

Toward the theory of the electron affinity of large dielectric clusters: Quantum size correction

I. T. Iakubov

Scientific Center for Applied Problems in Electrodynamics, Russian Academy of Sciences,
Izhorskaya Str. 13/19, 127412 Moscow, Russia

V. V. Pogosov

Theoretical Department, Institute for High Temperatures, Russian Academy of Sciences,
Izhorskaya Str. 13/19, 127412 Moscow, Russia and Department of Physics, Zaporozhye State Technical
University, Zhukovski str.64, 330063 Zaporozhye, Ukraine

(Received 23 April 1996; accepted 4 November 1996)

The consecutive procedure for the calculation of a size dependence of an electron affinity to a large dielectric cluster of radius R is presented. The perturbation theory over the small parameters \bar{r}/R and L/\bar{r} (L is the scattering length in the condensed medium, \bar{r} is the interatomic distance) is proposed for an electron binding energy in the frame of effective medium approach, using the theory of state of light quantum particle in a cellular medium. Estimations are fulfilled for liquid xenon clusters. © 1997 American Institute of Physics. [S0021-9606(97)51806-X]

I. INTRODUCTION

The state of charged particle in rare-gas liquids and clusters is the subject of many experimental and theoretical investigations.¹⁻³ Large clusters of these liquids are able to bind excess electrons and positrons. Measurements point to the existence of clusters consisting of some small "critical" numbers of atoms N^* realized the first bound state of an excess electron.⁴

An electron affinity (or binding energy) for small clusters may be calculated numerically only (e.g., Refs. 5, 6). In the opposite case of large clusters the affinity is close to the affinity for the bulk medium with the first curvature corrections.⁷ An affinity for the sphere of radius R and dielectric constant ϵ equals to the work needed to remove a unit charge from the center of sphere to infinity,

$$EA = -V_0(\infty) - \frac{e^2}{2R} \frac{\epsilon - 1}{\epsilon} - \frac{\hbar^2 \pi^2}{2mR^2} \quad (1)$$

where $V_0(\infty)$ is the ground state energy of an excess electron in the bulk dielectric. It is the conductivity band bottom which is disposed lower than the electron energy in the vacuum. The second term in Eq. (1) is the classical size correction originating as the energy of the polarization interaction of electron with N atoms,^{7,8} $R = N^{1/3}\bar{r}$, where \bar{r} is the mean interatomic distance. The third term is the kinetic energy of the electron. It is estimated for the smooth well with the large dimensionless strength.

The potential well of clusters is not smooth, but is curved in a high relief. The relief has a spatial scale of the mean interatomic distance. The thing is that the potential field, caused by atoms of the cluster, cannot be modelled satisfactory in the mean field approach. In the present paper the electron kinetic energy is determined taking account for this relief. The perturbation theory is developed over small parameter L/\bar{r} , where L is the scattering length of particle in the condensed medium.^{9,10} The results of calculations show that these quantum mechanical effects prove to be very im-

portant and the first order perturbation correction to Eq. (1) has a noticeable value. For Xe-clusters it consists of about 40 per cent of the electron kinetic energy.

The proposed theory can be applied to liquid (and may be solid) clusters made of a matter in the bulk of which an excess electron can be considered as almost free. Such are "the high mobility liquids," e.g., Refs. 9,13. Heavy noble liquids (argon, krypton and xenon) belong to that class of liquids. An injected electron acquires a mobility even exceeding a mobility in a rarified gas. The mean free path of electron can exceed radius of a cluster, and electron is rather rarely scattered inside it. Hence, the theory cannot be applied to clusters with localized electron, e.g., to clusters in polar liquids (like water) where an electron induces the restructuring of environment.

II. EFFECTIVE MEDIUM APPROACH FOR ELECTRON AFFINITY

The wave function of electron localized in a liquid cluster satisfies the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \Delta \Psi(\mathbf{r}) + \sum_{i=1}^N V(\mathbf{r} - \mathbf{R}_i) \Psi(\mathbf{r}) = -EA \Psi(\mathbf{r}), \quad (2)$$

where $V(\mathbf{r})$ is the electron-atomic potential, N is the number of atoms in cluster. In a liquid the potential field is characterized by the average translation symmetry. Let us represent the cluster by an array of N spherical Wigner-Seitz cells. The cell potential is symmetrical relative to each atom. In the liquid the potential may be expressed in the form of the sum of the electron interaction with the central atom of the cell $V_a(r)$ and with the cell environment.¹³ We assume that the short-range component of the $V_a(r)$ has a range which is much smaller than the size of the cell. The long-range component $V_a(r)$ has the polarization character ($-\alpha e^2/2r^4$), where α is the atomic polarizability.

