

## Electronic properties of Sodium clusters in spherical Jellium model

C. A. Madu and B. N. Onwuagba

Department of Physics  
Federal University of Technology, Owerri, Nigeria.

### Abstract

We have investigated a wide range of electronic properties for Na clusters of sizes between 2 and 36 with  $r_s = 3.93a.u$  using first-principles local spin density functional calculations. The Kohn-Sham single particle equations were solved self-consistently on a one-dimensional mesh according to Herman and Skilman's scheme. The Coulombic part of the energy is obtained by solving Poisson equation while Gunnarsson and Lundqvist parameterization technique was adopted in the calculation of the exchange-correlation energy density and potential. The studies were carried out in the spherical Jellium model approach. Peaks occurred at the magic numbers that correspond to the complete filling of the shells which explain the prominent role played by the kinetic energy of the Kohn-Sham independent electrons in the determination of the relatively greater stability at the magic numbers. The results compared favourably with previous experimental and theoretical values.

pp 267 - 274

### 1.0 Introduction

Clusters are midway between molecules and solids. Materials clusters display unique physical and chemical properties which are functions of cluster size, state of aggregation and composition. In the past few years, researchers have worked extensively on clusters because of their usefulness in the production of thin films and applications in catalysis and chemisorptions. Most calculations on the structural and electronic properties of simple metal clusters have been performed only for clusters with small numbers of atoms [1, 2].

Clusters with certain number of atoms have been found to be more abundant. These numbers are referred to as magic number [3]. For simple metal clusters, Knight and associates [4] found the particular stability and abundance of clusters with 8, 20, 40, 58 and 92 electrons. Stability of clusters can also be got from studies of ionization potentials [3] and the polarizabilities [5] of clusters. The existence of magic clusters has been explained using different physical factors. For noble gas clusters, it has been attributed to the geometrical sphere-packing [6], for semiconductor cluster to the micro-crystal model [7], while magic clusters appear in alkaline metals because of the existence of electronic shell structure [4].

Recently, a lot of work has been reported on cluster studies. Arvati et al [8] studied the ground-state properties of sodium micro-clusters with up to 138 atoms within the framework of the density functional theory. They used the spherical jellium model to calculate the cluster cohesive energy and the fragmentation channels with a view to providing a deeper understand of the mechanisms leading to the magic number clusters. Onwuagba [9] used the local spin density approximation in the density functional calculation of the stability of noble metal clusters within the context of a jellium-like model for neutral Ag cluster he obtained the binding energy to be about one fifth the dissociation energy. In addition, the results he obtained in the ionization potentials. For neutral Ag cluster and in the cluster abundance for the neutral Ag and singly charged  $Ag^+$  and  $Cu^+$  clusters provided useful information for the understanding of the enhanced stability of these noble metal clusters.

In this work the spherical jellium model of a metal in which N cluster ions are replaced by a uniform, rigid and spherical background of positive charge is used in the calculation of the binding energy, relative binding energy and ionization potential of neutral sodium cluster in the framework of the local spin density approximation (LASDA) of the density functional theory (DFT) [10]. The Kohn-Sham single particle equations [11] were solved self consistently on a one dimensional mesh according to Herman and Skilman's scheme,



The paper is organized as follows: Section 2 outlines the formalism used. In section 3, the results are presented and discussed. Finally, conclusions are given in Section 4.

## 2.0 Formalism

An efficient and accurate scheme for solving the many electron problem of a crystal (with nuclei at fixed positions) is the local spin density approximation (LSDA) within density functional theory (DFT) [10, 11]. The key quantities in the LSDA OF DFT are spin densities  $n_{\sigma}(r)$ .

