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IONIC AND ELECTRONIC PROPERTIES OF SODIUM CLUSTERS

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ABSTRACT

The Cylindrically Averaged Pseudopotential Scheme (CAPS) is used within the local density approximation to study the ground-state ionic and electronic properties of sodium clusters. In this approach calculations were carried out for the bond length of dimer, the total energies, binding energies per atom, as well as volume and surface energies of sodium clusters. The results obtained compare very well with the ones obtained from quantum chemical methods, distance-dependent Huckel type model and car Parrinello method who used full three dimensional approach.

INTRODUCTION

The study of metal clusters had attracted keen interest in recent years due to its relevance in catalysis and chemisorption. The metal clusters are used for studying transition form the atom to the metal. Presently, bimetallic clusters are used as catalysis for the conversion of automobile exhausts to non-toxic gas and refinement of crude oil in the petroleum industry. For this purpose many models had been used for the study of clusters and theoretical results obtained are compared with the various experimental values provided by the development of the molecular beam techniques. In this regard therefore, alkali metals with one electron per atom are particularly studied as prototypes of metal clusters.

In the theory of alkali metals clusters, the jellium model [1,2] was a very unique technique for the determination of the properties of clusters with sizes n = 2 – 2000. In this jellium model, all emphasis are based on the electron structure whereas the ionic background is treated as a smooth positive charge distribution [3]. Here, the interaction between electrons and ion is included by an external potential. According to the jellium model, the exact localization of nuclei is not important in explaining the electronic properties of alkali clusters due to the large screening. Nevertheless, major goals of the jellium model are the understanding of the magic numbers and in the prediction of the shell structure [2,4]. Despite the success recorded by using the jellium model in explaining the electronic properties of simple metal clusters, some properties calculated with the jellium assumption did not always fall in close quantitative agreement with accurately measured properties when these were available, for instance, with regard to ionization potentials [5]. The failure of the jellium model in this regard is due to neglect of information on the ionic structure. On the other hand, the quantum chemical methods which provide more realistic results are very elaborate and limit the range of applicability to small clusters. Thus, there was need to bridge the gap between both methods. In the effort to bridge this gap, there arose some extensions which added some average ionic structure information to the jellium model thus giving self-consistent dynamics also to the

jellium background [6-7]. With large clusters in mind, Inigueze and co-workers [8] introduced granularity of the ions by using pseudopotential to describe electron – ion interaction, although the method made several drastic approximations concerning the net external pseudopotential in order to simplify the solution of the Kohn-Sham equations for large clusters. In this way, Inigueze and co-workers [9] arrived at the Spherically Averaged. Pseudopotential Scheme (SAPS). Despite this simplification, the SAPS method goes a long way beyond the jellium model, since SAPS potential is less smooth than the extra potential of the spherical jellium model. In the next year, Perdew and co-workers [9] added the average effect of the ionic structure to the mean field and the Madelung energy for the ionic bulk was taken into account in order to obtain the correct total energy in the volume. This approach gave rise to the Stabilized Jelluim Model (SJM). A few years later, Montag and Reinhard [10] included average ionic structure information into the jellium model by introducing the average ionic effect on the electronic mean field potential and the ionic modeling energy of the bulk. This is Structure Averaged Jellium Model (SAJM). Recently, Montag and Reinhard [11] considered the pseudopotential for the ionic cores and valence electrons in a metal by treating the ions in three dimensions and the electrons restricted to axial symmetry. This gave rise to the Cylindrically Averaged Pseudopotential Scheme (CAPS). More recently, Kummel and co-workers [12] calculated in a self-consistent manner, with the ionic structure and the photo absorption spectra of medium-size sodium clusters beyond Na-20. In this case, the ionic positions are optimized by simulated annealing in a Monte Carlo approach.

In this paper, the Cylindrically Averaged Pseudopotential Scheme (CAPS) is used to study the ground state properties of sodium cluster. The results obtained will be compared with the quantum chemical calculations [13 – 15], from Car-Parrinello calculations [16], and from a distance –dependent Huckel type model [17] where full three-dimensional results are displayed. The outline of the paper is as follows. Section II will provide a brief theory of CAPS formalism. The result will be displayed in section III and the attendant conclusion drawn in section IV.

