

ESTIMATING THE STABILITY OF SOME ALKALI METAL CLUSTERS Li , Li^+ AND Na , Na^+ USING LOCAL SPIN DENSITY FUNCTIONAL FORMALISM

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ABSTRACT

We present a self-consistent Local Spin Density Approximation (LSDA) used in the Density Functional calculation of the stability of the alkali metal clusters Li , Li^+ , Na , Na^+ in the framework of a jellium - like model. Here for the neutral Li and Na clusters, the binding energy per atom obtained is about one fifth of the dissociation energy. Also, the results for the ionisation potentials for neutral Li and Na clusters and for the cluster abundance for the same Li and Na and singly charged Li^+ and Na^+ clusters enable us to understand and account for the enhanced stability of these alkali metal clusters.

INTRODUCTION

Many workers in cluster have extensively discussed the stability of alkali metal clusters in the framework of self consistent Density Functional Formalism. Chou and Cohen 1984 [1] Chou and Cohen 1986 [2], Rao et al 1987 [3] Knight et al (1987) (4). Kohn and Sham, 1965 [5] in their approach used Local Spin density Approximation (LSDA) for exchange and correlation. Balbas et al 1988 [6] in their approach used the spherical jellium model and self - consistent Density Functional theory to study the stability of Ag^{+2}N , Ag^+N , AgN and NaN clusters. Chou et al (1984) [7] calculated the ionisation potentials for jellium spheres for lithium, sodium and potassium as a function of cluster size N using local density functional (LDF) scheme. Ishili et al [1986] [8] using Perdew and Zunger formalism, (1981) [9], calculated the ionisation energies of sodium within LDF and SIC and compared them with their photo-ionization measurements. Onwuagba (1990) [10] used the Local Spin Density Approximation (LSDA) and its self interaction correction (SIC) in a self-consistent calculation of the total energies of K , Mg , Al , and Pb clusters as a function of N , the number of atoms using a jellium model in the framework of Density Functional Theory. He computed the binding energies. Binding energy change and ionisation potentials for these clusters. Lammers and Borstel (1993) [11] in their investigation of the electronic and structural properties of small ($N = 20$) and medium sized ($N = 50$) clusters of Cu using first principles Tight - Binding Linear Muffin - Tin Orbital (TB - LMTO) method with real space recursion scheme discovered that shell closing effects were in the ionization potentials. Becker et al (1994) [12] in their study of the stability of gold cluster ions Au^+N , $N = 23$ via collision induced dissociation in a Penning trap observed that the cluster stability exhibited a pronounced odd -

even alternation, illustrating the fact that clusters with an odd number of atoms N , are more stable than the ones with even numbers. We noted that this can apply to all metals including those under investigation.

In this work we used Local Spin Density Approximation in the self consistent Density Functional Calculation of the stability of the alkali metal clusters Li , Li^+ and Na , Na^+ in the frame work of a jellium - like model. We thus obtained the binding energy per atom, the dissociate ion energy and the ionization potentials for neutral Li clusters. Additionally, the results in the cluster abundance for the neutral Li , Na and their singly charged Li^+ , Na^+ clusters enable us to account for the enhanced stability of these alkali metal clusters. The rest of the paper is organised as follows; - In Section II, we give the formalism. In Section III, we outline the method of calculation while results and discussions are presented in Section IV. In Section V, the attendant conclusion is drawn

II FORMALISM

In this formalism, we calculated approximately the structure and properties of the valence electron gas in the cluster in the framework of the Density Functional Theory (Kohn and Sham), (1965) [5] where the clusters are considered as a uniform distribution of positive charge (of ionic background) with spherical shape

$$n+(r) = \begin{cases} n_0 & r < R \\ 0 & r \geq R \end{cases} \quad (1)$$

Here the radius of the homogeneously charge sphere, R , is given by $R = (zN)^{1/3} r$ where $r = (3/4\pi n_0)^{1/3}$ is the Wigner Seitz radius of the bulk matter in atomic units, z is the number of electrons in the cluster, N is the number of atoms in the cluster. It is clear that in the case of these alkali metals, r is the radius of a sphere of volume equal to the volume per conduction electron and is 3.25 a.u. and 3.95 a.u. for Li and Na respectively. Approximately, the external potential for the electrons is taken to be the electrostatic potential of a uniformly charged sphere. In the Density Functional formalism, Kohn and Sham, 1965 [5], we express the total energy of the electronic system due to a given external potential as a function of the electron density only. Using the variational method, and the local approximation for the exchanged correlation energy functional a set of one particle Kohn - Sham equations, was derive. The electron-electron interactions are included via the effective potential. The functional form of Gunnarsson and Lundqvist (1976) [13] was adopted as the exchanged correlation energy functional. In this work, we have calculated the total energy of the spherical jellium Li , Li^+ , Na , Na^+ in the Local Spin Density Approximation with the following equation.