The polarization component $V_p(r)$ of the environment potential may be defined in the usual way,

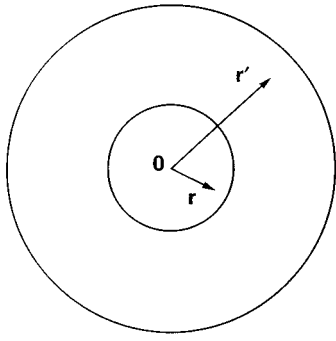


FIG. 1. An electron in the central Wigner–Seitz cell of the dielectric sphere.

$$V_p(r) = -\frac{1}{2} \int d\mathbf{r}' \mathbf{P}(\mathbf{r}, \mathbf{r}') \mathbf{E}_0(\mathbf{r}, \mathbf{r}'), \quad (3)$$

where $\mathbf{P}(\mathbf{r}, \mathbf{r}')$ is the dipole moment induced at the point \mathbf{r}' by an electron disposed at \mathbf{r} , \mathbf{E}_0 is the electron field in the vacuum. Using the definition $\mathbf{P} = \mathbf{E}_m(\varepsilon - 1)/4\pi$, Eq. (3) can be reduced to the form,

$$V_p(r) = \frac{1 - \varepsilon}{8\pi} \int d\mathbf{r}' \mathbf{E}_m \mathbf{E}_0 = \frac{1 - \varepsilon}{8\pi} \int d\mathbf{r}' \nabla \varphi_m \nabla \varphi_0, \quad (4)$$

where $\varphi_0 = -e/|\mathbf{r} - \mathbf{r}'|$, $\varphi_m(\mathbf{r}, \mathbf{r}')$ is the electrostatic potential of an excess electron in the dielectric sphere,¹¹

$$\varphi_m = \frac{-e}{\varepsilon |\mathbf{r} - \mathbf{r}'|} + \frac{-e}{\varepsilon} \sum_{k=1}^{\infty} \frac{(\varepsilon - 1)(k + 1)}{k(\varepsilon + 1) + 1} \times (rr')^k R^{-2k-1} P_k(\cos \theta), \quad (5)$$

where θ is the angle between the vectors \mathbf{r} and \mathbf{r}' . The dielectric constant is given by the Clausius–Mossotti formula, $\varepsilon = 1 + 3\alpha/(\bar{r}^3 - \alpha)$, provided that $\alpha/\bar{r}^3 \ll 1$. Consider an electron in the Wigner–Seitz cell positioned at the cluster center (Fig. 1). Then $r < \bar{r}$ and $\bar{r} < r' < R$. The environment potential is created by the atoms outside the cell where they are settled in accordance with the pair correlation function $g(r)$. To transform $V_p(r)$ [Eq. (4)] we assume that $g(r) = \{0, r < \sigma; 1, r \geq \sigma\}$, where σ is the parameter of the Lennard–Jones potential responsible for the interatomic repulsion ($\sigma > \bar{r}$),

$$V_p(r) = \frac{1 - \varepsilon}{8\pi} \left[\oint_{\sigma} \varphi_m \nabla \varphi_0 d\mathbf{S} + \oint_R \varphi_m \nabla \varphi_0 d\mathbf{S} - \int d\mathbf{r}' \varphi_m \Delta \varphi_0 \right]. \quad (6)$$

The first and second integrals should be taken over the surfaces of radii σ and R respectively, and the third integral should be taken over the volume between these surfaces. With the use of the multipole expansion $|\mathbf{r} - \mathbf{r}'|^{-1} = \sum_{k=0}^{\infty} r^k r'^{-k-1} P_k(\cos \theta)$ and the orthogonality rule of the Legendre polynomials, the straightforward integration leads to the explicit result,

$$V_p(r, R) = V_p(0, \infty) \left[1 - \frac{\sigma}{R} + \sum_{k=1}^{\infty} \frac{k+1}{2k+1} \left(\frac{r}{\sigma} \right)^{2k} - \frac{2\varepsilon + 4}{3(\varepsilon + 2)} \frac{\sigma}{R} \left(\frac{r}{R} \right)^{2k} \right], \quad (7)$$

