

# An optimized "jellium" model for metallic clusters with screened Coulomb interaction

V. K. Ivanov, A. N. Ipatov, and V. A. Kharchenko

St. Petersburg Technical University, 195251 St. Petersburg, Russia

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We examine an optimized nonparametric "jellium" model for polyatomic clusters that ensures the absolute minimum of the total energy of a system consisting of the delocalized electrons and a positive core with screened Coulomb interparticle interaction. We use the variational method to determine the optimal distribution of the charge density of the cluster core. The total cluster energy is minimized when the potential generated by the positive and negative charges are locally equal. Numerical calculations of the electron structure are done for alkali-metal clusters in the Hartree–Fock approximation. We discovered that screening of the interparticle interaction has a strong effect on the stability of the system and that there is a strong dependence of the electron structure on the distribution of the positive background.

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## 1. INTRODUCTION

Studies of the electronic structure of atomic clusters carried out in the last decade (see the paper by Ekardt<sup>1</sup> and the review articles by de Heer<sup>2</sup> and Brack<sup>3</sup>) have shown that *ab initio* calculations of such objects are difficult even for the case of several atoms<sup>4</sup> due to the large number of degrees of freedom in the system. At the same time it has been found that a number of approximate methods make it possible to considerably simplify the problem of calculating the structure and the physical characteristics of clusters. An example is the successfully used "jellium" model,<sup>1</sup> in which a cluster is represented by two subsystems: the ionic background (or core) whose positive charge is distributed over the entire volume, and the delocalized valence electrons, forming a shell structure in the field of the core.<sup>1–3</sup> The first calculations that made it possible to explain the formation of electron shells in alkali-metal clusters<sup>1–3</sup> were done with the model of a spherically symmetric uniformly charged core whose radius  $R$ , being the only macroscopic parameter of the model, was determined from the interatomic distance in the respective metal (the bulk material, or *BM*, model):

$$R = r_s \sqrt[3]{N},$$

where  $N$  is the number of atoms in the cluster. Here the stability of the system is determined by the total energy of the positive core charge and the delocalized electrons:

$$E_{\text{tot}} = E_{\text{core}} + E_{el}.$$

It was found that the choice of distribution function for the core's charge density has a strong effect on the results of calculations.<sup>5–7</sup> Attempts were made to "optimize" the distribution function  $\rho_{\text{core}}(\mathbf{r})$  by varying its geometric parameters,<sup>5,7</sup> but a common drawback of such an approach is the dependence on the choice of parameters in which the optimization is carried out.

In Ref. 6 we suggested a nonparametric optimized jellium model (*OJM*) ensuring the absolute minimum of the total energy of the system. The aim of the present investiga-

tion is to generalize the optimized jellium model to the case of a non-Coulomb interaction between the core particles and the electrons and to study the effect of the interaction parameters on the stability of the cluster system and its structure.

In contrast to the traditional jellium model with an *a priori* fixed distribution  $\rho_{\text{core}}(\mathbf{r})$ , the idea of an optimized jellium model is based on a self-consistent solution of the many-body problem involving the interacting electron system and the positive background in conditions where the total cluster energy  $E_{\text{tot}}$  is at its absolute minimum. This requires simultaneously solving two problems: calculating the multielectron wave function in an external field, and calculating the external field generated by the positive charge with an unknown distribution  $\omega_{\text{core}}(\mathbf{r})$  that ensures the total energy of the system being at its minimum. Using a double variational procedure, we find the condition for the absolute minimum of the total energy  $E_{\text{tot}}$  of the system, under which, as we show below, the potentials of the positive and negative charges balance each other. Here the same nature of the ion–ion and ion–electron interaction (say, purely Coulomb) in the cluster leads to local electric neutrality of the system.<sup>6</sup> This results in a nonlinearity in the Schrödinger equation for the multielectron wave function and in the system of Hartree–Fock equations if the single-particle approximation is used for the system of delocalized electrons. Thus, the electron wave functions and energies and the "optimal" distribution function for the positive-charge density,  $\rho_{\text{core}}(\mathbf{r})$ , are obtained as a result of numerically solving a system of coupled nonlinear integro-differential equations. It appears that the total cluster energy and, hence, the cluster stability depend not only on allowing for the nonlocal interelectronic interaction<sup>5,8,9</sup> and the positive charge distribution<sup>5,6,8,9</sup> but also on the nature of the interaction between the core ions and the electrons; for instance, on the screening of the ion–electron and ion–ion Coulomb interactions.

Throughout the article we use natural units:  $\hbar = |e| = m_e = 1$ .

## 2. VARIATION OF THE FUNCTIONAL OF THE TOTAL ENERGY OF THE SYSTEM

According to the jellium model, the total cluster energy consists of the total energy  $E_{el}$  of the delocalized electrons moving in an external field  $U(\mathbf{r})$  and the potential energy  $E_{core}$  of the distributed positive charge, which can be assumed purely electrostatic if we ignore the motion of the core particles:<sup>1,6</sup>

$$E_{core} = \frac{1}{2} \int \rho_{core}(\mathbf{r}) U(\mathbf{r}) d\mathbf{r} \quad (1)$$

(here and in what follows integration is over the entire cluster volume).

The total energy of the electron system in the ground state is

$$E_{el} = \langle \Psi^* | \hat{H}_{el} | \Psi \rangle, \quad (2)$$

where  $\Psi$  is the total wave function of the electron system (normalized to unity) satisfying the Pauli principle, and  $\hat{H}_{el}$  is the Hamiltonian of the electron system in the potential  $U(\mathbf{r})$ :

$$\hat{H}_{el} = \sum_i \left( -\frac{\Delta_i}{2} - U(\mathbf{r}_i) \right) + \sum_{i \neq j} V_{el-el}(\mathbf{r}_i, \mathbf{r}_j), \quad (3)$$

where  $V_{el-el}$  is the interelectronic interaction potential (not necessarily the pure Coulomb interaction  $V_{Coul}(\mathbf{r}_i, \mathbf{r}_j) = |\mathbf{r}_i - \mathbf{r}_j|^{-1}$ ).