$$E_{\text{Tot}}^{\text{LSDA}} = \int V_{\text{ext}}(r)n(r)d^3r + \frac{1}{3} \int \frac{n(r)n(r')d^3r d^3r'}{|r-r'|} + T_s(n) + E_{\text{xc}}^{\text{LSDA}}[n \uparrow(r)n \downarrow(r)] + \frac{3}{5} \frac{(\text{Ne})^2}{R} \quad (2)$$

where

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

Is the exchange and correlation energy expressed in the local - spin density approximation in the form of Gunnarsson & Lundqvist (1976) [13], $n(r)$ is the electron density and $T_s(n)$ is the total kinetic energy of the non-interacting system of the particles with electron \rightarrow density $n_{\sigma}(r)$ and is given by

$$T_s[n_{\sigma}] = \sum_i^N \left\langle \Psi_{i\sigma} \left| -\frac{1}{2} \nabla^2 \right| \Psi_{i\sigma} \right\rangle \quad (4)$$

where $\Psi_{i\sigma}$ is the single - particle wave functions that obey the Kohn - Sham equation of the form

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) \right] \Psi_{i\sigma}(r) = \varepsilon_i \Psi_{i\sigma}(r) \quad (5)$$

The effective potential V_{eff} is given by

$$V_{\text{eff}} = V_{\text{ext}}(r) + \int \frac{n(r')d^3r'}{|r-r'|} + \frac{\delta E_{\text{xc}}[n \uparrow n \downarrow]}{\delta n_{\sigma}(r)} \quad (6)$$

In this context the external potential due to the homogeneously charged sphere of radius R is given by

$$V_{\text{ext}}(r) = \begin{cases} -\frac{zN}{r} & r > R, \\ -\frac{3}{2} \frac{zN}{R^3} \left[R^2 - \frac{r^2}{3} \right] & r \leq R \end{cases} \quad (7)$$

With R satisfying the equation

$$\frac{4}{3} \pi R^3 n_0 = zN. \quad (8)$$

In the local spin density approximation (LSDA) for a closed shell structure the electron density is spherically symmetric and is of the form

$$n_{i\sigma}(r) = \sum_i f_{i\sigma} |\Psi_{i\sigma}(r)|^2 \quad (9)$$

Here i runs over the Kohn - Sham single particle wave functions and $f_{i\sigma}$ is the occupancy of any given state (0 or 1). For an open shell configuration where the resultant electron density is not spherically symmetric, the spherical jellium model replaces $n_{i\sigma}(r)$ by taking the form

$$n_{i\sigma}(r) = \frac{1}{4\pi} \int d\Omega n_{i\sigma}(r) \quad (10)$$

III METHOD OF CALCULATION

We calculated the total energy by solving Kohn-Sham equation self - consistently in a spherical symmetric potential. In this framework, the wave function separates into radial and angular parts. Eventually, the Kohn-Sham equation was reduced to a one dimensional mesh and was solved self-consistently with a modified Hermann and Skillman Code (Hermann and Skillman, 1963) [14]. For the convenience of the present computation, we extended the mesh points up to 1081 with constant spacing between the blocks.

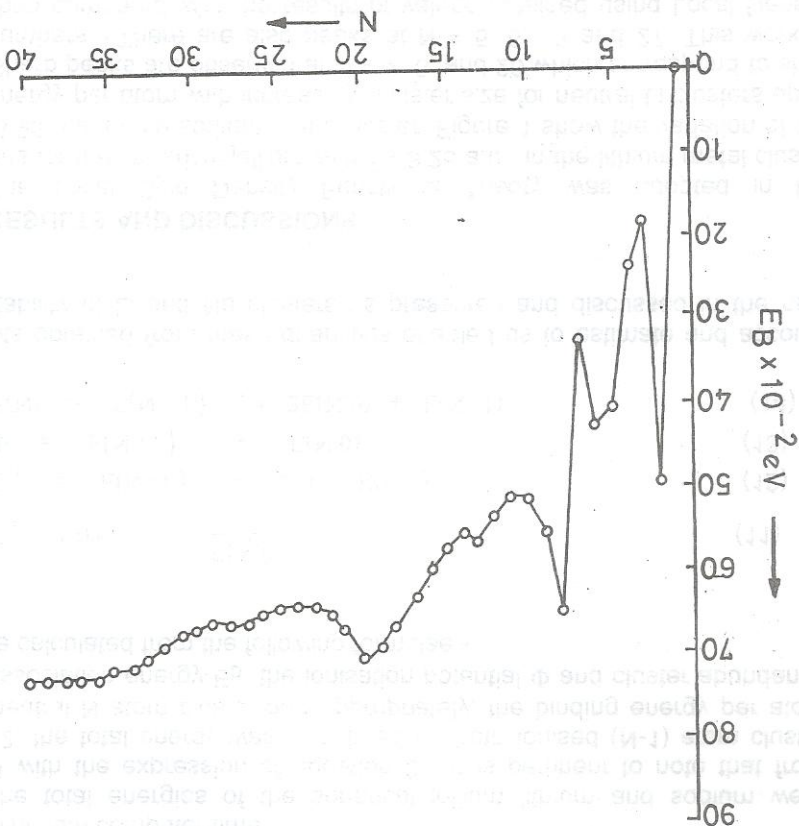
The radial part of the Schrodinger equation was solved numerically using Noumerov method (Koonin, 1976) [15] with the number of modes determined by the quantum number $n_r = n - 1$.

