IC/92/364

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

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INTERNATIONAL ATOMIC ENERGY AGENCY

UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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ABSTRACT

The ground state electronic and chemical properties of divalent barium and trivalent indium are investigated in a self–consistent manner using the spin–polarized local density approximation in the framework of Density Functional Theory. A jellium model is adopted in the spirit of Gunnarsson and Lundqvist exchange and correlation energies and the calculated properties primarily associated with the $s-p$ orbitals in barium and p orbitals in indium provide deepened insight towards the understanding of the mechanisms to the magic numbers in both clusters.

MIRAMARE – TRIESTE

November 1992

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1. INTRODUCTION

Recent experimental and theoretical studies of the electronic and chemical properties of metal and semiconductor clusters have received much attention especially in chemisorption and catalysis [1, 2]. In the past few years, a lot of work has been done in alkali–metal clusters, in particular, sodium [3–5], whereas little work is done in the higher valent clusters. It is now known that barium ferrite is a very promising material for high–density magnetic recording due to their special intrinsic magnetic properties as well as to their high quality of the particle ensemble, which make these particles suitable for investigating the size dependence of different collective magnetic properties [6]. On the other hand, indium clusters are found to be very reactive with hydrocarbons in a strongly size dependent manner [7]. In view of the varied interests in barium and indium, it is important to have a basic knowledge of the electronic and chemical properties of both clusters in different charge states using a jellium model.

A jellium model is used to handle large clusters in the framework of local density theory. In this model, a metal is modelled to consist of two charge contributions, namely, an ionic distribution which is represented by a uniform background of positive charge with spherical shape, and an electronic distribution resulting from the valence electrons of the atoms forming the cluster, which is in turn, associated with the effective potential one to the positive background and the electronic distribution itself [8].

Seidl *et al.* [9] used a semiclassical variational calculation of liquid–drop model to obtain surface tensions and work functions evaluated for an infinite plane metal surface. Also, Mañanes and co–workers [10] adopted a semiclassical variational approach in the investigation of the size dependent behaviour of chemical potential, electron affinities and ionization potentials. Nevertheless, Penzar and Ekardt [11] used the self–consistent spheriodal jellium model in the investigation of the ground state electronic properties of monovalent clusters and compared to recent experimental data of ionization potentials, electron affinities and binding energies of these clusters. In the past few years, Chou

and Cohen [12] calculated the total energies of simple metal clusters Na, Mg and Al in the spherical jellium approximation using the local density-functional scheme. They discussed the discontinuities found in the mass spectrum of sodium and indicated that similar behaviour is found theoretically for magnesium and aluminium, but the magic numbers should occur at different positions. Later Iniguez *et al.* [13] investigated the electronic structure of some higher valent clusters such as Mg, Al and Pb in addition to the monovalent Na by considering the electronic levels in a 'spherically averaged' effective potential and the optimized geometries calculated from ions embedded in a spherically symmetric, although not homogeneous electronic background. Onwuagba [14] used the LSDA and LSDA–SIC to calculate the binding energies and ionization potentials of the higher valent Mg, Al and Pb clusters in addition to the monovalent K. Recently, Kumar and Car [15] studied the structure, growth and bonding nature of Mg clusters using the density functional molecular dynamics method and the stimulated annealing technique within the local density approximation. But more recently, Ray and co-workers [16] used ab initio techniques in the calculation of the equilibrium geometries, total energies and fragmentation energies for the small neutral and cationic boron clusters.

In this paper, the ground state electronic and chemical properties of divalent barium and trivalent indium are theoretically investigated for the first time using spin-polarized local density approximation in the framework of Density Functional Theory [17, 18]. In this approach, a self-consistent field calculation was carried out in the jellium model using Gunnarsson and Lundqvist exchange and correlation energies with a view to obtaining dissociation energies, binding energies and ionization potential in both metal clusters. Comparison of present results with the previous theoretical results in magnesium [15] shows that present results are characterized by lower dissociation and binding energies, and provide data for larger cluster size. In indium, comparison of present ionization potentials with experimental data of Rayane *et al.* [7] is not quite good because indium is not free electron like. Nevertheless, the present results follow the prediction of the classical model of the work function of a conducting sphere [7].

In Section 2, a brief description of the formalism of the investigation is presented. In Section 3, the results are discussed and the conclusion is drawn in Section 4.

