

# Electronic structure and adiabatic oscillations of metal clusters

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The electronic structure of metal clusters is analyzed as a function of geometric parameters. The Hartree–Fock approximation is used to calculate the electron energies and wave functions as a function of the radius of the cluster core,  $R$ . New equilibrium values of  $R$  are derived for clusters with various numbers of atoms  $N$ . A collective motion of a new type is predicted and studied: adiabatic oscillations of the space charge density of the cluster core or (equivalently) of the effective core radius  $R$ . The frequencies and amplitudes of these parametric oscillations are calculated for clusters with various values of  $N$ .

**1.** The purposes of this study were to learn how the electronic structure and physical properties of metal clusters containing tens or hundreds of monovalent atoms depend on the geometric parameters of the clusters and to identify the role played by a nonlocal exchange interaction in such clusters. The basis for the theoretical description of the metal-atom clusters is the jellium model.<sup>1</sup> According to this model a cluster consists of two subsystems: a system of valence electrons and a system of positive ions, the latter constituting the core.<sup>1,2</sup> This core is represented as a smeared positive charge with a spherically symmetric density distribution  $\rho(r)$ , in which the valence electrons forming the shells are moving. We have also studied how the physical properties of a cluster depend on this core charge distribution  $\rho(r)$ .

Essentially all recent calculations of the electronic structure have used model potentials with a local exchange to deal with volume effects; examples are the Kohn–Shen potential<sup>3</sup> and the Hartree–Fock–Slater potential.<sup>1,3</sup> Recent calculations on the structure of clusters in the Hartree–Fock approximation and on the polarizability of a cluster in the random phase approximation<sup>4</sup> have shown that a nonlocal nature of the exchange interaction plays an extremely important role in determining the electron spectrum and oscillator strengths. However, all the corresponding calculations in Ref. 4 were carried out for clusters with filled electron shells, and only on the basis of the cluster size as determined by the equilibrium interatomic distance in a solid. No detailed study has been made of how the spectrum and physical properties of a cluster depend on its size or the  $\rho(r)$  distribution.

In the present paper we calculate the one-electron and total energies of clusters as a function of the radius of the cluster core,  $R$ , and of the number of atoms  $N$ . We work from the  $R$  dependence of the total energy to calculate the spectrum of adiabatic size oscillations of a cluster. The wave functions and energies of the valence electrons forming the shells are calculated in the Hartree–Fock approximation with complete nonlocal exchange. The total and one-electron energies of the cluster calculated with

and without exchange are compared. Calculations are carried out for various distributions of the positive charge density of the core,  $\rho(r)$ .

2. The wave functions and energies of the valence electrons in a cluster are determined by the solution of the system of self-consistent Hartree–Fock equations (here and below we are using the atomic system of units:  $e = m_e = \hbar = 1$ ):

$$-\frac{\Delta}{2}\phi_j(x) - eV(r)\phi_j(x) - \sum_k \int \phi_k(x') \frac{e^2}{|\mathbf{r}' - \mathbf{r}|} [\phi_j(x)\phi_k(x') - \phi_j(x')\phi_k(x)] dx' = E_j\phi_j(x),$$

where  $\phi_j(x) = (1/r) P_{nl}(r) Y_{lm}(\varphi, \phi) X_\sigma$  is the electron wave function,  $x = (r, \sigma)$ , and  $V(r)$  is the field potential of the positive core, given by

$$V(r) = \frac{4\pi}{r} \left( \int_0^r [\rho(r')r'^2] dr' + \int_r^\infty [\rho(r')r'^2] \frac{r}{r'} dr' \right).$$

For the jellium model (the simplest), the  $\rho(r)$  distribution is taken to be constant; i.e., the positive core is represented as a uniformly charged sphere of some radius  $R$  (Refs. 1 and 4). In all papers,<sup>1-6</sup> the atomic spacing in the core has been assumed equal to the size of a unit cell in a solid,  $r_s$  (this is the “bulk material” model). The core radius has thus been taken to be  $N^{1/3}r_s$ , where  $N$  is the number of atoms in the cluster. In the present paper we solve the Hartree–Fock equations for various cluster radii, treating  $R$  as an independent parameter. For a uniformly charged sphere of radius  $R$  we have

$$V(r) = \begin{cases} \frac{N}{2R} [3 - (r/R)^2], & r \leq R, \\ \frac{N}{r}, & r > R. \end{cases}$$

In addition, to determine the sensitivity of the wave functions and the energy to the particular functional distribution of the charge density,  $\rho(r)$ , we represent the cluster core as a sphere with a nonuniform distribution  $\rho(r)$ , e.g., a Fermi function:

$$\rho(r) = \frac{\rho_0}{1 + \exp [(r - R)/\beta]},$$

where  $\rho_0$  is the charge density at the center of the cluster, and  $\beta$  is a diffusion parameter. Correspondingly, the integral of  $\rho(r)$  over all space is normalized to the total core charge  $Z$  (for monovalent metals,  $Z = N$ ). The problem thus has two adjustable parameters,  $R$  and  $\beta$ ; they were varied in the determination of the electron spectrum. This parametric behavior is important for finding the minimum electron energy of the cluster, i.e., in calculating the geometric parameters of the equilibrium state.

