

## Size dependence of electronic structure and adiabatic type of collective vibration in small metal clusters

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The electronic structure of atomic clusters is studied as a function of the geometrical parameters and number of atoms  $N$  in the clusters. Self-consistent electron wave functions and energies are calculated for the clusters with closed and open shells for  $N$  ranging from 4 to 40 and for the various radii of positive cluster cores. These calculations are done both for the homogeneous and inhomogeneous jellium models of the cluster core. The equilibrium values of jellium core radius have been obtained using *ab initio* Hartree-Fock calculations for the valence electrons. The importance of the role of nonlocal exchange interaction in the creation of the equilibrium cluster structure is also shown. An adiabatic type of collective vibrational mode is predicted. Vibrational frequencies and amplitudes are calculated for the "magic" number clusters. The influence of the geometrical parameters on the physical properties of clusters is discussed.

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### INTRODUCTION

The problem of *ab initio* electronic-structure calculations for the atomic clusters is important now, because experimental methods of cluster spectroscopy can give detailed information about energies and dynamical properties of ground and excited cluster states. The great interest in the atomic cluster physics is associated with the discovery of the electron shells and "magic" numbers of atomic clusters [1-4]. There is close analogy between atomic clusters and other finite Fermi systems such as atomic nuclei or many-electron atoms. The electronic cluster structure traditionally is calculated using the functional-density method with local-density approximation (LDA) for the electron exchange interaction [2-5]. As a rule, LDA calculations give accurate values of total electronic energies of ground state, but are not so successful in the description of dynamic properties of finite Fermi systems [4,6]. The comparison of the nonlocal exchange Hartree-Fock (HF) calculations with the results of LDA methods has been done in [6] for the excitation spectrum and oscillator strength of sodium atomic clusters. There it was shown that the results are sensitive to the approximation of the electron-electron interaction.

In the present paper we have studied the parametric dependencies of the cluster electronic structure on the cluster core radius  $R$  for the homogeneous and inhomogeneous positive-core charge distribution. For the simplest homogeneous jellium approximation the electron Hamiltonian depends only on a single parameter  $R$ . Usually, the solid state parameter of internuclear distance is used to obtain the magnitude of the cluster core radius  $R$ . It is expressed as  $R_b = N^{1/3}a_0$  where  $N$  is a number of atoms in the cluster and  $a_0$  is an internuclear distance in the bulk material, which consists of the same atoms. Due to the different physical conditions near the free-cluster

boundary and inside the bulk material the internuclear distances in the small clusters can be different from the bulk internuclear distances  $a_0$ . We calculated the  $R$  dependencies of the cluster total energy and obtained the equilibrium position  $R_0$  as a function of the number of atoms. It is important in these calculations that we used the Hartree-Fock approximation for a description of the cluster valence electrons, as it gives more accurate size dependences of the cluster characteristics than other approximate methods.

We found collective oscillations which do not exist in nuclei and atoms. These are adiabatic oscillations of the charge density of the positive-core ions, which look like the core radius vibrations near equilibrium position  $R_0$ . And variable  $R$  plays the role of the collective coordinate for this motion. The energies and amplitudes of core vibrations are obtained for the clusters with various numbers of atoms  $N$ . Size dependences are calculated for the electron charge distribution, energies, and electronic diamagnetic susceptibilities.

### SELF-CONSISTENT ELECTRON ENERGIES AND WAVE FUNCTIONS

The jellium approximation gives a possibility to apply the advanced methods of many-body atomic theory to the calculations of the electronic energies and wave functions for the valence cluster electrons. It was done for the closed-shell clusters and bulk material approximation of the internuclear distance inside the core in a recent article [6]. We present the results of the HF calculations of the electronic structures for the clusters with various geometrical core parameters and number of atoms changed from  $N = 4$  to  $N = 40$ . The dependences of total cluster energies on  $W(N, R)$  have been obtained for both the

clusters with closed and open electron shells. The accurate magnitudes of the total cluster energies  $W$  were calculated using minimization of  $W(N, R)$  with respect to the core cluster radius  $R$ .

