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PSEUDOPOTENTIAL CALCULATION OF SHELL STRUCTURE IN SODIUM CLUSTERS

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The electronic structure and charge density of two model sodium clusters of 13 and 15 atoms in fixed structures are calculated using pseudopotentials within the local-density-functional formalism. The results provide some confirmation of the calculated shell structure obtained using jellium models of alkali clusters.

1. INTRODUCTION

A NUMBER OF PAPERS HAVE recently described calculations based on a jellium model for clusters of alkali atoms [1–3]. In this model, the alkali ions are replaced by a spherical, uniformly charged sphere with total charge equal to that of the ions in the cluster. The radius of the sphere is given by $R = N^{1/3} r_s$, where N is number of ions and r_s is the radius of the Wigner–Seitz sphere in the bulk metal. The valence electrons are confined to the sphere, and the ground state total energy and electron charge density are calculated using local density functional theory. The only adjustable parameter within the jellium approximation is the value of r_s.

One reasonably clear success of this model is an explanation for the existence of peaks in the spectrum of sodium clusters produced in the supersonic expansion of sodium vapor [4]. Since the electrostatic jellium potential is spherically symmetric, the electron energy eigenstates are eigenstates of total angular momentum. Each energy eigenvalue is associated with an angular momentum quantum number l with degeneracy $2(2l + 1)$ and is identified as a shell. As atoms are added, the cluster size is increased and the electrons fill each shell in turn. The total cluster energy decreases gradually while each shell is being filled, but increases discontinuously when an electron is placed in a new shell. Clusters with enough electrons to just fill a shell are therefore more stable than clusters with slightly more or fewer atoms. The jellium model predicts a sequence of shells with angular momentum degeneracies such that the jumps in total energy match very well with the drops in abundance in the mass spectra.

The detailed applicability of the jellium model is not obvious since the electrostatic potential from discrete ions in a real cluster is not spherically symmetric. Hence there is no *a priori* reason for the existence of energy shells with the correct degeneracies. These considerations have motivated the present calculation, which can serve as a test of the appropriateness of the jellium model. The calculation uses pseudopotentials within local density functional theory. Similar calculations have been reported previously, where clusters with 2 to 8 and 13 atoms were treated [5]. In these cases, the authors reported the geometric configurations having the lowest total energy but did not publish the electron eigenvalues.

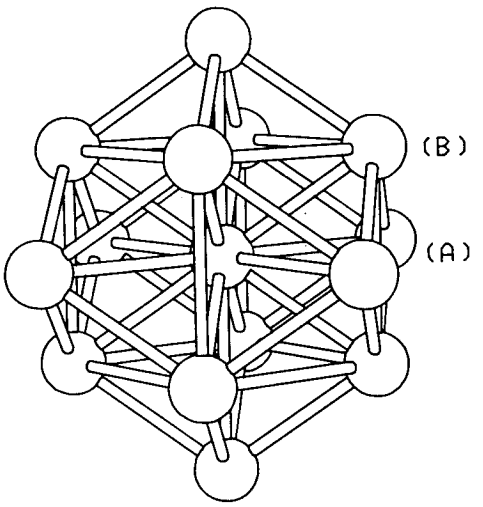

Fig. 1. The 15 atom cluster in a b c c-type structure; the letters A and B mark the planes for which total charge densities have been plotted.