The total effective potential was finally calculated as the sum of three part namely; the coulombic contribution, the exchange correlation contribution and the external potential contribution. In this paper we achieved self - consistency when at each iteration step, it was ensured that the maximum difference between initial and final potential at any mesh point was less than 1×10^{-3} a. u.; while the tolerance for the convergence to the eigenvalues when solving the Schrodinger equation was put at 1.0×10^{-15} a.u.

The effectiveness of the above computational procedure was a function of many factors namely:

- (i) The integration technique used on the modified mesh
- (ii) The choice of the starting potential in the initial self - consistency loop

Fig. 1 (a) The binding energy in neutral Li cluster as a function of number of atoms N.



additional peaks at $N = 13, 23$ and 38 corresponding to half-filled shell numbers which are associated with high spin configuration. But comparing Figures 1 and 2, we notice that the binding energy per atom is one fifth the dissociation energy. This is explained by the fact that this decrease in the binding energy per atom arises from the fact that part of the energy gained in binding the atom is redistributed among the other atoms in the cluster. We observe the same trend in

(iii) The choice of the starting eigenvalues in the solutions of the Schrödinger equation

(iv) The adjustment of the eigenvalues to the number of modes when solving the Schrödinger equation and

(v) The procedures used to make convergence toward self consistency quicker. In this work, we achieved quicker convergence by suitable combination of the Pratt and Arithmetic Average Method, Koonin (1978) [16] and the appropriate adjustment of the eigenvalues to the number of modes when solving the Schrödinger equation. In this way, the convergence was achieved at minimum number of iterations and minimum computer time.

The total energies of the spherical jellium lithium and sodium were computed with the expression of equation 2. It is pertinent to note that from equation 2, the total energy was calculated for both ionised (N-1) atom cluster and the neutral N atom cluster and appropriately, the binding energy per atom E_B , the dissociation energy E_D , the ionisation potential Φ and cluster abundance $\delta(N)$ were calculated from the following formulae:-

$$E_B = E(1) - \frac{E(N,0)}{N} \quad (11)$$

$$E_D = E(N-1) + E(1) - E(N,0) \quad (12)$$

$$\Phi = E(N-1) - E(N,0) \quad (13)$$

$$\delta(N) = E(N+1) + 2E(N,0) + E(N-1) \quad (14)$$

The results obtained from these quantities enabled us to estimate and account for the stability of Li and Na clusters as presented and discussed in the next section.

IV. RESULTS AND DISCUSSIONS

The Local Spin Density Functional Theory was adopted in the calculations for the spherical jellium with $r = 3.25$ a.u. in the lithium metal cluster and $r = 3.95$ a.u. in the sodium metal cluster. Figure 1 show the variation of the binding energy per atom with increase in cluster size for neutral Li clusters up to $N = 40$. Sharp peaks are observed at $N = 2, 8, 13$ and 20 which correspond to shell closing numbers. There are also peaks at $N = 5, 6, 13$ and 27 . This work in LSDA, when compared with the results of values obtained using Local Density approximation (LDA) Iniguez et al [17] 1986 correspond to the enhancement at half-filled shell numbers that are associated with high spin configuration. In Figure 2, the graph of dissociation energy versus cluster size is plotted for neutral Li clusters up to $N = 40$. Pronounced peak are observed at $N = 2, 5, 8, 27, 36$ which correspond to the shell-closing numbers. We also notice

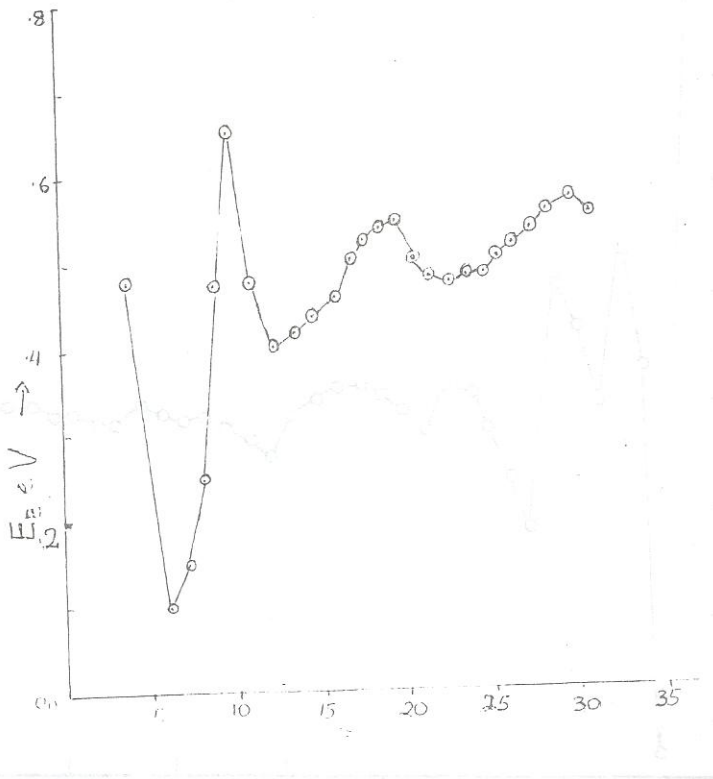


Fig. 1 (b) The binding energy in neutral Na cluster as a function of number of atoms N