Let us briefly describe the procedure of the calculation of the total cluster energy  $W(N, R)$ . If we neglect the kinetic energies of the positive ion motion inside the cluster core, total cluster energy  $W$  is equal to a sum of the electronic  $E_{el}(N, R)$  and the positive core electrostatic energies  $E_c$ :

$$W(N, R) = E_c(R) + E_{el}(N, R), \quad (1)$$

$$E_c(N, R) = \frac{3}{5} \frac{N^2}{R}, \quad (2)$$

$$E_{el}(N, R) = \langle \hat{H}_{el}(N, R) \rangle, \quad (3)$$

where  $\langle \rangle$  is the mean value of the valence cluster electron Hamiltonian with respect to their many-electron wave functions. The main computational problem is the calculation of the  $R$  dependence of the many-electron wave function. Using HF approximation we obtain a system of integrodifferential equations for the single-electron wave

functions  $\psi_i$  and orbital energies  $\epsilon_i(R)$ :

$$\{\hat{h}_0 - \epsilon_i\} \psi_i(\mathbf{r}) = \sum_j' \left\langle j(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| i(\mathbf{r}') \right\rangle \psi_j(\mathbf{r}), \quad (4)$$

where  $\hat{h}_0$  is a single-particle Hamiltonian for the Hartree approximation:

$$\hat{h}_0 = -\frac{1}{2} \Delta + \sum_j' \left\langle j(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| j(\mathbf{r}') \right\rangle + v(r) \quad (5)$$

and  $v(r)$  is a cluster core potential

$$v(r) = \begin{cases} -\frac{N}{2R} \left[ 3 - \left( \frac{r}{R} \right)^2 \right] & r < R \\ -\frac{N}{r} & r \geq R. \end{cases} \quad (6)$$

The system of Eq. (4) is solved numerically using standard procedure of atomic HF calculations. All orbital wave functions and energies are functions of  $R$ , and the cluster core radius is the only physical parameter for the electronic Hamiltonian. The total energy of the cluster valence electron  $E_{el}(R, N)$  is obtained according to the HF method and, of course, it is a function of the core radius  $R$ :

$$E_c(N, R) = \sum_{i=1}^N \epsilon_i(R) - \frac{1}{2} \sum_{i,j} \left\langle i(\mathbf{r}) j(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| i(\mathbf{r}) j(\mathbf{r}') - i(\mathbf{r}') j(\mathbf{r}) \right\rangle. \quad (7)$$

As an illustration of such  $R$  parametric behavior, the size dependences of single-electron energies are shown in Fig. 1(a) for the cluster consisting of 34 atoms (1s, 1p, 1d, 2s, and 1f levels in the quantum well notations [2]). The single-particle eigenenergies  $\epsilon_i$  as functions of core radius  $R$  are given for a wide interval of

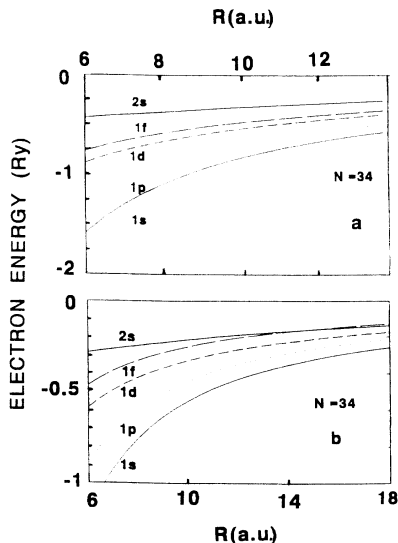


FIG. 1. Size dependences of single orbital energies  $\epsilon_i(R)$  for the  $N = 34$  cluster: (a) HF approximation with nonlocal exchange interaction; (b) Hartree approximation.