According to the spherical jellium model, the positive density of a charged sphere  $n^{+}$  is assumed to be the same as the electron density,  $n^{-}$  is the bulk, that is

$$n^{+} = \left(\frac{4}{3}\pi r_s^3\right)^{-1} \quad (2.1)$$

within the sphere, where  $r_s$  is the bulk Wigner-Seitz radius for the electron system. The radius  $R$  of a jellium sphere with  $Z$  total valence electrons is

$$R = Z^{1/3} r_s \quad (2.2)$$

In the density functional formalism, the Kohn-Sham single particle equations which are solved self-consistently to obtain the kinetic part of the total energy is in the form

$$\left[-\frac{1}{2}\nabla^2 + \nabla\sigma_{eff}(r)\right]\psi_{i\sigma}(r) = \varepsilon_i\psi_{i\sigma}(r) \quad (2.3)$$

Atomic Rydberg units  $\left(\hbar = 2m_e = \frac{e^2}{2} = 1\right)$  are used throughout. In equation (2.3),  $V_{eff}(r)$  is the spherically symmetric one particle effective potential written as

$$V_{eff}(r) = V_{ext}(r) + \int d^3r' \frac{n(r')}{|r-r'|} + \frac{\delta E_{xc}[n\uparrow, n\downarrow]}{\delta n_{\sigma}(r)} \quad (2.4)$$

where the external potential due to the homogeneously charged sphere is given by

$$V_{ext}(r) = \begin{cases} -\frac{N}{r}, & r > R \\ \left[-\frac{3N}{2R^3} \left(R^2 - \frac{r^2}{3}\right)\right], & r \leq R \end{cases} \quad (2.5)$$

$E_{xc}[n\uparrow, n\downarrow]$ , the exchange correlation energy in the local spin density approximation is expressed as

$$E_{xc}[n\uparrow, n\downarrow] = \int d^3r n_{\sigma}(r) E_{xc}[n\uparrow(r), n\downarrow(r)] \quad (2.6)$$

$n_{\sigma}(r)$  is the total spin density of the system,

$$n_{\sigma}(r) = (n\uparrow)(r), n\downarrow(r) \quad (2.7)$$

The groundstate total energy can be minimized by means of the variational principle by introducing the orbitals  $\psi_{ik}^{\sigma}$  constrained to construct the spin densities as

$$n_{\sigma}(r) = \sum_{\zeta k} n_{ik}^{\sigma} |\psi_{ik}^{\sigma}(r)|^2 \quad (2.8)$$



with  $n_{ik}^\sigma$  as occupation numbers such that  $0 \leq n_{ik}^\sigma \leq \frac{1}{\omega_k}$ , where  $\omega_k$  is the symmetry required weight of point  $k$ .

The Kohn-Sham equations are then solved self-consistently is an iterative process on a one-dimensional mesh according to the Herman and Skilman's scheme [12]. The Coulombic part of the equation is obtained by solving the Poisson equation on the same mesh point while Gunnarsson and Lundqvist [13] parameterization technique was adopted in the calculation of the exchange-correlation energy density and potential.

The total energies of the spherical jellium model are the calculated with the expression

$$E_{\text{tot}}^{SJM} = T_S [N_\sigma] + \int V_{\text{ext}}(r) n_\sigma d^3r + \frac{1}{2} \int \frac{n_\sigma(r) n_\sigma(r')}{|r-r'|} d^3r d^3r' + \int d^3r n_\sigma(r) \epsilon_{xc} [n_\sigma(r)] + \frac{3(Ne)^2}{5R} \quad (2.9)$$

### 3.0 Results

In this paper we report the results of calculations for the electronic properties of neutral sodium clusters with  $2 \leq n \leq 36$ . We used a spherical jellium model in which the ionic charges are smeared out in a uniform positive background in the framework of the local spin-density approximation of the density functional theory to calculate the groundstate total energies of sodium cluster.

On their own, these values of total energies have no physical meaning because of the lack of detailed information about the core electrons. But from the total energy we calculated the binding energy  $E_B$  from the relation.

$$E_B = E_{\text{tot}}(1) - \frac{E_{\text{tot}}(N)}{N} \quad (3.1)$$

While by comparing  $E(N)$  with  $E(N-1)$  and  $E(N)+1$  we got the relative binding energy change  $\Delta N$ , that is

$$\Delta N = E_{\text{tot}}(N+1) + E_{\text{tot}}(N-1) - 2E_{\text{tot}}(N) \quad (3.2)$$

The energy difference between the groundstates of the neutral and ionized cluster yields the ionization potential  $\phi$ . Thus

$$\phi = E_{gs}^{N-1} - E_{gs}^N \quad (3.3)$$

where  $E_{gs}^{N-1}$  is the groundstate energy of the ionized cluster and  $E_{gs}^N$  is the groundstate energy of the neutral  $N$ -electron clusters. These results are displayed in Figures 1 to 4.