where $V_p(0, \infty) = -3\alpha e^2 f / (2\bar{r}^3 \sigma)$, and $f = (1 + 2\alpha/\bar{r}^3)^{-1}$ is the Lorentz–Lorentz factor of the local field.¹² In the limit $R \Rightarrow \infty$ the expression (7) takes the correct form.⁹ One can see that the curvature corrections decrease the polarization contribution to the electron ground state energy. It is a result of the deficiency of neighbors in the comparison with the bulk liquid. Let conveniently represent $V_p(r, R) = U_0(R) + U_{\text{env}}(r, R)$, where $U_0(R) = V_p(0, \infty)(1 - \sigma/R)$ in accordance with Eq. (7). By this we extract the spatial dependence of the potential profile. Then the Eq. (2) may be rewritten in the form,

$$-\frac{\hbar^2}{2m} \Delta \Psi(\mathbf{r}) + \sum_{i=1}^N [V_a(\mathbf{r} - \mathbf{R}_i) + U_{\text{env}}(\mathbf{r} - \mathbf{R}_i)] \Psi(\mathbf{r}) = -(EA + U_0(R)) \Psi(\mathbf{r}). \quad (8)$$

The term $U_0(R)$ is the shift of the energy due to the mean polarization of the medium.

The electron wave function of the ground state can be written in the form,

$$\Psi(\mathbf{r}) = \psi_c(\mathbf{r}) u(\mathbf{r}), \quad (9)$$

where the function $\psi_c(\mathbf{r})$, varying on the cluster size scale, is modulated on the atomic scale by the function $u(\mathbf{r})$. The function $u(\mathbf{r})$ is the superposition of the usual Wigner–Seitz solutions $u_0(|\mathbf{r} - \mathbf{R}_i|)$ inside cells, centered at \mathbf{R}_i .

For the cell centered at $\mathbf{R}_i = 0$ (at the center of cluster)

$$-\frac{\hbar^2}{2m} \Delta u_0(r) + [V_a(r) + U_{\text{env}}(r)] u_0(r) = T_0(R) u_0(r) \quad (10)$$

with the boundary conditions

$$\nabla u_0(r)|_{\bar{r}} = 0, u_0(r)|_{L(R)} = 0, \quad (11)$$

where $T_0(R)$ is the cellular energy eigenvalue, $L(R)$ is the electron scattering length in the liquid cluster of radius R . It appears that $L(R) = L(\infty) + O(1/R^3)$, where $L(\infty)$ is the scattering length in the bulk.⁹ For the validity of our theory it should be small in comparison with the mean interatomic distance, $L/\bar{r} \ll 1$. The wave function $u_0(r)$ has the following form,

$$u_0(r) = \frac{A}{\sqrt{4\pi}} \frac{\sin\{q_0[r - L(R)]\}}{q_0 r}. \quad (12)$$

The wave vector q_0 is given by the well known equation¹³ $\tan\{q_0[\bar{r} - L(R)]\} = q_0 \bar{r}$. The size dependence of $T_0(R) = \hbar^2 q_0^2(R)/2m$ is formed by the dependence $L(R), T_0(R) = T_0(\infty) + O(1/R^3)$. Below we shall neglect this weak size dependence. In order to simplify the analysis we introduce the Fermi optical approximation,

$$q_0^2/2 = 3L/2\bar{r}^3, \quad (13)$$

which contains the independent small parameter $\xi = L/\bar{r}, L \equiv L(\infty)$.

Substitution of Eq. (9) into Eq. (8), with the use of Eq. (10), yields the wave equation for $\psi_c(\mathbf{r})$,

$$-\frac{\hbar^2}{2m}\Delta\psi_c(\mathbf{r}) - \frac{\hbar}{m}\sum_{i=1}^N \frac{\nabla u_0(|\mathbf{r}-\mathbf{R}_i|)}{u_0(|\mathbf{r}-\mathbf{R}_i|)}\nabla\psi_c(\mathbf{r}) = -(EA + V_0(R))\psi_c(\mathbf{r}), \quad (14)$$

where $V_0(R) = U_0(R) + T_0(R)$. In the limit $R \Rightarrow \infty$ it coincides with the conductivity band bottom for electrons injected into the infinite dielectric,

$$V_0(R) = V_0(\infty) + \frac{3}{2} \frac{\alpha e^2}{\bar{r}^3 R} f + O\left(\frac{\bar{r}^{-3}}{R^3}\right) \quad (15)$$

where $V_0(\infty) = -3\alpha e^2 f / (2\bar{r}^3 \sigma) + 3\hbar^2 L / (2m\bar{r}^3)$. The remaining terms are negligible. In the frame of classical electrodynamics, $EA = -V_0(R)$ [see Eq. (1)]. Further we describe how quantum effects modify this expression.

