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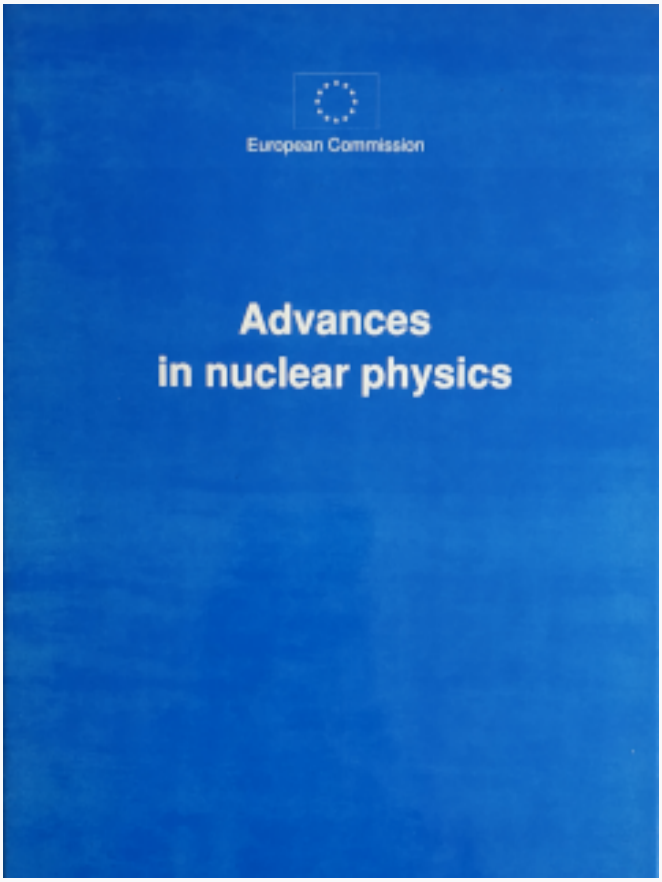


# Particle Number Dependence of Size and Energy Quantities in Sodium Clusters

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# PARTICLE NUMBER DEPENDENCE OF SIZE AND ENERGY QUANTITIES IN SODIUM CLUSTERS.

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## Abstract

The effective radial electronic potentials for neutral sodium clusters, which were determined by Ekardt on the basis of the local density approximation and the jellium model, are parametrized by means of the (symmetrized) Woods-Saxon and "Wine-Bottle" symmetrized Woods-Saxon potentials with the aim of investigating the dependence of size and energy quantities on the cluster particle number. The potential parameters are determined by various least-squares fitting procedures. It is found that for the radius $R$ of the above potentials, complex expressions are more appropriate than the standard one $R = r_0 N^{1/3}$ for relatively small values of $N$. Furthermore, N-power expansions are derived for those complex expressions of $R$, as well as for the r.m.s. radius of the potential. It is also found that improved results in these cases are obtained with an expression of the form $R = r_0 N^{1/3} + b$, which is still very simple. There is also investigated the variation of energy quantities, such as the single particle energies of the $1s$ and $1p$ states, the level spacing $|E_{1p} - E_{1s}|$ and the average energy level spacing, with respect to the particle number N. Expressions for the first three of these quantities with N-dependent terms of the form $aN^{-2/3} + \beta N^{-1}$ give good results.

## 1. Introduction

The knowledge of the mean field potentials for electrons in metal clusters is needed in various calculations, such as in the case of single-particle level densities, and electronic binding energies [1,2]. In practice, it is sometimes convenient to use parametrized forms of these potentials, as in ref. [2] where the shell and supershell structure were studied for $Na$ clusters.

In this paper we consider in some detail the effective radial electronic potential $V_{eff}(r)$ in the spherical and homogeneous jellium model as determined by using the local-density approximation. The density functional theory of Hohenberg, Kohn and Sham [3] has been used repeatedly in studies of metallic clusters, such as those in refs. [4]-[8]. Ekardt used the above mentioned method in his spherical-jellium- background model(SJBM) study of the metal cluster work function , the self consistent determination of the charge density and of the self consistent effective one-particle potential.

Ekardt's potentials have been parametrized in ref. [2] by a spherical Woods-Saxon (W-S) potential

$$V_{WS}(r) = -\frac{V_0}{1+e^{(r-R)/a}}, \quad 0 \leq r < \infty \tag{1}$$

with $V_0 = 6eV, R = r_0 N^{1/3}, r_0 = 2.25\mathring{A}$ and $a = 0.74\mathring{A}$

Nishioka et al [2] have also considered another type of potential obtained in ref. [9] through a combination of a semiclassical approximation and application of the Kohn-Sham density functional method to a positive jellium background. The inner part of this potential is slightly shallower while the outer part is deeper than the Woods-Saxon potential. This potential of "wine-bottle" shape has also been used in ref. [2] for the study of supershells.

In this paper we consider Ekardt's effective potentials for neutral sodium clusters and discuss a parametrization procedure, mainly by means of symmetrized Woods-Saxon potentials as well as "wine-bottle symmetrized Woods-Saxon" ones, and determine their parameters through least squares fittings. Our main objective is to investigate the variation of size and energy quantities of those clusters with respect to the particle number N. The layout of the paper is as follows: In the next two sections we discuss the above mentioned potentials, specify the notation and give some useful relevant formulae. In section 4 we report the numerical results of the various

least squares fittings and we investigate the way in which the potential radius $R$ and the root mean square radius of the potential varies with $N$ by deriving the corresponding analytic expressions and their expansions in powers of $N$. In section 5, the problem of the variation of such quantities as the lower single particle energies and the energy level spacings with respect to the particle number N is investigated and relevant analytic expressions are also discussed. The final section is devoted to a summary and conclusions.