To determine the condition for the minimum of the total cluster energy, let us assume that the interaction  $V(\mathbf{r}_i, \mathbf{r}_j)$  between any two point unit charges in the system depends only on the distance between the points, monotonically decreases as the charges are moved apart, and tends to zero at infinity:

$$V(|\mathbf{r}_i - \mathbf{r}_j|) \xrightarrow{|\mathbf{r}_i - \mathbf{r}_j| \rightarrow \infty} 0. \quad (4)$$

Note that this assumption simplifies the real picture, since we ignore possible nonlocal effects in the interaction that involve electrons of the inner shells of the core atoms.

In the interaction between two unit point charges we can isolate the pure Coulomb factor  $V_{Coul}$  and a bounded function  $K$  (nonnegative over the entire domain of definition), the latter allowing, in particular, for screening:

$$V(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{K(|\mathbf{r}_i - \mathbf{r}_j|)}{\varepsilon |\mathbf{r}_i - \mathbf{r}_j|}, \quad (5)$$

where the coefficient  $\varepsilon$  acts as the dielectric constant of the medium. We write the interaction of a charge with an arbitrary charge-density distribution  $\rho(\mathbf{r})$  in the usual form

$$U(\mathbf{r}) = \int \rho(\mathbf{r}') V(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \int \rho(\mathbf{r}') V(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (6)$$

where we have allowed for the condition that the interaction of point charges depends only on the relative distance (Eq. (5)).

The condition for the minimum of the free energy  $F$  of the system in an equilibrium state at absolute zero is equivalent to the requirement that the total energy  $E_{tot}$  be minimal,

which for an electrically neutral cluster is reduced to determining the conditions for stationarity of the functional<sup>6</sup>

$$G\{\Psi, \Psi^*, \rho\} = E_{tot}\{\Psi, \Psi^*, \rho\} - \mu \langle \Psi^* | \Psi \rangle - \lambda \int \rho(\mathbf{r}) d\mathbf{r} \quad (7)$$

under small variations  $\delta\Psi^*(\mathbf{r})$  and  $\delta\rho(\mathbf{r})$ , where  $\mu$  and  $\lambda$  are arbitrary Lagrange multipliers. The last two terms on the right-hand side of Eq. (7) are related to the normalization of the wave function and the conservation of the total core charge for a neutral system.<sup>6</sup> If we combine Eq. (7) with (1), (2), and (6), we can write

$$\begin{aligned} G\{\Psi, \Psi^*, \rho\} &= \langle \Psi^* | \hat{H}_{el} | \Psi \rangle \\ &+ \frac{1}{2} \int \int \rho(\mathbf{r}) \rho(\mathbf{r}') V_{ion-ion}(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &- \mu \langle \Psi^* | \Psi \rangle - \lambda \int \rho(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (8)$$

where  $V_{ion-ion}(\mathbf{r}, \mathbf{r}') \equiv V_{ion-ion}(|\mathbf{r} - \mathbf{r}'|)$  is the interaction of two unit point charges from the positive core.

Thus, we must find the solution of the following system of variational equations:<sup>6</sup>

$$\frac{\delta G(\Psi, \Psi^*, \rho)}{\delta \Psi^*} = 0, \quad (9a)$$

$$\frac{\delta G(\Psi, \Psi^*, \rho)}{\delta \rho} = 0. \quad (9b)$$

Equation (9a) leads to the ordinary Schrödinger equation for the total wave function  $\Psi(x)$  of the system of electrons in the potential field (6):

$$\hat{H}_{el} \Psi(X) = E_{el} \Psi(X), \quad (10)$$

where  $X = \{x_1, x_2, \dots, x_i, \dots, x_N\}$ ,  $x_i = (\mathbf{r}_i, \sigma_i)$ , is the set of coordinates and spins of all  $N$  electrons,  $E_{el}$  is the total electron energy of the system, identical to the Lagrange multiplier  $\mu$  in (7) and (8),  $\hat{H}_{el}$  is the Hamiltonian (3), which together with (6) can be written as

$$\begin{aligned} \hat{H}_{el} &= \sum_i \left( -\frac{\Delta_i}{2} - \int \rho(\mathbf{r}') V_{ion-el}(|\mathbf{r}_i - \mathbf{r}'|) d\mathbf{r}' \right) \\ &+ \sum_{i,j} V_{el-el}(|\mathbf{r}_i - \mathbf{r}_j|), \end{aligned} \quad (11)$$

where  $\rho(\mathbf{r}) \equiv \rho_{core}(\mathbf{r})$  is the *a priori* unknown positive charge density distribution function, and  $V_{ion-el}(\mathbf{r}, \mathbf{r}') \equiv V_{ion-el}(|\mathbf{r}_i - \mathbf{r}'|)$  is the interaction of the  $i$ th electron with an elementary point charge from the positive core.

