PHYSICAL REVIEW B VOLUME 34, NUMBER 10 15 NOVEMBER 1986

Structures of small alkali-metal clusters

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(Received 26 June 1986)

Structures of clusters of monovalent metals have been calculated using the Kohn-Sham method in the local-density approximation. The metal atoms are described by a local pseudopotential. Instead of using any basis-set expansion, the single-electron wave functions are solved on a three-dimensional grid using a relaxation method. Since the relaxation method is also used to solve the Poisson equation, the electronic structure as well as the ion positions can be relaxed simultaneously for finding the ground-state configuration. The structures obtained for small clusters ($N < 8$) agree well with the results of earlier calculations. These structures are found to be independent of the pseudopotential parameter and common to all alkali metals. It is shown that the geometries of these clusters are similar to those of small clusters of electron-hole plasma, and can be understood in terms of single-electron states in a spherical potential (jellium model). The electric polarizabilities of the clusters are calculated and the results agree well with the experimental results. For a diatomic cluster the two-electron wave function is solved exactly in the finite grid and the results are compared with those obtained using the local-density approximation.

I. INTRODUCTION

Ab initio calculations have revealed that alkali-metal clusters have fascinating geometries.[1-6] For up to five atoms the lowest-energy state of the cluster has a planar structure, and clusters of six or seven atoms have fivefold symmetry. Even in the largest clusters studied, Na_{13}, the structure seems not to have the symmetry of the infinite metal.[4] The measured abundances of clusters formed in a rare gas show "magic numbers" which coincide with the magic numbers of nuclei and can be explained in terms of the shell structure of the single-particle energy levels in a spherical potential.[7,8] The spherical jellium model thus gives the correct magic numbers for sodium and potassium clusters.[9,10]

The calculations of the cluster geometry in its ground state are based on the minimization of the total energy with respect to the ionic positions. This has been done using Hartree-Fock and perturbative configuration-interaction (CI) methods for Li clusters[5,6] and using the local-density approximation for sodium clusters.[3,4] The resulting geometries are similar in all cases for clusters containing less than eight atoms. For larger clusters a complete search for the ground-state structure has not been done. In all these calculations the molecular orbitals are expressed in terms of small number of atomic basis functions.

In the present paper we report calculations of alkali-metal clusters using a simple pseudopotential model and the local-density approximation. Instead of using any basis set, the single-electron wave functions are solved numerically on a finite three-dimensional grid. Using relaxation methods[11] for solving the Schrödinger equation and the Poisson equation, rapid convergence is obtained for the ground-state electronic structure and for the cluster geometry. A similar relaxation method has been successfully applied earlier for solving the Schrödinger equation of a localized positron[12] and a hydrogen atom[13,14] in metals and on metal surfaces. The obtained cluster geometries agree well with earlier calculations and it is shown that these are common structures for all alkali-metal clusters.

The results of the pseudopotential calculations are compared with the results obtained from the spherical jellium model and with the structures of plasma clusters. The latter are shown to have the same geometry as the pseudopotential clusters and form a natural bridge in understanding the cluster structures in terms of the spherical jellium model. In the case of a nondegenerate electronic structure the cluster shape is nearly spherical and can have a high symmetry (no Jahn-Teller distortion[15,16]). In these cases the cluster structures can be understood by minimizing an electrostatic energy term corresponding to the classical Madelung energy in an infinite lattice.[10] The results of all the different approaches are used to discuss why the magic numbers can be determined by the spherical jellium model even if the actual geometries of the small clusters are drastically nonspherical.

The present computational method allows a straightforward determination of the electronic polarizability of a pseudopotential cluster. The polarizability is strongly dependent on the orientation of the molecule with respect to the direction of the electric field, but the average polarizability agrees well with the results obtained with the spherical jellium model,[17] and is in a good qualitative agreement with the experimental results for sodium clusters.[18]

The plan of this paper is as follows. In Sec. II the theory and the computational methods are presented. In Sec. III results are given for the cluster geometries, electronic structure, total energy, and electronic polarizability. In this section it is also discussed why the magic numbers can be obtained from the spherical jellium model. Finally, Sec. IV gives the discussion and conclusions.

II. THEORY

A. Local-density approximation

The electronic structures of the clusters are calculated using the density-functional Kohn-Sham method in the local-density approximation. For the exchange-correlation energy we have used the interpolation formula of Perdew and Zunger[19] to the numerical data of Ceperley and Alder.[20] Only spin-independent calculations were performed in the present work, except in the case of a dimer where the local-density results are compared with the results of an exact many-body calculation. The spin-dependent formalism would change slightly the results for clusters with odd numbers of electrons and for open-shell jellium clusters,[5] but the basic conclusions of this paper would be the same. A local pseudopotential is used to describe the electron-ion interaction so that only valence electrons are included in the computations. The adiabatic Born-Oppenheimer approximation is used to separate the ionic motion from the electronic motion.