$R$ . For the purpose of comparison, in Fig. 1(b) we present the energies of single-particle orbitals calculated for Hartree approximation (HA). It is shown that the nonlocal exchange interaction influences not only the magnitude of the single-particle energies, but it also changes the relative energy gaps between orbital energy levels and the parametric dependences of  $\epsilon_i(R)$ . For example, parametric “velocities”  $\frac{d\epsilon_i}{dR}$  for the  $i = 1d, 2s$  strongly depend on the exchange interaction and, of course, this strongly influences the  $R$  dependence of electron polarizability of clusters.

For the HA we found the energy orbital 1f-2s crossing at  $R \sim 15$  [Fig. 1(b)]. A similar crossing effect was found for these orbitals in LDA calculations [4]. The nonlocal exchange interaction causes the avoidance of the level crossing for the orbitals with different types of symmetry [Fig. 1(a)]. This means that there is strong exchange interaction between orbitals with different angular momenta (for example, interaction between 1f-2s orbitals in the  $N = 34$  cluster). This effect strengthens the electron angle correlations in the large radius clusters and it should be taken into account in the problem of the correct determination of electronic orbital configuration or mixture of configurations for the ground state.

Information about  $R$  dependence of single-particle orbital wave functions is available now, and these functions are used as a basis set for the calculations of the cluster response to the external fields [5,6]. We obtained the  $R$  dependence of the orbital functions  $\psi_I$  for various val-

ues  $N$  and  $R$ . Positions of the maximums of the radial wave functions for the single-electron orbitals depend on the magnitude of the core radius. The large separation between maximums of single-particle electronic HA orbitals showed considerable shell effects [Fig. 2(a)], but after inclusion of the nonlocal exchange interaction these maximums have become closer to each other [Fig. 2(b)].

Nonlocal exchange interaction makes the single-particle orbitals more compact and absolute values of the single-electron energies are increased. Nevertheless, we found that magnitude of the total electronic energy practically does not depend on the exchange interaction. The total energy of the cluster valence electron  $E_{el}(R, N)$  is calculated by using the HF method and it is a function of the core radius  $R$ . In Fig. 3 the total electron energies per atom  $E_{el}(N, R)/N$  are shown for the HF and HA calculations for the clusters with  $N = 8$  and  $N = 18$ . One can see that the influence of the exchange interaction on the magnitude of total electron energy is weak and the difference between HF and HA energies is less than 3%. The total electronic energies calculated in LDA also are close to HF and HA results [2,5]. A more significant difference arises between results of HA, LDA, and HF methods in calculations of amplitudes of physical processes such as optical absorption and dynamical polarizability of atomic clusters [5,6]. Since these approximations give sufficiently different single-particle orbitals, which form the basis set for the many-body perturbation theory, it is not surprising to observe significant difference between the three methods for calculations of the physical processes to which they pertain.

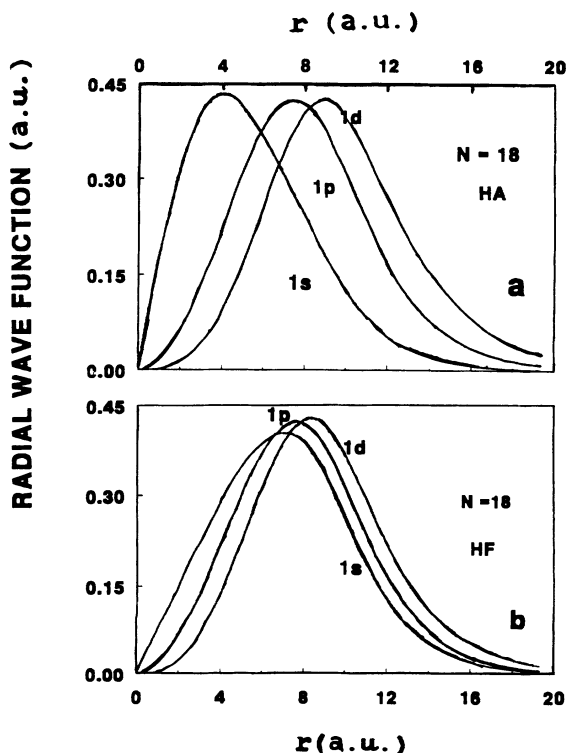


FIG. 2. Radial orbital wave functions for the cluster with  $N = 18$  atoms: (a) HA; (b) HF approximation.