The l.h.s. of Eq. (14) contains a cross-term. It can be treated as a perturbation. Earlier, analogous procedures were carried out in infinite metals for calculations of ground energies and effective masses of electrons by Bardeen,¹⁴ Cohen and Ham,¹⁵ and for positrons by Kubica and Stott.¹⁶ In Refs. 14 and 15 the set of cellular wave functions was used, and $\psi_c(\mathbf{r})$ was chosen as the plane wave. In Ref. 16 the function $\psi_c(\mathbf{r})$ was expanded in the set of plane waves in a crystal. However, we are interested in the finite system where the boundary condition for $\psi_c(\mathbf{r})$ leads to the discrete energy spectrum of an excess electron.

III. PERTURBATION PROCEDURE

If the kinetic energy is much smaller than $|V_0(R)|$, that is $mR^2|V_0(R)|/\hbar^2 \gg 1$, the cluster potential can be modeled by the infinitely deep square well. Therefore the wave function should be small on the surface of the cluster. The boundary condition for Eq. (14) takes the form,

$$\psi_c(r=R) = 0. \quad (16)$$

The solution can be obtained, by expanding the function $\psi_c(r)$ in terms of the complete orthonormal set of eigenfunctions of the deep potential well. In this case, the electron affinity can be written as the series, truncated in the second order,

$$EA = -V_0(R) - \left(\frac{\hbar^2 \pi^2}{2mR^2} + E^{(1)} + E^{(2)} \right). \quad (17)$$

As the perturbation, the operator $\delta V(r)$ is used,

$$\delta V(r) = -\frac{\hbar^2}{m} \sum_{i=1}^N \frac{\nabla u_0}{u_0} \nabla. \quad (18)$$

The diagonal matrix element of the perturbation,

$$E^{(1)} \equiv \langle \delta V(r) \rangle = \int_{r < R} d\mathbf{r} \psi_1(r) \delta V(r) \psi_1(r), \quad (19)$$

is the potential field $\delta V(r)$, averaged over the ground state with the quantum numbers $n=1$ and $\ell=0$,

$$\psi_1(r) = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{2}{R}} \frac{\sin(\pi r/R)}{r}. \quad (20)$$

The straightforward estimation for $E^{(1)}$ gives the following result:

$$\langle \delta V(r) \rangle = \left\langle \left(\frac{\nabla u_0}{\bar{r} u_0} \right) (R \psi_1 \nabla \psi_1) \right\rangle \frac{\hbar^2 \bar{r}}{m \bar{r}^2 R} \equiv \frac{\hbar^2 \bar{r}}{m \bar{r}^2 R}, \quad (21)$$

where $\langle \dots \rangle$ denotes the integration over the cluster volume. It seems as if $E^{(1)}$ is proportional to $1/(\bar{r}R)$. In this case the hierarchy of terms in our expansion (17) would be broken, because the previous term is proportional to $1/R^2$. However, below we shall demonstrate the emergence of an extra factor to $E^{(1)}$ which is proportional to $(\bar{r}/R)\xi$. It is a result of the integration in Eq. (19) over angles.

The perturbation $\delta V(r)$ has the cell's scale of variation. We shall integrate in Eq. (19) over the volume of i th cell. Using the spatial integration by parts one can write

$$E^{(1)} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \int_{L < |r - R_i| < \bar{r}} d\mathbf{r} \nabla \ln[u_0(|\mathbf{r} - \mathbf{R}_i|)] \nabla \psi_1^2(r) = -\frac{\hbar^2}{2m} \sum_{i=1}^N \left[(\ln u_0) \right]_{\bar{r}} \oint_i d\mathbf{S} \nabla \psi_1^2 - \int_i d\mathbf{r} (\ln u_0) \Delta \psi_1^2. \quad (22)$$