In the case of the spherical jellium model the one electron wave functions form a shell structure related to that of a free atom. The valence-electron states can then be classified in terms of the angular-momentum quantum number. The states are filled in the order[21] 1*s*, 1*p*, 1*d*, 2*s*, 1*f*, 2*p*, etc. Since the resulting wave functions in the real clusters have similar symmetries, we use the language of the spherical jellium model. For example a *p* state then means a wave function which has a *p*-like symmetry with respect to the center of the cluster.

B. Relaxation method

The three-dimensional space is divided into a uniformly spaced grid (simple cubic) and the single-particle wave functions and the potentials are discretized in this grid. The ion sites, however, are not restricted to be grid points. The single-particle Schrödinger equation is solved using a relaxation method. The Laplace operator ∇^2 is approximated using only the six nearest neighbors. The equations to be solved iteratively for each single-electron state are[14] (atomic units are used throughout this paper)

$$\psi_{i,j,k}^{(n+1)}=\frac{\sum'_{\langle i,j,k\rangle}[\psi_{i,j,k}^{(n)}]}{6+2h^2(V_{i,j,k}^{(n)}-\varepsilon^{(n)})}\,, \tag{1}$$

$$\varepsilon^{(n+1)}=\frac{\sum_{i,j,k}\left[-\frac{1}{2h^2}\psi_{i,j,k}^{(n)}\left(\sum'_{\langle i,j,k\rangle}[\psi_{i,j,k}^{(n)}]-6\psi_{i,j,k}^{(n)}\right)+V_{i,j,k}^{(n)}\,|\,\psi_{i,j,k}^{(n)}\,|^2\right]}{\sum_{i,j,k}|\,\psi_{i,j,k}^{(n)}\,|^2}\,, \tag{2}$$

where we have used the following notation for the (restricted) sum,

$$\sum'_{\langle i,j,k\rangle}[\psi_{i,j,k}]\equiv\psi_{i+1,j,k}+\psi_{i-1,j,k}+\psi_{ij+1,k}+\psi_{ij-1,k}+\psi_{ij,k+1}+\psi_{ij,k-1}\;. \tag{3}$$

$\psi_{i,j,k}^{(n)}$ is the single-electron wave-function value at the grid point (i,j,k) in iteration n. V is the effective potential of the Kohn-Sham scheme (usually denoted by V_{eff}), ε the single-particle energy eigenvalue, and h the mesh size. The iteration of Eqs. (1) and (2) converges if the mesh size is small enough,[11] as compared to the variation in ψ and V. The initial guess for the wave function has to be general enough so that it is not linearly independent of the resulting self-consistent wave function. The wave function corresponding to the lowest-energy eigenvalue is directly the solution of Eqs. (1) and (2). For higher-energy states the wave function has to be orthogonalized against each lower-energy states. This is done in each iteration cycle of the wave function.

The effective potential V consists of the local exchange-correlation potential, the electrostatic potential ϕ, corresponding to the electron density, and the external potential provided by the pseudopotentials. The electrostatic potential ϕ can be integrated directly once the electron density is known. However, in the present method it is much more effective to solve the Poisson equation using a similar relaxation method as for the wave functions. The iterative equation is then

$$\phi_{i,j,k}^{(n+1)}=\tfrac{1}{6}(\phi_{i+1,j,k}^{(n)}+\phi_{i-1,j,k}^{(n)}+\phi_{ij+1,k}^{(n)}+\phi_{ij-1,k}^{(n)}+\phi_{ij,k+1}^{(n)}+\phi_{ij,k-1}^{(n)})+\frac{4\pi h^2}{6}\rho_{i,j,k}^{(n)}\,, \tag{4}$$

where $\rho_{i,j,k}^{(n)}$ is the electron density in the cluster at the site (i,j,k) in iteration n. Using the relaxation method in solving also the Poisson equation has two advantages. (i) Close to the self-consistent solution $\phi^{(n)}$ does not change very much from the previous one and only a few iterations of Eq. (4) are needed to update the potential. This is much faster than the direct (three-dimensional) integration of the potential from the density. (ii) The wave functions and the electrostatic potential can be relaxed simultaneously.

Conventionally, the self-consistent iteration goes as follows: Starting from an initial potential, the single-particle wave functions corresponding to this potential are solved (numerically) *exactly* from the Schrödinger equation. Then a new potential is derived again corresponding *exactly* to the electron density provided by the wave functions. In the present relaxation method we also start from an initial potential, but the Schrödinger equation is solved only approximately [a few iterations of Eqs. (1) and (2)] and then a new potential is derived, but again only approximately, using Eq. (4) for the electrostatic potential. Close to self-consistency, only one iteration of Eqs. (1) and (2) is done alternately with Eq. (4). Only when self-consistency is achieved are the one-particle wave functions an exact solution (within the numerical accuracy) of the Schrödinger equation, and the electrostatic potential is an exact solution to the Poisson equation.