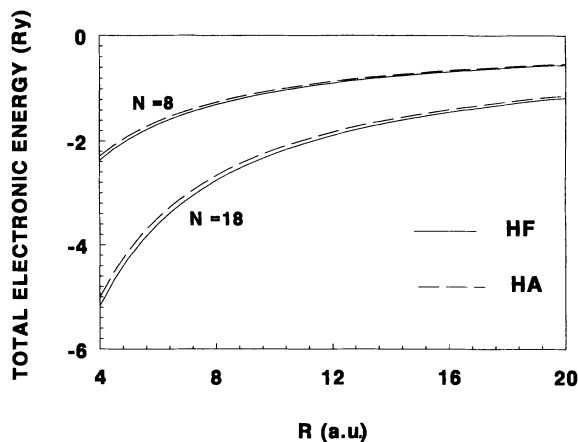


FIG. 3. Total electronic energies  $E_{el}(N, R)$  for the clusters with  $N = 8$  and  $N = 18$ . Solid line—HF calculation, dashed line—HA.

Additional information about the electronic wave function could be obtained from the diamagnetic susceptibility  $\chi$  of atomic clusters. At present we are not aware of any such experimental measurements of the diamagnetic susceptibility of the sodium clusters. Although  $\chi$  does not change dramatically due to the approximation used to compute the exchange interaction, it would be possible to use experimental data to establish the validity of the approximations by comparing the experimental values with the theoretical predictions for  $\chi(N)$  resulting in each case. In Fig. 4 we show the magnitude of diamagnetic susceptibility  $\chi$  per atom as a function of  $N$  for the HF and HA calculations. The difference between the results is several percent and it increases for the clusters with the larger numbers of atoms.

The total cluster energy per atom  $w(N, R) = W(N, R)/N$  is a function of the core radius  $R$  and it has a minimum at the magnitude  $R_0$ , which differs from the bulk material approximation of the core radius  $R_b$ . We show in Fig. 5 the  $R$  dependences for the  $w(N, R)$  of the

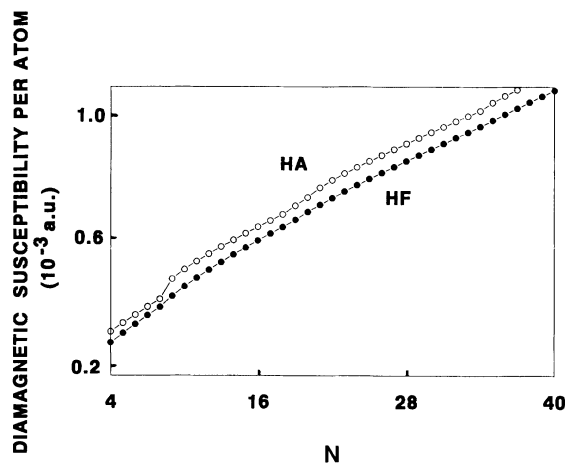


FIG. 4. Diamagnetic susceptibility per atom  $\chi$  of sodium atomic cluster with different numbers of atoms  $N$ . Dark circle—HF and open circle—HA calculations.