Equation (9b) relates the electron charge density and the jellium charge density at the absolute minimum of the total energy:

$$\begin{aligned} \int \delta\rho(\mathbf{r}') \left( -\sum_i \int |\Psi(X)|^2 V_{ion-el}(|\mathbf{r}_i - \mathbf{r}'|) dX \right. \\ \left. + \int \rho_{core}(\mathbf{r}) V_{ion-ion}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} \right) d\mathbf{r}' = 0, \end{aligned} \quad (12)$$

which holds for an arbitrary variation of the positive charge density provided that the expression in parentheses vanishes. Allowing for (6), we can write Eq. (12) as follows:

$$\int \delta\rho(\mathbf{r})(U_{\text{ion-el}}(\mathbf{r}) - U_{\text{ion-ion}}(\mathbf{r}))d\mathbf{r} = 0, \quad (13)$$

where  $U_{\text{ion-el}}$  is the electrostatic potential generated by the total electron charge in the interaction with the core charge at point  $\mathbf{r}$ , and  $U_{\text{ion-ion}}$  is the interaction of the distributed positive charge with itself.

Thus, the basic conclusion that can be drawn is that the optimal distribution of the jellium charge is such that the potentials of the positive and total electron charges balance, which constitutes the condition for local equality of potential at the absolute minimum of the total energy:  $U_{\text{ion-el}}(\mathbf{r}) = U_{\text{ion-ion}}(\mathbf{r})$ . Here the distribution of the positive charge corresponding to the minimum of the total energy of the system can generally be determined, according to (6) and (12), by solving the inverse problem with respect to the desired function  $\rho_{\text{core}}(\mathbf{r})$ :

$$\int \rho_{\text{core}}(\mathbf{r}')V_{\text{ion-ion}}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = U_{\text{ion-el}}(\mathbf{r}), \quad (14)$$

where the potential  $U_{\text{ion-el}}(\mathbf{r})$  is determined, according to (6), from the distribution of the electron density  $|\Psi(X)|^2$  found by solving the Schrödinger equation

$$\left( -\frac{1}{2}\sum_i \Delta_i - \sum_i \int \rho_{\text{core}}(\mathbf{r})V_{\text{ion-el}}(|\mathbf{r}-\mathbf{r}_i|)d\mathbf{r} + \frac{1}{2}\sum_{i \neq j} V_{el-el}(|\mathbf{r}_i-\mathbf{r}_j|) \right) \Psi(X) = E_{el}\Psi(X) \quad (15)$$

consistently with (14). The fact that the system of equations (14) and (15) is self-consistent leads to nonlinear equations for the total wave function even for a single electron in the field of a positive charge. This sets the optimized jellium model apart from the traditional model of a rigid core with a given distribution of the charge density  $\rho_{\text{core}}(\mathbf{r})$ , where Eq. (10) is linear in the wave function  $\Psi(X)$ .

When the interactions of the elementary point charges,  $V_{\text{ion-el}}(|\mathbf{r}-\mathbf{r}'|)$  and  $V_{\text{ion-ion}}(|\mathbf{r}-\mathbf{r}'|)$ , are the same for neutral clusters, in which the core charge is equal to the total charge of the delocalized electrons,  $\int \rho_{\text{core}}(\mathbf{r})d\mathbf{r} = N$ , Eq. (12) leads to electrical local neutrality of the system,<sup>6</sup> i.e., the optimal positive-charge density is equal to the total electron charge density at each point in the cluster volume:

$$\rho_{\text{core}}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)|\Psi(X)|^2 dX. \quad (16)$$

Such nonlinear dynamic interaction of the electrons with the particles belonging to the cluster core resembles polaron effects in a solid,<sup>10</sup> where a similar situation emerges in a system with a single electron. In metallic clusters we are forced to deal with a multielectron system.

### 3. THE HARTREE-FOCK APPROXIMATION

In a multielectron system an exact solution of Eq. (10) is impossible, with the result that we must employ the approxi-

mate methods of many-body theory. In the present paper we use the Hartree-Fock approximation, in which we can write similar equations for the single-electron wave functions  $\varphi_i(\mathbf{r})$  (normalized to unity) and energies  $E_i$ . For instance, in the optimized jellium model the system of self-consistent single-particle equations corresponding to Eqs. (15) and (16) can be written as follows:

$$\left( -\frac{\Delta_i}{2} + \sum_j \int \varphi_j^*(x')\varphi_j(x')\{V_{el-el}(|\mathbf{r}'-\mathbf{r}|) - V_{\text{ion-el}}(|\mathbf{r}'-\mathbf{r}|)\}dx' \right) \varphi_i(x) - \sum_j \varphi_j(x) \int \varphi_j^*(x')\varphi_i(x')V_{el-el}(|\mathbf{r}'-\mathbf{r}|)dx' = E_i\varphi_i(x), \quad (17)$$

where summation is over all values of  $j$  (including  $j=i$ ), and  $x=(\mathbf{r},\sigma)$ . In the single-particle approximation, the total energy of the system of electrons (Eq. (2)) is

$$E_{el} = \sum_i E_i - \frac{1}{2} \sum_{i,j} (\langle ij|V_{el-el}(\mathbf{r},\mathbf{r}')|ij\rangle - \langle ji|V_{el-el}(\mathbf{r},\mathbf{r}')|ij\rangle). \quad (18)$$

If the potentials of the ion-electron and interelectronic interactions are assumed equal (say, if there are only pure Coulomb forces,  $V_{\text{ion-el}}(\mathbf{r},\mathbf{r}') = V_{el-el}(\mathbf{r},\mathbf{r}') = V_{\text{Coul}}(\mathbf{r},\mathbf{r}') = |\mathbf{r}-\mathbf{r}'|^{-1}$ , in the system) and the jellium charge density is optimal, the Hartree terms of the direct Coulomb interaction are balanced by the terms describing the interaction with the positive charge except for the term with  $j=i$ . This term produces the only "unbalanced" contribution from the potential well of the positive core, and it creates a spatial inhomogeneity in the problem. From the standpoint of the electron system the term with  $i=j$  corresponds to the electron's "self-action."<sup>6</sup> Then the Hartree-Fock equations can be written as

$$-\frac{\Delta}{2}\varphi_i(x) - \sum_j \varphi_j(x) \int \varphi_j^*(x')\varphi_i(x')\frac{1}{|\mathbf{r}-\mathbf{r}'|}dx' = E_i\varphi_i(x), \quad (19)$$

i.e., we have a system of nonlinear integrodifferential equations for the single-particle wave functions of electrons coupled through a nonlocal exchange interaction, including self-action.