II FORMALISM

In the Density functional approach, the ground state energy for the valence electrons with pseudopotentials for the electron-ion interaction is expressed in the form.

$$E_{tot}\left(\rho_{el}, R_{i\in\{1,\ldots N\}}\right) = T\left[\rho_{el}\right] + E_{xc}\left[\rho_{el}\right] + \frac{1}{2}e^2\int d^3r\int d^3r'\frac{\rho_{el}(r)\rho_{el}(r')}{|r-r'|}$$

$$+\sum_{i=1}^{N}\int d^3r\,\rho_{el}(r)\,V_{ps}\left(|r-R_i|\right) + \frac{1}{2}Z^2e^2\sum_{i=1}^{N}\sum_{j\neq i=1}^{N}\frac{1}{|R_i-R_j|} \qquad (1)$$

where ρ_{el} is the density of the valence electron, R_i, i = 1, ..., N describes the ionic positions and $V_{ps}(|r-R_i|)$ is the local pseudopotential which corresponds to the total ionic potential $V_{ion}(r, R_{i\in\{1,\ldots,N\}})$.

In the CAPS approach, the treatment of the electrons is reduced to axial symmetry using the cylindrical coordinates (ρ,z). Thus the cylindrical average of the pseudopotential seen by the electrons is of the form

$$V_{ps}(z,\rho;z_i,\rho_i)=\frac{1}{2\pi}\int_0^{2\pi} d\varphi V_{ps}(|r-R_i|) \tag{2}$$

Now the total energy is thus approximated by

$$E_{tot}(\rho_{el}, R_{i\in\{1,\ldots N\}}) \approx T[\rho_{el}(z,\rho)]+E_{xc}[\rho_{el}(z,\rho)]+E_{con}[\rho_{el}(z,\rho)]$$
$$+2\pi\sum_{i=i}^{N}\int dz\int d\rho\rho\rho_{el}(z,\rho)\,V_{ps}(z,\rho;z_i,\rho_i)+\frac{1}{2}Z^2e^2\sum_{i=i}^{N}\sum_{j\neq i=i}^{N}\left|\frac{1}{R_i-R_j}\right| \tag{3}$$

Eqn (3) constitutes the energy functional of the Cylindrically Averaged Pseudopotential Scheme (CAPS). Here we use the exchange and correlation energy density functional of Gunnarsson and Lundqvist [18].

The ground state of a cluster is found by solving the variational equations:

$$\frac{\delta E_{tot}}{\delta\varphi}=0, \qquad \frac{\partial E_{tot}}{\partial R_i}=0 \tag{4}$$

The variation with respect to the electron wave-functions yields the Kohn-Sham equations in the pseudopotential field of ions and the variation with respect to the ionic positions yields classical stationary conditions for the ions. The Kohn-Sham equations are solved on an axial coordinate space grid.

Since we are dealing with valence electrons, we have to employ pseudopotentials for the individual ionic potentials [19]. For simple metals, one may use the local pseudopotential, for instance, Ashcroft's empty core pseudopotential [20]

$$V_{Ash}=-\frac{Ze^2}{r}\theta(r-r_c) \tag{5}$$

And its strength becomes

$$S_{Ash} = \int d^3r \frac{Ze^2}{r}\theta(r_c - r) = 2\pi Ze^2 r_c^2 \tag{6}$$

Here, r_c is the core radius and Z the effective ionic charge. The core radius is to be adjusted such that the Wigner-Seitz radius r_s of a given bulk metal is reproduced by the equilibrium point of the energy functional in equation (1). The value of the strength of the Ashcroft empty core pseudopotential is chosen in order to reproduce the experimental value of r_s, namely

$$\frac{\partial E_{tot}}{\partial r_s}\Big|_{r_s=3.96} = 0 \tag{7}$$

Accordingly, from eqn (6), we get

$$r_c^2 = \frac{Z^{2/3} r_s^2}{5} + \frac{1}{6}\left(\frac{9}{4\pi^2}\right)^{1/3} r_s^2 - \frac{2}{15e^2}\frac{\hbar^2}{2m}\left(\frac{9\pi}{4}\right)^{2/3} r_s + \frac{2r_s^4}{9e^2}\frac{\partial \varepsilon_c}{\partial r_s}\left(\rho_{el}(r)\right)\Big|_{r_s=3.96} \tag{8}$$