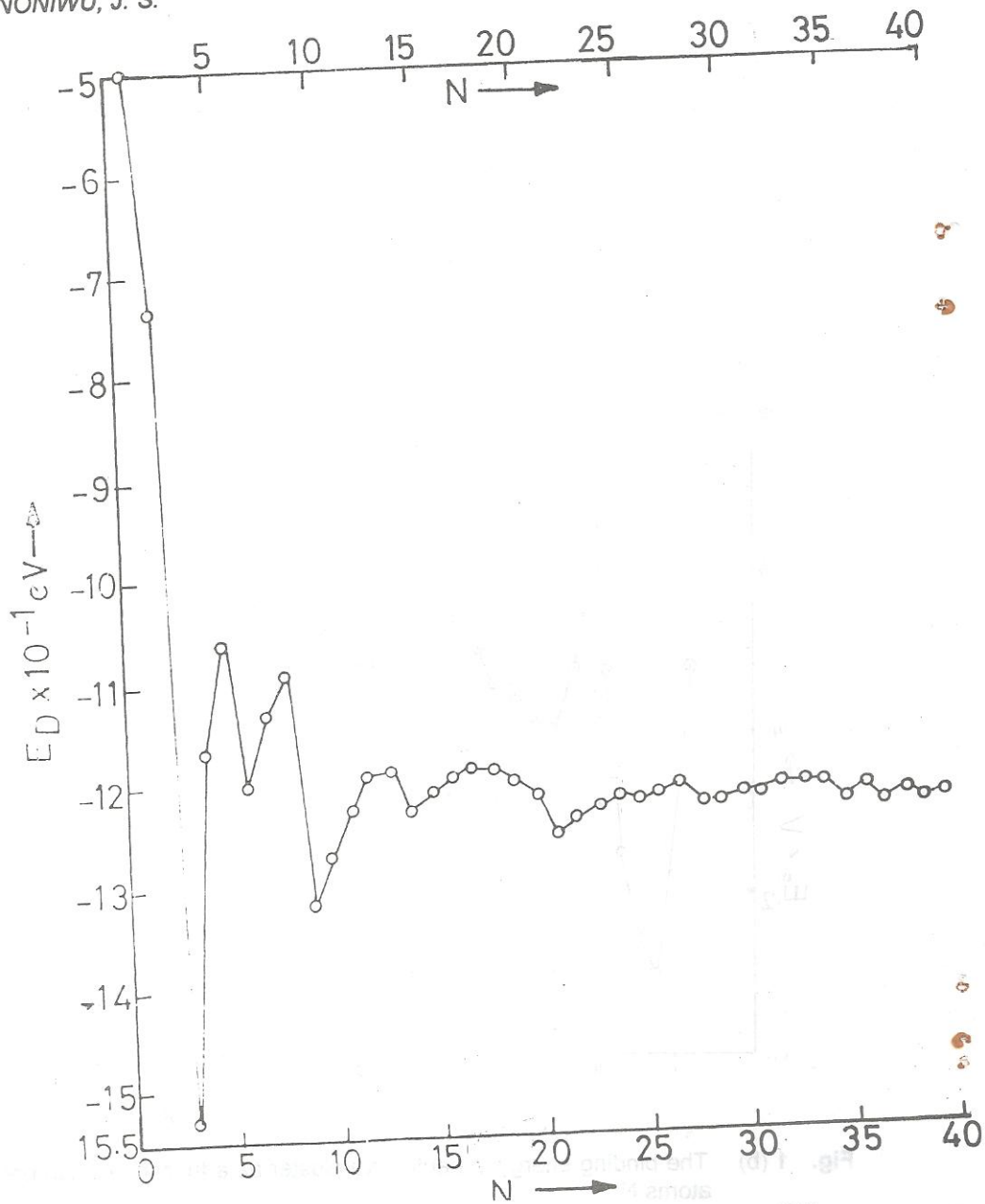


Fig. 2 (a) The dissociation energy in Li cluster as a function of atoms N.

