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On the applicability of deformed jellium model to the description of metal clusters

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Abstract. This work is devoted to the elucidation the applicability of jellium model to the description of alkali cluster properties on the basis of comparison the jellium model results with those derived from experiment and within *ab initio* theoretical framework. On the basis of the Hartree-Fock and local-density approximation deformed jellium model we have calculated the binding energies per atom, ionization potentials, deformation parameters and the optimized values of the Wigner-Seitz radii for neutral and singly charged sodium clusters with the number of atoms $N \leq 20$. These characteristics are compared with the results derived from the *ab initio* all-electron simulations of cluster electronic and ionic structure based on the density functional theory as well as on the post Hartree-Fock perturbation theory on many-electron correlation interaction. The comparison performed demonstrates the great role of cluster shape deformations in the formation cluster properties and the quite reasonable level of applicability of the deformed jellium model.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 36.40.Mr Spectroscopy and geometrical structure of clusters

1 Introduction

During the last decade, investigation of the detailed structure and properties of small sodium clusters attracted a lot of attention (see, *e.g.*, [1–3] and references therein). With the discovery of electronic shell structure in free alkali clusters [4,5] the essential role of the quantized motion of delocalized valence electrons in the mean field created by ions in a cluster has been understood. Under different experimental conditions, the detailed ionic structure has been found not to affect the properties of alkali and other simple metal clusters very much (see, *e.g.*, [6–8] for review). This behavior suggests the validity of a jellium model, defined by a Hamiltonian which treats the electrons in the usual quantum mechanical way, but approximates the field of the ionic cores by treating them as a uniform positively charged background. This naturally leads to a description of the electron density in terms of single particle wave functions that extend over the entire cluster.

The jellium model provides a very useful basis for studying various collision processes, such as photabsorption, photoionization elastic and inelastic scattering, electron attachment, photon emission, atomic cluster fission process and others, involving metal clusters (see, *e.g.*, [1, 9–12] and references therein). As elucidated in the papers cited above, many-electron correlations are quite essential for the correct description of various characteristics of the cluster systems.

Structural properties of small metal clusters have been widely investigated using quantum chemistry *ab initio* methods. Here we refer to the papers [3,13–20], in which optimized geometries, binding energies, ionization potentials, electron structure and electron transport properties of small lithium and sodium clusters have been calculated.

In spite of the fact that both jellium model results and results of *ab initio* frameworks do exist in literature there have been performed no systematic comparison of the results of the two different theoretical schemes so far. In the present paper we demonstrate that such a comparison is rather illustrative and explains essential physical aspects of the formation of various cluster characteristics and properties. Comparison performed in our work demonstrates the great role of cluster deformations in the formation cluster properties and the quite reasonable level of applicability of the deformed jellium model.

We use the atomic system of units $\hbar = |e| = m_e = 1$ in this paper.

2 Numerical results and discussion

2.1 Cluster deformations

In the axially deformed jellium model clusters can either be spherical or have a shape of ellipsoid of

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revolution (spheroid) with principle diameters a and b. The spheroidal shape can be of the two types prolate or oblate, depending on the sign of the deformation parameter δ, which characterizes the families of the prolate ($\delta > 0$), and the oblate ($\delta < 0$) spheroids of equal volume $V_c = 4\pi ab^2/3 = 4\pi R^3/3$. The principle diameters a and b of the spheroid can be expressed as follows:

$$a = \left(\frac{2+\delta}{2-\delta}\right)^{2/3} R, \qquad b = \left(\frac{2-\delta}{2+\delta}\right)^{1/3} R. \tag{1}$$

$R = r_s N^{1/3}$ is the radius of an undeformed spherical cluster with N atoms, r_s is the Wigner-Seitz radius, which for the bulk sodium is equal to 4.0.

