

Optimized jellium model for metal clusters

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An optimized parameter-free jellium model is proposed for polyatomic clusters. This model leads to an absolute minimum of the total energy of a system consisting of delocalized electrons and a positive core. A double-variation method is used to determine the optimum distribution of the charge density of the cluster core and the electronic structure. The total energy of the cluster reaches a minimum under the condition of local electrical neutrality. Numerical calculations have been carried out on the electronic structure in the Hartree–Fock approximation with various numbers of atoms. The electron system, with a shell structure, has a strong effect on the charge distribution of the positive background. Basic physical characteristics of the metal clusters calculated from this model are compared with experimental data and with the results of other calculations. © 1994 American Institute of Physics.

1. The electronic structure of atomic clusters has recently been the subject of active research.^{1–5} *Ab initio* calculations on entities of this sort are quite difficult, even if there are only a few atoms,⁶ because of the large number of degrees of freedom in the system. Progress has been achieved with the help of a jellium model, which pictures a cluster as consisting of two quasi-independent subsystems: a subsystem of delocalized valence electrons and a subsystem of an ion core. The positive charge of the core is distributed over the entire volume. This model substantially simplifies the problem of calculating the structure and dynamic characteristics of clusters.^{2,3,5–11} It turns out that the results of the calculations depend on the particular distribution of the core charge which is selected and on the geometric parameters. The first calculations which explained the formation of a shell structure in clusters of alkali metal atoms^{1–5} were carried out under the assumption that the core charge is distributed uniformly in a spherically symmetric cluster. Its radius was determined from the interatomic distance in a solid. This is the “bulk material” (BM) model. Attempts were subsequently made to “optimize” the distribution of the positive jellium by varying geometric parameters,^{7,9–11} but those calculations suffer from a dependence on the choice of parameters on which the optimization is based.

Our purpose in the present letter is to find the optimum distribution of the positive core charge, $\rho(\mathbf{r})$, by which we mean the distribution which corresponds to an absolute minimum of the total energy of the system. We propose a parameter-free optimized jellium model (OJM), which is based on a self-consistent solution of a many-body problem jointly for the delocalized electrons and the positive core. On the one hand, the many-electron wave function and the energy are functionals of the core charge distribution $\rho(\mathbf{r})$; on the other, $\rho(\mathbf{r})$ is a functional of the electron density, because of the Coulomb interaction between the electrons and the positive background. A nonlinear dynamic

interaction of the electrons with particles of the cluster core is similar to polaron effects in a solid,¹² in which a similar situation arises in a system with one electron. In the case of metal clusters we are dealing with a many-electron system. It is thus necessary to solve two self-consistent problems simultaneously: calculate the many-electron wave function in an external field and calculate the external field itself. This external field is set up by the positive background, with a distribution $\rho(\mathbf{r})$ which is not known at the outset.

The solution method proposed here is based on a double-variation procedure. This procedure yields a condition for an absolute minimum of the total energy of the system. Under this condition, the density of the nonuniform charge of the OJM core is precisely equal to the electron density over the entire volume of the cluster, as we will show below. This condition leads to a nonlinear equation for the many-electron wave function or, in the one-particle approximation, to a system of Hartree–Fock equations. The electron wave functions and energies and also the optimum charge distribution $\rho(\mathbf{r})$ of the OJM jellium are thus found through a numerical solution of a system of coupled nonlinear integrodifferential equations. The total energies which are calculated are absolute minima among all possible distribution functions of the core density and geometric parameters of clusters with various numbers of atoms.

We use an atomic system of units: $\hbar = |e| = m_e = 1$.

2. According to the jellium model, the total energy of the cluster, E_{tot} , is the sum of the total energy of the system of delocalized electrons, which are moving in the core field $U(\mathbf{r})$, and the Coulomb potential energy of the distributed positive charge of the core.

The total energy of the system of electrons in the ground state is $E_{\text{el}} = \langle \Psi^* | \hat{H}_{\text{el}} | \Psi \rangle$, where Ψ is the total wave function of the electron system, which satisfies the Pauli principle and which is normalized.