Introduce the gradient expansion of the squared wave function $\psi^2(r)$ near the point \mathbf{R}_i ,

$$\psi^2(r) = \psi^2(R_i) + \nabla \psi^2|_{R_i} (\mathbf{r} - \mathbf{R}_i) + \frac{1}{2} \Delta \psi^2|_{R_i} (r^2 - 2\mathbf{r}\mathbf{R}_i + R_i^2) + \dots \quad (23)$$

Using Eq. (23) and expansions of derivatives over the small parameter \bar{r}/R_i we have

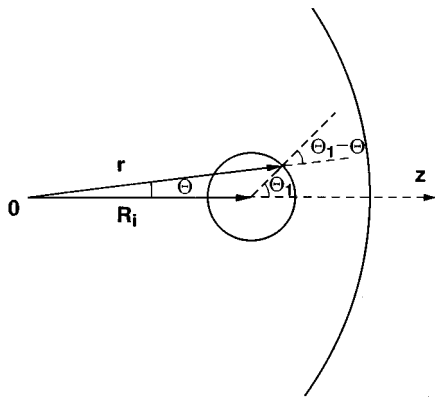
$$\nabla \psi^2(r) = \left(\frac{d\psi^2(R_i)}{dR_i} + \frac{d^2\psi^2(R_i)}{d^2R_i} \frac{\bar{r}}{R_i} \right) \frac{\mathbf{r}}{r} = \frac{d\psi^2(R_i)}{dR_i} \left[1 + O\left(\frac{\bar{r}^2}{R_i^2}\right) \right] \frac{\mathbf{r}}{r}, \quad (24)$$

$$\Delta \psi^2(r) = \Delta \psi^2(r)|_{R_i}. \quad (25)$$

In Eq. (22) we can take the derivatives over \mathbf{r} at the centers of cells \mathbf{R}_i , then

$$E^{(1)} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \left[\frac{d\psi_1}{dR_i} (\ln u_0) \right]_{\bar{r}} \oint_i \frac{\mathbf{r}}{r} d\mathbf{S} - \Delta \psi_1^2(r) \Big|_{R_i} \int_i d\mathbf{r} \ln u_0, \quad (26)$$

where

FIG. 2. The scheme for calculation of the integral over surface of i th cell.

$$(\ln u_0)|_{\bar{r}} = -\frac{3}{2}(\xi - \xi^2) + O(\xi^3). \quad (27)$$

The terms under the sum in Eq. (26) have the opposite signs.

The integral over the surface of i th cell is evaluated exactly (see Fig. 2),

$$\begin{aligned} \oint_i \frac{\mathbf{r}}{r} d\mathbf{S} &= 2\pi\bar{r}^{-2} \int_0^\pi d\theta \cos(\theta_1 - \theta) \sin \theta_1 \\ &= 4\pi\bar{r}^{-2} \left\{ \left(1 - \frac{1}{3} \frac{R_i}{\bar{r}} \right) \quad \text{for } r < \bar{r}; \right. \\ &\quad \left. \frac{2}{3} \frac{\bar{r}}{R_i} \quad \text{for } r \geq \bar{r} \right\}. \end{aligned} \quad (28)$$

Hence, the integration over angles gives the additional power of \bar{r}/R_i . Further, taking account for the factor $1/R_i$ from Eq. (28), we change in Eq. (26) summation to integration and obtain the following result,

$$\sum_{i=1}^N \frac{d\psi_1}{dR_i} \frac{1}{R_i} = \frac{3}{4\pi\bar{r}^3} \int_0^R dr 4\pi r^2 \frac{1}{r} \frac{d\psi_1}{dr} = -\frac{3}{\bar{r}^3 R^2} C_0, \quad (29)$$

where $C_0 = 0.709$. Further, after the change of the summation over cell numbers to the integration over the cluster volume it is possible to reduce the second term in Eq. (26) to a surface integral. The integral vanishes due to the boundary condition (16). Finally, using Eqs. (26)–(29), we have for $E^{(1)}$,

$$E^{(1)} = -\frac{\hbar^2 \pi^2}{2mR^2} [(\xi - \xi^2)C_1 + O(\xi^3)] + O\left(\frac{\bar{r}^{-3}}{R^3}\right), \quad (30)$$

where $C_1 = 12C_0/\pi$. It is worth noting, that the excluded volumes inside the cells contribute to neglected terms ($\sim \xi^3$).