2. METHOD OF CALCULATION

Each cluster is chosen to have the sodium ions in a fixed structure with a fixed bond length. The 15 atom cluster is placed in a b c c-type structure, shown in Fig. 1, with a nearest-neighbour bond length of 6.917 a.u., which is equal to that in bulk sodium [6]. The 13 atom cluster has the same nearest-neighbour spacing but is

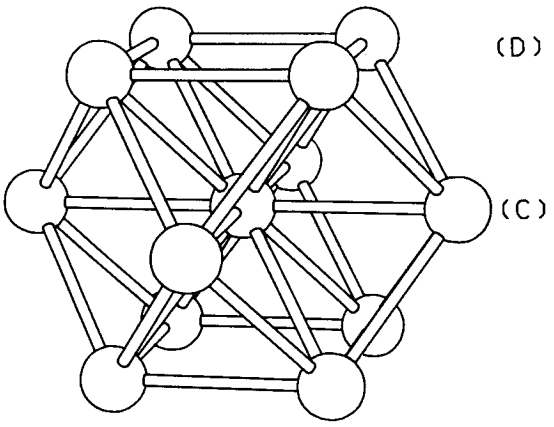

Fig. 2. The 13 atom cluster if a fcc-type structure; the letters C and D mark the planes for which charge densities have been plotted.

placed in a fcc-type structure, shown in Fig. 2. The clusters are repeated in real space on a simple cubic lattice, such that each cluster is surrounded by a supercell of empty space [7]. This scheme allows the use of a discrete symmetrized plane wave basis for the eigenfunction and potential expansions. The 15 atom cluster is placed in a supercell 29.8 a.u. on a side with plane wave having kinetic energies up to 4 ryd; the 13 atom cluster is placed in a supercell 26 a.u. on a side with plane waves having kinetic energies up to 5 ryd.

The ions potentials are replaced by angular-momentum dependent pseudopotentials [8]; the s, p and d pseudopotentials are chosen to give the atomic ground-state electron eigenenergies and some excited state eigenenergies to within 2 mryd, or about 1%. The many-body Hamiltonian for the cluster is approximated through the use of local density functional theory [9] and the one-particle Kohn–Sham equations [10]. The exchange-correlation energy functional of Perdew and Zunger [11] is chosen. This parametrized form is based on the electron gas calculations of Ceperley and Alder [12]. The formalism for the pseudopotential local-density functional scheme has been described previously [13] for solids. The energies are solved for at the Γ-point in Brillouin zone reciprocal to the supercell lattice. The Kohn–Sham equations are iterated until the potential function appearing in those equations is reasonably self-consistent, i.e. when the potential changes by less than 0.5 mryd from one iteration to the next.

3. RESULTS

The geometries chosen for the clusters have cubic symmetry, as may be seen from Figs. 1 and 2. The solutions of the Kohn–Sham equations at the Γ-point will therefore have full O_h symmetry: the energy eigenvalues will have degeneracies of one, two, or three, corresponding to the dimensions of the irreducible representations of the O_h group, and the eigenfunctions will transform according to those representations under rotations belonging to the group. It is furthermore expected that the eigenfunctions with the lowest energies will identify closely with eigenstates of angular momentum; states with s, p, and d angular dependence, which are expected to have low energies, transform as basis functions of the irreducible representations of the O_h group.

The calculated eigenvalues of the Kohn–Sham equations and their associated degeneracies are displayed in Table 1, for both the jellium [14] and cluster calculations. The state notation is that of [1]. The angular momentum labels are indeed found to apply to the cluster states, as more than 98% of each state's wavefunction lies in the appropriate subspace of the total angular momentum operator. This is determined by calculating for each state the projection integral

$$I_l = \int (P_l\psi)^*(P_l\psi)\,dV \qquad (1)$$

where P_l is a projection operator and the integration is over the volume of the largest sphere fitting inside the supercell cube.

A direct comparison of the eigenvalues in this table indicates that the cluster calculation agrees with the jellium results to within 10% for nearly all the states, with most of the cluster values somewhat higher than

Table 1. Electron eigenvalues (in eV) for 13 and 15 atom clusters. Degeneracies are noted in parentheses. The electrons occupy the lowest energy levels

State	Na_{13}		Na_{15}	
	Jellium	Cluster	Jellium	Cluster
1s	−5.037 (2)	−4.805 (2)	−5.097 (2)	−4.933 (2)
1p	−3.985 (6)	−3.675 (6)	−4.104 (6)	−3.930 (6)
1d	−2.718 (10)	−2.498 (6)	−2.916 (10)	−2.930 (4)
		−2.255 (4)		−2.636 (6)
2s	−2.265 (2)	−2.195 (2)	−2.505 (2)	−2.433 (2)