If the ion sites are to be relaxed to the equilibrium positions, that is also done simultaneously with the electronic-structure calculation. In each self-consistency cycle the Hellmann-Feynman forces for each ion are derived and the ions are relaxed in the direction of the force. Again it is not effective to solve for the equilibrium sites corresponding to a given electron density in the middle of the self-consistency iteration. Instead, we do only a few (usually one or two) iterations of the ion positions before doing the next self-consistency cycle. This simultaneous relaxation is closely related to the unified approach to the molecular-dynamics and density-functional theory developed by Car and Parrinello.[22]

C. Electron-ion pseudopotential

The pseudopotential describing the ions has to be a smoothly varying local function. Any discontinuity of the total potential would require special care in choosing the grid points or restrict the ion sites to be in similar positions on the grid. The widely used discontinuous Heine-Abarenkov—type[23] potentials are thus not applicable in the present method. We have chosen to use the following model potential,

$$V_{\mathrm{ps}}(r)=\begin{cases} -\dfrac{Z}{r} & \text{if } r>r_c\ , \\[2ex] -\dfrac{3Z}{2r_c^3}\left[r_c^2-\dfrac{r^2}{3}\right] & \text{if } r<r_c\ , \end{cases} \tag{5}$$

which is the electrostatic potential of a homogeneously charged sphere of radius r_c. This pseudopotential does not, however, mean that our clusters are the same as interacting jellium spheres, since the pseudopotential is only used for the electron-ion interaction, whereas the ion-ion interaction is kept to be Z^2/r at all distances.

The equilibrium densities of bulk metal corresponding to different parameter values of the model pseudopotential have been estimated by minimizing the total energy per electron (in first-order perturbation theory),

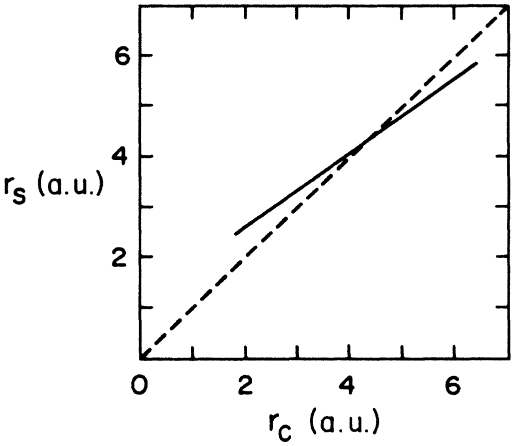

FIG. 1. The equilibrium density of a metal described with the pseudopotential of Eq. (5) as a function of the parameter r_c. The density is expressed in terms of the density parameter $r_s=(3/4\pi n_0)^{1/3}$, where n_0 is the valence-electron density.

$$\lim_{N\to\infty}(E_{\mathrm{tot}}/N)\approx\varepsilon_0(n_0)+\frac{Z^{5/3}\alpha_M}{2r_s}+4\pi n_0\int_0^{r_c}dr\,r^2\left[V_{\mathrm{ps}}(r)+\frac{Z}{r}\right]\ , \tag{6}$$

where ε_0 is the energy per electron in a homogeneous electron gas of density n_0, and α_M is the Madelung constant for the lattice in question. The relation of the pseudopotential parameter r_c to the electron-density parameter r_s of the homogeneous electron gas is shown in Fig. 1. The difference between fcc and bcc structures (arising from the different Madelung constant) is negligible (less than the thickness of the line in the figure).

D. Mesh size and test calculations

The benefit of the relaxation method, that no basis functions are needed, brings in the drawback that one has to use a finite and small number of mesh points in describing the electron density, potentials, and the wave functions. For testing what the minimum number of lattice points is for describing the electronic structure of the cluster, several computations were first performed for spherical jellium clusters of different sizes. For a cluster with up to ten electrons, it was found that the resulting electronic structure and the total energy, as well as the electronic polarizability of the cluster, were accurate enough by using $12\times12\times12$ points in the three-dimensional lattice with mesh size $2r_s/3$. The error in the single-electron energy eigenvalues and in the total energies of the clusters was less than 1 mRy, and the relative error in the polarizability was less than 5%.

If a one-electron jellium cluster was moved around in this mesh, the variation in the total energy was less than 1 mRy. This variation comes from the fact that the total energy depends on the relation of the center of the cluster (external potential) to the mesh points. The interatomic interaction in a diatomic pseudopotential cluster was calculated at different orientations of the cluster with respect to the mesh points. The variation in the binding energy of the dimer was less than 1 mRy and the variation in the bond length about 0.2 a.u. For the purpose of the present model calculation this accuracy was considered to be satisfactory and all the results shown for the pseudopotential clusters are calculated using $12\times12\times12$ mesh points with the mesh size $h=2r_c/3$. The small number of mesh points needed is a result of the smoothness of the pseudopotential chosen.

