $l \lesssim \lambda_\beta$, where l is the mean free path. If it is less than the wavelength, then, again according to Mott[7], this indicates localization.

As N increases (at constant T), the role of the interatomic interaction grows. At sufficiently large densities the interatomic repulsion can inhibit cluster formation. Since the atom density inside a cluster differs insignificantly from the mean density, it is sufficient to estimate the role of the interatomic interaction for the mean density. In Fig. 2 the curve 3 corresponds to the density at which $N|B(T)| \approx 1$ ($B(T)$ is the second virial coefficient). At densities lying below the curve 3, the interatomic interaction can be taken into account with the aid of $B(T)$. This would lead to the replacement of N in (23) by $N(1 - NB(T))$, which would somewhat decrease $N_c(T)$. Since the values of $N_c(T)$ lie substantially below the curve 3 in Fig. 2, the assumption that the interatomic interaction is weak is justified.

Let us consider experimental methods for the detection of the clusters. Since the mobility of the clusters, like that of heavy particles and that of bubbles in He[2], is very low, for $N \gg N_c$ the mobility of the injected electrons should decrease by several orders of magnitude. The observation of the discontinuity in the mobility allows the measurement of $N_c(T)$. The presence of clusters leads, for $N \geq N_c$, to the appearance of infrared light absorption bands in a region of perfect transparency of the gas. Its appearance is due to the photoionization of the clusters, and lies in the frequency region $\nu \approx \epsilon/\hbar$. Consequently, its measurement will enable us to determine the electron binding energy in a cluster.

For $N > N_c$ the mobility of the injected electrons is very low. But if we irradiate the gas with an external source of light of frequency of the order of ν, then free electrons appear as a result of photoionization. Therefore, the discontinuity in the mobility should be measured the moment the source is switched on. Such an experiment has been performed in liquid He, in which electrons form bubbles[14].

ALLOWANCE FOR THE INTERATOMIC INTERACTION

Allowance for the interatomic interaction primarily inside a cluster may turn out to be obligatory in clusters of small radii. The tendency towards the formation of such clusters along with the already considered clusters of large radii can be followed in Fig. 1. As λ decreases the ΔF curve undergoes a new qualitative change (the curve 3 corresponding to large N/T), going through a second maximum and subsequently decreasing without restriction. At too low values of λ we go outside the limits of applicability of our theory (the inequalities (7) are not fulfilled). But at still moderate—from this point of view—values of λ allowance for the repulsion of the atoms inside a cluster could stabilize the cluster, as shown by the dashed line in Fig. 1. Then clusters of small radii exist side by side with large clusters, the ratio of their number to that of the large clusters being given by $\exp[-\beta(\Delta F_s - \Delta F_l)]$, where ΔF_s and ΔF_l are the values of ΔF at the corresponding minima of the $\Delta F(\lambda)$ curve.

Let us take the interatomic interaction into account in the pair approximation, as is done in Krivoglaz and Lekhtsier's paper[15] in connection with the theory of fluctuons in solutions:

$$\beta\Delta F=-\beta\varepsilon+N\int d\mathbf{r}\left[(c+1)\ln(c+1)-(c_0-c)\ln\frac{c_0-c}{c_0}\right]-N^2a\beta\int c^2\,d\mathbf{r}. \quad (30)$$

The repulsion of the atoms is taken into account in (30) in the cellular approximation, which prevents them from coming too close together: c(r) cannot exceed $c_0 = (Nb)^{-1} - 1$, where b is the constant of the van der Waals equation. The other constant a characterizes the attraction if it decreases rapidly with distance.

The variation with respect to c(r) gives

$$c=(\exp\{-\beta(\bar{V}+2aNc)\}-1)\,[1+c_0^{-1}\exp\{-\beta(\bar{V}+2aNc)\}]^{-1}, \quad (31)$$

which, in the limiting cases of high and low densities, yields the correct expression, amounting in the second case to a virial correction. The subsequent analysis is carried out numerically. The values of a and b are known from experiment: $b = 8.5 \times 10^{-23}$ cm^3 and $a = 1.17 \times 10^{-35}$ erg-cm^3[16].

Figure 3 shows the results of the computation for three values of T at densities when $\Delta F_l = 0$, i.e., when the number of free of electrons is equal to the number of electrons localized in clusters of large radii. It follows from Fig. 3 that clusters of small radii are absent at high temperatures (curve 1). They appear as the temperature is lowered, and can even predominate (curve 3).

We can hardly assert that they exist under precisely these conditions in Xe since the necessary inequalities (7) and the condition $4\pi N/3\,|\psi(0)|^2 \gg 1$, requiring that the system be macroscopic are poorly fulfilled. Nevertheless, we should, in analyzing the experimental situation in Xe or other gases, bear clusters of small radii in mind. Also of interest from this standpoint is the question of localized non-fluctuonic states. Although localization on one Xe atom is impossible (no stable Xe$^-$ ion exists), the possibility of localization on several atoms cannot be excluded.

