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Magic clusters Na_{57}^{-} and Na_{59}^{+}

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Abstract. The electronic structure of positively charged sodium cluster with 59 atoms and negatively charged sodium cluster with 57 atoms (both having 58 electrons) have been studied using an ab initio molecular dynamics method. Although the geometries of both clusters are nearly spherical, the results show differences in the electronic shells.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters

1 Introduction

The electronic shell structure is based on the assumption that the valence electrons of a metal are almost free and move in a nearly constant potential. This is the basic idea of jellium model. The electron numbers corresponding to full shells are particularly stable and the clusters having a full shell are called "magic" clusters. If an atom is added to a magic cluster, the new valence electron (or electrons) occupies a state with considerably higher energy. This will reduce the stability of the cluster and can be seen in the mass spectrum as reduced abundance [1].

The large degeneracy of an energy shell is only possible with a complete spherical symmetry [2]. In the case of real clusters, the shell energies split due to reduced symmetry of the cluster. However, in the case of sodium clusters the splitting is so small that large energy gaps remain between shells: sodium is the best representative of a free electron metal [3]. Therefore it is possible to observe the electronic shell structure in real sodium clusters.

The first reported experiment on electronic shell structure was published in 1984 by Knight et al. [4]. Electronic shell structure can be demonstrated experimentally by measuring the ionization energy as a function of cluster size. A more direct way to observe the electronic shell structure is the use of photoelectron spectra. Theoretically the shell structure was first predicted by the jellium model [5,6].

Photoelectron spectroscopy is an experimental method, which can be used to extract the electronic structure and excitation spectra of atoms, molecules and condensed phases. For molecules and clusters a comparison of the measured photoelectron spectra with the electronic density of states obtained from ab initio calculations provides information about the underlying geometrical structure.

The Issendorff et al. have made the most comprehensive experiment of size selected, negatively [7] and positively [8] charged sodium clusters by using photoelectron spectroscopy. They observed the electronic shell structure directly and found that it was in qualitative agreement with jellium model predictions.

2 Simulation methods

The jellium model replaces the ions with a uniform positive background and ignores the discrete ionic structure. The valence electrons are then confined by this positively charged background [9]. For looking the ion positions, we turn this model around and replace the valence electrons with a uniform negatively charged background. The ion positions can then be found by using classical molecular dynamics for point charges in a harmonic external potential provided by the uniform electron distribution. Similar model has been used to study the ion localization in traps [10] and results to consecutive nearly spherical shells of ions. These structures can then be used as starting geometries for ab initio computations.

The ab initio calculations were performed using a Born-Oppenheimer-Local-Spin-Density molecular dynamics (BO-LSD-MD) simulation method devised by Barnett and Landman [11]. In the Born-Oppenheimer method the Kohn-Sham one-electron equations are solved at each molecular dynamics calculation time step to get the single-electron states of the valence electron of the system corresponding to a given nuclear configuration of the ions for that instance of time. For the converged solution the Hellmann-Feynman forces on the ions can be calculated and together with the Coulomb repulsion of the positive ion cores, one can determine the total forces of ions. The electronic structure calculation is done explicitly for the sodium $3s^1$ electrons by using norm-conserving nonlocal

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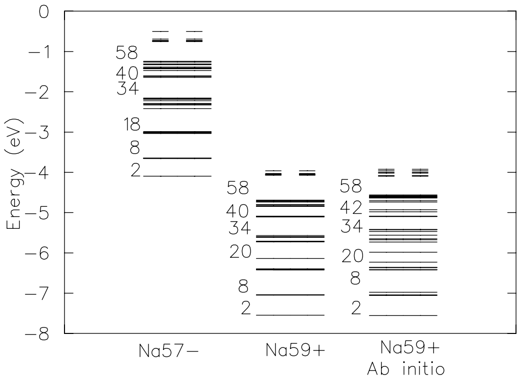

Fig. 1. Kohn-Sham energy levels for Na_{57}^{-} and for two different geometries of Na_{59}^{+}. The main energy gaps are shown by the numbers of electrons. The energy levels above the Fermi surface are shown as dashed lines. The spectrum denote 'Ab initio' is the lowest energy geometry found using simulation annealing technique [14].

pseudopotentials [12] and a plane-wave basis set. More details of the method can be found in the paper by Barnett and Landman [11] and the parameters for sodium have been described and tested in our previous papers [13].

3 Results

The classical ion model for finding the geometry of spherical clusters give shell like structures. The outermost shell tends to be as spherical as possible and for small sizes the number of ions in each shell do not follow that of icosahedral or FCC structures. For example, the 59 atom cluster has 1 atom in the center, 12 in the second shell and 46 in the outermost shell. However, other stable nearly degenerate geometries exist having 13 or 14 atom in the second shell.

The meaning of the simple model becomes clear with the comparison to the low-energy structure obtained by simulation annealing technique in cluster size $N = 59$ [14]. The second atomic shell of the best ab initio structure has 14 atoms and the surface shell 44 atoms. The comparable structure has 12 atoms in the first shell and 46 atoms in the second shell. The important point is that in both cases the surface shell is nearly spherical.