In the second order of the perturbation theory

$$E^{(2)} = \sum_{n,\ell} \frac{\langle n,\ell | \delta V | 1,0 \rangle \langle 1,0 | \delta V | n,\ell \rangle}{E_{1,0} - E_{n,\ell}}. \quad (31)$$

Integrations over angles in the nondiagonal matrix elements select states with the orbital quantum number $\ell=0, E_{n,0} = \hbar^2 \pi^2 n^2 / (2mR^2)$. The series (31) is a rapidly convergent. Therefore we account for the terms with $n \leq 4$. The result is

$$E^{(2)} = \frac{\hbar^2 \pi^2}{2mR^2} [\xi^2 C_2 + O(\xi^3)] + O\left(\frac{\bar{r}^{-3}}{R^3}\right), \quad (32)$$

where $C_2 = 0.093(8/\pi)^2$. Assembling Eqs. (13), (17), (30), and (32) we obtain the desired expression for electron affinity,

$$\begin{aligned} EA &= \frac{3}{2} \frac{\alpha e^2}{\bar{r}^3 \sigma} f\left(1 - \frac{\sigma}{R}\right) - \frac{3}{2} \frac{\hbar^2}{m\bar{r}^2} \xi - \frac{\hbar^2 \pi^2}{2mR^2} [1 - C_1 \xi \\ &\quad + C_3 \xi^2 + O(\xi^3)] + O\left(\frac{\bar{r}^{-3}}{R^3}\right), \end{aligned} \quad (33)$$

where $C_3 = C_1 + C_2$.

IV. DISCUSSION

The obtained expression for EA refines the formula for the binding energy of charged quantum particles (electron or positron) in a finite system. We can consider now the hierarchy of inequalities as criterions for the validity of our results. The estimations are carried out for xenon at the particle density $\rho = 1.41 \times 10^{22} \text{ cm}^{-3}$. The input data are: $\alpha = 27a_0$, $\sigma = 7.6a_0$, $\bar{r} = 4.855a_0$; the electronic scattering length $L = 0.7a_0$, a_0 is the Bohr radius.

(1) First of all, the medium must provide the well for an electron, that is $V_0(\infty) < 0$ in the limit of $R = \bar{r}N^{1/3} \Rightarrow \infty$. The condition corresponds to the following inequality,

$$\alpha/(a_0 \sigma L) > 1.$$

The calculated value of $V_0(\infty) = -0.61 \text{ eV}$ is in a satisfactory agreement with the measured value $V_0(\infty) = -0.71 \pm 0.05 \text{ eV}$.¹⁷

The first curvature correction to the polarization shift $U_0(\infty)$ must be small, $R \gg \sigma$.

The next inequality, $|T_0| = 3\hbar^2 |L| / (2m\bar{r}^3) \gg \hbar^2 \pi^2 / 2mR^2$, results in $N \gg (\pi^2 \bar{r} / 3 |L|)^{3/2}$. For the xenon cluster it means that

$$N \gg 109.$$

Thermal excitation should be sufficiently small compared with the spacing between the electron energy levels in the cluster, $kT \ll E_{2,0} - E_{1,0} = 3\hbar^2 \pi^2 / 2mR^2$. If $T = 300 \text{ K}$,

$$N \ll 3.3 \cdot 10^4.$$

On the other hand, we neglect the terms of the order of $(\bar{r}/R)^3$ in Eq. (33). Therefore, the additional condition takes place,

$$\xi > \bar{r}/R.$$

We have $\xi = 0.144$, that leads to $N > 300$.

Finally, the range of applicability of our results for $T = 300 \text{ K}$ is

$$300 < N \leq 3.3 \times 10^4.$$

For these clusters the first new term $E^{(1)}$ modifies the kinetic energy in the well by 40%. There are three additional questions one can ask concerning the validity of present calculations.

- (i) Is it reasonable to treat the equivalence of all the cells?
- (ii) Does the approximate boundary condition (16) influence the final result of our perturbation theory?
- (iii) Is it necessary to take into account the effect of a self-compression of cluster under the surface tension?^{18,19}

The calculations were done as if cluster cells are equivalent one to others, i.e., the surface effects are small. In reality, near the cluster surface cells are partially “destroyed.” Let us estimate the contribution of surface layer of thickness x to $E^{(1)}$. It is given by the integration in Eq. (29) between $(R-x)$ and R . The result is proportional $x/(\bar{r}R)^3$ and small since $x \sim \bar{r}$.