2. FORMALISM

In the jellium model, the positive ionic charge distribution is replaced by a homogeneous background density, ρ_0 inside a sphere of radius $R = [ZN]^{1/3} r_s$, where $r_s = [4\pi\rho_0/3]^{-1/3}$ is the Wigner–Seitz radius, N the number of atoms and Z is the valence.

The energy functional $E[\rho_\sigma]$ is given by the sum of kinetic, electrostatic and exchange–correlation energies. In Rydberg atomic units the kinetic energy is

$$T_s[\rho_\sigma] = \sum_i \varepsilon_i - \sum_\sigma \int V^\sigma_{eff}(\bar{r})\ \rho_\sigma(\bar{r})\ d^3r \tag{2.1}$$

where ε_i are the eigenvalues of the spin–dependent Kohn–Sham equations.

The spin densities $\rho_\sigma(\bar{r})$ are obtained by solving the spherically symmetric Kohn–Sham equation [18] self–consistently in the Density Functional Theory [17, 18]. In this approach, we have

$$-\frac{1}{r^2}\ \frac{d}{dr}\left[r^2\ \frac{d\varphi_i}{dr}\right] + \left[V^\sigma_{eff}(\bar{r}) + \frac{\ell(\ell+1)}{r^2} - \varepsilon_i\right]\varphi_i = 0\ . \tag{2.2}$$

Here, $\varphi_i = \varphi_{n,l,m,\sigma}$ is the radial wave function with quantum numbers n, l, m, σ. Also, $V^\sigma_{eff}(\bar{r})$ is the spin–σ component of the effective potential in the form

$$V^\sigma_{eff}(\bar{r}) = \int V_{ext}(\bar{r})\ \rho_\sigma(\bar{r})\ d^3r + \frac{1}{2}\int\int\ \frac{\rho_\sigma(\bar{r})\ \rho_\sigma(\bar{r}')}{|\bar{r}-\bar{r}'|}\ d^3r\ d^3r' + E_{XC}[\rho_\sigma] \tag{2.3}$$

where the first term is the interaction of the electrons with the external potential which is the electrostatic potential due to the positive background in the form

$$V_{ext}(\bar{r}) = \begin{cases} \frac{ZN}{2R}\left[3 - \left(\frac{r}{R}\right)^2\right] & r \le R \\ \frac{ZN}{r} & r > R \end{cases}\ . \tag{2.4}$$

The second term in Eq.(2.3) is the electron–electron interaction which is the electrostatic potential due to the electron density $\rho_\sigma(\bar{r})$, while the last term is the exchange and correlation energy which is taken in the local density approximation of Gunnarsson and Lundqvist [19] in the form

$$E_{XC}[\rho_\sigma] = \int d^3r\ \rho_\sigma(\bar{r})\ \varepsilon_{XC}[\rho_\sigma(\bar{r})]\ . \tag{2.5}$$

The spin–σ component of the electronic density is replaced by its spherical average

$$\rho_\sigma(\bar{r}) = \frac{1}{4\pi}\sum_{n,l}|\varphi_{n,l,\sigma}(\bar{r})|^2 \tag{2.6}$$

in order to maintain the spherical symmetry of the equations. The electrostatic potential is computed by solving the Poisson equation numerically on the same mesh points. The total effective potential is obtained and the radial part of the Schrödinger equation is solved numerically using the Noumerov Method [20] in the modified Herman and Skillman Code [21] with 1081 mesh points. The total energy per atom becomes

$$E(N) = T_s[\rho_\sigma] + \frac{1}{2}\int\int\frac{\rho_\sigma(\bar{r})\ \rho_\sigma(\bar{r}')}{|\bar{r}-\bar{r}'|}\ d^3r\ d^3r' + \int d^3r\ \rho_\sigma(\bar{r})\ \varepsilon_{XC}[\rho_\sigma(r)] + \int V_{ext}(\bar{r})\ \rho_\sigma(\bar{r})\ d^3r + U_{II}\ . \tag{2.7}$$

The last term U_{II} is the self–interaction of the positive background.

The above approach is appropriate for studying cluster properties with $N \geq 8$ and from the ground state energy given in Eq.(2.7), dissociation energy E_D, binding energy E_B, the second derivative of the energy $\Delta(N)$ and the ionization potential Φ are derived namely

$$E_D = E(N-1) + E(1) - E(N,0) \tag{2.8}$$

$$E_B = E(1) - \frac{E(N,0)}{N} \tag{2.9}$$

$$\Delta(N) = E(N+1) + E(N-1) - 2E(N,0) \tag{2.10}$$

and

$$\Phi = E(N-1) - E(N,0)\ . \tag{2.11}$$

The results obtained from these quantities are shown and discussed in the next section.