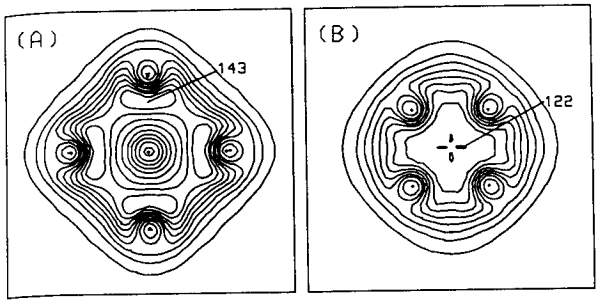

Fig. 3. The total charge density in the 15 atom cluster for the planes marked A and B in Fig. 1. The units are electrons per $(a.u.)^3$; contour lines are every 15 elecctrons/$(a.u.)^3$. The plot boundaries indicated the supercell size.

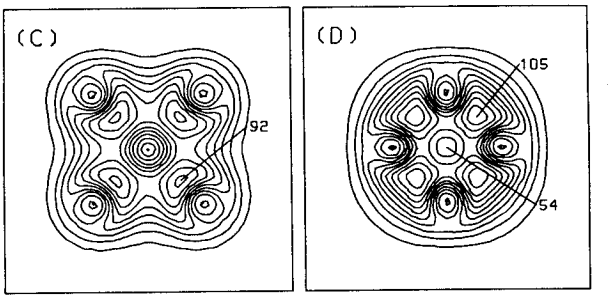

Fig. 4. The total charge density in the 13 atom cluster for the planes marked C and D in Fig. 2. The units are electrons per $(a.u.)^3$; contour lines are every 10 electrons/$(a.u.)^3$. The plot boundaries indicate the supercell size.

those of jellium. These differences might change if the cluster were allowed to relax to the ion configuration with the lowest total energy.

A somewhat more interesting effect may also be seen from the table: the energy levels have nearly the same sequence of degeneracies in both the jellium and cluster calculations, i.e. the ordering in energy of the angular momentum eigenstates is almost identical. The only difference is that in both the 13 atom and 15 atom clusters, the 1*d* level has split into two sublevels; however, the energy difference between the sublevels is quite small. From this ordering of levels with their respective degeneracies, it appears that at least for these small clusters the jellium model is in good agreement with this more realistic calculation, and therefore offers a good basis for computing the peaks in the abundance curves.

The final charge densities at two planar cuts through each cluster are shown in Figs. 3 and 4. These plots appear to provide further justification for the jellium model. That model assumes that the ion potentials are completely smeared out by electron screening, and that no interion bonds form. From the charge density contours it is clear that the screening is quite good, even for these small clusters, and that there is only slight evidence of bond formation. The electrons appear to be well delocalized. It seems reasonable that for larger clusters this delocalization will be even more apparent.

There are many refinements and other calculations that could be done to further test the jellium model. Relaxing the positions of the ions would give an indication of how much energy is involved in cluster distortions. This would indicate how sensitive the eigenvalues are to ion locations. It should be noted that in this calculation the two clusters had rather different structures (one f c c-based and the other b c c-based); yet this seemed to have little effect on the eigenvalues. As mentioned above, calculations have been reported on smaller clusters where the clusters were allowed to relax; these calculations indicate that Jahn–Teller distortions do take place, but that the electrons still fill a series of levels of type *s*, *p* and *d*. Larger clusters could also be calculated; it would perhaps be possible to do a cluster large enough to see whether the peak in the abundance curve at $N = 34$, predicted by the jellium but not seen in the experiments, would disappear in a more realistic calculation. Finally, clusters of different elements should be studied.

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