When the kinetic energy of the atomic ions within the core is ignored, the total cluster energy is  $E_{\text{tot}} = E_{\text{el}} + E_{\text{bkg}}$ , where

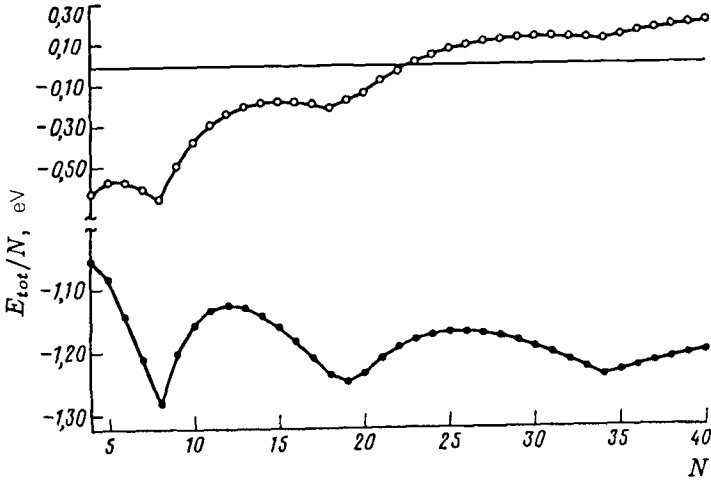


FIG. 1. Total energy of the cluster per atom (in eV) versus the number of atoms in the cluster,  $N$ . Lower curve—Exchange is taken into account; upper curve—is not. The core radius  $R$  is assumed everywhere to be equal to  $N^{1/3}r_s$ .

$$E_{cl} = \sum_j E_j - \frac{1}{2} \sum_{jk} \left( \langle jk | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | jk \rangle - \langle kj | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | jk \rangle \right)$$

is the total energy of the system of valence electrons, and  $E_{bkg}$  is the potential energy of the positive core, given by

$$E_{bkg} = 2\pi \int_0^\infty \rho(r) V(r) r^2 dr.$$

For a uniformly charged core, we find  $E_{bkg} = 3N^2/5R$ .

As a result of the calculations, we find the wave functions of the valence electrons, their one-particle energies, the electron density distribution, the total energies, and certain physical characteristics of the clusters, e.g., the diamagnetic susceptibility. These results were found for clusters ranging in size from 4 to 40 atoms. In order to determine the role played by the exchange interaction, we carried out all calculations with and then without full account of the nonlocal exchange interaction. Figure 1 shows the results calculated for the total energy of a cluster, per atom,  $E_{tot}/N$ , as a function of the number of atoms. These results confirm the result, which has been found by many investigators, that the largest binding energy per atom corresponds to the formation of filled electron shells. The total energies calculated in the Hartree-Fock approximation for clusters with filled shells ( $N=8, 18, 20, 34, 40$ ) turn out to be the same as those found in Ref. 6. However, incorporation of the exchange interaction may lead to deviations from the sequence of "magic numbers" (Fig. 1). For example, a cluster of 19 atoms with the electronic configuration  $1s^2 1p^6 1d^{10} 2s^1$ , i.e., a cluster with

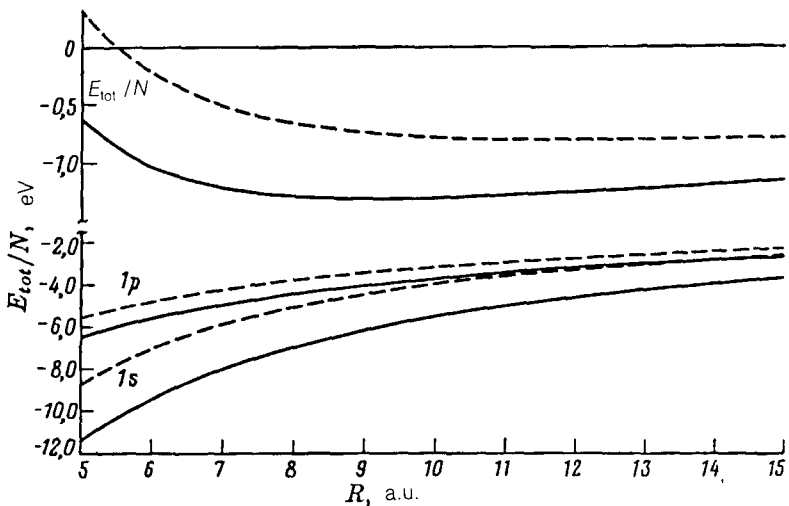


FIG. 2. One-particle energies (in eV) of the 1s and 1p levels and total energies of the cluster per atom versus the core radius  $R$  (in atomic units) for an eight-atom cluster. Solid curves—With exchange; dashed—without.

a single unpaired electron, has a binding energy higher than those of clusters with closed electron shells,  $N=18$  and  $N=20$ , according to the model adopted, in the Hartree-Fock approximation.