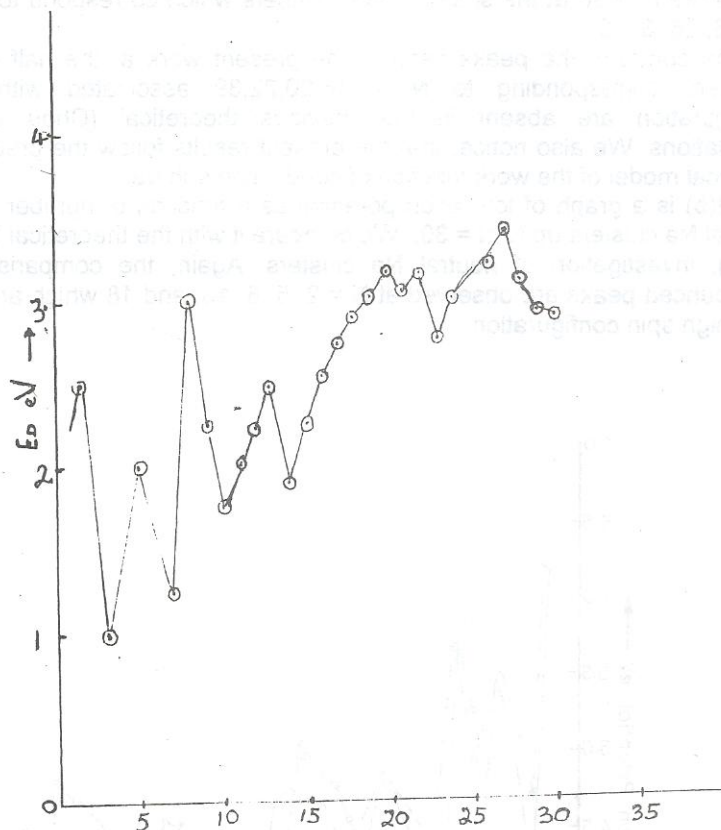


Fig. 2(b) The dissociation energy in Na cluster as a function of atoms N .

We present the results for the ionisation potential as a function of cluster size in Figs.3 a, b, for the alkali metal clusters Lithium and Sodium. As can be seen from the figures, there is remarkable enhancement of the ionisation potential at the Shell - closing and half-filled shell numbers due to high spin configurations.

Fig. 3(a) is a graph of ionization potential as a function of number of atoms for neutral Li clusters up to $N=40$. The present work is compared with the theoretical, Chou et al [7] 1984, investigations of neutral Li clusters. The comparison of the present work with the previous theoretical work is quite good.

Particularly, in both cases, the oscillatory behaviours are reproduced and the peaks are noticed at the shell closing numbers which correspond to $N = 2, 6, 8, 13, 18, 26, 34, 36$.

On the contrary, the peaks seen in the present work at the half-filled shell numbers corresponding to $N = 16, 20, 22, 39$ associated with high spin configuration are absent in the previous theoretical (Chou et al 1984) calculations. We also notice, that the present results follow the prediction of the classical model of the work function of conducting sphere.

Fig. 3(b) is a graph of ionisation potential as a function of number of atoms for neutral Na clusters up to $N = 30$. We compare it with the theoretical (Ishii et al [8] 1986); investigation of neutral Na clusters. Again, the comparison is good. Pronounced peaks are observed at $N = 2, 5, 8, 13$, and 18 which are associated with high spin configuration.

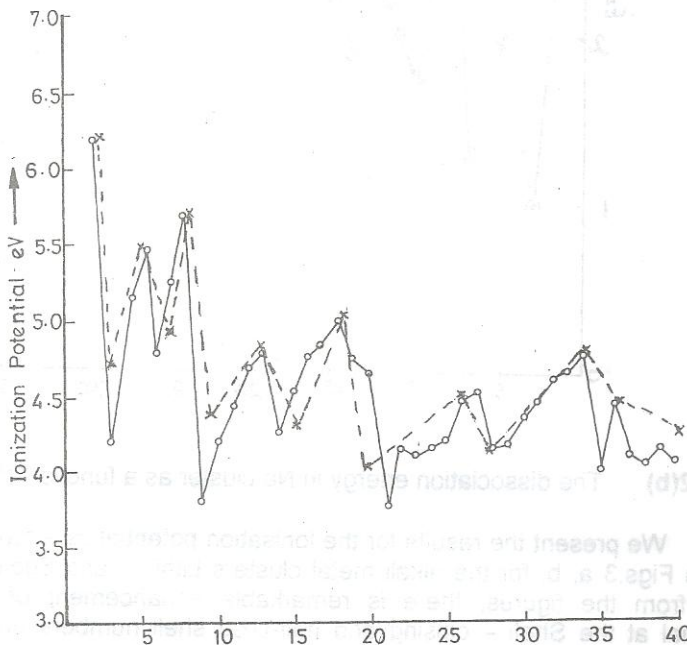


Fig. 3(a) The ionization potential in neutral Li clusters as a function of number of atoms N —o—o—present; —x—x—Chou et al, 1984.