The Hamiltonian of the system of electrons in the field $U(\mathbf{r})$ is

$$\hat{H}_{\text{el}} = \sum_i \left(-\frac{\Delta_i}{2} - U(\mathbf{r}_i) \right) + \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (1)$$

The potential $U(\mathbf{r})$, set up by the distributed positive charge of the core, with a density $\rho(\mathbf{r})$, satisfies the Poisson equation. The potential energy of the positive core can thus be expressed in terms of $U(\mathbf{r})$:

$$E_{\text{cor}} = \frac{1}{8\pi} \int U(\mathbf{r}) \Delta U(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (2)$$

For an electrically neutral cluster consisting of N monovalent atoms of an alkali metal we would have

$$\int \rho(\mathbf{r}) d\mathbf{r} = -\frac{1}{4\pi} \int \Delta U(\mathbf{r}) d\mathbf{r} = N.$$

The condition for a minimum of the free energy of the system, F , in an equilibrium state at absolute zero is equivalent to the requirement that the total energy of the cluster, E_{tot} , be at a minimum. For an electrically neutral cluster, satisfying this requirement reduces to determining the conditions for a stationary state of the functional

$$G\{\Psi, U\} = \langle \Psi^* | \hat{H}_{el} | \Psi \rangle + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \epsilon \langle \Psi^* | \Psi \rangle - \lambda \int \rho(\mathbf{r}) d\mathbf{r} \quad (3)$$

under small variations $\delta\Psi^*(\mathbf{r})$ and $\delta\rho(\mathbf{r})$. Here ϵ and λ are arbitrary Lagrange multipliers. The last two terms in (3) are associated with the normalization of Ψ and with conservation of the total charge of the core. The condition which fixes the total core charge can be omitted from functional (3), since we are calculating an absolute minimum of the total cluster energy for arbitrary distributions of the core charge. As we will see below, an absolute minimum of the energy is reached only in the case of electrically neutral clusters, with the core charge equal to the total number of delocalized electrons.

We are thus required to find a solution of the system of variational equations

$$\frac{\delta G\{\Psi^*, U\}}{\delta\Psi^*} = 0, \quad \frac{\delta G\{\Psi^*, U\}}{\delta\rho(\mathbf{r})} = 0. \quad (4)$$

The first of Eqs. (4) leads to an ordinary Schrödinger equation for the total wave function $\Psi(x)$ of the system of electrons: $\hat{H}_{el}\Psi(x) = E_{el}\Psi(x)$, where $x = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N\}$ is the set of coordinates of all N electrons, and E_{el} is the total energy of the electron system, which is identical to the Lagrange multiplier ϵ in (3).

The second equation in (4) relates the electron density and the charge density of the jellium in the state of an absolute minimum of the total energy:

$$\int \delta\rho(\mathbf{r}') \left(- \sum_i \int \frac{|\Psi(x)|^2 dx}{|\mathbf{r}_i - \mathbf{r}'|} + \int \frac{\rho(\mathbf{r}) d\mathbf{r}}{|\mathbf{r} - \mathbf{r}'|} \right) d\mathbf{r}' = 0. \quad (5)$$

This relation holds for an arbitrary variation of the density of the positive core charge if the expression in parentheses is zero.

The main conclusion is thus that the "optimum" density of the positive background is equal to the total electron density at each point in the cluster volume:

$$\rho(\mathbf{r}) = \sum_i \int \delta(\mathbf{r} - \mathbf{r}_i) |\Psi(x)|^2 dx. \quad (6)$$

Using (6), we can write a Schrödinger equation for the total wave function $\Psi(x)$ with Hamiltonian \hat{H}_{el} from (1):

$$\left(- \frac{1}{2} \sum_i \Delta_i - \sum_{ij} \int \frac{|\Psi(x')|^2 dx'}{|\mathbf{r}_j - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(x) = E_{el} \Psi(x). \quad (7)$$

Because of the second term in (7), the equation for the total wave function is nonlinear. A point of particular importance is that this equation is nonlinear even for a system consisting of a single electron in the field of a positive charge. Here we are seeing a difference between the OJM and the standard model of a "rigid" core.