3. RESULTS

In the present work, calculations were carried out for $r_s = 3.71$ and 2.41 in barium and indium respectively. In this section Figs.1–5 display new results in eigenvalues, dissociation energies E_D, binding energies E_B, second derivative of the energies $\Delta(N)$ and ionization potentials Φ.

In Fig.1(a) the computed electron eigenvalues of a spherical jellium barium for $1s, 1p, 1d, 2s, 1f, 2p$ and $1g$ are plotted as functions of N and Fig.1(b) provides a similar graph for indium in $1s, 1p, 1d, 2s, 1f, 2p, 1g, 2d, 3s$ and $1h$. In the present work, the divalent barium gives higher electron eigenvalues than in indium for same cluster size. Peaks in barium and indium clusters are noticed at $N = 4$ and 6 respectively which are associated with magic numbers corresponding to 8 and 18 electrons.

Fig.2 displays graphs of dissociation energy versus cluster size. In Fig.2(a) peaks in barium are observed at $N = 4$ and 9 which correspond to the magic numbers [3] at $N = 8$ and 18 in monovalent clusters. Also peaks in indium are noticed in Fig.2(b) at $N = 6$ and 19 which are the shell closing numbers. The probabilities of dissociation are determined by comparing the total energies of X_N and $X_{N-\alpha} + X_\alpha$, which shows that a cluster can break into two pieces of sizes α and $N - \alpha$.

In Fig.3, the graphs of the binding energies per atom E_B in barium and indium clusters are plotted as a function of cluster size N. Here, peaks in barium are seen in Fig.3(a) at $N = 4$ and 10 which correspond to the shell closing numbers at $N = 8$ and 20 in monovalent clusters. The result is similar to previous works [13–15] carried out in Mg but with lower binding energy per atom. Also, peaks in indium are observed in Fig.3(b) at $N = 3, 7$ and 13 corresponding to 9, 21 and 39 electrons. The trend here is similar to previous results [13, 14] in Al clusters. In both Figs.2 and 3, the binding energy per atom is about half the dissociation energy. This decrease in binding energy per atom arises due to the fact that part of the energy gained in binding the atom is redistributed among the other atoms in the cluster.

The graphs of abundance of barium and indium clusters as a function of cluster size are shown in Fig.4. In Fig.4(a), peaks in barium are observed at $N = 4$ and 10 and from the second derivative of the energy it is clear that 4 and 10 are magic numbers and should be abundant in the mass spectrum. Comparison of present results with previous works in magnesium [13–15], shows that barium is associated with higher peaks at same cluster size. A similar graph is plotted in Fig.4(b) and peaks in indium are noticed at $N = 3, 7, 13$ and 19 corresponding to 9, 21, 39 and 57 electrons.

In Fig.5, graphs of ionization potential against cluster size N are shown. For the case of barium clusters displayed in Fig.5(a), the normal oscillatory behaviour is achieved and peaks are seen at $N = 4$ and 9 which correspond to the shell closing numbers at $N = 8$ and 18. By comparing present results with previous work carried out in Mg [14], it is found that barium is associated with lower ionization potential than magnesium. In Fig.5(b), the present work is compared with experimental values of the ionization potentials in indium [7] and it is observed that jellium model does not quite reproduce the experimental data because indium is not free electron like. Nevertheless, present results tend to follow the prediction of the classical model of the work function of a conducting sphere.

4. CONCLUSION

In this paper, the properties of barium and indium clusters have been investigated in the jellium model by using the spin–polarized local density approximation in the framework of Density Functional Theory. Here, exchange and correlation energy of Gunnarsson and Lundqvist was used in the computations. In Section 3, the results obtained in the present work were given, thus, for barium and indium, the eigenvalues, dissociation energies, binding energies and ionization potentials were calculated as a function of cluster size. For most of these properties investigated, it is shown that peaks in barium were noticed at $N = 4, 9$ and 10 whereas similar peaks in indium were observed at $N = 3, 7, 13$ and 19 corresponding to 9, 21, 39 and 57 electrons.

In conclusion, the spin–polarized local density approximation in the framework of Density Functional Theory has greatly explained barium and indium clusters and the results obtained provide a better understanding of the basic electronic and chemical properties of both clusters.