Values of the total energy have been plotted as  $N$  versus the core radius for clusters with various values of  $N$ , both with and without the exchange interaction. It turns out that in the jellium model, with a uniform charge distribution in the core, an atomic spacing equal to the size of the unit cell in a solid does not correspond to the minimum of the total energy. Figure 2 shows the total energy and the single-particle energies of a cluster with  $N=18$  as a function of the cluster radius. We see that the single-particle electron energies are smooth functions of  $R$ , and the minimum of the total energy corresponds to a value of  $R$  slightly larger than  $N^{1/3}r_s$ . The nonlocal exchange interaction plays an important role. Looking at the total electron energy  $E_{el}$ , we see that the exchange makes a relatively small contribution, about 1%. We should point out that this circumstance is the main reason for the good agreement between the total electron energies found in various studies, which have dealt in different ways with the local exchange interaction. However, the positive potential energy of the core,  $E_{bkg}$ , is also large, and it goes a long way toward cancelling the electron energy, with the result that the total energy of the entire cluster is sharply reduced. The role of the exchange interaction increases in a relative sense and amounts to a few tens of  $E_{tot}$ . This result means that an accurate account of the exchange interaction is necessary in order to find a good description of the electron energy spectrum of clusters and—an extremely important point—to find the correct set of wave functions.

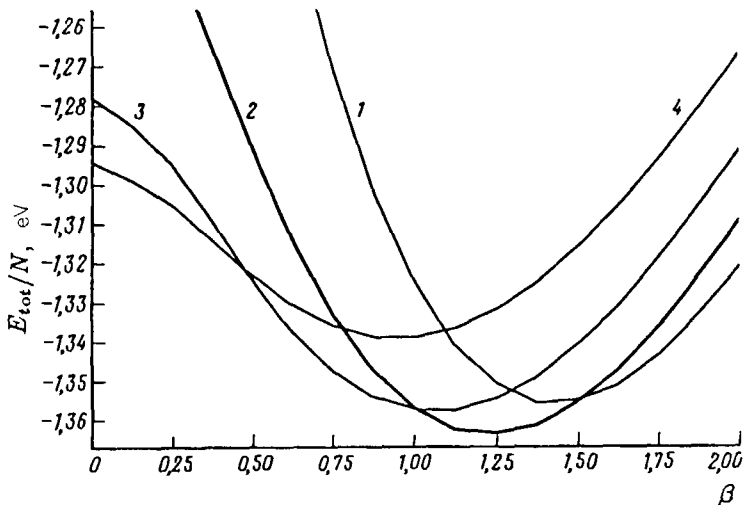


FIG. 3. Total energy per atom (in eV) of an eight-atom cluster with a Fermi-function distribution of the core charge density versus the diffusion parameter  $\beta$  for various radii  $R$ . 1)  $R=6$  a.u.; 2) 7; 3) 8; 4) 9 a.u.

However, the total energy of a cluster depends strongly on the radial variations in the positive charge distribution. Figure 3 shows  $E_{\text{tot}}(R, \beta)/N$  for a cluster with  $N=8$ . At  $\beta > 0$ , the stablest clusters form at values of  $R$  smaller than are found for a uniformly charged core. The "absolute" minimum of the total energy, corresponding to the position of a stable equilibrium according to our jellium model, is reached at  $R=7$  a.u. and  $\beta = 1.25$ .

3. The minimum on the plot of the total energy of the cluster versus the core radius,  $E_{\text{tot}}(R)$ , gives rise to adiabatic oscillations of the core radius. The quantity  $R$  serves as a coordinate of the collective motion of the core ions. In the Born-Oppenheimer approximation the total wave function of the overall system can be written as the product

$$\Psi(r, R) = \Phi(r, R)\psi(R),$$

where  $\Phi(r, R)$  is the total wave function of the electron system. In the Hartree-Fock approximation,  $\Phi(r, R)$  is a Slater determinant constructed from the one-particle functions  $\phi_j(r, R)$  which are the solutions of the Hartree-Fock equations for the potential  $V(R)$ , and  $\psi(R)$  is a spherically symmetric wave function which depends on a single generalized coordinate. We assume this single coordinate to be the adiabatically varying cluster radius  $R$ . To determine the spectrum and amplitudes of the adiabatic oscillations of the cluster, we solved the Schrödinger equation for the function  $\psi(R)$  for a cluster of  $N$  atoms:

$$\frac{1}{2M} \frac{d^2\psi(R)}{dR^2} - [E_{\text{tot}}(R) - \epsilon]\psi(R) = 0,$$

TABLE I. Spectrum of adiabatic oscillations for an eight-atom cluster (all energies are in meV).