The iterative procedure for the numerical solution of the system of equations (17) requires fixing the initial approximation for the wave functions  $\varphi_i(x)$ . For these we used the Hartree-Fock wave functions of delocalized electrons calculated for a cluster with a uniform positive charge distribution  $\rho_{\text{core}}(\mathbf{r})$ . The system (17) of Hartree-Fock equations was solved for neutral metallic clusters with an optimal distribution of the background charge on the assumption that the system is spherically symmetric, i.e.,  $\rho_{\text{core}}(\mathbf{r}) \equiv \rho_{\text{core}}(r)$ , which simplified the solution considerably because of separation of the angular and radial variables. In a spherically symmetric charge distribution with radial density  $\sigma(r) = 4\pi r^2 \rho(r)$ , where  $\int \rho(\mathbf{r})d\mathbf{r} = \int_0^\infty \sigma(r)dr = N$  for a neutral cluster, the potential (6), after we allow for (5) and integrate over the angular variables, assumes the form

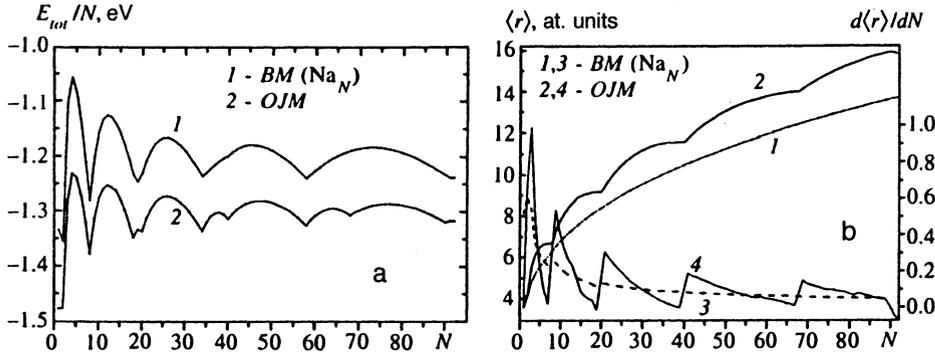


FIG. 1. The dependence of the total energy per atom,  $E_{\text{tot}}/N$  (a), the mean radius  $\langle r \rangle$  (curves 1 and 2 in (b)), and the derivatives  $d\langle r \rangle/dN$  (curves 3 and 4 in (b)) on the number of atoms  $N$  calculated in the Hartree–Fock approximation for clusters consisting of sodium atoms ( $r_s = 4$  at. units) for the *BM*- and *OJM*-distributions with a pure Coulomb interparticle interaction ( $\alpha = 0$  and  $\varepsilon = 1.0$ ).

$$U(r) = \frac{1}{2\varepsilon r} \int_0^\infty \frac{\sigma(r')}{r'} \int_{|r-r'|}^{r+r'} K(x) dx dr', \quad (20)$$

and the condition (13) for the total-energy minimum can be written as

$$\int_0^\infty \delta\sigma_{\text{core}}(r) \{U_{\text{ion-el}}(r) - U_{\text{ion-ion}}(r)\} dr = 0, \quad (21)$$

where  $\delta\sigma_{\text{core}}(r)$  is a small variation in the radial density of the positive jellium charge (provided that there is charge conservation, i.e.,  $\int_0^\infty \delta\sigma_{\text{core}}(r) dr = 0$ ), and the potentials  $U_{\text{ion-el}}$  and  $U_{\text{ion-ion}}$  of the ion–electron and ion–ion interactions are generally defined in the following way:

$$U_{\text{ion-el}}(r) = \frac{1}{2\varepsilon_{\text{ion-el}}(r)} \int_0^\infty \frac{\sigma_{\text{core}}(r')}{r'} \times \int_{|r-r'|}^{r+r'} K_{\text{ion-el}}(\xi) d\xi dr', \quad (22)$$

$$U_{\text{ion-ion}}(r) = \frac{1}{2\varepsilon_{\text{ion-ion}}(r)} \int_0^\infty \frac{\sigma_{\text{core}}(r')}{r'} \times \int_{|r-r'|}^{r+r'} K_{\text{ion-ion}}(\xi) d\xi dr'. \quad (23)$$

In our numerical calculations we took for the point-charge interaction potential (5) the screened Coulomb potential, i.e.,  $K(r) = \exp(-\alpha r)$ :

$$V(\mathbf{r}_i, \mathbf{r}_j) \equiv V(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{\exp(-\alpha r)}{\varepsilon r} = \frac{\exp(-r/D)}{\varepsilon r}, \quad (24)$$

where  $r = |\mathbf{r}_i - \mathbf{r}_j|$ , and  $D = \alpha^{-1}$  is the screening radius. In the solution we assumed that the parameters of the ion–

electron and ion–ion interaction potentials are equal:  $\varepsilon_{\text{ion-ion}} = \varepsilon_{\text{ion-el}}$  and  $\alpha_{\text{ion-ion}} = \alpha_{\text{ion-el}}$ . According to (12), this leads to local neutrality (Eq. (16)) in the “optimal” system. The interelectronic interaction in (17) was assumed to be pure Coulomb, i.e.,  $\varepsilon_{el-el} = 1$  and  $K_{el-el}(x) \equiv 1$ , since in the first approximation the screening effect of the inner electron shells of the core atoms on the interaction of delocalized valence electrons can be ignored.