In Figure 1, the total energy per atom is plotted as a function of cluster size. Dips are observed at  $N = 2, 3, 8, 13, 20$  and  $34$ . While these kinks are prominent in  $N = 2$  and  $8$ , they are very slight as  $N$  increases. The minima at  $N = 2, 8, 20, 34$  correspond to a complete filling of the shell  $1s, 1p, 2s$  and  $1f$ . The dips at  $N = 5$  and  $13$  correspond to the half-filled shell numbers.

In Figure 2, where the binding energy is plotted against number of clusters, the value  $E_B$  is found to be positive for all cluster sizes. Peaks are seen at  $N = 8, 13, 20$  and  $34$ , this compares favourably well in the region  $2 \leq N \leq 10$  with the work by Arvati et al [8].

Figure 3 shows variation of relative binding energy change with cluster size. Peaks are observed at  $N = 2, 5, 8, 13, 18,$  and  $20$ . The peaks at  $N = 8, 18$  and  $20$  correspond to the magic numbers which can be explained as being due to the closing of electronic shells. The peak at  $N = 5$  and  $13$  correspond to the half-filled shell numbers because of high spin configuration. The peak is highest at  $N = 8$ . The results are in agreement with previous results by De Heer et al [3].

The graph of ionization potential versus number of atoms per cluster is shown in Figure 4. The dimer has the highest ionization potential. Prominent peaks are observed at  $N = 5, 8, 13, 18$  and  $27$ . The saw teeth pattern of the plot is as observed by Arvati et al [8].