E. Two-electron wave function

In the case of only two electrons, the ground state of the molecule is a spin triplet and has a symmetric spatial wave function. In that case it is straightforward to diagonalize the many-body wave function without making the local-density approximation. In the present model calculation this is done in a slightly smaller grid of only $8\times8\times12$ points. This does not decrease the accuracy in the case of a diatomic cluster. The relaxation method is a generalization of Eqs. (1) and (2):

$$\psi_{\alpha,\beta}^{(n+1)}=\frac{\sum'_{\langle\alpha,\beta\rangle}[\psi_{\alpha,\beta}^{(n)}]}{12+2h^2(V_{\alpha,\beta}^{\text{ext}}+1/r_{\alpha,\beta}-\varepsilon^{(n)})}\ , \tag{7}$$

$$\varepsilon^{(n+1)}=\frac{\sum_{\alpha,\beta}\left[-\frac{1}{2h^2}\psi_{\alpha,\beta}\left(\sum'_{\langle\alpha,\beta\rangle}[\psi_{\alpha,\beta}^{(n)}]-12\psi_{\alpha,\beta}^{(n)}\right)+(V_{\alpha,\beta}^{\text{ext}}+1/r_{\alpha,\beta})\,|\psi_{\alpha,\beta}^{(n)}|^2\right]}{\sum_{\alpha,\beta}|\psi_{\alpha,\beta}^{(n)}|^2}\ . \tag{8}$$

Here, $\psi_{\alpha,\beta}$ is shorthand notation for $\psi(\mathbf{r}_\alpha,\mathbf{r}_\beta)$, where r_α and r_β are grid points and $\sum'_{\langle\alpha,\beta\rangle}[\cdots]$ means, as in Eq. (3), summation over the nearest-neighbor points. $V_{\alpha,\beta}^{\text{ext}}$ is the external potential provided by the electron-ion pseudopotentials. The energy expression contains singular terms $|\psi_{\alpha,\alpha}|^2/r_{\alpha,\alpha}$ which are an artifact of the finite mesh. These have been approximated by

$$\left[\frac{|\psi_{\alpha,\beta}|^2}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}\right]_{\beta=\alpha}\rightarrow\frac{3}{2h}\left[\frac{3}{4\pi}\right]^{1/3}|\psi_{\alpha,\alpha}|^2\ , \tag{9}$$

which is the electrostatic interaction energy between a point charge and a homogeneously charged sphere of volume h^3.

F. Madelung energy in spherical clusters

In the case of a weak pseudopotential, the total energy of a cluster can be approximated by applying first-order perturbation theory to the result for a spherical jellium cluster[10,24] (in the same way that the jellium model has been used to describe, for example, surfaces and vacancies in simple metals[25,26]). The total energy can then be expressed as[10]

$$E=E_{\text{jellium}}+E_M+\Delta E_{\text{ps}}\ , \tag{10}$$

where E_{jellium} is the total energy of the jellium cluster, E_M is the Madelung energy of the cluster (defined below), and ΔE_{ps} is an energy term which depends on the form of the pseudopotential. The jellium energy is independent of the structure of the molecule. The Madelung energy is the electrostatic energy of a cluster consisting of point charges (ions) and a homogeneously charged sphere of density n_0 (electrons). This term is strongly dependent on the structure, and determines the structure of the molecule. The last term is a correction arising from the fact that the pseudopotentials are not potentials of point ions and that the electron density is not homogeneous. This term does not depend as much on the structure as the Madelung energy, and in an earlier paper it was then argued that the structures of the closed-shell clusters (spherical electron density) can be determined simply by minimizing the Madelung energy (no electronic-structure calculation is needed).[10]

III. RESULTS

A. Cluster geometry

The calculated ground-state structures of clusters with two to eight atoms are shown in Fig. 2. These results are for a monovalent metal with the pseudopotential parameter $r_c=4$ a.u. which would correspond to a bulk metal with $r_s=4.1$ a.u. This is slightly larger than the electron-density parameter for sodium, $r_s=3.93$ a.u. The structures of the clusters were found to be independent of the pseudopotential parameter when it was varied between 2 and 6, which corresponds to r_s values from 2.6 to 5.6 a.u. This range includes all alkali metals, and the results therefore suggest that the geometrical structure of small clusters is similar in all alkali metals.

The clusters of up to five atoms are planar, the six- and seven-atom clusters have fivefold symmetry, and the eight-atom cluster consists of two squares rotated by 45° with respect to each other. The structures for up to seven atoms are in excellent agreement with the results of CI calculations of Rao *et al.*[5,6] for Li clusters and pseudopotential local-density-approximation (LDA) calculations of Martins *et al.*[3,4] for Na. The eight-atom cluster has the most compact nearly spherical structure. It has been shown earlier that the structures of small alkali-metal clusters are dominated by the filling of the single-particle