3. In the case of a many-electron system, Eq. (7) cannot be solved exactly. In this letter we use the Hartree-Fock approximation,¹³ in which we can derive corresponding equations for normalized one-electron wave functions $\Phi_i(\mathbf{r})$ with an energy ϵ_i . For the optimized density distribution, the Hartree terms of the direct Coulomb interaction are

cancelled exactly by terms describing the interaction with the positive charge. From the interaction with the core we are left with only the $i=j$ term, which corresponds to a "self-effect" of an electron, which arises because of a redistribution of the positive charge density. In this case the Hartree-Fock equations can be written in the form

$$-\frac{\Delta}{2}\Phi_i(x) - \sum_{j=1} \Phi_j(x) \int \Phi_j^*(x')\Phi_i(x') \frac{1}{|\mathbf{r}-\mathbf{r}'|} dx' = \epsilon_i \Phi_i(x), \quad (8)$$

where the summation is over all values of j (including $j=i$), and where we are using $x=(\mathbf{r},\sigma)$.

In the Hartree-Fock approximation we thus find a system of equations for one-particle electron wave functions which are coupled by a nonlocal exchange interaction, which includes a self-effect.

Using (6), we can also find an expression for the total energy of the cluster in terms of the one-particle wave functions $\Phi_i(\mathbf{r})$:

$$E_{\text{tot}}^{\text{OJM}} = \sum_i \epsilon_i + \frac{1}{2} \sum_{ij} \left\langle ij \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| ji \right\rangle. \quad (9)$$

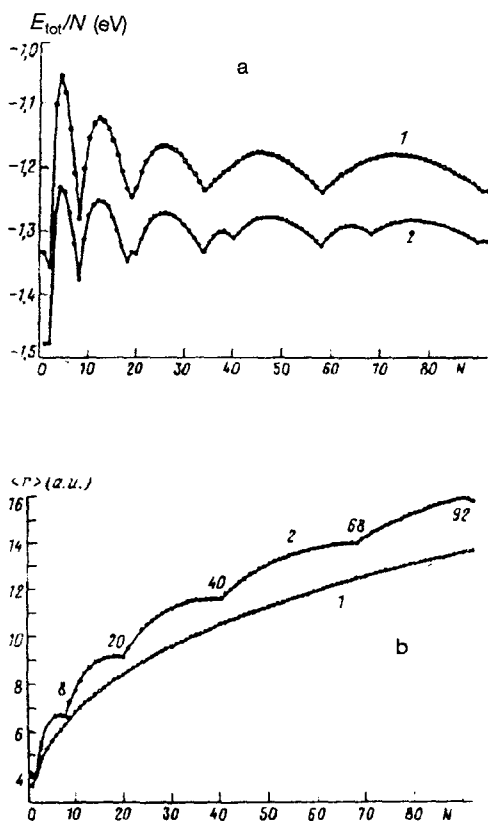


FIG. 1. Total energy of a cluster per atom, E_{tot}/N (eV; part a), and the average radius $\langle r \rangle$ (a.u.; part b), versus the number of atoms, N , in the Hartree-Fock approximation. 1—For the "bulk material" model with a unit cell of size $r_s = 4$ a.u. (sodium); 2—for the optimized jellium model.