In the *ab initio* approach, the cluster shape is determined by the optimized coordinates of all the ions and it can be characterized by the tensor R_{ij}

$$R_{ij} = \sum x_i x_j. \tag{2}$$

Here, the summation is performed over all ions in the system. The principle values of this tensor R_{xx}, R_{yy} and R_{zz} define the dimensions R_x, R_y and R_z of the ionic charge distribution in the cluster along the principle axes x, y and z. Note that tensor R_{ij} is closely connected with the cluster moment of inertia tensor and the quadrupole moment tensor of the ionic distribution.

The tensor R_{ij} can also be defined for the jellium model. In this case, sum in (2) should be replaced by the integral and the integration to be performed over the homogeneous spheroidal distribution of the ionic density in the cluster. Then, the principal values of the tensor R_{ij} can easily be determined. The result of this calculation reads as

$$R_{xx} = R_{yy} = \frac{b^2}{5}N, \qquad R_{zz} = \frac{a^2}{5}N. \tag{3}$$

Here, a and b are the principle diameters of the spheroid defined in (1).

In Figure 1, we present the principle values R_{xx}, R_{yy} and R_{zz} calculated for the neutral sodium clusters with $N < 20$ in the framework of the deformed jellium model according to (3). The diameters a and b have been determined by minimizing the total cluster energy in the LDA approximation, using Gunnarsson and Lundqvist type of the exchange-correlation potential. The details of calculation are fully described in [21]. This calculation has been performed with optimized value of the Wigner-Seitz radius. The cluster energy minimization on Wiger-Seitz radius will be discussed in Section 2.4 in more detail. The LDA deformed jellium model results are shown in Figure 1 by the filled triangles. The filled triangles pointing up correspond to R_{xx}=R_{yy}, while those pointing down to R_{zz}. The opened triangles are the results of the all-electron *ab initio* framework derived in [3] with the use of the B3LYP density functional. The opened triangles pointing up and down show R_{xx} and R_{zz} respectively, while the opened triangles pointing right represent R_{yy}.

Figure 1 demonstrates rather good agreement of the jellium model and *ab initio* results. In most of the cases

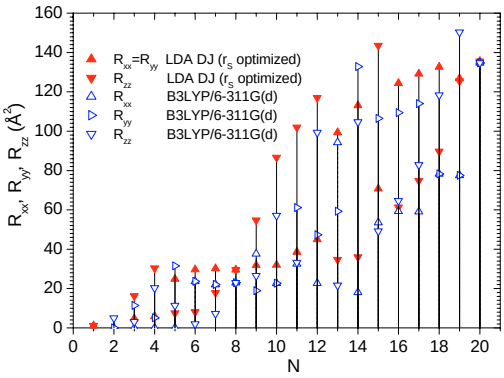

Fig. 1. The principal values of the tensor R_{ij} for neutral sodium clusters with optimization on Wigner-Seitz radius r_s as a function of cluster size calculated in the LDA deformed jellium (LDA DJ) model (filled triangles) and *ab initio* B3LYP framework [3] (opened triangles).

the jellium model predicts correctly the type of the dominant cluster deformation, prolate or oblate one. Of course, *ab initio* calculations include tri-axial deformations of the cluster, which turned out to be noticeable for the clusters with the open subshells and play important role for clusters like Na_{12}−Na_{14}, Na_{17}. The axially symmetric deformed jellium model does not take into account tri-axial deformations and thus in this case always $R_{xx} = R_{yy}$. The axially symmetric jellium model gives the wrong type of deformation in the open shell clusters, like Na_5, Na_{16}−Na_{19}. However, it is necessary to note that for all these clusters there are almost degenerate oblate and prolate isomers within the axially symmetric jellium model [21]. Thus, accounting for tri-axial deformations in these clusters plays the crucial role as it becomes clear from the comparison of the jellium and *ab initio* results.

For the magic clusters Na_8 and Na_{20}, the principle values $R_{xx} = R_{yy} = R_{zz}$ are almost identical in both approaches, which demonstrates the closeness to the sphericity of the *ab initio* magic cluster shapes.