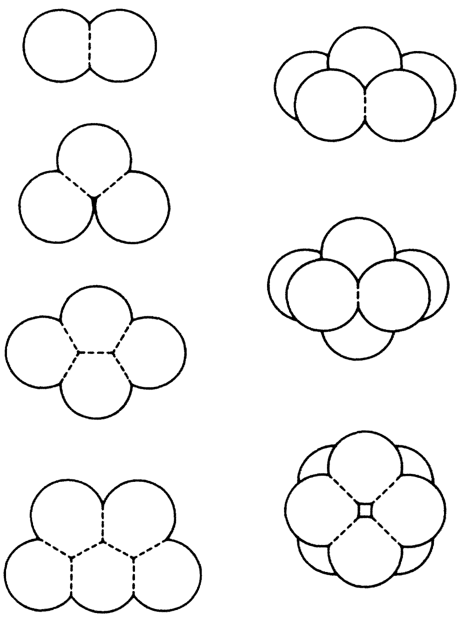

FIG. 2. The calculated structures of the pseudopotential clusters for $r_c = 4$ a.u. The sphere radii describing the atoms are equal to r_c. The cluster with two to five atoms are planar. In the six- and seven-atom clusters the fifth atom of the fivefold ring cannot be seen. The eight-atom cluster consists of the squares of atoms rotated 45° with respect to each other.

energy levels of different symmetries.[7,8] The energy levels as a function of the cluster size are shown in Fig. 3. In the cases where the nearly degenerate energy levels are filled the cluster prefers to take a spherical shape. This is expected to happen at the magic numbers determined by the jellium model (these numbers, are 2, 8, 18, 20, 34, 40, ...). In addition to the trivial case of the dimer, the eight-atom cluster is magic. In that case the structure agrees exactly with the prediction of a simple consideration of the electrostatic Madelung energy of the cluster,[10] and gives further support to the idea that the structures of alkali-metal clusters with a magic number of atoms can be predicted by minimizing the classical Madelung energy of a spherical cluster. The resulting clusters have fascinating structures which are very different from the lattice structure of the bulk metal.[10,24]

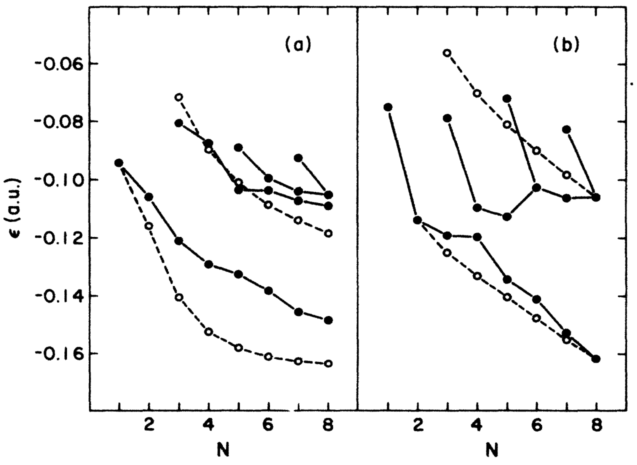

FIG. 3. Electron-energy levels as a function of the cluster size. (a) shows the results for the pseudopotential clusters with $r_c = 4$ a.u. (solid points) and for the spherical jellium model with $r_s = 4$ a.u. (open points). The results for the plasma clusters (solid points) and spherical plasma clusters (open points) are shown in (b).

B. Plasma clusters

The electronic structure of a two-component electron-hole plasma can be calculated from Kohn-Sham equations which are similar to those for the electronic structure of the pseudopotential clusters. If the electrons and the holes have same mass, then the resulting cluster, in the local-density approximation, does not have nonzero charge density anywhere. The hole density exactly cancels the electron density. The effective potential consists only of the local exchange-correlation potential

$$V(\mathbf{r}) = V_{\mathrm{xc}}(n(\mathbf{r})) + V_{\mathrm{corr}}^{\mathrm{e\text{-}h}}(n(\mathbf{r}))\ ,$$

where V_{xc} is the usual exchange-correlation potential for the electrons and $V_{\mathrm{corr}}^{\mathrm{e\text{-}h}}$ is the additional correlation energy arising from the electron-hole correlation. This local potential can be calculated (as can V_{xc}) for the homogeneous system.[25,26] In the present study, however, since we merely want to compare the results of the plasma model with those of the jellium and pseudopotential models, the electron-hole correlation has been totally neglected. One way to think of this model is then a completely relaxable jellium, i.e., the rigid positive background density of the normal jellium is replaced with a relaxable density which always minimizes the electrostatic energy by taking exactly the same density distribution as the electron density.

The resulting one- and two-electron clusters are spherically symmetric since the one or two electrons occupy the $1s$ state. The following clusters from three to seven electrons, however, are not spherical. The electrons from three to eight occupy the p states, and the resulting electron density and the effective potential are not spherically symmetric until the p shell is full in the case of the eight-electron cluster. To maximize the local exchange-correlation energy, the four-electron cluster has the two p electrons in the same state, say p_x, and similarly the four p electrons in the six-electron cluster occupy the two p states p_x and p_y. Thus the clusters with three or four electrons have a cigar shape, whereas five- and six-electron clusters are planar disklike in shape, in the same way (and for the same reason) as the pseudopotential clusters. In the density-functional Kohn-Sham formalism the electron states, in principle, can also be partially filled, and a spherical cluster can be formed for any number of electrons. However, these clusters are always higher in energy as compared to the clusters where the local electron density is maximized by fully occupying a state whenever it is possible. The filling of the electron states in the (local-density) plasma clusters is then different from that of free atoms. In the plasma clusters there is no direct Coulomb repulsion between the two electrons in the same state (this is compensated for by the hole density). In atoms the direct Coulomb repulsion makes it energetically favorable to fill the levels according to the Hund's rules.