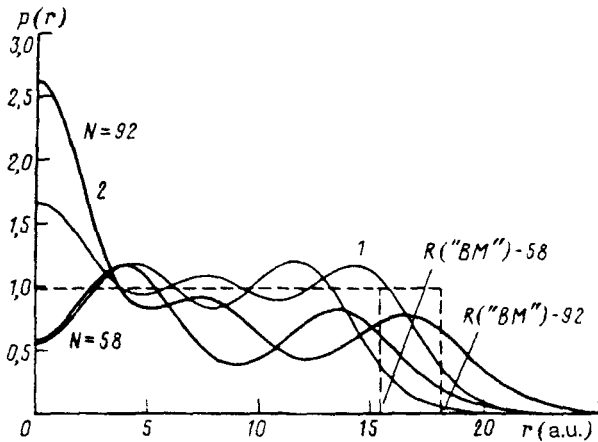


FIG. 2. Electron density distribution $\rho(r)/\rho_0$ in the volume of the cluster for $N=58$ and 92 , in units of the density of the uniformly distributed core charge of the BM model (dashed lines). 1—BM model, $r_s=4$ a.u. (sodium); 2—OJM.

In other words, E_{tot} contains the one-particle energies ϵ_i , the exchange interaction (the terms with $i \neq j$), and the electron self-effect ($i=j$).

4. System (8) has been solved numerically for metal clusters of 1 to 92 atoms with an "optimum" background charge distribution $\rho(\mathbf{r})$. As a result, we plotted the total energy per atom, as shown in Fig. 1a. Here we can clearly see some magic numbers, which correspond to the stablest configurations of clusters with closed shells. The many-electron "polaron" effect makes these magic numbers considerably more prominent, for $N=40$ ($1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$) and $N=68$ ($1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6 1g^{18} 2d^{10}$), for example. The difference between the total energies of the clusters with an OJM core and with a uniform background distribution under the approximation of Ref. 10, $[E_{\text{tot}}^{\text{OJM}}(N) - E_{\text{tot}}^{\text{BM}}(N)]/N$, turns out to be approximately constant at about 0.1 eV/atom.

The average radius $\langle r \rangle = \sum \langle \Phi_i^* | r | \Phi_i \rangle$ acquires its typical dependence on the number of atoms, N (Fig. 1b). In contrast with the corresponding plot for the BM model, the plot for the OJM has local minima at $N=8, 20, 40, 58$, and 92 , i.e., for clusters whose spherical symmetry has been confirmed experimentally and agrees with calculations on the basis of the Nilsson spheroidal model.⁵ This is a result of a modulation of the positive jellium by the electron density. As a result, the electronic configurations with closed shells form a more compact structure. The average radius $\langle r \rangle_{\text{OJM}}$ calculated for the optimum distribution $\rho(\mathbf{r})$ is significantly larger than $\langle r \rangle_{\text{BM}}$ (for the bulk material model) at all values of N . The effect should be a substantial increase in the static dipole polarizability α of a cluster upon the switch to the "optimized" model.

Figure 2 shows curves of the electron density $\rho^{\text{el}}(\mathbf{r})$ for the BM and OJM distributions of the core charge density. Since the condition of local electrical neutrality holds in a "self-consistent" cluster, it becomes possible, for the first time, to speak of an internal structure of the ion core within the framework of a jellium model. It can be seen from these curves that the positive charge is distributed nonuniformly over volume, forming