Solving eqn (8) gives r_c as 1.76 a.u.

The local pseudopotential is generated by the ionic charge distribution via Poisson's equation of the form

$$\rho_{ps}(r) = \frac{\Delta V_{ps}(r)}{4\pi e^2} \tag{9}$$

By expressing the ionic charge distribution in the form

$$\rho_{ps}(r) = (\rho_1 - \rho_2)\theta(r_1 - r) + \rho_2\theta(r_2 - r) \tag{10}$$

And using the parameters ρ_1, ρ_2, r_1, and r_2 we arrive at the local pseudopotential of the form

$$V_{ps}(r) = e^2 \begin{cases} \frac{2\pi}{3}\rho_1 r^2 + C_1 & r < r_1 \\ \frac{4\pi(\rho_1 - \rho_2)r_1^3}{3r} + \frac{2\pi}{3}\rho_2 r^2 + C_2 & r_1 \le r < r_2 \\ -\frac{Z}{r} & r \ge r_2 \end{cases} \quad (11)$$

Where

$$C_1 = -2\pi(\rho_1 - \rho_2)r_1^2 + C_2 \quad (12)$$

and

$$C_2 = \frac{4\pi(\rho_1 - \rho_2)r_1^3 - Z}{3r_2} - \frac{2\pi}{3}\rho_2 r_2^2 \quad (13)$$

The most essential feature of the pseudopotential is its total strength S_{ps} which is defined as the volume integral over its non-coulomb part, namely,

$$S_{ps} = \int d^3r \left(V_{ps} + \frac{Ze^2}{r} \right) \quad (14)$$

The constraint for the correct strength S_{ps} and the conservation of charge eliminates ρ_1 and ρ_2 in the form

$$\rho_1 = \frac{3}{4\pi r_1^3 (r_1^2 - r_2^2)} \left[Z r_2^2 \left(\frac{r_1^5}{r_2^5} - 1 \right) + \frac{5S_{ps}}{2\pi e^2} \left(1 - \frac{r_1^3}{r_2^3} \right) \right]$$

$$= \frac{3Z}{4\pi r_1^3} - \frac{r_2^3 - r_1^3}{r_1^3}\rho_2 \quad (15)$$

And

$$\rho_2 = -\frac{3}{4\pi r_2^3 (r_1^2 - r_2^2)} \left[Z r_1^2 - \frac{5S_{ps}}{2\pi e^2} \right]$$

$$= \frac{3Z}{4\pi r_2^3} \quad \frac{5r_c^2 - r_1^2}{r_2^2 - r_1^2} \quad (16)$$

Having known all the parameters except r_1 and r_2 the pseudopotential is related to the choice of both matching radii. Accordingly, we have chosen our pseudopotential by taking $r_1 = 1.15a_0$ and $r_2 = 3.85a_0$ which are below r_s.

The solution of the ground-state equations proceeds in an interlaced iteration of the Kohn-Sham and the ionic stationarity conditions. The Kohn Sham equations are solved by a damped gradient iteration [21]. The ionic configuration is iterated with a simulated annealing technique using a Metropolis Algorithm.

III RESULTS

The bond length of dimer Na_2 obtained from the present work is $5.8a_0$ which is compared with other previous theoretical and experimental values displayed in Table 1. It is found that the present result perfectly agrees with the experimental value [22]. However, the results obtained by Martins and co-workers [22] using DFT calculations and results from CAPS [11] under estimate the bond length of dimer. It is interesting to observe that the present result is also better than the results obtained from quantum chemical calculation [14], Car-Parrinello calculations [16] and the distance –dependent Huckel type model [17] where full three dimensional treatment were used.