We calculated the single-particle Hartree–Fock wave functions, the delocalized-electron energies, and the total energies  $E_{\text{tot}} = E_{el} + E_{\text{core}}$  for neutral clusters, with the number of atoms  $N$  ranging from 1 to 92 both for an “optimal” distribution of the background charge density  $\rho_{\text{core}}(r)$  and for a positive core in the form of a uniformly charged ball of radius  $R$ , which corresponds to the bulk material model<sup>1</sup> for clusters consisting of sodium atoms ( $r_s = 4$  at. units). The calculations were done in both models for various values of the screening parameter  $\alpha$  and the dielectric constant  $\varepsilon$ .

#### 4. A DISCUSSION OF THE NUMERICAL RESULTS

Our calculations show that allowing for the interaction of the electron system with the unbalanced charge of the positive core in the optimized jellium model leads to considerable changes in the electronic structure of the cluster. Primarily this is manifested by a redistribution of the charge density in the cluster as a result of “optimization,” which leads to local neutrality of the system. Thus, the jellium core acquires internal structure. The positive charge winds up distributed over the volume nonuniformly and forms regions of maxima and minima corresponding to the equilibrium positions of the ions in the lattice of the polyatomic cluster. This irrevocably changes the other physical parameters of the

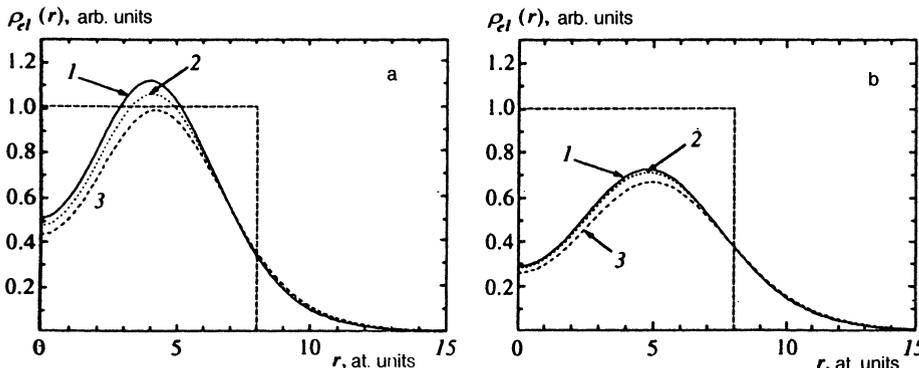


FIG. 2. The electron density distributions  $\rho_{el}(r)$  in an optimal eight-atom cluster with the screened Coulomb interaction (24). The calculations were done in the Hartree–Fock approximation for different values of the screening parameter  $\alpha$  and the dielectric constant  $\varepsilon = 1.0$  (a) and 1.025 (b). The dashed curves depict the positive charge distribution  $\rho_{\text{core}}(r) \equiv \rho_0$  in the  $\text{Na}_8$  cluster for the *BM* model ( $R = 8$  at. units):  $\alpha = 0.0001$  (curves 1), 0.01 (curves 2), and 0.015 (curves 3).

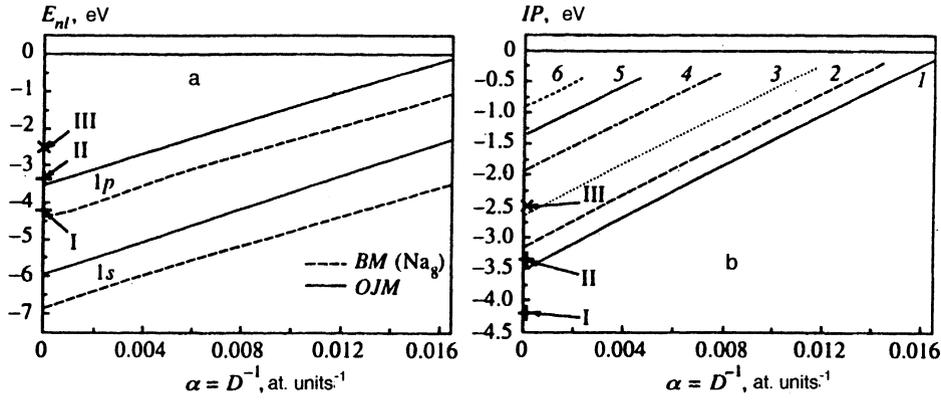


FIG. 3. a) Hartree-Fock single-electron energy levels  $E_i$  of an eight-atom ( $1s^2 1p^6$ ) cluster as functions of the screening parameter  $\alpha$  of the interparticle interaction calculated in the bulk material model (dashed curves) and the optimized jellium model (solid curves) at  $\epsilon = 1$ . b) Ionization potentials for an  $OJM$ -cluster,  $IP(\alpha) = E_{1p}$ , at different values of the dielectric constant:  $\epsilon = 1.00$  (curve 1), 1.01 (curve 2), 1.025 (curve 3), 1.05 (curve 4), 1.075 (curve 5), and 1.10 (curve 6). The  $\times$ 's stand for the ionization potentials: I and II stand for the experimental values of  $IP$  for the  $Na_8$  and  $K_8$  clusters,<sup>12</sup> and III stands for the results of calculations in the local density approximation.<sup>13</sup>