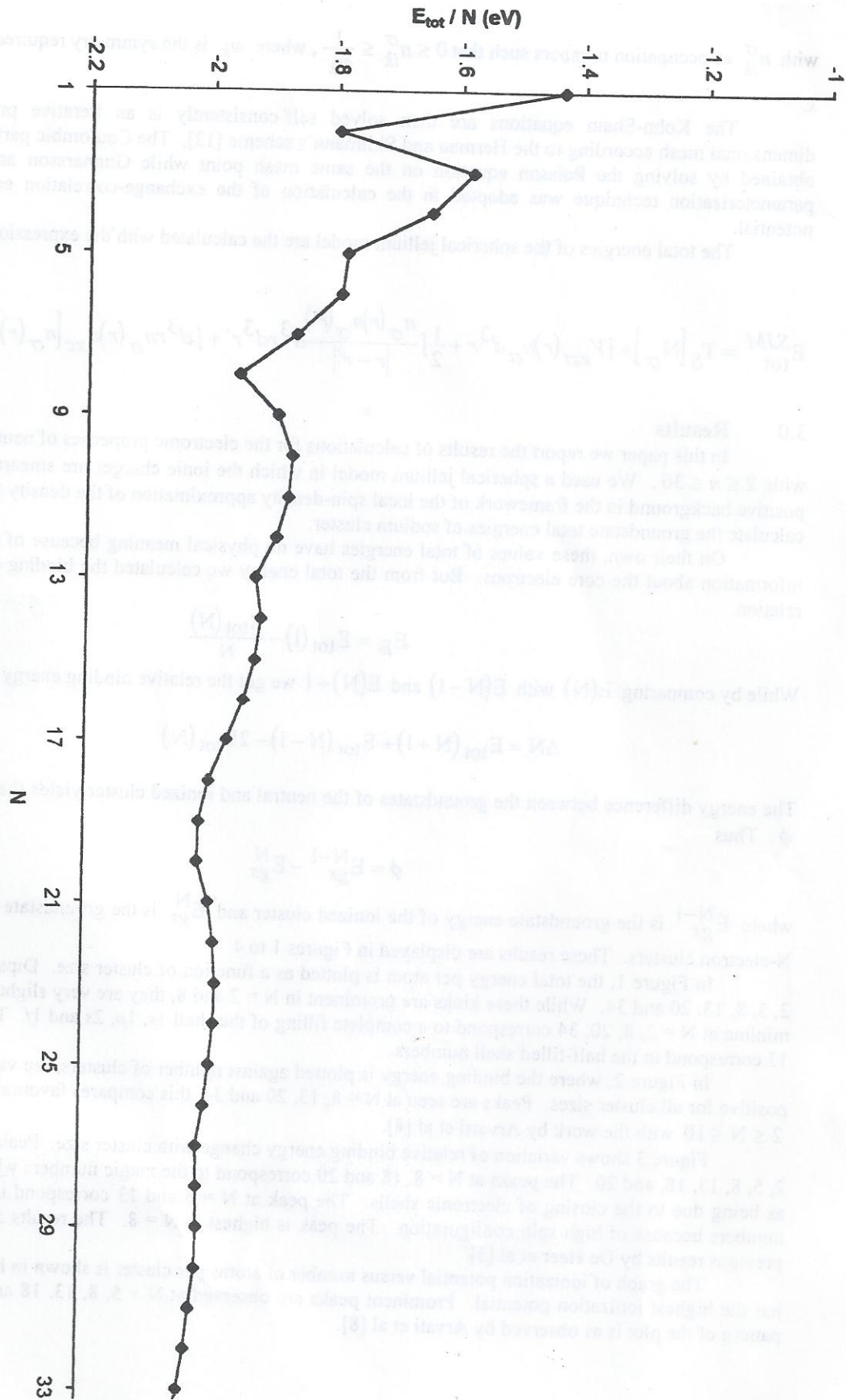


Fig 1: The total energy per atom in neutral sodium cluster as a function of number of atoms, N.