Acknowledgments

The author would like to thank the Swedish Agency for Research Cooperation with Developing Countries, SAREC, for financial support during his visit at the ICTP under the Associateship scheme. He would also like to thank Professor Abdus Salam, the International Atomic Energy Agency and UNESCO for hospitality at the International Centre for Theoretical Physics, Trieste.

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FIGURE CAPTIONS

Fig.1 The electron eigenvalues of barium and indium clusters as a function of number of atoms N (a) barium (b) indium.

Fig.2 The dissociation energy in barium and indium clusters as a function of number of atoms N (a) barium (b) indium.

Fig.3 The binding energy in barium and indium clusters as a function of number of atoms N (a) barium (b) indium.

Fig.4 The abundance of barium and indium clusters against the number of atoms N (a) barium (b) indium.

Fig.5 The ionization potential in barium and indium clusters as a function of number of atoms N (a) barium (b) indium, +++ experimental data (Ref.7).

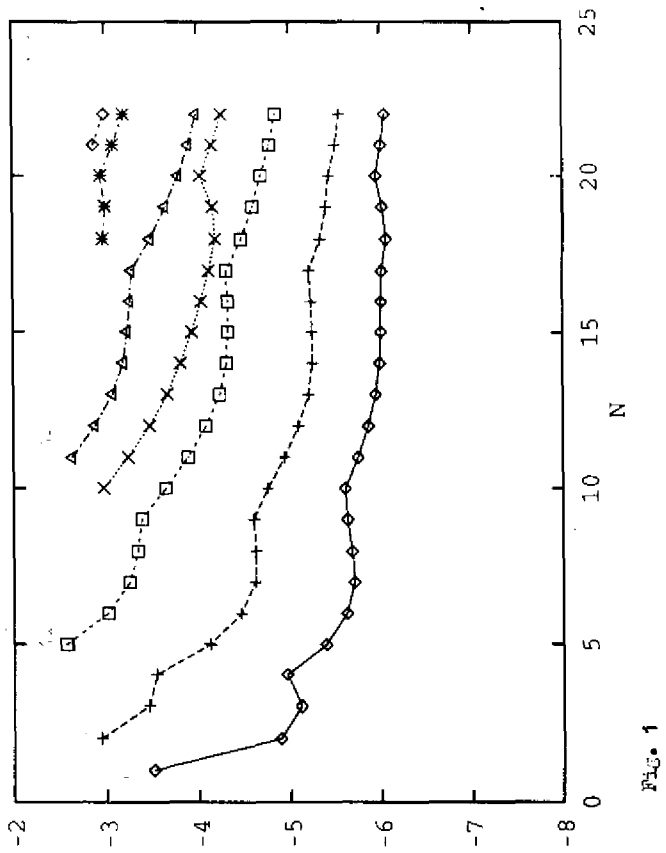

FIG. 1

EINGENVALUE (a.u.)

Fig. 1

DISSOCIATION ENERGY (eV)

Fig. 2

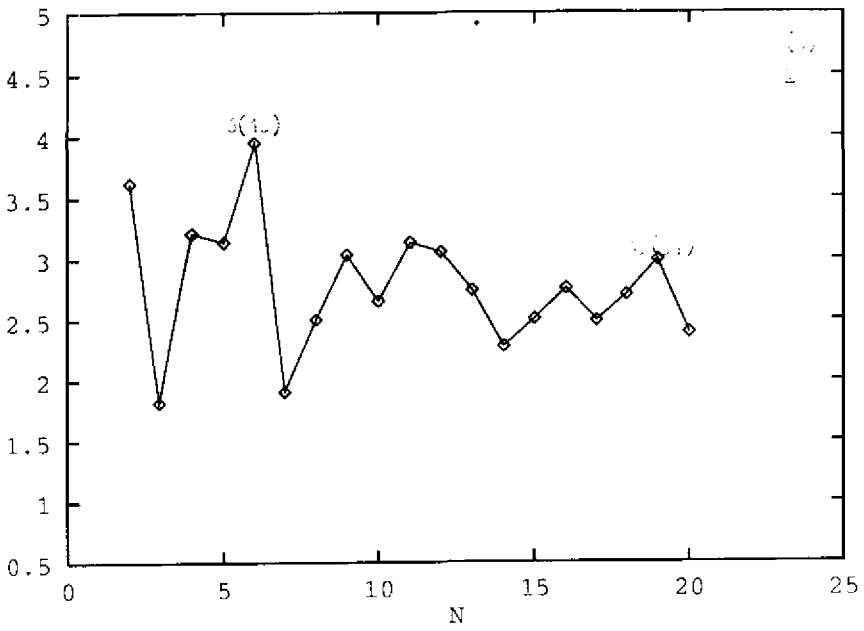
DISSOCIATION ENERGY (eV)
N
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
5
10
15
20
25