2.2 Binding energies per atom

In this paper we calculate the dependence of binding energy per atom in the deformed jellium model and compare it with *ab initio* results from [3]. The binding energies per atom for the neutral and singly charged clusters are defined as follows:

$$E_b/N = E_1 - E_N/N \tag{4}$$

$$E_b^+/N = \left((N-1)E_1 + E_1^+ - E_N^+\right)/N, \tag{5}$$

where E_N and E_N^+ are the total energies of a neutral and singly-charged N-atomic jellium cluster respectively.

Figure 2 shows the dependence of the binding energy per atom for neutral (Fig. 2a) and singly charged (Fig. 2b) clusters as a function of cluster size calculated in the deformed jellium model. We compare the calculated dependences with the *ab initio* results from [3] obtained by the

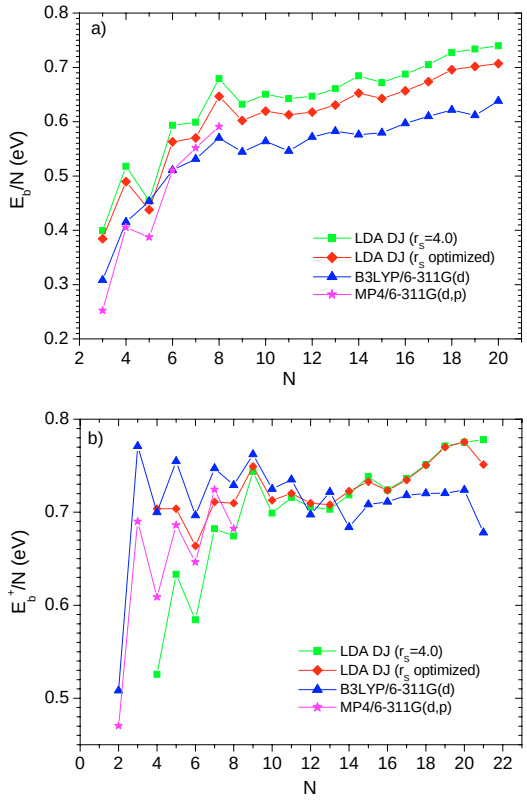

Fig. 2. Binding energy per atom for neutral (a) and singly charged (b) sodium clusters as a function of cluster size calculated in the LDA deformed jellium model and compared with *ab initio* B3LYP and MP4 results from [3].

B3LYP and MP4 methods. In Figure 2 we show the jellium model results obtained with bulk and optimized values of the Wigner-Seitz radius. It is seen that the cluster optimization on the Wigner-Seitz radius brings the cluster energies down and makes them closer to the *ab initio* results.

Figure 2 demonstrates that the general trend of the curves calculated within the jellium framework turns out to be very close to the one obtained from the *ab initio* calculation. The similarity of the the jellium and *ab initio* curves is higher for $N \leq 10$. In the region $10 \leq N \leq 20$ small discrepancy in the behaviour of the curves can be attributed to the tri-axial cluster deformations taken into account in the *ab initio* approach and omitted in the axially symmetric jellium model.

Note that the jellium model results for both neutral and singly charged sodium clusters are somewhat closer to the predictions of the MP4 method. This method is based on the accounting of the many-electron correlations up to the fourth order of the perturbation theory and is free of any adjustable parameters.

Figure 2 demonstrates that in spite of the simplicity, the jellium model turns out to be rather reliable approximation able to reproduce reasonably well the dependence of binding energy per atom for both neutral and singly charged sodium clusters.

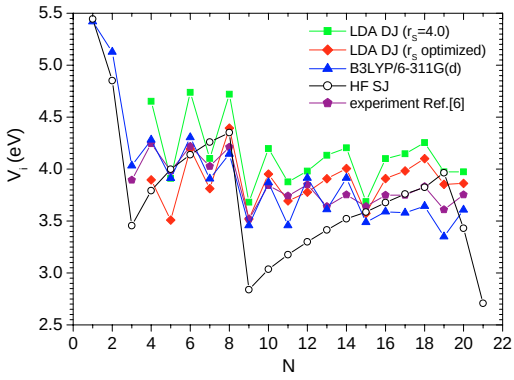

Fig. 3. Ionization potentials of neutral sodium clusters calculated in the LDA deformed jellium model and compared with Hartree-Fock spherical jellium model, *ab initio* results from [3] and with experiment [6].