“optimal” system in comparison to results obtained on the basis of the model with a uniformly charged core. In particular, the electronic Hartree-Fock levels transform considerably,<sup>6</sup> especially in clusters with completely filled electron shells. Figure 1(a) depicts the dependence of the total energy per atom,  $E_{tot}/N$ , on the number of atoms in a cluster calculated in the Hartree-Fock approximation for two models ( $BM$  and  $OJM$ ) with only Coulomb forces (i.e.,  $K(r) \equiv 1$  and  $\epsilon = 1$ ) in a spherically symmetric system. Clearly visible are the magic numbers<sup>1</sup> corresponding to the most stable cluster configurations with closed electron shells. For some values of  $N$ , say,  $N = 40$  ( $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$ ) and  $N = 68$  ( $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 1g^{18} 2d^{10}$ ), the minima in the total energy are much more pronounced. The difference in the total energies of clusters with an  $OJM$ -core and with a uniform background distribution in the  $BM$  approximation,  $(E_{tot}^{OJM}(N) - E_{tot}^{BM}(N))/N$ , in the case of pure Coulomb interparticle interaction remains approximately constant and amounts to about 0.1 eV per atom.

The dependence of the mean radius  $\langle r \rangle = \sum_i \langle \varphi_i^* | r | \varphi_i \rangle$  on the number of atoms<sup>6</sup> also changes considerably as we go from the  $BM$  model to  $OJM$ : local minima appear in curves 1 and 2 in Fig. 1(b) at  $N = 8, 20, 40, 58, 92, \dots$ , i.e., clusters with closed electron shells, whose spherical symmetry has been verified experimentally and agrees with computations done for the spherical Nilsson model,<sup>3</sup> form a more compact system as a result of modulation of the positive jellium by the electron density. On the whole, the size of clusters in  $OJM$  is somewhat greater than in the ordinary jellium model, i.e., they form a looser structure with a lower total energy. This is accompanied by enhancement of the “shell effect” in comparison to the  $BM$  model because of a redistribution of charge in the positive core, which acquires a shell structure. This results in the appearance of magic numbers in the dependence of  $\langle r \rangle$  on the number  $N$  of the atoms. For instance, curves 3 and 4 in Fig. 1(b) represent the derivatives  $d\langle r \rangle/dN$  and show that the mean radius calculated in  $OJM$  is much more sensitive to the population of electron shells than the  $BM$  model.

As a result of studying the physical characteristics of clusters with different numbers of atoms we found that a multielectron system is extremely sensitive to minute variations in the nature of the interparticle interaction forces. The distributions of the electron density in an optimal eight-atom system ( $1s^2 1p^6$ ) clearly show (Fig. 2) that screening of the Coulomb interaction with a positive charge and especially the fact that the dielectric constant  $\epsilon$  in (24) differs from unity lead to significant suppression of the electron density at the center and to an increase in the mean radius of the system. The reason lies in the increase in the role of the unscreened Coulomb repulsion between electrons, but as Fig. 2 clearly shows, the dependence on the screening parameters proves to be extremely strong. This affects the stability of the cluster system and the size of other parameters.

Figure 3(a) depicts the Hartree-Fock energy levels  $E_i$  as functions of the screening parameter  $\alpha$  calculated in the bulk material and optimized jellium models for an eight-atom cluster. Note the linear nature of the curves in both models. This behavior is exhibited for all values of the dielectric constant in (24), as is clearly visible in Fig. 3(b), which depicts the behavior of the ionization potential  $IP(\alpha)$  of the same cluster. A similar linear dependence of the energy levels  $E_i(\alpha)$ , whose slope, as we found, is independent of the core model and is essentially independent of the dielectric constant in the potential, is exhibited by clusters with more atoms, say  $N = 20$  [Figs. 4(a) and 4(b)], with the “polaron” effect transforming the electron structure of the  $OJM$ -system and thus changing the order in which the  $2s$ - and  $1d$ -levels appear.

The dependence of the total energy of the system on the parameters of the screening of the interparticle interaction is also linear in both models and at essentially all values of the dielectric constant  $\epsilon$ . Figure 5 depicts the curves representing the dependence of the binding energy of an eight-atom cluster ( $1s^2 1p^6$ )  $E_{tot}(\alpha)/N$ , calculated in the Hartree-Fock approximation for the bulk material and optimized jellium models with a screened Coulomb potential (24) at  $\epsilon = 1.0$ . We found that the stability of the system strongly depends on the screening parameter and on the dielectric constant in the

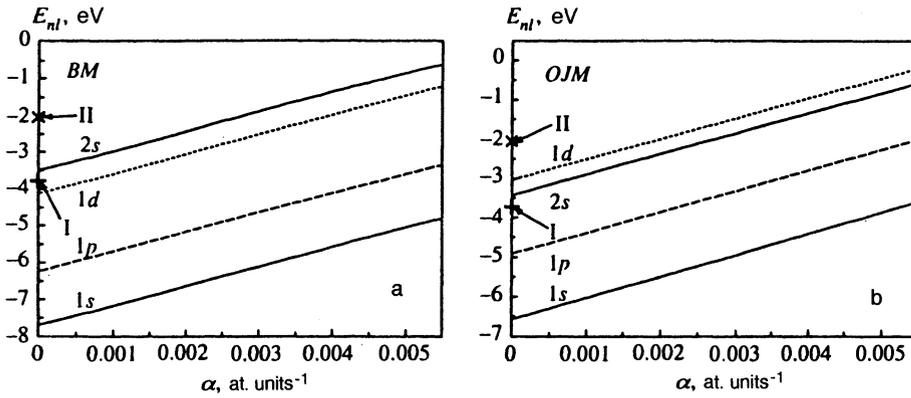


FIG. 4. Hartree-Fock electron energy levels  $E_i$  of a 20-atom ( $1s^2 1p^6 1d^{10} 2s^2$ ) cluster as functions of the screening parameter  $\alpha$  calculated in the bulk material model (a) and the optimized jellium model (b) at  $\epsilon = 1.0$ . The  $\times$ 's stand for the ionization potentials: I stands for the experimental values of  $IP$  for the  $Na_{20}$  cluster,<sup>12</sup> and II stands for the results of calculations in the local density model.<sup>13</sup>