In Fig. 1, the present total energies of Na_N cluster compare favorably with the previous theoretical result by Poteau and Spiegelmann [17] who employed Monte Carlo ensemble growth method (MCGM) algorithm to a systematic investigation of the low energy isomers for sodium clusters. In addition, our present total energy for Na_{18} agrees very well with the results of extensive computer simulation using the Car-Parrinello method [16].

The binding energies per atom

$$\frac{E(N)}{N} = E(1) - \frac{E(N)}{N} \tag{17}$$

are plotted in Fig 2 for the ground state structures and compared with previous results. It is seen that present results follow the trend of the results obtained in *ab initio* calculations [13] in the topological Huckel model [24] and the distance-dependent extension of the Huckel model [17]. Our results are very close to the results reported by Spiegelmann and Pavolini [25] for $N \leq 6$, but with values higher than results reported by Bonacic-Kontecky and co-workers [24] who used smaller basis set and excluded the core-valence correlation effects. The binding energies obtained by DFT [16,26] are systematically larger than other calculate values, and exhibit a quicker increase towards the bulk value. Again, our result perfectly agrees with the experimental value for the dimer [27].

The binding energy of finite clusters can be parameterized in the Liquid Drop Model (LDM) as

$$E(N) \approx \epsilon_{bulk} N + \sigma 4\pi r_s^2 N^{\frac{2}{3}} \tag{18}$$

Where ϵ_{bulk} is the binding energy per atom in the bulk and σ the surface energy. This means that $E(N)-\epsilon_{bulk}\ \alpha N^{-1/3}$. Therefore, we use this trend in the total binding energies to explain the asymptotic to bulk like behaviour with increasing particle number. Accordingly, eqn (18) can be expressed in the form

$$\frac{E(N)}{N} \approx a_v + a_s N^{-\frac{1}{3}} \tag{19}$$

Where the first two terms of the expansion define the volume and surface energies. The coefficient for the volume energy, a_v, is just the binding energy per valence electron in the bulk and the surface energy, α_s, is related to the surface tension σ in the form

$$\alpha_s = 4\pi r_s^2 \sigma \tag{20}$$

In fig 3, the total energies per valence electron of the neutral sodium clusters with even N are plotted versus $N_{el}^{-1/3}$. The results for α_v and a_s are displayed in table 2. The deduced volume energy agrees with CAPS [11] and the value obtained in bulk matter by using the Thomas-Fermi model in the Atomic - Sphere - Approximation (TF-ASA) with the same S_{ps} [10]. Again the deduced surface energy from the present work agrees with CAPS [11] and the experimental bulk surface energy obtained by using the zero-temperature-extrapolation of the surface tension [28].

IV CONCLUSION

The present work has consistently incorporated ionic structure information within the local density approximation in the investigation of the ground state properties of the electronic structure of Na_N clusters with even numbers of atoms, up to N = 40. The present result for the bond length of dimer now provides excellent agreement with experimental value. Our present total energy for Na_{18} compares very well with the result obtained with MD simulation and present total energies favorably compare with previous results from Monte Carlo Growth Method. Furthermore, our present results compare well with the binding energies per atom obtained by several workers who used distance-dependent Huckel type model, quantum chemical and Car-Parrinello methods where full three dimensional treatment were used. Finally, our results for volume and surface energies compare favorably with previous values.