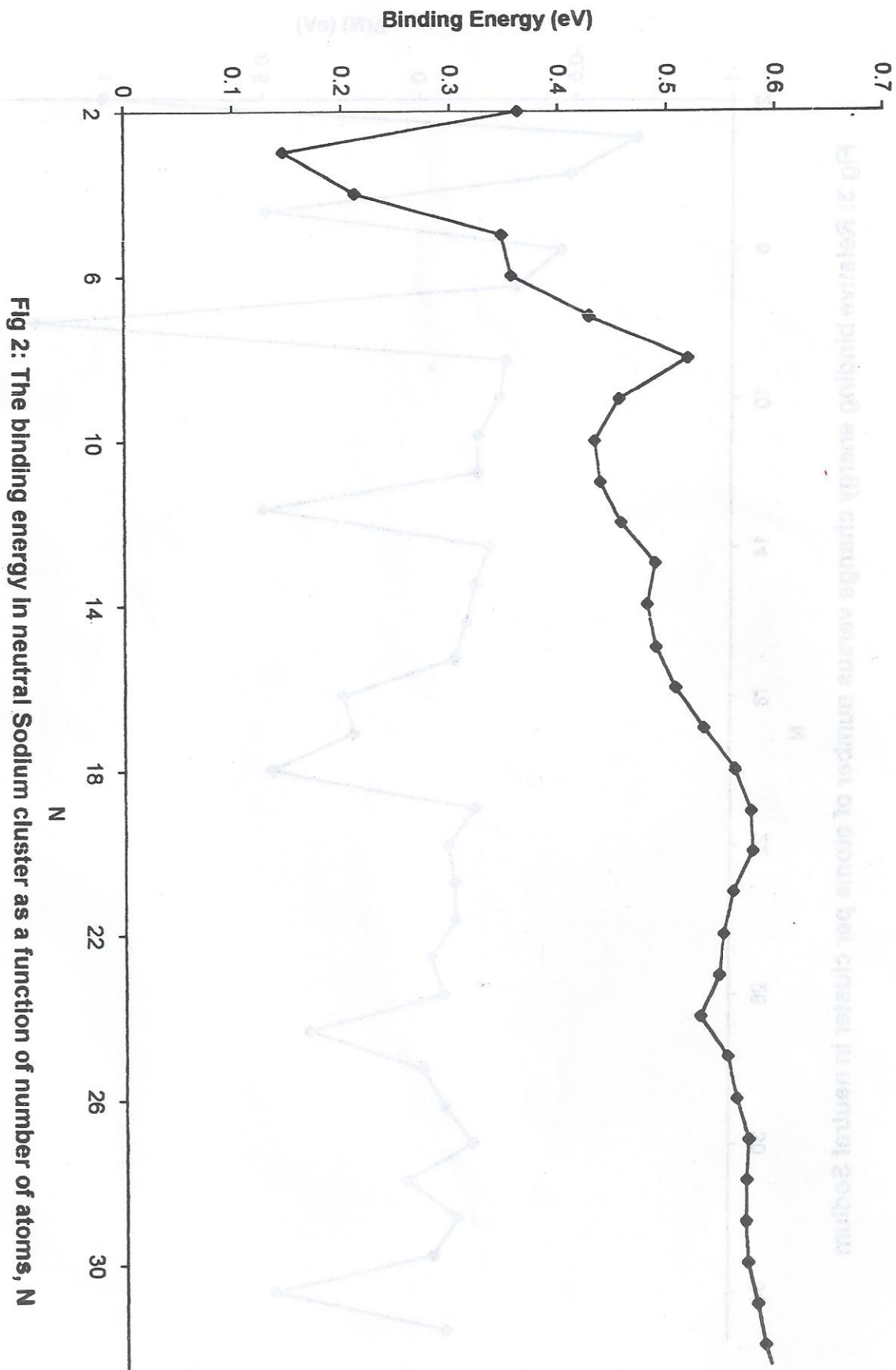


Fig 2: The binding energy in neutral Sodium cluster as a function of number of atoms, N