These two structures were first optimized at zero temperature using the ab initio method. The ab initio structure [14] has only 8.3 meV/atom (0.49 eV/cluster) lower total energy than the structure obtained by optimizing the ions in a harmonic trap. The simple model is thus useful in getting initial structures for simulations of sodium clusters. It is interesting to note that the ab initio structure is more stable although its Fermi gap is smaller, as seen in Figure 1.

The Kohn-Sham energy levels of both of these clusters are presented in Figure 1. The electronic structure of cluster obtained from the classical model is jellium like with clear energy gaps at $N = 2$, 8, 20, 34, 40 and 58. The ab initio structure is slightly deformed and this is the reason why this cluster have gap at $N = 42$ instead of 40.

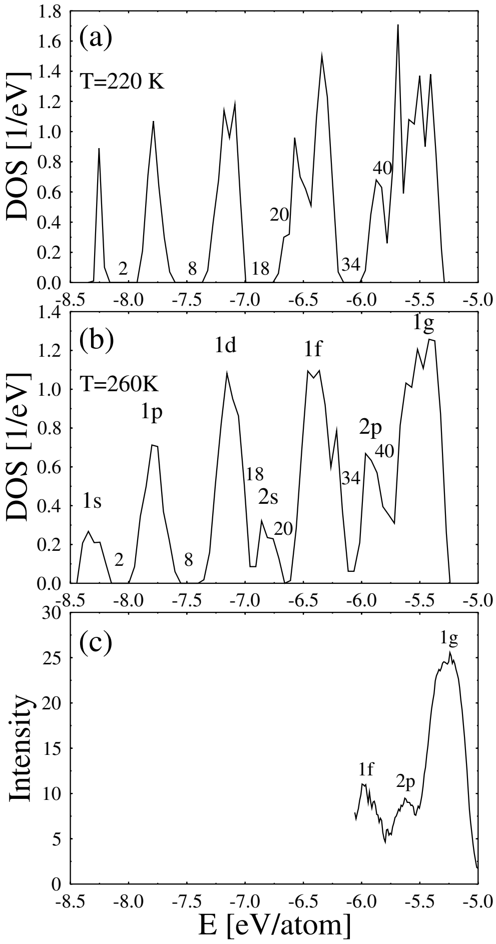

Fig. 2. Calculated density of states (DOS) for Na_{57}^{-} (a) and for Na_{59}^{+} (b) compared to the experimental result [8] for Na_{59}^{+} (c). The different jellium model energy shells and corresponding electron numbers are denoted in the figures. The energy scale for Na_{57}^{-} (a) is shifted so that the 1*g* peak is in the same place as in (b).

The Kohn-Sham energy levels of Na_{57}^{-} ground state geometry are presented in Figure 1. Both Na_{57}^{-} and Na_{59}^{+} have a magic number of 58 electrons, but their geometry has to be different due to a different number of atoms. Figure 1 compares their ground state electronic structures. The Na_{57}^{-} cluster has larger Fermi gap than the ab initio structure of Na_{59}^{+}. From Figure 1 it can be seen also that the Na_{57}^{-} is jellium like. The binding energy per atom is for Na_{57}^{-} 1.01 eV/atom and for Na_{59}^{+} 0.93 eV/atom.

Finding a global ground state geometry is always an exhaustive task. But in studying liquid clusters the initial geometry does not anymore have an important role unless the melting properties are studied. Here we consider only the photoemission spectra of liquid clusters and, consequently, the simple classical model can be used as a starting geometry of the simulation for Na_{57}^{-}.

For calculating the photoemission spectra we performed ab initio simulations at finite temperatures. The constant energy simulation for Na_{57}^{-} was performed at a temperature of 220 K and for Na_{59}^{+} at 260 K [14]. Figure 2 shows the time-averaged electron density of state (DOS) for Na_{57}^{-} (Fig. 2a) and for Na_{59}^{+} (Fig. 2b). The experimentally measured photoelectron spectrum [8] is also showed in the same figure (Fig. 2c). As we can see, the calculated DOS of Na_{57}^{-} and Na_{59}^{+} show the characteristics of the jellium model, but there are some small differences, for example, the Na_{57}^{-} cluster shows a surprisingly large gap between the $1d$ and $2s$ shells (after 18 electrons). It should be noted that the simulations in both cases are quite short, being 2 ps in the case of Na_{59}^{+}, but only 1 ps for Na_{57}^{-}. For easy comparison of the spectra the DOS of Na_{57}^{-} is sifted so that the 1g peak is at the same energy as the corresponding peak in the spectrum of Na_{59}^{+}. The experimental PES correlates very well with experimentally measured photoelectron spectrum apart from a shift of 0.2 eV in the position of the first peak. This deviation comes from the slight overestimation of the second ionization potential of the Na_{59}^{+} cluster by DFT.

4 Conclusion

In summary, we have studied electronic structure of magic Na_{57}^{-} and Na_{59}^{+} clusters with 58 electrons using an ab initio molecular dynamics method based on the density functional theory. Both clusters show clearly the shell structure of the jellium model. However, the energy gaps between the jellium subshells are different. In Na_{57}^{-} the magic number 20 disappears and is replaced with a new magic number 18. Our results for Na_{59}^{+} are in good agreement with the experimental results. It would be important to be able to extend the experimental measurement for the whole energy range of the conduction band.

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