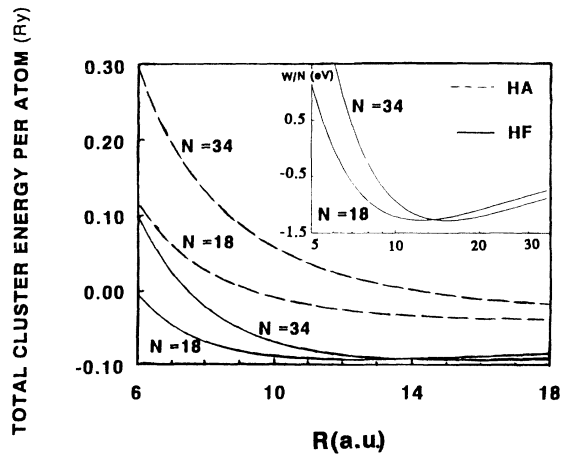


FIG. 5. Total cluster energies  $w(N, R)$  as a function of the cluster core radius  $R$  for the magic clusters  $N = 18$  and  $N = 34$ . Solid line—HF and dashed line—HA calculations. The inset shows the same HF energy curves for a wider interval of the variable  $R$ .

clusters with  $N = 18$  and  $N = 34$ . The equilibrium value of the core radius  $R_0$  and magnitude of the minimal cluster energy  $w_0$  are very sensitive to the electron exchange interaction. This behavior is expected, because near the equilibrium position  $R_0$  the electron  $E_{el}(N, R)$  and core  $E_c(R)$  energies essentially compensate each other and the absolute value of total energy is much smaller than both electronic and core energies:

$$|W(N, R)| = |E_c + E_{el}| \ll E_c(N, R), |E_{el}(N, R)|. \quad (8)$$

In this case even small variation of electronic energies, which arises due to the exchange interaction approximation, could give considerable relative variation of the total energies  $w$ . The  $w$ -function maximum is very sensitive to the inclusion of the exchange interaction. An illustration of this fact is shown in Fig. 6 where the total cluster

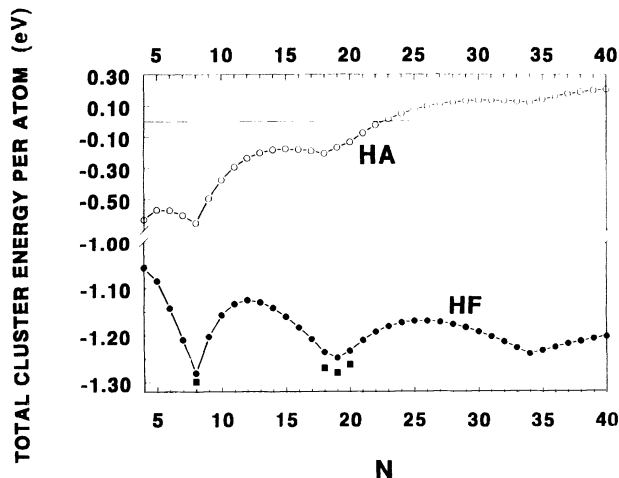


FIG. 6. Total cluster energy  $w(N, R)$  per atom for the HF and HA calculations as a function of the number of atoms  $N$  in the cluster.

energy per atom  $w = w(N)$  is calculated for the Hartree and HF approximations with the bulk material magnitude of cluster core radius. These calculations were done for the clusters with open and closed shells. The value of  $(-w)$  plays the role of the atomic binding energy and according to our HA calculations this binding energy is negative for the clusters with  $N \geq 23$ . This means that these clusters are unstable without electronic exchange interaction. Nonlocal exchange interaction reduces the total cluster energies and makes the cluster with  $N \geq 23$  also stable.

The value of binding energy  $(-w)$  increases by several percent for the calculations with equilibrium core radius  $R_0$ . This effect was also found in the clusters with closed and open shells. Additional minimization of the total cluster energy has been achieved by using inhomogeneous distribution of the core charge. For the Fermi-like charge density distribution  $\rho(r)$  [6],

$$\rho(r) = \rho_0 \{1 + \exp[(r - R)/\beta]\}^{-1} \quad (9)$$

we calculated total cluster energies as the functions of  $R$  and diffuseness parameter  $\beta$ . Figure 7 shows the total energy of the cluster with  $N = 8$  and illustrates that the minimization with respect to inhomogeneity parameter  $\beta$  gives the reduction of total energy about 5–7%. The magnitude of the equilibrium diffuseness parameter  $\beta$  indicates the length of the inhomogeneous part of the charge distribution for the clusters with different core radii  $R$ . The rectangular points in Fig. 6 are the results of double minimization of the total cluster energies  $w$  for the magic clusters  $N = 8, 18, 20$  and the cluster with open electronic shell  $N = 19$ .