Fig. 2

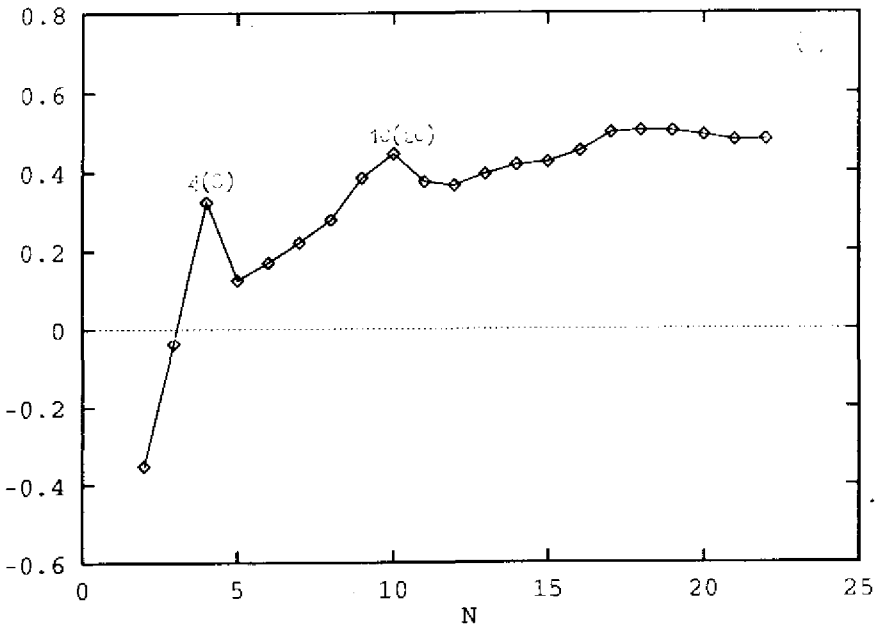
BINDING ENERGY (eV)/Atom)
N
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
5
10
15
20
25

Fig. 3

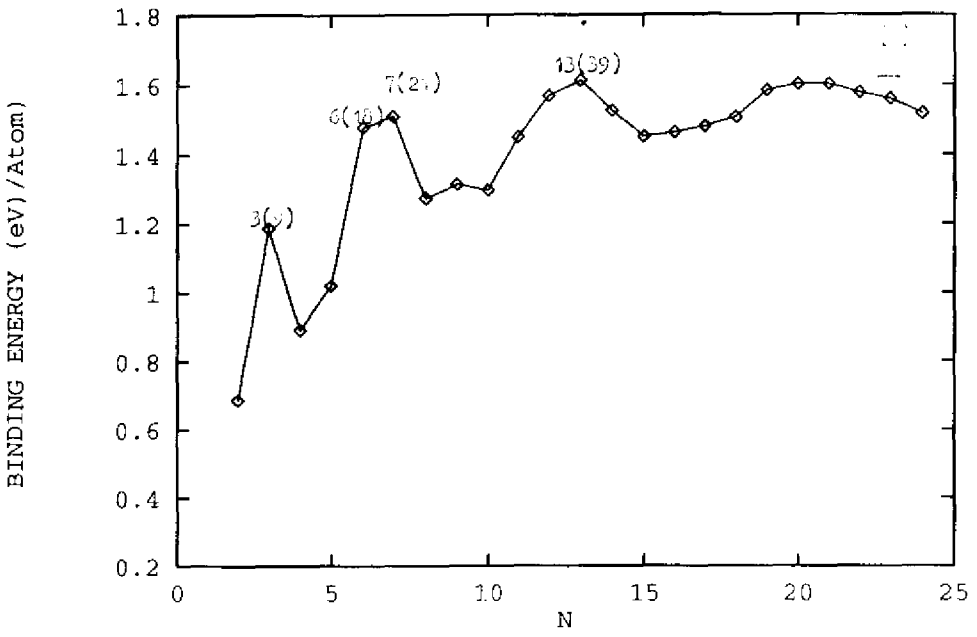
BINDING ENERGY (eV)/Atom
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
5
10
15
20
25
N
3(9)
6(18)
7(21)
13(39)