ON THE ELECTRON STATE IN LOW-POLARIZABILITY GASES

In gases in which an electron is largely repelled from the atoms, allowance for the polarizability can yield appreciable corrections. They can be determined on the basis of the expression (18) obtained above.

Figure 4 shows, in reduced units, the dependence $N_c(T)$ in He, H$_2$, and, for comparison, Xe. The numerical computations were carried out with the formulas (18), (13), and (14). We used the scattering-length and polarizability values given in[11]. For He, $a = 1.14a_0$ and $\alpha = 1.39a_0^3$; for H$_2$, $a = 1.36a_0$ and $\alpha = 5.52a_0^3$. For the sake of visualizability, we present in Fig. 3 phase-coexistence curves for He and Xe. The phase-coexistence curve for H$_2$ lies between the first two.

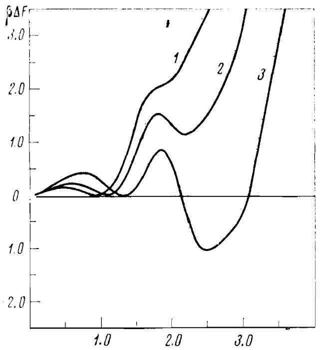

FIG. 3. Dependence of $\beta\Delta F$ on the quantity λ_β/λ in Xe (calculated from the formula (30)). Presented are curves for which $\Delta F_l = 0$. They correspond to the cases when: 1) T=700°K and $N = 2.5\times10^{21}$ cm^{-3}; 2) T=600°K and $N=1.9\times10^{21}$ cm^{-3}; 3) T=500°K and $N=1.3\times10^{21}$ cm^{-3}.

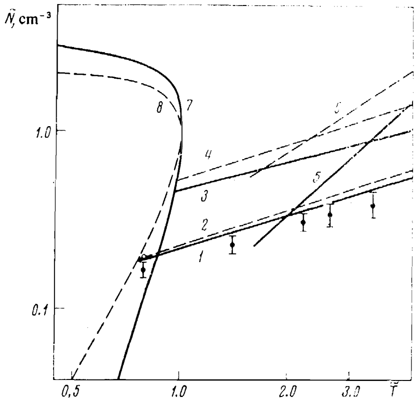

FIG. 4. Value of the reduced density $\tilde{N}_c(T)=N_c(T)/N_{c0}$ at which electron localization occurs—the curves 1-6. $\tilde{T}=T/T_{c0}$. 1), 2) for He; 3), 4) for H$_2$ (the curves 2 and 4 were constructed without allowance for the polarization interaction); 5), 6) for Xe (the curve 6 was constructed in the Gauss approximation with allowance for the interatomic interaction); 7), 8) phase-coexistence curves for Xe and He respectively. The points denote values measured in He [17].

The computations for He and H$_2$ were carried out both with (the solid curves in Fig. 4) and without (the dashed curves) allowance for the polarization interaction. It can be seen that allowance for the polarization interaction leads to a decrease in N_c, the decrease being such that the higher the temperature, the larger it is. For He the correction due to this effect is small (as was to be expected in view of the smallness of α). For H$_2$ allowance for the polarization interaction decreases N_c by 20–50%.

In Fig. 4 we also present the values of N_c obtained in experiments on the measurement of the mobility of injected electrons in gaseous He[17]. The dependence of N_c on T can be analytically derived if the polarization interaction is neglected[18,19]:

$$N_c a^{5/3}\lambda_\beta^{4/3}=\text{const}\approx 1,\ N_c\sim T^{2/3}. \quad (32)$$

Figure 4 shows that the expression (32) is in good agreement with experiment[17]. The dimension λ_m^0 of the optimal bubble on this curve (i.e., on the $N = N_c(T)$ curve) is given by

$$\lambda_m^0\approx(2a\lambda_\beta^2)^{1/3}. \quad (33)$$

At T = 4.2°K the quantity $\lambda_m^0 \approx 24$ Å, while at T = 18.1°K it is ~15 Å.

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[1] Let $\varphi(r)$ and $\varphi_1(r)$ be the radial wave functions in the fields V(r) and $V_1(r)$. For low-momentum electrons we have the expression

$$\varphi_1(R)\varphi'(R)-\varphi(R)\varphi'(R)=\frac{2m}{\hbar^2}\int_0^R d\mathbf{r}\,V_2(r)\varphi(r)\varphi_1(r).$$

Allowing R→∞, and setting

$$\varphi(r)\sim\sin(r/\lambda+\delta_0),\qquad \varphi_1\sim\sin(r/\lambda+\delta_0')$$

in this expression, we obtain in the Born approximation $r_1 \gg (\alpha/a_0)^{1/2}$) the expression

$$\delta_0-\delta_0'\approx-\frac{2m}{\hbar^2}\lambda\int_0^\infty d\mathbf{r}\,V_2(r)\varphi^2(r).$$

For large λ we have $\varphi^2\lambda^2=r^2$, $\delta_0(\lambda)=-a_1/\lambda$, $\delta'_0=-a_1/\lambda$ and arrive at (8).

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