interparticle interaction potential. For instance, even an optimized cluster becomes unstable (i.e., the total energy changes sign) at a screening radius  $D \approx 75$  nat. units, which exceeds the mean radius of the electron system  $\langle r \rangle = 6.5$  nat. units by a factor of ten (Fig. 1(a)). As Fig. 5 shows, the critical value of the screening parameter rapidly decreases as  $\epsilon$  grows. The differences in the behavior of electron systems with uniform and "optimal" positive charge distributions, induced by changes in the interparticle interaction forces, show up in the dependence of the total energy on the dielectric constant  $\epsilon$  (Fig. 6). The more adaptive OJM-system retains its stability over a much broader range in  $\epsilon$ , and the corresponding  $E_{tot}$  vs.  $\epsilon$  dependence acquires a nonlinearity, in contrast to the BM-model.

The linear dependence of the total and single-particle energies on the screening parameter can be explained if we replace the exponential factor in (24) :

$$K(r) = \exp(-\alpha r) \approx 1 - \alpha r.$$

Thus, in the first approximation and with allowance for (23), the potential energy of the positive core (Eq. (1)) can be written as (Fig. 7(a))

$$E_{core}(\alpha) = \frac{1}{4\epsilon} \int_0^\infty \frac{\sigma_{core}(r)}{r} \int_0^\infty \frac{\sigma_{core}(r')}{r'} dr dr'$$

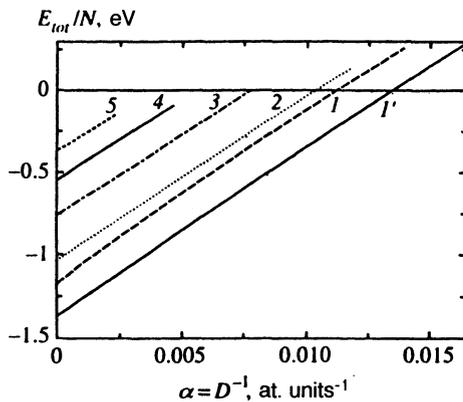


FIG. 5. Dependence of the total energy per atom,  $E_{tot}/N$ , of an eight-atom cluster on the screening parameter  $\alpha$  calculated in the Hartree-Fock approximation for the bulk material model (curve 1) and the optimized jellium model (curve 1') at  $\epsilon = 1.0$ , and for an "optimal" system at different values of the dielectric constant:  $\epsilon = 1.025$  (curve 2), 1.05 (curve 3), 1.075 (curve 4), and 1.01 (curve 5).

$$\times \int_{|r-r'|}^{r+r'} K(\xi) d\xi dr' dr \approx E_{core}(0) - \alpha \frac{N^2}{2\epsilon}, \quad (25)$$

where  $\sigma_{core}(r) = 4\pi r^2 \rho_{core}(r)$  is the radial positive charge density, and  $E_{core}(0)$  is the energy of a core with a pure Coulomb interaction ( $\alpha = 0$ ). As Fig. 7a demonstrates for a 20-atom cluster, the approximation (25) holds for a uniform distribution  $\rho_{core}(r) = \rho_0$  over essentially the entire range of  $\alpha$ , and the slight deviation for the optimized jellium model can be accounted for by a shift of the charge density (positive or negative) in the direction of large radii as  $\alpha$  increases (Fig. 2), where we must allow for the higher-order terms in the expansion of  $K(r)$ .

Similarly, with allowance for (17) and (22), the total energy of the electron system  $E_{el}$  (Eq. (19)) can be written as

$$E_{el}(\alpha) \approx E_{el}(0) + \alpha \frac{N^2}{\epsilon}. \quad (26)$$

Then as a result of adding (25) to (26) the total cluster energy  $E_{tot} = E_{core} + E_{el}$  becomes

$$E_{tot}(\alpha) \approx E_{tot}(0) + \alpha \frac{N^2}{2\epsilon}. \quad (27)$$

For an optimal distribution, as a result of the condition (17) for local neutrality, the nonlinearities in  $E_{core}(\alpha)$  (Fig. 7(a)) and  $E_{el}(\alpha)$ , which are due to the redistribution of the

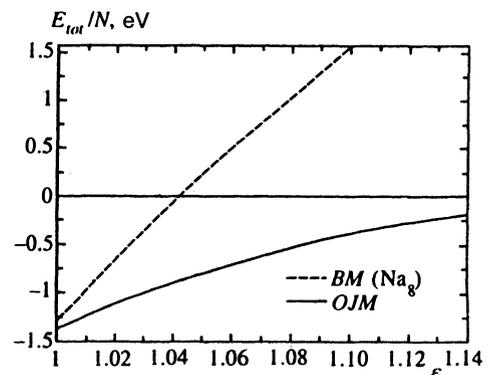


FIG. 6. Dependence of the total energy per atom,  $E_{tot}/N$ , of an eight-atom cluster on the dielectric constant  $\epsilon$  in the interparticle interaction potential (24) for the bulk material model (dashed curve) and the optimized jellium model (solid curve) at  $\alpha = 0$ .