The ground state of the plasma clusters have qualitatively the same geometries and electronic structures as the pseudopotential clusters. For three- to six-electron clusters the geometries are planar (or cigar shaped), the seven-electron cluster starts to be spherical, and finally the eight-electron cluster is a sphere. The plasma clusters are expected to have the same magic numbers as the pseudopotential clusters, i.e., those determined by the spherical shell model. The inclusion of the electron-hole correlation would not change the results qualitatively. It only increases the local potential and changes the equilibrium density of the plasma slightly, but not the conclusions of the shape of the clusters or the filling of the single-particle energy levels.

C. Comparison of the structures of the jellium, plasma, and pseudopotential clusters

The one-electron energy eigenvalues of the occupied states of different clusters are shown in Fig. 3. The eigenvalues for the spherical jellium clusters ($r_s = 4$ a.u.) and for the pseudopotential clusters ($r_c = 4$ a.u.) are given in Fig. 3(a) and the eigenvalues for the plasma clusters are given in Fig. 3(b). The lowest state in each case is an s state and all the higher states are p-like. It is interesting to see that the qualitative behavior of the eigenvalues as a function of the cluster size is very similar for the pseudopotential clusters and for the plasma clusters. In the six-atom pseudopotential cluster the two p states do not have exactly the same energy eigenvalue since in the finite grid the cluster does not have exact fivefold symmetry. For the same reason the two lowest p states in the seven-atom clusters are not exactly degenerate. The results show once again that in a metal with a weak pseudopotential it is the electron-density distribution of the shell model which determines the cluster structure. The electron-density distribution takes the form which minimizes the kinetic energy and the exchange-correlation energy, whereas the electrostatic Hartree energy is minimized by relaxing the ions to compensate for the charge density of the electron distribution. In the case of a plasma cluster the positive charge density exactly cancels the electron density. Both in the plasma clusters and in the pseudopotential clusters the variation of the total energy of the cluster as a function of the cluster size is dominated by the electronic shell structure in a spherically symmetric potential and this leads to the magic numbers found experimentally. For closed-shell clusters the electron-density distribution is spherical and thus the resulting ionic configuration is as spherical as possible, and can be estimated by minimizing the classical Madelung energy, which is the most structure-dependent energy term in the pseudopotential clusters.

The total energies of the clusters are shown in Fig. 4. For the pseudopotential clusters, the variation of the total energy as a function of the cluster size is qualitatively independent of the pseudopotential parameter r_c. The results for the plasma clusters are very similar to those for the pseudopotential clusters with $r_c = 4$ a.u. This is a consequence of the fact that the total energy of a jellium has a minimum at the density corresponding to about $r_s = 4.8$ a.u., which is only slightly larger than the equilibrium bulk density corresponding to the pseudopotential metal with $r_c = 4$ a.u. The results for the clusters with an odd number of electrons would be decreased slightly if the spin-dependent formalism would be used. This would decrease the odd-even variation seen clearly in the case of the plasma clusters.