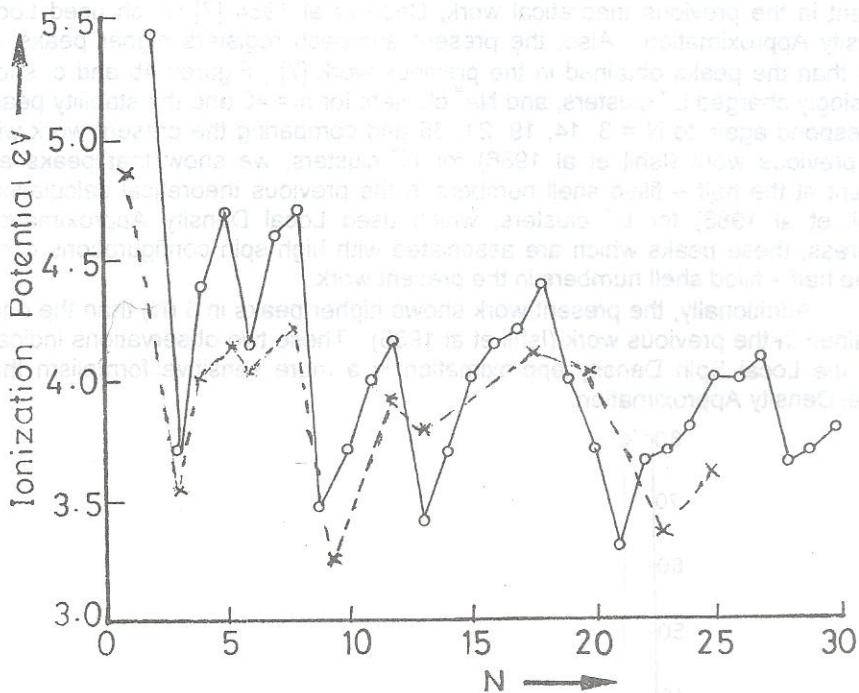


Fig. 3(b) The ionization potential in neutral Na clusters as a function of number of atoms N o-o-o— present, --x-x-x--- Ishii et al, 1986.

At best we study the relative stability of neutral or charged clusters in Fig. 4 by plotting the abundance of Li, Li^+ and Na and Na^+ cluster as function of Cluster size. **Essentially, the second derivative of the energy must have a peak if a cluster with N atoms is more stable relative to those with one atom more or one atom less.**

The peaks therefore indicate enhanced relative stabilities. Fig. 4(a) shows $\delta(N)$ as a function of cluster size for neutral Li cluster up to $N = 40$. The stability sharp peaks are observed at $N = 2, 6, 13, 18, 20, 34, 40$ which are in agreement with previous calculations for noble metals, [6], even though volume per atom is the difference between the alkali and noble metals. The stability here corresponds to the filled electronic shells in the order is, $1p, 1d, 2s, 1f, \dots$. There are also dips at $N = 3, 8, 15, 21, 23, 29, 35$, and 37 . Equally, the appearance of peaks in $\delta(N)$ at N shows that a cluster with N atoms is comparatively stable and has a larger mass spectrum than a cluster with $N + 1$ atoms. By comparing the present work with the previous, Chou et al 1984, [7] it is observed that the half-filled shell numbers which correspond to $N = 10, 16, 18, 22, 24, 27$, and 38 are

absent in the previous theoretical work, Chou et al 1984 [7] which used Local Density Approximation. Also, the present approach registers higher peaks for $\delta(N)$ than the peaks obtained in the previous work [7]. Figures 4b and c, show the singly charged Li^+ clusters, and Na^+ clusters for $n = 40$ and the stability peaks correspond again to $N = 3, 14, 19, 21, 35$ and comparing the present work with the previous work (Ishii et al 1986) for Li^+ clusters, we show that peaks are absent at the half-filled shell numbers in the previous theoretical calculations (Ishii et al 1986) for Li^+ clusters, which used Local Density Approximation, whereas, these peaks which are associated with high spin configurations occur at the half-filled shell numbers in the present work.

Additionally, the present work shows higher peaks in $\delta(N)$ than the ones obtained in the previous work (Ishii et al 1986). These two observations indicate that the Local Spin Density approximation is a more sensitive formalism than Local Density Approximation.

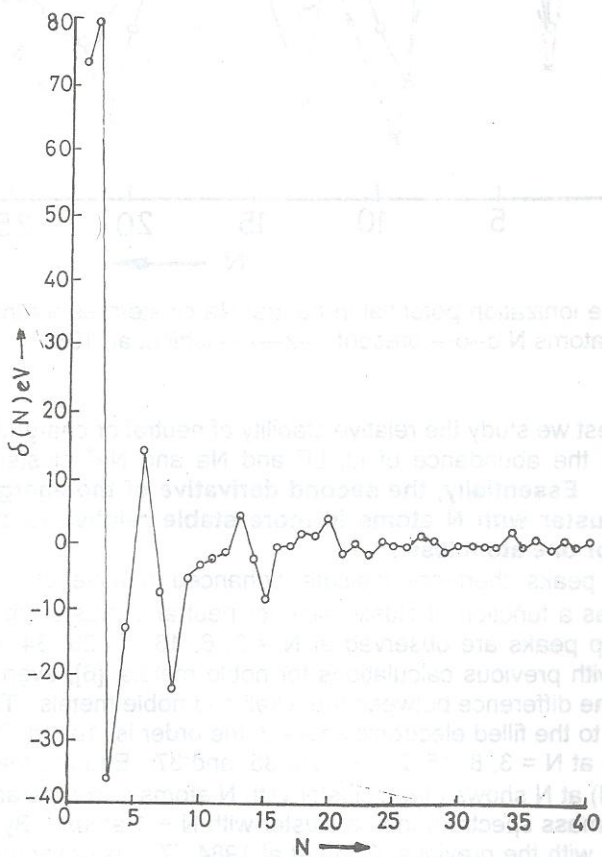


Fig. 4. (a) The abundance of neutral Li clusters versus number of atom N.