TABLE 1 :Bond length of dimer Na_2 (in a_0)

CAPS (MR) ref. 11	DFT (MBC) ref. 23	DFT (RA) ref. 16	DDHM O (PS) ref. 17	ECP-CT(BFK) ref. 14	Expt ref. 22	Present work
5.56	5.5	5.56/5.68	5.9	6.1	5.8	5.8

TABLE 2 : The volume energy a_v and surface energy a_s of Na

Coeff	Method	Value (Ryd)
a_v	Present work	-0.4630
	CAPS [11]	-0.4702
	TF – ASA [10]	-0.4708
a_s	Present work	0.0588
	CAPS [11]	0.0634
	Bulk (Expt) [28]	0.0669

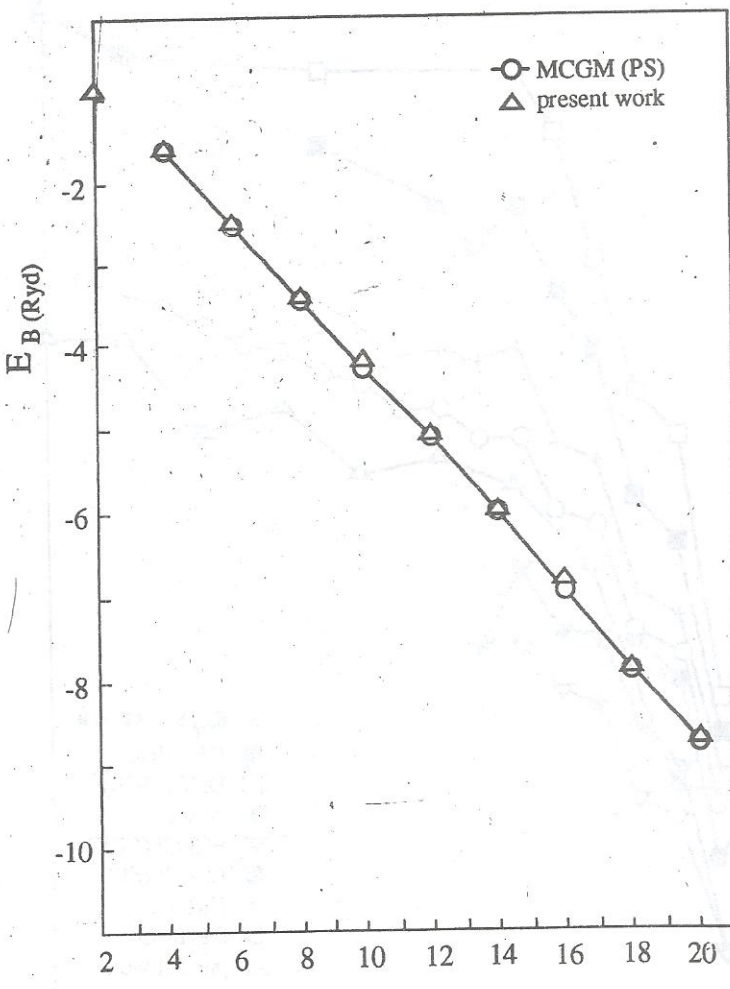

Fig 1: Total energies versus cluster size N.