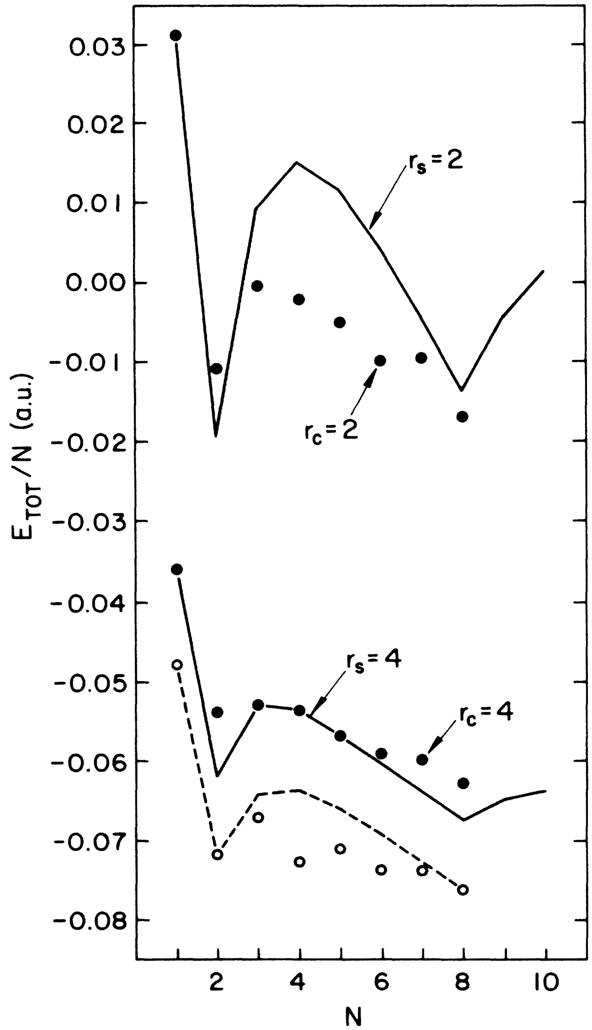

FIG. 4. The total energies of pseudopotential clusters with $r_c = 2$ and 4 a.u., for jellium clusters with $r_s = 2$ and 4 a.u., for the plasma clusters (open points), and for the spherical plasma clusters (dashed line). The electrostatic self-energy of the pseudopotential core (homogeneously charge sphere) is added to the results of the pseudopotential model to make the comparisons of different results easier.

Figure 4 shows that the strong size dependence of the total energy of the spherical jellium model is reduced in the pseudopotential model. However, the pseudopotential results still show the same basic shape arising from the shell structure of the jellium model. This indicates that the energy term that varies mostly as a function of the cluster size is the kinetic energy of the electrons. This result is in agreement with the earlier model calculation for spherical clusters,[10] which shows that the variation of the

Madelung energy (the dominating structure-dependent term) is slightly smaller than the variation of the total energy of the spherical jellium model. This means that in monovalent pseudopotential clusters and in plasma clusters it is the kinetic energy of (independent) electrons (in a spherical potential) which determines the magic numbers. The resulting cluster structure is not necessarily spherical in shape since the ions relax according to the nonspherical electron-density distribution to minimize the electrostatic energy. Thus both the magic numbers and the geometry of small clusters can be understood in studying the energy levels of independent electrons in a spherical potential. In metals with higher valency, the direct ion-ion as well as electron-ion interaction becomes stronger and the simple shell model is not necessarily applicable any longer as shown by Upton.[27]

D. Electric polarizability

The electric polarizability α of the pseudopotential clusters of $r_c=4$ a.u. was calculated by applying a small static electric field $\mathbf{F}$ to the cluster and calculating the change in the total energy:

$$\Delta E=-\tfrac{1}{2}\alpha\,|\mathbf{F}|^2\ .$$

The ion positions were kept fixed in the sites of the ground state (in the zero field). The contribution of the ionic relaxation was therefore not included in the polarizability (this could be done only in the principal directions since otherwise the ion would turn towards the field to maximize the polarizability). For each cluster the polarizability was calculated by directing the electric field along the three principal axes of the molecules. The results are shown in Fig. 5. The average polarizability agrees well with the spherical jellium results (not shown), whereas individual polarizability components show large variations for clusters with a nonspherical shape.

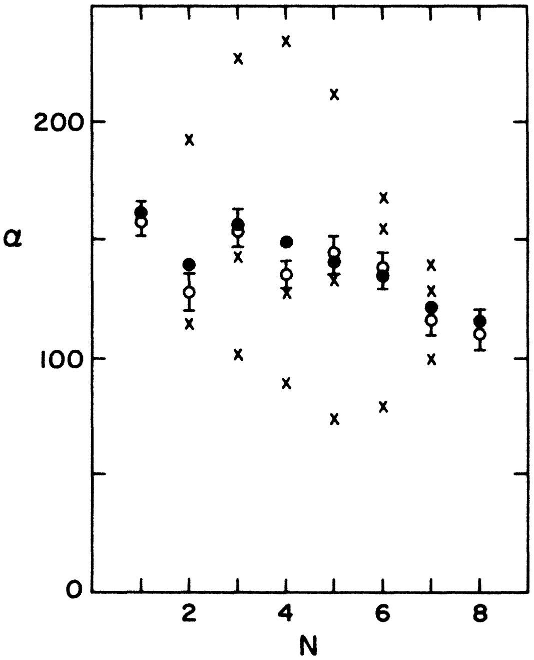

FIG. 5. The polarizability per electron of the pseudopotential clusters as a function of the cluster size. The solid points are the calculated average polarizability for $r_c=4$ a.u., the open points with the error bars are the experimental results for sodium clusters (Ref. 7), and the crosses are the principal polarizability components.

The results are in good qualitative agreement with the measured polarizabilities for small sodium clusters. The agreement of the absolute values with the experimental ones does not have so much meaning since the pseudopotential parameter $r_c=4$ a.u. is slightly too large for sodium. It has been shown earlier[17] that at least part of the discrepancy between the experimental and theoretical results is due to the use of the local-density approximation for the exchange-correlation energy.