Level $n$	Excitation energy $\epsilon_n - E_{\text{tot}}(R_0)$	Energy $\Delta E$ $\epsilon_n - \epsilon_{n-1}$	Amplitude $\Delta R/R_0$ (%)
0	2.81	...	3.43
1	8.41	5.607	5.95
2	14.01	5.602	7.68
3	19.61	5.597	9.09
4	25.20	5.591	10.31
...	...	...	...
8	47.51	5.567	14.19
9	53.07	5.560	15.00
10	58.62	5.552	15.77

where  $M = (3/5)\Sigma^N M_{\text{at}}$  is the reduced mass of the collective motion of the core ions,  $M_{\text{at}}$  is the mass of a single atom (expressed in units of the electron mass  $m_e$ ), and  $\epsilon$  is an eigenenergy of the oscillations.

We obtained spectra and amplitudes of the adiabatic oscillations for various clusters. For low-lying excited states, the results are a set of essentially equidistant levels with characteristic energies  $\Delta E \approx 1-10$  meV. The oscillation amplitudes were determined by the classical turning points. For an 18-atom cluster, for example, the energy of the zero-point vibrations of the ground state is  $E_0 \approx 2$  meV at an oscillation amplitude amounting to about 2% of the equilibrium value  $R_0$ , where  $R_0 \approx 12.3$  a.u. is the cluster radius corresponding to the minimum  $E_{\text{tot}}(R) = -22.86$  eV. Higher-lying excited states form a system of levels with  $\Delta E \approx 4.13$  meV (Tables I and II).

The predicted spectrum of adiabatic oscillations of the cluster size can be observed experimentally in a study of the temperature dependence of static and dynamic characteristics of the clusters. The collective oscillations which we studied can of course be observed only at sufficiently low "temperatures" of the motion of the ions in the core. High kinetic energies of the core ions smear out the structure in the electron

TABLE II. Spectrum of adiabatic oscillations for an 18-atom cluster.

Level $n$	Excitation energy $\epsilon_n - E_{\text{tot}}(R_0)$	Energy $\Delta E$ $\epsilon_n - \epsilon_{n-1}$	Amplitude $\Delta R/R_0$ (%)
0	2.01	...	1.95
1	6.20	4.135	3.38
2	10.34	4.134	4.37
3	14.47	4.132	5.17
4	18.60	4.130	5.86
...	...	...	...
8	35.01	4.121	8.05
9	39.22	4.119	8.52
10	43.33	4.116	8.95

spectra. Beams of metal clusters with a core “temperature” of about 500 K are currently being produced experimentally.<sup>8,9</sup> In a real experimental situation, it should thus be the high-lying vibrational modes with  $n=8-10$  and large vibration amplitudes which are primarily filled. It can be seen from Tables I and II that the relative vibration amplitude reaches  $\approx 10\%$ . For the cluster with  $N=18$ , for  $n=10$ , for example, the cluster radius varies within  $\approx 9\%$ .

It follows from the adiabatic jellium model that the electronic characteristics depend strongly on the cluster size; in particular, the ionization potential at  $N=18$  varies within an interval  $3.55-3.30=0.25$  eV for these variations in size. Preliminary calculations show that the dynamic characteristics of the clusters, in particular, the distribution of oscillator strengths and the photoionization cross section, vary markedly. In experiments with clusters, it is thus necessary to consider thermal effects or to carry out the experiments at low temperatures, i.e., to produce beams of clusters containing only the low-lying modes.

4. In conclusion we should point out that calculations incorporating a nonlocal exchange interaction provide a correct basis for further study of electronic processes in metal clusters. The size dependence of the total energy reported here reveals a deviation from the “bulk material” model of a cluster core. The behavior found for the total energy as a function of the number of atoms in the cluster, with allowance for the exchange interaction, not only confirms that clusters with filled electron shells are the stablest but also demonstrates that there can be deviation from the old sequence of magic numbers, in the example of the cluster with  $N=19$ . The collective oscillations of the cluster core predicted here are important for describing the electron spectra, since they may strongly influence the electron–electron interaction at low temperatures, playing the role of acoustic phonons in a solid.

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