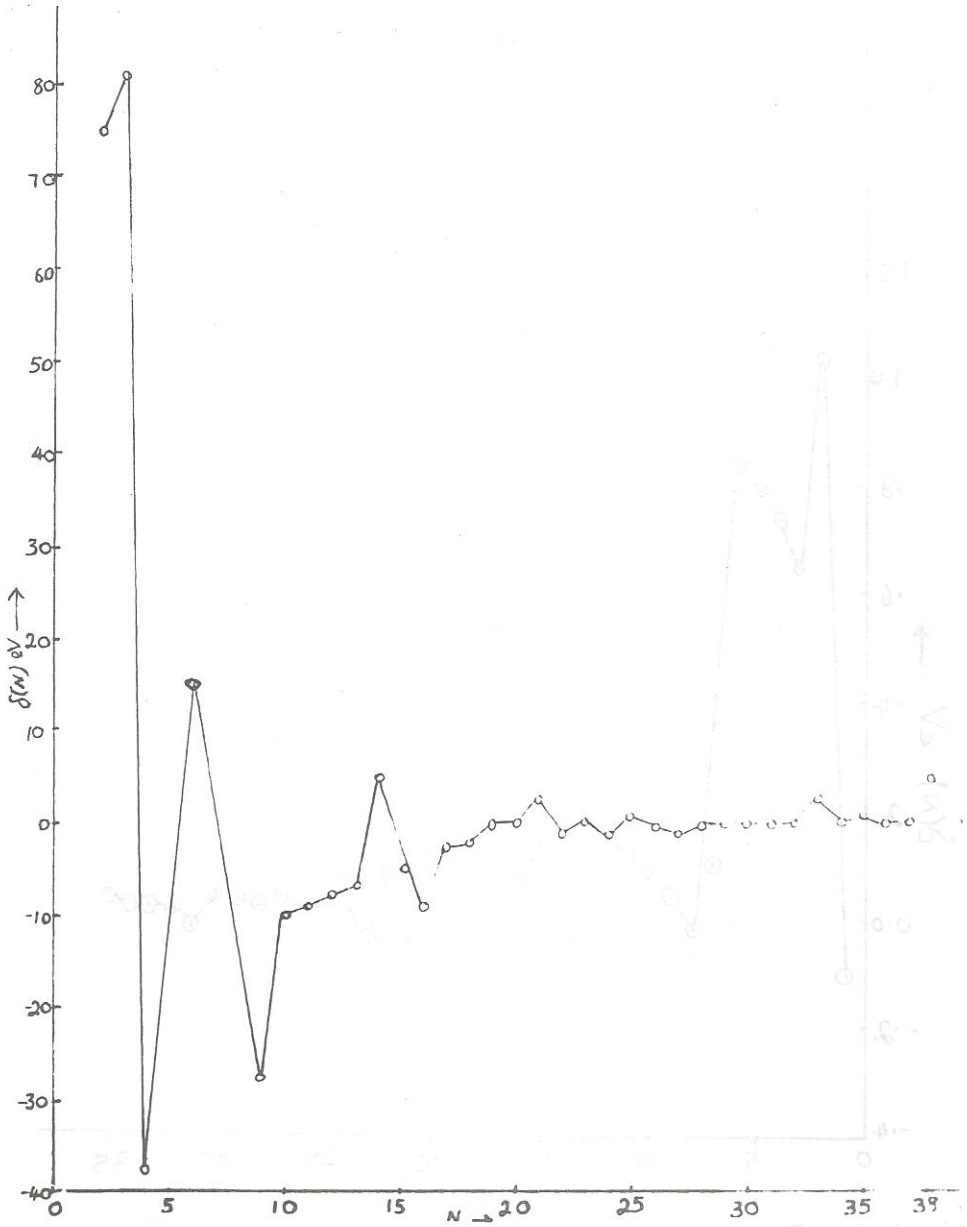


Fig. 4. (b) The abundance of singly charged Li^+ clusters versus number of atoms N .