E. Exact model calculation for the dimer

The six-dimensional Schrödinger equation (7) for the spatially symmetric two-electron wave function was solved exactly using an $8\times8\times12$ grid with a mesh size of 2.67 a.u. and $r_c=4$ a.u. The result for the interatomic potential is shown in Fig. 6, and compared to the results of the local-density (LDA) and local-spin-density approximations (LSDA). These were calculated using the same mesh size. The LSDA gives a good estimate for the binding energy, whereas the LDA strongly overestimates the binding. The difference between the LSDA and LDA comes solely from the different total energy values for the free atom in these two approximations: the one-electron atom is totally spin polarized and thus the LSDA gives a much lower total energy for it. At the distances shown the dimer is always totally spin compensated, the two electrons occupying the same state, and the LSDA and LDA give exactly the same result. At larger distances it becomes preferential for the two electrons to occupy spatially orthogonal states to create a spin density and decrease the exchange-correlation energy.

The differences between the exact result and the LSDA result is less than 10% both in the binding energy and in the bond length. Note that the LDA gives exactly the same bond length as the LSDA. The difference between

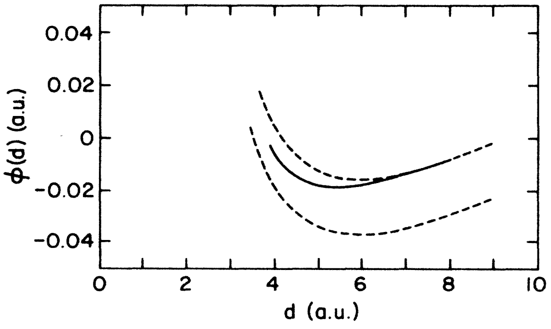

FIG. 6. The interatomic potential of a diatomic pseudopotential cluster ($r_c=4$ a.u.). The solid line is the (numerically) exact result of the two-electron calculation, the upper dashed line is the result of the local-spin-density approximation, and the lower dashed line is the result of the local-density approximation.

the exact result and the LSDA is qualitatively similar to that obtained for the hydrogen molecule[28] and for alkali-metal dimers.[29] The exact calculation gives a slightly shorter bond length and slightly larger binding energy. The LSDA is successful only in calculating the binding energy of the molecule, but not in calculating its total energy or that of a monoatom. As discussed often earlier, the cancellation of errors result good results for the binding energies.[30]

IV. DISCUSSION AND CONCLUSIONS

The relaxation method for solving the one-electron Schrödinger equation is straightforward if the potential is smoothly varying function. The use of variable mesh sizes would make additional complications for the present calculations. If, for example, there were to be more points near the core of the pseudopotential, the mesh would have to be changed when the atom is relaxed toward its equilibrium site. This would make the simultaneous relaxation of the electronic structure and ion sites awkward. Nevertheless, the relaxation method has been used lately successfully in quantum chemistry in applications where all electrons are included[31] (but the nuclear positions are kept fixed). In the case of simple pseudopotential clusters as in the present study, the relaxation method is especially attractive, since it overcomes any difficulties of choosing a large enough basis set (since no basis sets are used) and allows simultaneous relaxation of the single-particle wave functions, self-consistent potential, and atomic sites in the cluster.

The results show that the structures of the alkali-metal clusters are governed by the filling of single-electron energy shells in a spherical potential. The fact that the resulting self-consistent potentials is not spherical is due to the nonspherical charge distribution of the partially filled shell and to the relaxation of the ions to compensate for the charge density provided by the electrons. A consequence of this is the nearly planar geometries for clusters containing less than seven atoms. It is also expected that the shell structure dominates the structures of larger alkali-metal clusters, containing several tens of atoms. This can be predicted both from the experimentally found magic numbers and from the theoretical consideration of the cluster-size dependence of different energy terms. As shown by Upton,[27] however, the shell model cannot explain the structures of clusters of polyvalent metals, like aluminum.

Of the alkali metals, sodium has an electron density which is close to the equilibrium value of a homogeneous electron gas. This makes sodium the metal which is best described by the simple jellium model. It gives reasonable results for the surface energy[32] and vacancy-formation energy[33] of the bulk metal, as well as for the properties of the clusters. However, the jellium model cannot, of course, give information on the geometry of the cluster, except by letting the background density relax to an arbitrary shape. An ultimate limit of this is the plasma model where the background density totally balances the charge-density distribution of the electrons. This model indeed results in cluster geometries which are in agreement with the pseudopotential calculations. The structures of the plasma clusters as well as the magic numbers are again in accord with the spherical shell model.

The results for the average electric polarizability are in good qualitative agreement with the experimental results and with the results of the spherical jellium model. There is a large variation in the different components of the polarizability tensor as a function of the cluster size, but the average polarizability is a smooth function showing minima at the magic numbers.

In conclusion, the structures of small alkali-metal clusters differ drastically from the structures of the bulk metals. The magic numbers and the cluster structures are dominated by the electronic shell model applied to the nearly free valence electron. The variation of the kinetic energy of the electrons as a function of the cluster size gives the magic numbers. The ions relax according to the electron-density distribution to minimize the electrostatic energy.

ACKNOWLEDGMENTS

The author wishes to thank J. W. Wilkins, N. W. Ashcroft, and J. H. Davies for useful discussions. This work was supported by the U.S. Office of Naval Research.

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