One of the results of our calculations is the avoidance of the magic number rule for the clusters with  $N = 18$  and 20 atoms. HF calculations give the minimum energy  $w$  for the cluster with open shell  $N = 19$ , but not for the neighbor clusters with closed shells  $N = 18, 20$ . This effect does not exist in HA and LDA [2] calculations and

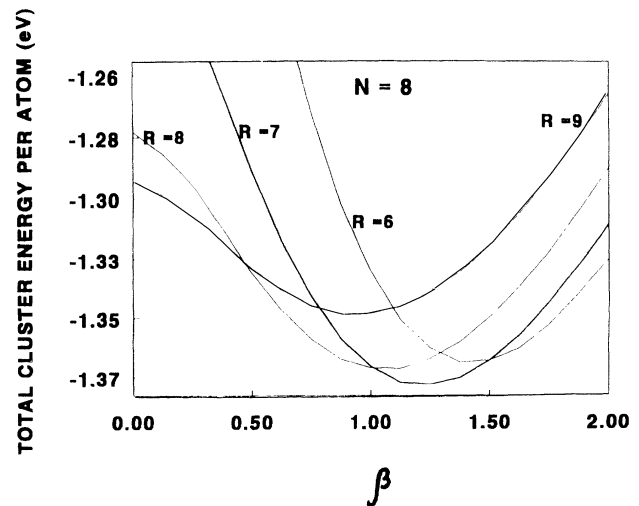


FIG. 7. Total energy  $w$  of the cluster with  $N = 8$  atoms as a function of diffuseness parameter  $\beta$  for the different cluster core radius  $R$ .

the avoidance of magic numbers is a result of nonlocal exchange interaction.

### ADIABATIC CORE VIBRATIONS

The  $R$  dependences of the total cluster energy  $W = W(N, R)$  provide an opportunity to resolve the problem of the adiabatic modes for the collective motion of the cluster core nuclei. Each calculated curve  $W(N, R)$  has a smooth minimum as a function of the cluster core radius  $R$ , for example,  $W$  curves for the HF calculations in Fig. 5. This minimum arises as a result of the competition between two factors: the Coulomb repulsion between positive-core ions producing the expansion of the cluster core volume, and the electron-ion attraction compressing the cluster core. The balance of these factors gives the minimum of the total cluster energy  $W(N, R = R_0)$  at some magnitude of the core radius  $R_0$ . The energy of the cluster ground state is equal to the equilibrium value  $W(N, R_0)$  only for the classical description of the motion of the core ions, but the quantum systems oscillate near a position of classical equilibrium. The frequency and amplitude of these small oscillations depend on the effective mass of the collective motion of ions and curvature of the corresponding potential curve near minimum. In the case of the spherical jellium model the  $R$  dependence of the total cluster energy  $W(N, R)$  plays the role of the potential curve for the dynamic variable  $R$ . The cluster core radius is an external parameter for the electronic part of the cluster Hamiltonian and simultaneously is the coordinate of collective motion of the core ions. (Simple examples of such parametric oscillations are the vibrations of the internuclear distance in diatomic molecules or adiabatic collective motions of the atomic particles in the acoustic phonon modes in solids.) These  $R$  vibrations are equivalent to the small quantum oscillations of the core volume and it is possible due to the compressibility of the cluster's jellium core. This type of low energy collective motion is realizable for the low-temperature clusters, when the other degrees of freedom are frozen. The typical values of temperature will be discussed after numerical calculation of the vibrational energies.