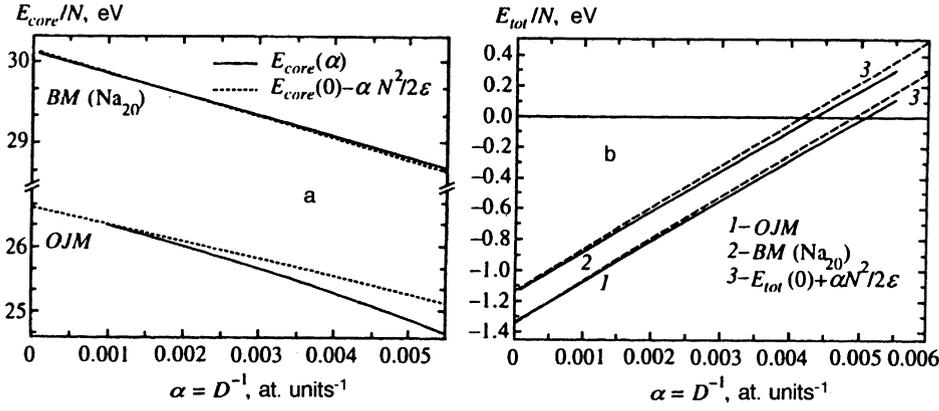


FIG. 7. Positive-core potential energy per atom  $E_{core}/N$  (a) and the total energy per atom  $E_{tot}/N$  (b) of a 20-atom cluster as functions of the screening parameter  $\alpha$  calculated for the bulk material and optimized jellium models at  $\epsilon = 1.0$ .

charge density in the system, are balanced and the  $E_{tot}$  vs.  $\alpha$  dependence for both models becomes linear (Fig. 7(b)).

Allowing for screening of the interaction between delocalized electrons constitutes a separate, more difficult computational problem. An estimate similar to that done above shows that when such screening is present, the total energy of the electron system (for an arbitrary distribution of the positive charge density) can be written for the special case in which the parameters of interelectronic and electron-ion interactions are equal, to first order in  $\alpha$  in the expansion of  $K(r)$ , as

$$E_{el}(\alpha) \approx E_{el}(0) + \alpha \frac{N(N+1)}{2\epsilon}, \quad (28)$$

and the total energy of the system, with allowance for (25), can be written as

$$E_{tot}(\alpha) \approx E_{tot}(0) + \alpha \frac{N}{2\epsilon}. \quad (29)$$

Thus, comparing (27) with (29), we see that allowance for screening in the electron system, while retaining the linear nature of the  $E_{tot}$  vs.  $\alpha$  dependence, makes the system more stable against changes in the screening parameter than in the case of a pure Coulomb interelectronic interaction, and increases the value of the "critical"  $\alpha$  at which the total cluster energy vanishes. This increase in the stability of the system resulting from screening of the Coulomb repulsion between delocalized electrons shows up more readily in clusters with a large number of atoms  $N$ , as expected.

Allowing for the fact that the clusters become unstable at small values of  $\alpha$ , we can perform a more general analysis of the linear dependence of the energy as screening of the pairwise interaction grows. This requires using parameter-dependent Hamiltonians. Indeed, if we employ the relationship<sup>11</sup>

$$\frac{\partial E_n(\alpha)}{\partial \alpha} = \left\langle \psi_n \left| \frac{\partial \hat{H}}{\partial \alpha} \right| \psi_n \right\rangle \quad (30)$$

and the fact that the Hamiltonian  $\hat{H}$ , which describes a cluster system with positively charged-jellium and the same pairwise interaction (24) as a whole, with only the potential energy being  $\alpha$ -dependent, we arrive at the following expression for the derivative on the right-hand side of Eq. (30):

$$\frac{\partial E_n}{\partial \alpha} = \left\langle \psi_n \left| \frac{1}{\epsilon} N^2 - \frac{1}{2\epsilon} N(N-1) - \frac{1}{2\epsilon} N^2 \right| \psi_n \right\rangle = \frac{1}{2\epsilon} N. \quad (31)$$

Here the first term between the bra and ket vectors appears because of electron-ion attraction, and the second and third appear because of electron-electron and ion-ion repulsion, respectively. The last term incorporates the nonphysical "self-action" of the positive charges, which is a consequence of using the jellium model. Equation (31) shows that in the general case we arrive at the same dependence of the total energy on  $\alpha$  as we did in the Hartree-Fock approximation (29).

For a more realistic approach we can replace the system of positive ions in the cluster by a system of point charges. Then self-action is eliminated from the term describing the contribution of ion-ion repulsion to the energy, and the derivative of this term with respect to  $\alpha$  is equal to  $N(N-1)/2\epsilon$ . Here the dependence of the total energy on the small parameter  $\alpha$  has the form

$$E_n(\alpha) = E_n(0) + \alpha \frac{N}{\epsilon}. \quad (32)$$

Thus, comparing (29) with (32), we see that the jellium model and the point-ion model yield different results for the dependence of the total energy on the screening parameter  $\alpha$ .

## 5. CONCLUSION

The results of our study of the dependence of the physical characteristics of a multielectron system on the parameters of the interparticle interaction potential show that for the limiting cases of clusters with an infinitely rigid ionic core (the bulk material model) and an infinitely compressible ionic core (the optimized jellium model), not only does the distribution of the unbalanced positive charge in the cluster volume have a considerable effect on the properties of the system (on the optical response, in particular), but so does the nature of the forces acting in it. For instance, as a result of screening of the atomic nuclei by the inner-shell atomic electrons, an increase in the average radius (Figs. 1 and 2) must lead to an increase in the dc dipole polarizability of the system and a decrease in the frequency of the giant dipole resonance.<sup>2,5</sup>

In addition to clusters, these data can be applied to any finite multielectron system in which there is interaction with a positive background.

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