Fig. 3

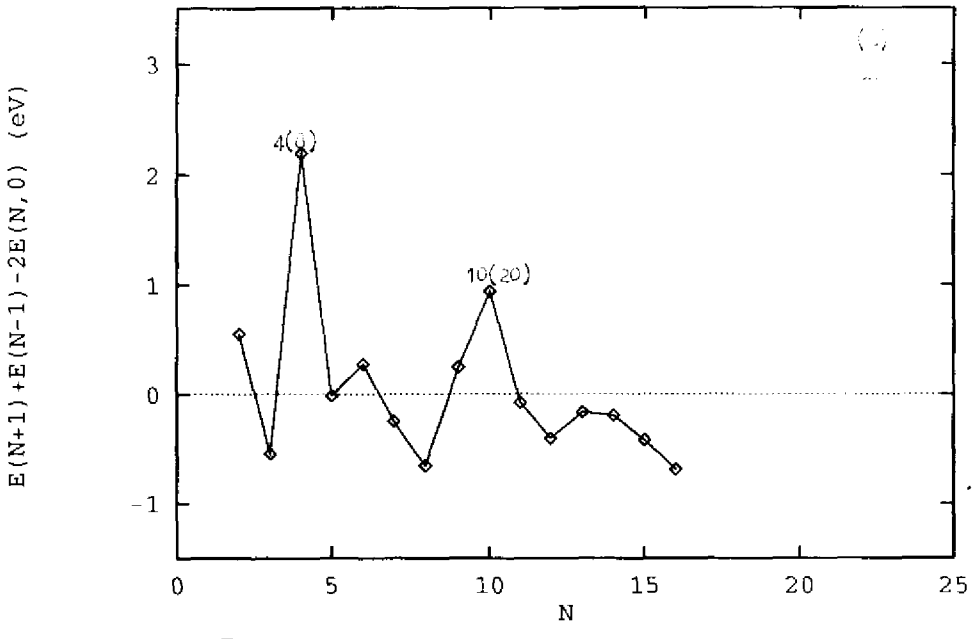
E(N+1)+E(N-1)-2E(N,0) (eV)
3
2
1
0
-1
0
5
10
15
20
25
N
4(8)
10(20)

Fig. 4

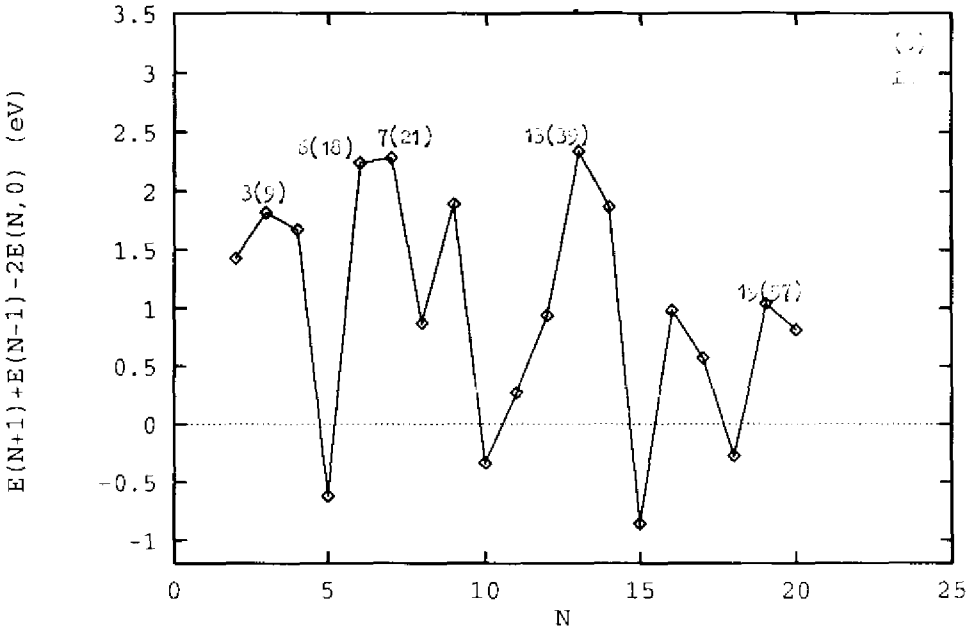
E(N+1)+E(N-1)-2E(N,0) (eV)
N
3(9)
6(18)
7(21)
15(39)
19(57)