The usage of the boundary condition (16) eliminates the second term in Eq. (26). An explicit check of the supposition can be made by a straightforward calculation. The calculations were fulfilled for an electron in the spherically symmetric potential well of radius R and $V_0(R)$ in depth. The eigenvalue problem was solved numerically for the wide range of N , using the exact boundary condition, $\psi_1(\infty)=0$. The results indicate the nice applicability of our formula for EA (33) in the range $N \cong 10^3 - 10^4$. However, if $N \cong 100$ both terms in Eq. (26) become equal.

In conclusion, we discuss the possibility of a deformation of clusters. There are two opposite processes: the pressing under surface stress and the strain induced by an excess electron. The electron free path in rare-gas liquids is very large, therefore electron is nearly free in a cluster containing thousand atoms. It allows us to estimate an electron pressure as $\pi \hbar^2 / (4mR^5)$. If the electron pressure term is not ignored, one can obtain from the equilibrium condition

$$2\gamma/R - \hbar^2 \pi / (4mR^5) - B \ln(V_0/V) = 0$$

the simple relation which describes the deformation. Here γ is the surface tension, B is the bulk modulus, V_0 and V are the cluster volumes in the nondeformed and deformed states, $R_0 = \bar{r}N^{1/3}$, and $R = (\bar{r} + \Delta\bar{r})N^{1/3}$, where $\Delta\bar{r}$ is the change in the interatomic spacing. The simple analysis points to the compression of liquid xenon cluster with $N > 20$ and to the strain if $N < 20$. However, these numbers of atoms are left beyond our approach. The quantitative estimation of an influence of the deformation on the electron affinity of small clusters requires a self-consistent consideration.

ACKNOWLEDGMENT

The work was supported by the Russian Foundation for Basic Research.

- ¹ *Large Finite Systems*, edited by J. Jortner (Reidel, Dordrecht, 1987).
- ² H. Haberland, *Clusters of Atoms and Molecules*, Springer Series in Chemical Physics, Vol. 56 (Springer, Berlin, 1994).
- ³ P. Stampfli, *Phys. Rep.* **255**, 1 (1995).
- ⁴ H. Haberland, T. Kölar, and T. Reiners, *Phys. Rev. Lett.* **63**, 1219 (1989).
- ⁵ P. Stampfli and K. Bennemann, *Phys. Rev. A* **38**, 4431 (1988); *Z. Phys. D* **20**, 53 (1991).
- ⁶ G. L. Martyna and B. Berne, *J. Chem. Phys.* **90**, 3744 (1989).
- ⁷ D. Jackson, *Classical Electrodynamics*, 2nd ed. (Wiley, New York, 1975).
- ⁸ G. Makov, A. Nitzan, and L. E. Bruce, *J. Chem. Phys.* **88**, 5076 (1988).
- ⁹ V. M. Atrazhev and I. T. Iakubov, *J. Chem. Phys.* **103**, 9030 (1995).
- ¹⁰ I. T. Iakubov and V. V. Pogosov, *Phys. Rev. B* **51**, 14941 (1995); V. M. Atrazhev, I. T. Iakubov, and V. V. Pogosov, *Phys. Lett. A* **204**, 393 (1995).
- ¹¹ V. V. Batygin and I. N. Toptygin, *Problem in Electrodynamics* (Academic, New York, 1964).
- ¹² J. Lekner, *Phys. Rev.* **158**, 130 (1967).
- ¹³ B. E. Springett, M. H. Cohen, and J. Jortner, *J. Chem. Phys.* **48**, 2720 (1968).
- ¹⁴ J. Bardeen, *J. Chem. Phys.* **6**, 367 (1938).
- ¹⁵ M. H. Cohen and F. S. Ham, *J. Phys. Chem. Solids* **16**, 177 (1960).
- ¹⁶ P. Kubica and M. J. Stott, *J. Phys. F* **4**, 1969 (1974).
- ¹⁷ R. Reininger, U. Asaf, and I. T. Steinberger, *Chem. Phys. Lett.* **90**, 287 (1982).
- ¹⁸ I. T. Iakubov and V. V. Pogosov, *Physica A* **214**, 287 (1995).
- ¹⁹ A. Kiejna and V. V. Pogosov, *J. Phys.: Condens. Matter* **8**, 4245 (1996).