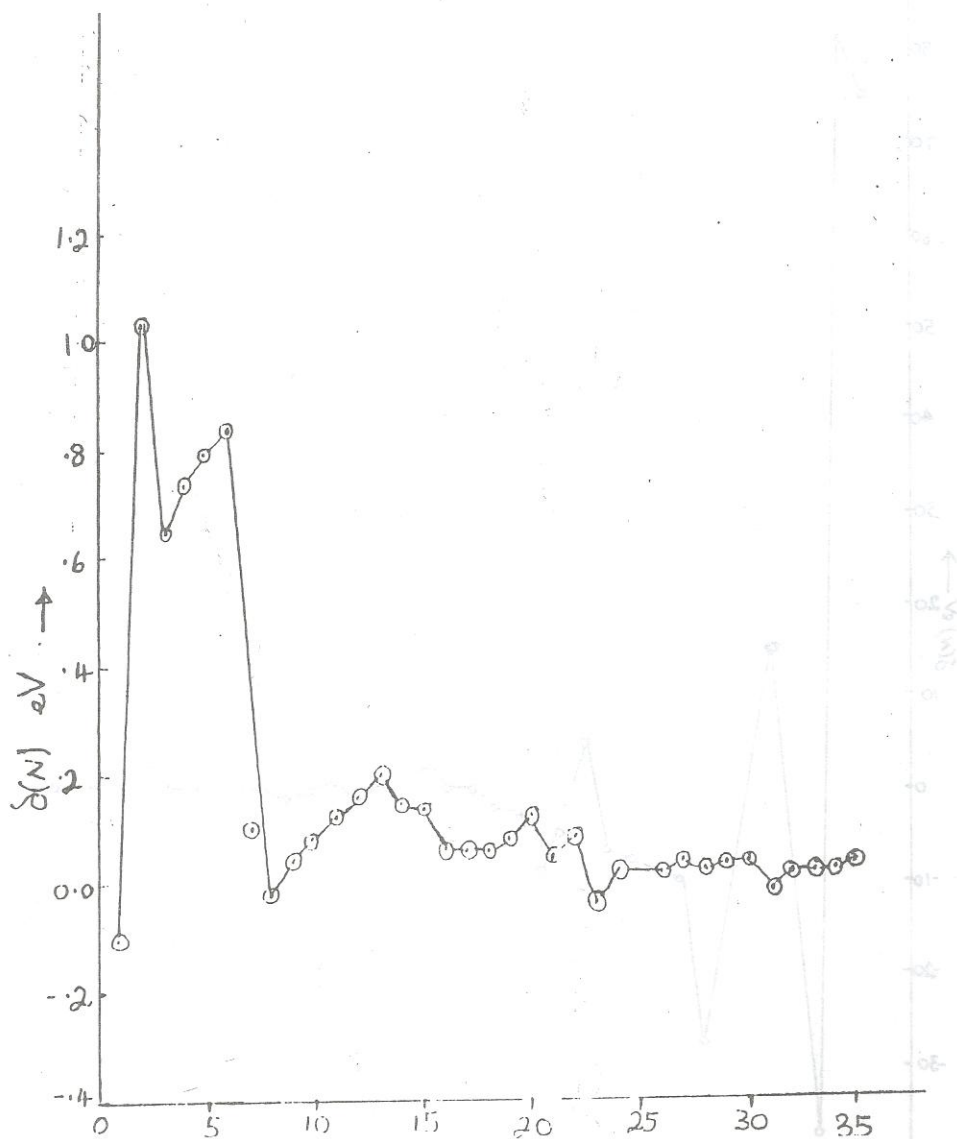


Fig. 4. (c) The abundance of singly charged Na^+ clusters versus number of atom N.

V CONCLUSION

In this paper, we have used a self – consistent Density Functional Theory in the framework of Local Spin Density Approximation to compute the stability of the alkali metal clusters within the context of a jellium – like model. In this context, the binding energy per atom E_B , the dissociation energy E_D , the ionization potential Φ , and the abundance of clusters $\delta(N)$ are derived from the computed total energy $E(N,0)$ using the aforementioned formalism. In the neutral Li clusters, the binding energy is about one fifth the dissociation energy. This decrease in the binding energy per atom is attributed to the fact that part of the energy gained in binding the atom is redistributed among the other atoms in the cluster. The ionization potential of neutral Li clusters up to $N = 40$, obtain in present work is compared with the previous theoretical calculations (Chou et al 1984). Furthermore, the stability of the neutral and charged alkali metal clusters Li , Li^+ and Na^+ for $N = 40, 30$ are investigated via the cluster abundance, $\delta(N)$, the second derivative of the energy, in the present work we observed the stability peaks at $n = 2, 6, 13, 18, 20, 34$, and 40 which are compared with the previous theoretical calculations (Chou et al 1984) in neutral Li clusters. Furthermore, for the singly charged Li^+ and Na^+ clusters, this present work shows stability peaks at $N = 3, 14, 19, 21$ and 35 . It is interesting to note the shift in the position of the stability peaks by 1 in these singly charged alkali clusters. One remarkable outcome of the present approach is that this present approach has clearly distinguished itself from the previous theoretical calculation [7] in the alkali metal clusters, Li , Li^+ and Na^+ by the occurrence of peaks at the half – filled shell numbers. These peaks, which are associated with high spin configuration, are found in neutral Li clusters at $N = 10, 16, 18, 22, 24, 27$ and 38 as well as at $N = 2, 6, 13, 20, 34$ in the singly charged Li^+ and Na^+ clusters. Therefore, the results of the present work provide useful information for the understanding of, and enable us to account for, the enhanced stability of these alkali metal clusters as adumbrated above.

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