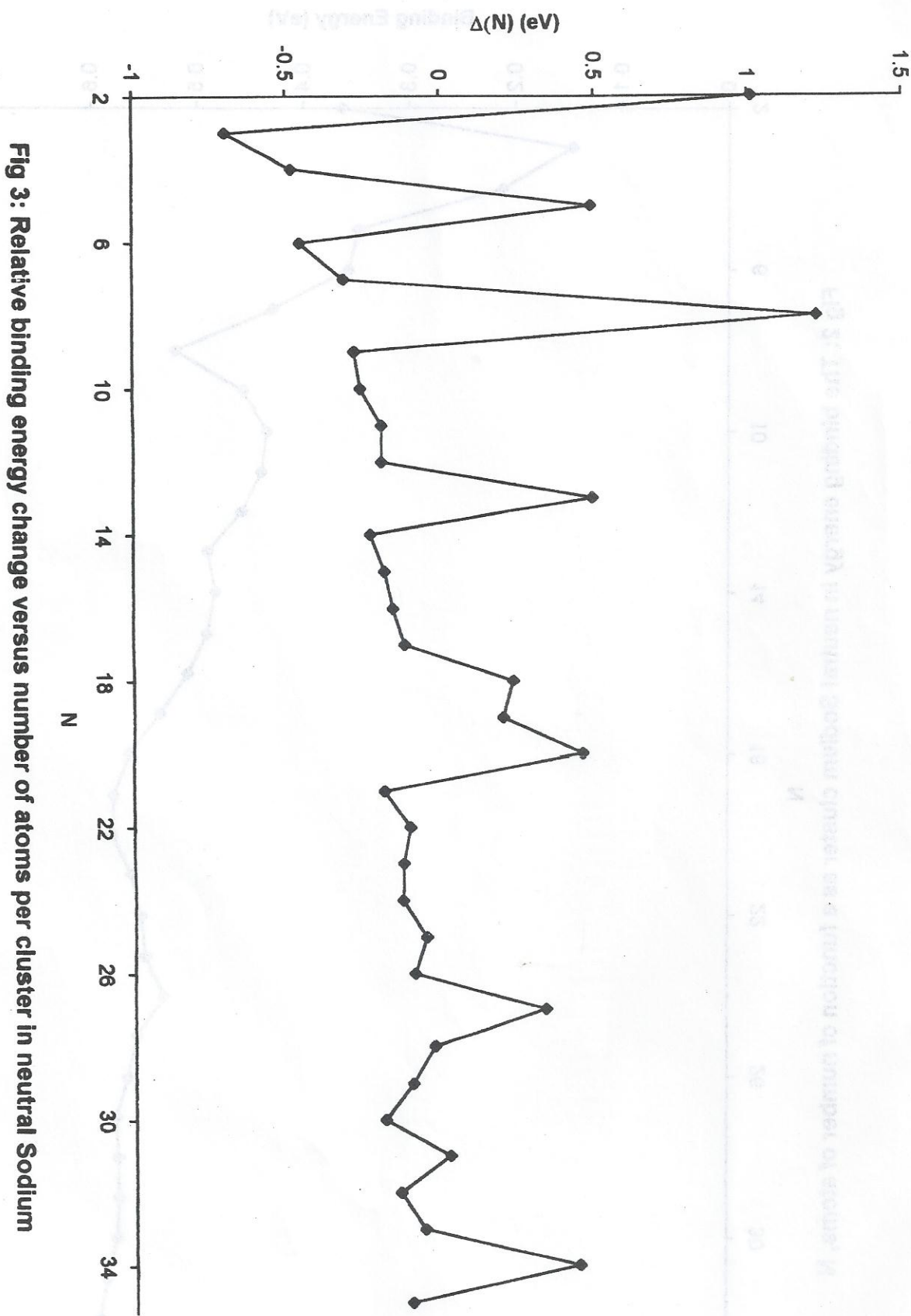


Fig 3: Relative binding energy change versus number of atoms per cluster in neutral Sodium