Fig. 4

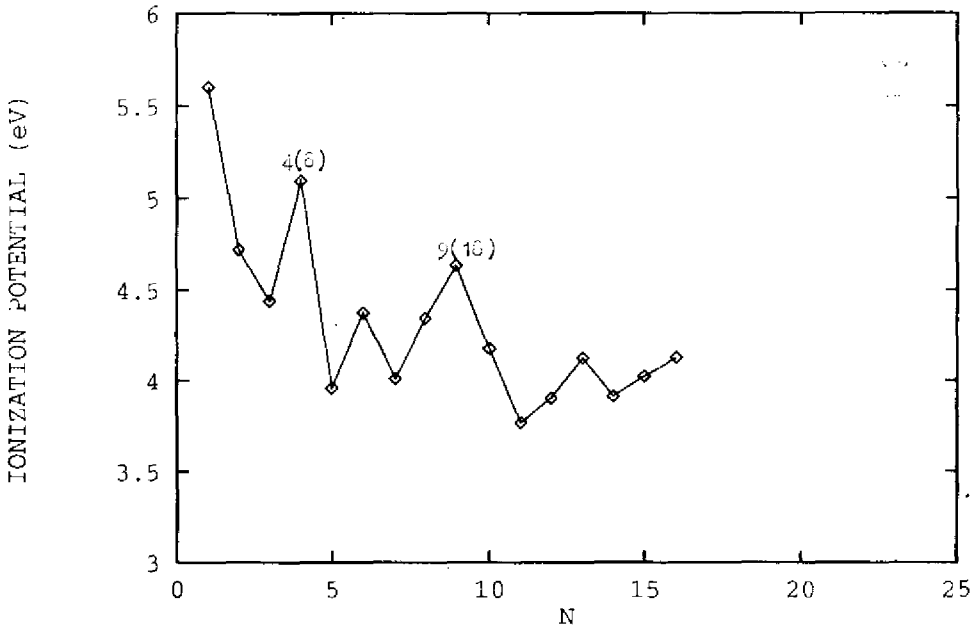
IONIZATION POTENTIAL (eV)
N
4(8)
9(18)

Fig. 5

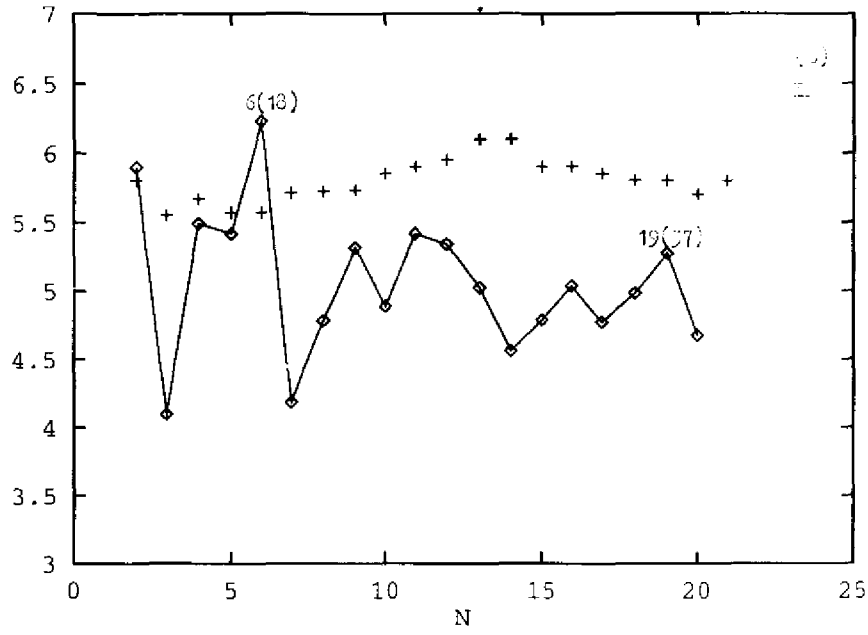
IONIZATION POTENTIAL (eV)
7
6.5
6
5.5
5
4.5
4
3.5
3
0
5
10
15
20
25
N
6(18)
19(37)

Fig. 5