2.3 Ionization potentials

Another important characteristic of the cluster system is its ionization potential. The ionization potential is determined by the energy needed to take an electron out of the cluster. It is equal to:

$$V_i = E_N^+ - E_N \tag{6}$$

In Figure 3, we present the ionization potential of neutral sodium clusters calculated within the jellium model as a function of cluster size. We compare the jellium model results with those obtained in [3] using *ab initio* theoretical framework and with the available experimental data [6]. This comparison demonstrates that the jellium model reproduces correctly most of the essential features of the ionization potential dependence on N. Some discrepancy, like in the region $11 \leq N \leq 14$, can be attributed to the neglection of the tri-axial deformation in the axially symmetric jellium model.

In spite of the fact that *ab initio* results are closer to the experimental points, one can state quite satisfactory agreement of the jellium model results with the experimental data, which illustrates correctness of the jellium model assumptions and its applicability to the description of sodium clusters.

Figure 3 also demonstrates the role of cluster deformations on the formation of the odd-even oscillations in the dependence of the cluster ionization potential on N. Indeed, for spherically symmetric clusters this dependence turns out to be monotonous within the range of the given shell contrary to the experimental observations. Allowing for the cluster deformation and introducing a single deformation parameter δ, we have achieved much better agreement of theoretical results with the experimental data as it is clear from Figure 3.

2.4 Wigner-Seitz radius variation

Calculations of the cluster total energy are usually performed at the certain value of the Wigner-Seitz radius r_s.

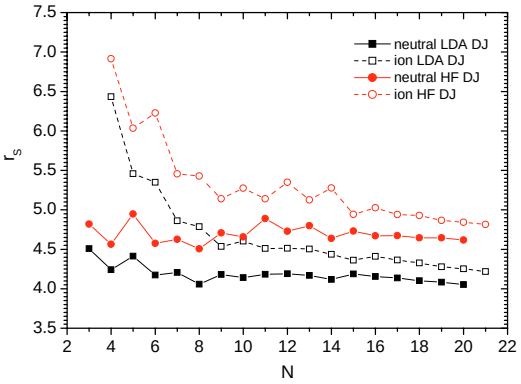

Fig. 4. Optimized Wigner-Seitz radii for neutral and singly charged sodium clusters calculated as a function of cluster size in the HF and LDA deformed jellium models.

The bulk value of the Wigner-Seitz radius for sodium is equal to 4.0. However, one can also perform the calculation minimizing the total cluster energy by variation of the Wigner-Seitz radius.

Figure 4 demonstrates the dependence of the optimized Wigner-Seitz radii on cluster size calculated for neutral and singly charged sodium clusters within the HF and LDA approximations. This figure shows that the alteration of the optimized r_s values is much larger for the cluster ions as compared to the neutral clusters. For neutral clusters, the optimized values are somewhat larger than the bulk value $r_s = 4.0$ in both LDA and HF approximations. The LDA dependence goes closer to the bulk limit. With increasing N this dependence approaches the bulk limit, being very close to it also for the magic numbers $N = 8$ and $N = 20$, which is another manifestation of the shell effect.

3 Conclusion

In this paper we performed systematic calculation of various characteristics of neutral and singly charged sodium clusters with $N \leq 20$ on the basis of the HF and LDA deformed jellium models. We compared the results of our calculations with the *ab initio* results obtained in [3] and with the available experimental data. From these comparisons, we have established the level of applicability of the jellium model to the description of various cluster characteristics. Our consideration shows that the deformed jellium model provides qualitatively correct description of the sodium clusters and their ions. The quantitatively reliable results with the accuracy below than 10 per cent one can expect from the jellium model description providing one allows for the tri-axial cluster deformations. We have performed our calculations for sodium clusters. However, most of the conclusions should be applicable to other alkali clusters, potassium for example. The level of applicability of the jellium approach to other metals, like alkali-earth, requires a separate careful consideration.

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