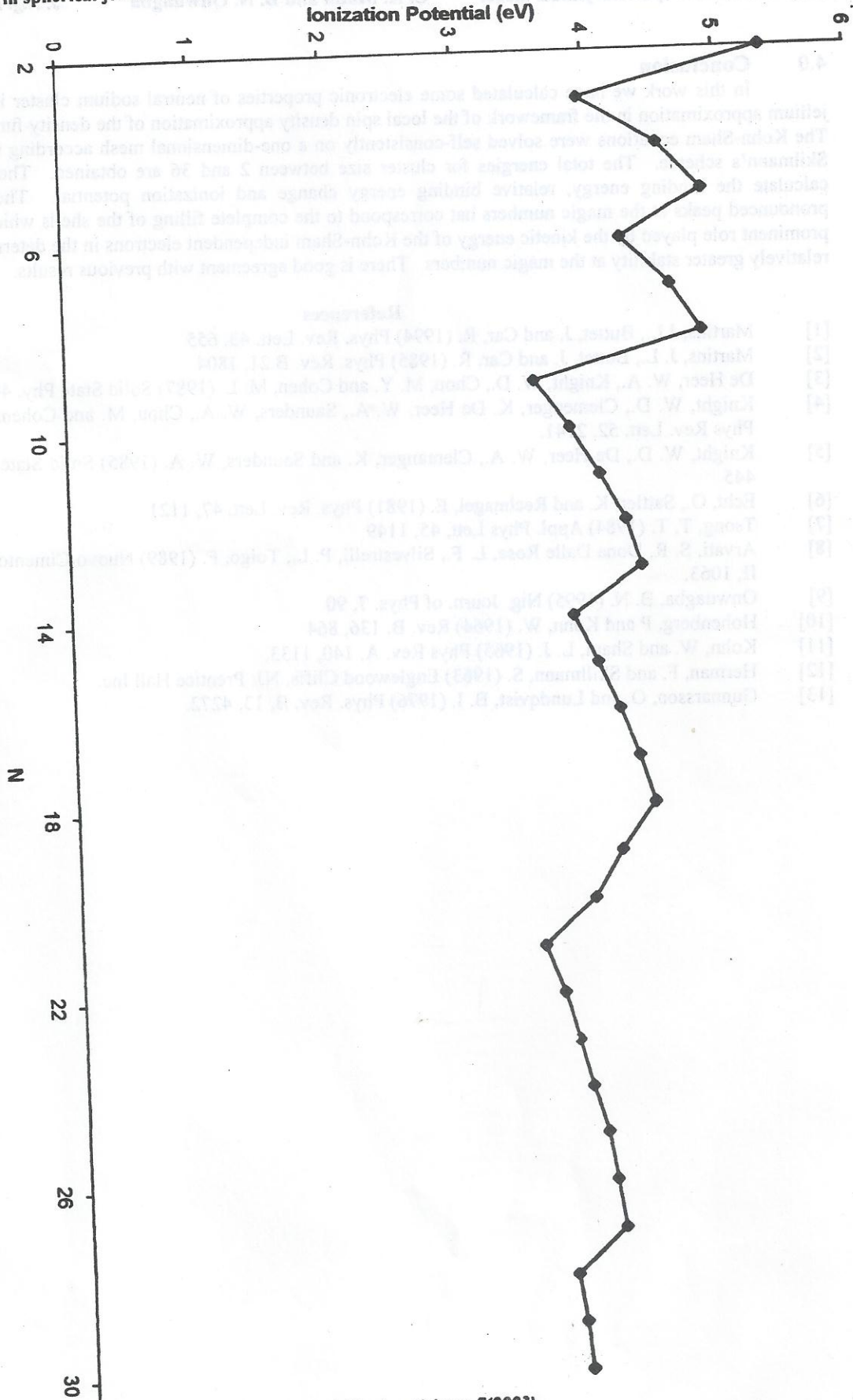


Fig 4: Ionization Potential versus cluster size N in neutral Sodium



#### 4.0 Conclusion

In this work we have calculated some electronic properties of neutral sodium cluster in the spherical jellium approximation in the framework of the local spin density approximation of the density functional theory. The Kohn-Sham equations were solved self-consistently on a one-dimensional mesh according to Herman and Skillmann's scheme. The total energies for cluster size between 2 and 36 are obtained. These are used to calculate the binding energy, relative binding energy change and ionization potential. The results show pronounced peaks at the magic numbers that correspond to the complete filling of the shells which explains the prominent role played by the kinetic energy of the Kohn-Sham independent electrons in the determination of the relatively greater stability at the magic numbers. There is good agreement with previous results.

#### References

- [1] Martins, J.L., Buttet, J. and Car, R. (1994) Phys. Rev. Lett. 43, 655
- [2] Martins, J. L., Buttet, J. and Car, R. (1985) Phys. Rev. B.21, 1804
- [3] De Heer, W. A., Knight, W. D., Chou, M. Y. and Cohen, M. L. (1987) Solid State Phy. 40.
- [4] Knight, W. D., Clemenger, K. De Heer, W. A., Saunders, W. A., Chou, M. and Cohen, M. L. (1984) Phys Rev. Lett. 52, 2141.
- [5] Knight, W. D., De Heer, W. A., Clemenger, K. and Saunders, W. A. (1985) Solid State Commun, 53, 445
- [6] Echt, O., Sattler, K. and Rehnagel, E. (1981) Phys. Rev. Lett. 47, 1121
- [7] Tsong, T. T. (1984) Appl. Phys Lett, 45, 1149
- [8] Arvati, S. R, Dona Dalle Rose, L. F., Silvestrelli, P. L., Toigo, F. (1989) Nuovo Cimento Soc. Ital. Fis. II, 1063.
- [9] Onwuagba, B. N. (1995) Nig. Journ. of Phys. 7, 90
- [10] Hohenberg, P and Kohn, W. (1964) Rev. B. 136, 864
- [11] Kohn, W. and Sham, L. J. (1965) Phys Rev. A, 140, 1133.
- [12] Herman, F. and Skillmann, S. (1963) Englewood Cliffs, NJ: Prentice Hall Inc.
- [13] Gunnarsson, O. and Lundqvist, B. I. (1976) Phys. Rev. B, 13, 4272.