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Brief Reports

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Electronic polarizability of small sodium clusters

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Small sodium clusters consisting of 1 to 40 atoms are described as spheres of interacting homogeneous electron gas (jellium model). The static electronic polarizability is calculated using self-consistent density-functional methods. An excellent agreement with recent experimental results is obtained.

Recently, Knight, Clemenger, de Haar, and Saunders[1] have reported on measurements of the static electronic polarizability of small sodium clusters consisting of up to 40 atoms. The size dependence of the polarizability is connected with the electronic structure of the cluster and shows (shell) structure similar to that found in earlier measurements of abundance spectra[2] and ionization potential.[3]

Theoretical *ab initio*–type calculations of the ground-state electronic and atomic structure of small metal clusters has been restricted to clusters consisting usually of less than 10 atoms,[4] and the polarizability has been calculated only for diatomic molecules.[5] However, several model calculations assuming a spherical symmetry have been presented for small metal clusters (see Ref. 6, and references therein). Typically, the metal sphere is described by noninteracting or interacting electrons moving in a spherically symmetric effective potential in a way analogous to the nuclear shell model. In a recent paper[6] we have calculated static and dynamical polarizabilities for small jellium spheres corresponding to the density of metallic lithium. The purpose of this paper is to do a more complete study of the static polarizability of jellium clusters corresponding to the density of sodium and compare the results with the very recent experiments of Knight, Clemenger, de Haar, and Saunders.[1] A similar calculation for closed-shell sodium clusters has been reported earlier by Ekard.[7] In the case of sodium the comparison of jellium results to the experimental ones is meaningful and interesting because (i) the jellium model gives good results for the surface energy[8] and vacancy formation energy[9] of sodium metal (meaning that the pseudopotential corrections are small[9]), and because (ii) the stability of sodium clusters (magic numbers) has been successfully explained in terms of the jellium model.[2]

In the jellium model the metal cluster is described in terms of an interacting electron gas which moves in the external electrostatic potential provided by a spherical homogeneous positive background charge distribution $n_+(r) = n_0\Theta(R-r)$, where n_0 is the average conduction electron density of the metal and R is the radius of the cluster ($R = N^{1/3}R_{\mathrm{WS}}$, N being the number of atoms in the cluster and R_{WS} the bulk Wigner-Seitz radius). The electronic structure and the (dipolar) response function needed for the polarizability determination are calculated using self-consistent density-functional techniques. For details of the method we refer to an earlier publication.[6] The formulation we use in calculating the response function is strictly valid only for clusters with closed electron shells. For open-shell clusters we use spin-independent formalism and energy-minimizing fractional occupation numbers for the degenerate energy levels. This method is found to give good results for free atoms.[6]

The results are compared to the experimental results[1] in Fig. 1. The polarizability of the cluster α_N is normalized by dividing by the polarizability of a free atom α_1 and by the number of atoms in the cluster. The theoretical value ($131a_0^3$) has been used for the atomic polarizability α_1. This is actually very close to the polarizability of a one-electron jellium cluster ($136a_0^3$) and the use of the latter would have given an equally good overall agreement between the theory and experiment. The opening of a new shell causes an increase in the polarizability of $N = 3$, 9, 19, 21, and 35 clusters. The same structure is seen also in the experimental values. The agreement between theory and experiment is best for closed-shell clusters of $N = 2$, 8, 18, 20, 34, and 40. For open-shell clusters the experimental values are slightly above the theoretical ones.

The excellent agreement displayed in Fig. 1 indicates that many properties of the clusters can indeed be understood in terms of electron levels in a spherical potential. This is rather surprising since *ab initio* calculations have shown that

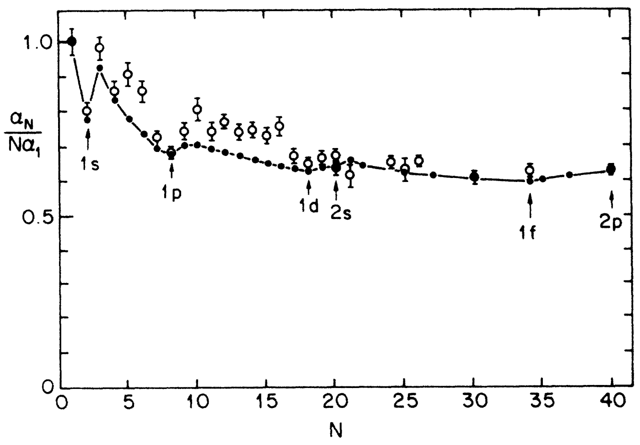

FIG. 1. Electrical polarizability as a function of the cluster size. N is the number of atoms in the cluster, α_N the polarizability of the cluster, and α_1 the polarizability of a free atom. The filled circles are theoretical results of the jellium model and the open circles experimental average polarizabilities from Ref. 1. The filling of energy levels in the jellium model are marked by arrows. Note that different values α_1 are used for scaling the theoretical ($\alpha_1 = 131a_0^3$) and experimental ($\alpha_1 = 159a_0^3$) results.

the actual structures of the smallest clusters ($N < 6$) are planar,[4,10] i.e., seemingly far from spherical. However, the planar structure is the result of the relaxation of the atomic position according to the electronic distribution of nonspherical valence-electron orbitals (e.g., p orbitals) as explained in detail by Martins, Buttet, and Car,[4] and does not necessarily mean that the valence-electron wave functions would be very different from those of a spherical potential. The delicate relationship between the orbital occupancy and structure will induce more structure to the $\alpha_N/N\alpha_1$ curve (for small N) than seen in the jellium model. For example, the weak minimum at $N = 4$ in the polarizability and the corresponding maximum in the ionization potential[4] is related to the structure of the cluster and cannot be predicted by the jellium model.

The absolute value of the polarizabilities from our calculations are about 20% below the experimental ones, i.e., the calculated α_1 is smaller than the experimental one. This atomic polarizability was calculated using exactly the same density-functional method as for the polarizabilities of the jellium clusters. The fact that the calculated atomic polarizability is within 4% of the polarizability of the one-electron jellium cluster indicates that the main discrepancy in the absolute values of the polarizabilities of small clusters may not be the use of the jellium model but the approximations made in solving the many-body problem. The use of spin-dependent formalism would change the absolute values of open-shell clusters and produce additional kinks in the jellium curve at N values corresponding to half-filled shells (due to the spin population determined by Hund's rules). In real metal clusters the magnetism would be connected with the actual atomic arrangement and reduced from the jellium value.[10] The large magnetic moments of jellium clusters might then lead to overestimation of the spin effects. The jellium model can be refined by taking into account the difference in the spherically averaged pseudopotential between a real metal and jellium[9] or by using the (related) pseudojellium model.[11] These refinements would not change the qualitative size dependence of the polarizability and in the case of sodium also the change in the absolute values would be very small.

In conclusion, we have calculated the static electronic polarizability for sodium clusters using the jellium model and density-functional techniques. The results are in good agreement with the experimental results giving further support to the ideas that many electronic and structural properties of sodium clusters can be understood in terms of single-particle electron levels in a spherical effective potential.

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