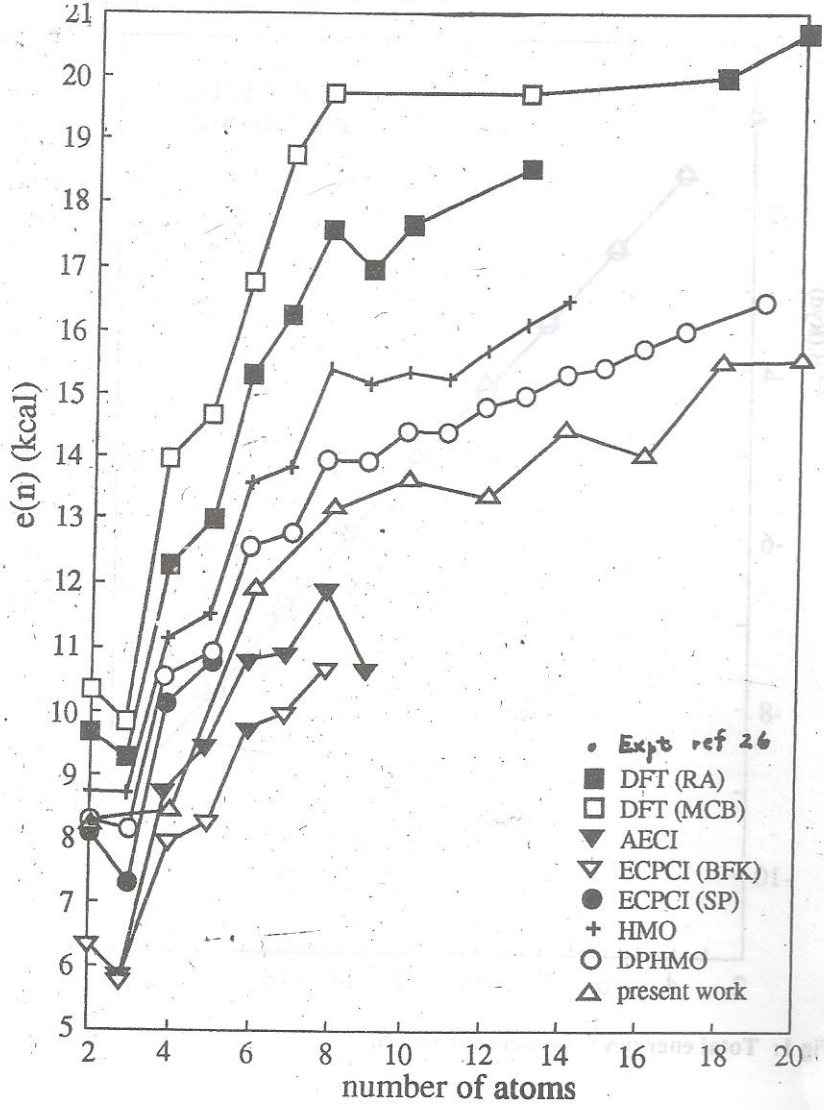

Fig 2: Binding energies per atom versus cluster size N.

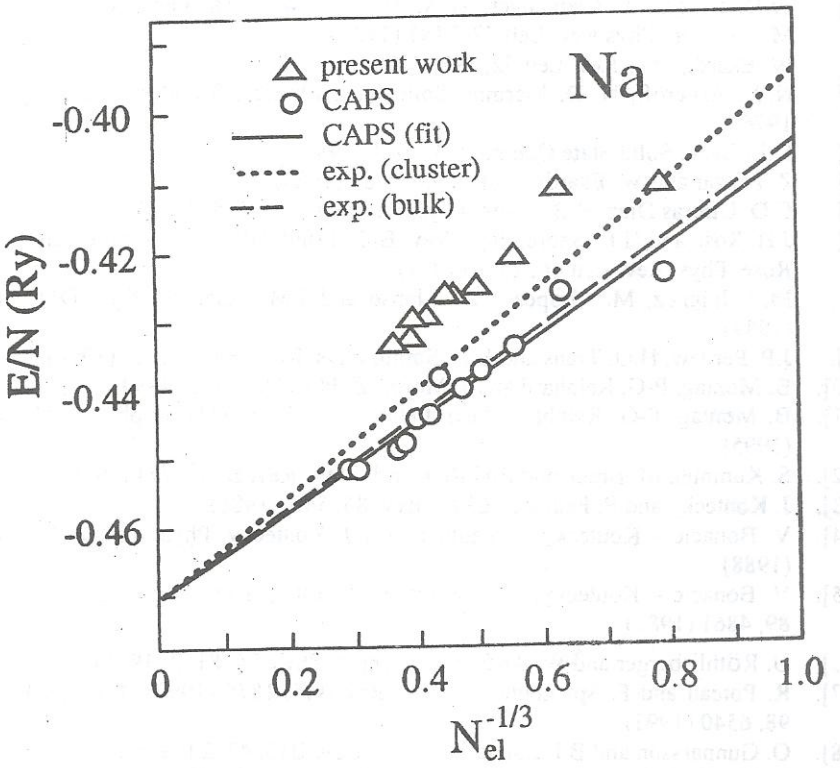

Fig 3: total energies per valence electron versus $N^{-1/3}$

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