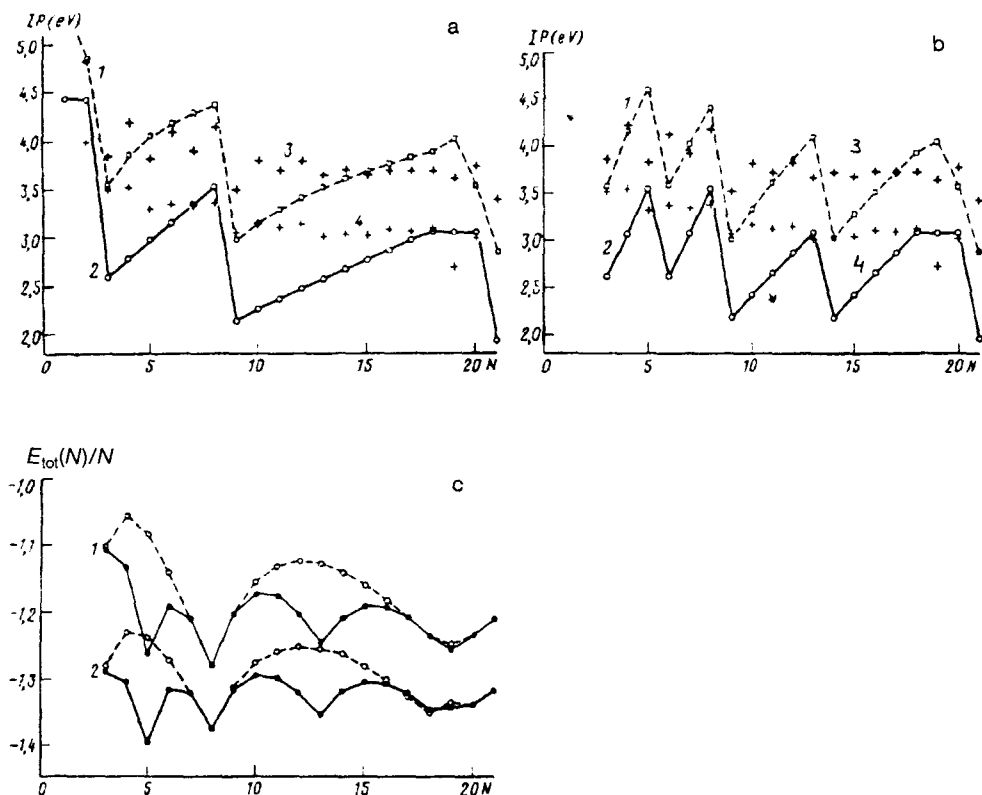


FIG. 3. The ionization potential IP (eV) and the total energy per atom, E_{tot}/N (eV), of a metal cluster versus the number of atoms, in the Hartree-Fock approximation. a— $IP(N)$, average term; b— $IP(N)$, spin-polarized version; c— $E_{tot}(N)/N$, average term (dashed curve) and spin-polarized version (solid curve). Curve 1) BM model, $r_s = 4$ a.u. (sodium); 2) OJM; 3) Na_N , experimental;⁴ 4) K_N , experimental.⁴

regions of maxima and minima, which correspond to ion coordination spheres.

Figure 3a shows ionization potentials $IP(N)$ calculated in the Hartree-Fock approximation for jellium models with the BM and optimized distributions of the core density. We see that the experimental values of IP of clusters of heavier elements (K_N) lie closer to the results of the OJM calculations than in the case of lighter atoms (Na_N). The shape of the $IP(N)$ curve for each model reflects a transition from electronic configurations with unfilled electron shells to filled shells, which correspond to maxima of the ionization potentials. These results agree with shell-structure arguments.^{1,4}

The polarized-spin method is widely used in calculations on electronic configurations with half-filled shells in atomic physics. It is convenient to break up each filled shell into two spin shells, which are characterized by definite directions of the projections of the spins of the electrons in it. These spin shells can be thought of as closed. If there is no exchange between electrons with different spin directions, the total energy of the

system is lowered. Figure 3b shows ionization potentials of clusters for the BM model and the OJM as calculated in the Hartree–Fock approximation by the polarized-spin method. We can clearly see maxima in the IP s of configurations with half-filled shells, which also correspond to minima of the total energy in Fig. 3c. The solid curves there are plots of $E_{\text{tot}}(N)/N$ corresponding to the spin-polarized method, while the dashed curves correspond to average terms.

A change in the distribution $\rho(\mathbf{r})$ has a strong effect on optical characteristics of the cluster. For example, the static dipole polarizability increases from 750 a.u. for the BM model^{7,11} to 1090 for the OJM. The frequency of the dipole resonance shifts from 2.67 to 2.15 eV. However, these values still differ from the experimental values⁴ 890 ± 17 a.u. and 2.5 eV. The reason is that both of these models are limiting cases—of “rigid” and infinitely compressible ion lattices of the cluster.

The results of this letter can be applied to entities other than clusters: to any finite many-electron systems in which there is an interaction with a positive external background.

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