The kinetic energy operator  $\hat{K}$  for the small vibrations of the collective coordinate  $R$  can be obtained using the adiabatic approximation, when the typical "radial" vibration velocity  $|dR/dt|$  is much smaller than the typical electron velocity in cluster shells. The Schrödinger equation for the cluster core vibration wave functions  $\xi_n(R)$  can be written as

$$\left( -\frac{1}{2\tilde{M}} \frac{\partial^2}{\partial R^2} + W(N, R) - W(N, R_0) \right) \xi_n(R) = K_n \xi_n(R), \quad (10)$$

where  $\tilde{M} = \frac{3}{5}M_0$  is the effective mass of the adiabatic vibrational mode for the cluster core with mass  $M_0$  and  $K_n$  is the vibration energies counted from the minimum of total cluster energy  $W(N, R_0)$ . These equations for the eigenfunctions and eigenenergies of the core vibra-

TABLE I. Characteristics of adiabatic vibrational mode.

| $n$      | $K_n$ (meV) | $R_1$ (a.u.) | $R_2$ (a.u.) | $\delta$ (%) |
|----------|-------------|--------------|--------------|--------------|
| $N = 8$  |             |              |              |              |
| 0        | 2.80        | 8.86         | 9.17         | 3.4          |
| 1        | 8.41        | 8.75         | 9.28         | 6.0          |
| 2        | 14.01       | 8.68         | 9.37         | 7.7          |
| 3        | 19.6        | 8.62         | 9.44         | 9.4          |
| 4        | 25.2        | 8.57         | 9.50         | 10.3         |
| $N = 18$ |             |              |              |              |
| 0        | 2.07        | 12.17        | 12.42        | 2            |
| 1        | 6.2         | 12.1         | 12.5         | 3.4          |
| 2        | 10.34       | 12.03        | 12.57        | 4.4          |
| 3        | 14.47       | 11.99        | 12.62        | 5.2          |
| 4        | 18.60       | 11.95        | 12.67        | 5.86         |

tions are resolved numerically. In Table I some characteristics of the spherical symmetric core vibrations for  $N = 8$  and  $N = 18$  are shown, such as  $K_n$ —the vibration energies for the ground and excited states;  $R_{1,2}$ —the positions of classical turning points for the  $R$  coordinate;  $\delta = |R_2 - R_1|/R_0$ —relative value of deviation from the equilibrium position. The magnitude of  $\delta/2$  is in analogy with the amplitude of classic core radius vibrations. It should be noted that the smooth minimums of the total cluster energies (Fig. 5) transform into pronounced minimums of the oscillator potential for the vibrational motion due to very large magnitude of the effective mass  $\tilde{M}$ . This gives a possibility to calculate the positions of the classical turning points with sufficient accuracy.

For the clusters with  $N = 8$  and 18 the excited energies of vibration modes are close to the simple oscillator model with the vibration frequencies  $\hbar\omega = 65$  and 48 K, respectively. The magnitude of the relative deviation  $\delta$  is small for the ground state of the vibrational mode (2 – 3%), but it is as high as 10 – 12% for the excited states with vibrational quantum numbers  $n \sim (8 - 10)$ . This fact is important for the analysis of the experimental spectrum of atomic clusters. The modern molecular-beam techniques provide the production of the metal-cluster beams with the "inner" cluster core temperature  $T$  about 500 K [3,7]. This means that in real experimental conditions there are high excited adiabatic vibrational modes of cluster core with  $n = T/\hbar\omega \sim (8 - 10)$  for  $N = 8$  or 18. In this case the amplitudes of the radius thermal vibrations are sufficiently large (10 – 15% of cluster core radius) and for the correct description of various cluster processes it is necessary to use quantum statistical methods. This applies both to the electronic and the nuclear core subsystems of the atomic cluster. It is possible to study the spectrum of collective vibrations of the cluster core for low-temperature cluster beams ( $T < 100$  K), when only the lowest vibrational modes are excited. It seems that at low temperatures the cluster core vibrations could strongly influence the electron-electron interaction in analogy with Cooper pair effects for the bulk materials, and core vibrations could play the role of the bulk material acoustic phonons [8]. Of course, renormalization of electron-electron interaction in small metal atomic clusters needs a more detailed investigation.

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