## 2. The symmetrized Woods-Saxon potential

The symmetrized Woods-Saxon potential we are using is the following:

$$V_{SF}(r) = -V_0 f_{SF}(r) \doteq -V_0 \frac{sinh(R/a)}{cosh(r/a) + cosh(R/a)} =$$

$$= -V_0 \left[ [1 + exp\frac{(r-R)}{a}]^{-1} + [1 + exp\frac{(-r-R)}{a}]^{-1} - 1 \right], \quad 0 \leq r < \infty \quad (2)$$

The form factor of this potential has the shape of the symmetrized Fermi distribution which has been used to describe successfully the densities of nuclei for a wide range of mass numbers [10]. The potential (2) has been used pretty recently in analyses of hypernuclei [11] and also as a nuclear single particle potential [12]. It is very closely related to the so-called "cosh" potential used in ref. [13] as a cluster-core potential in Nuclear Physics.

The potential (2), which, unlike the Woods-Saxon potential, has zero slope at the origin, resembles somehow the Gaussian one for small values of $R/a$, while for $R/a >> 1$ gets very close to the Woods-Saxon one.

One feature of the potential (2) is that its volume integral is given exactly by the following simple analytic expression:

$$\left| 4\pi \int_0^\infty V_{SF}(r) r^2 dr \right| = \frac{4\pi}{3} V_0 R^3 [1 + (\frac{\pi a}{R})^2] \quad (3)$$

The same holds for its m.s.radius:

$$< r^2 >_{SF} = \frac{3}{5} R^2 [1 + \frac{7}{3} (\frac{\pi a}{R})^2] \quad (4)$$

More generally, the n-th moment of potential (2) may be given analytically [12]. In the case of the Woods-Saxon potential there are additional exponential terms. Thus, the expression of its n-th moment becomes more complex.

Since the condition $R/a >> 1$ is well satisfied, both for nuclei and atomic clusters, except for the very light ones, the symmetrized Woods-Saxon potential gives results almost identical to the Woods-Saxon ones, even for small values of the mass number and particle number $N$, respectively. The present analysis corroborates also this fact.

## 3. The "Wine-bottle" symmetrized Woods-Saxon potential

Another parametrization of the effective potential, which seems to be rather interesting, is the following one which is of "wine- bottle" shape

$$V_{WB}(r) = -V_0(1 + \frac{wr^2}{R^2})\frac{sinh(R/a)}{cosh(r/a) + cosh(R/a)}, \quad 0 \leq r < \infty \qquad (5)$$

for suitable choices of the parameter $w$.

The volume integral of the potential (5) may be obtained analytically though its expression is a little more complex than that of the potential (2). The result of integration leads to:

$$\left|4\pi \int_0^\infty V_{WB}(r)r^2dr\right| = \frac{4\pi V_0}{3}R^3\left[(1 + \frac{3w}{5}) + (1 + 2w)(\frac{\pi a}{R})^2 + \frac{7}{5}w(\frac{\pi a}{R})^4\right] \qquad (6)$$

It is immediately seen that for $w = 0$ this expression goes over to (3), as should be the case. Analytic expressions for the various moments of the potential may be also derived. The mean square radius for the "Wine-bottle" potential (5) is given by the expression:

$$< r^2 >_{W.B.} = \frac{3(7 + 5w)R^6 + 35(2 + 3w)a^2\pi^2R^4 + 49(1 + 5w)a^4\pi^4R^2 + 155a^6\pi^6w}{7(5 + 3w)R^4 + 35(1 + 2w)a^2\pi^2R^2 + 49a^4\pi^4w} \qquad (7)$$

We note that potential (2), or alternatively (5), should also be able to roughly reproduce the effective potential in the inhomogeneous jellium model [14]. Moreover, potential (5) may also reproduce the modified jellium potential of ref. [15]. We also note that the substitution of a higher degree polynomial (or a suitable function of $r$) for $(1+w\frac{r^2}{R^2})$ in (5), is likely to reproduce the wavy character of the local equivalent potential of ref. [16] (see fig. 2, of this reference) for individual clusters. Finally, we may point out that

it would be of interest to also consider the possibility of parametrizations of the form (2) or (5) of the average potential for the atom in the cluster, in the spirit of ref. [17].

## 4. The particle number depedence of quantities related to the radial extension of the effective electronic potential.

In this section we investigate the problem of the determination of the explicit dependence of the radius $R$ and of the root-mean-square radius $< r^2 >^{1/2}$ of the potentials (2) and (5) on the particle number. We considered Ekardt's effective local mean field potentials for the valence electrons in neutral sodium clusters with particle numbers $N$ = 8,18,20,34,40,58,68,90,92,106, 132,138,168,186, 198 [7] and we performed "a global least squares fit" of the symmetrized Woods-Saxon potential to the potential values for all these clusters by treating $V_0$, $a$ and the parameter $r_0$ in $R = r_0 N^{1/3}$ as adjustable parameters. According to the size of each cluster, about 15-30 points covering the interval where the potential differs practically from zero have been considered and the corresponding potential values were estimated from the figures of ref. [7]. The best fit values are: $V_0 = 6.05eV$, $r_0 = 2.34\ AA$, $a = 0.79\ AA$.

The same procedure was repeated by adopting as $R$ a fairly complex function of N. That function results from the observation that to a good approximation, the volume integral of the symmetrized Woods-Saxon potential for each cluster varies with $N$ as $cN + d = c(1 + \frac{d}{cN})N$, where $c$ and $d$ are constants. That functional dependence is obvious from Fig.1.

Thus we may write, by means of (3):

$$R^3 + (a\pi)^2 R = r_0'^3 N \tag{8}$$

where $r_0' = r_0(1 + \frac{\beta}{N})^{1/3}$ , $r_0 = (\frac{3c}{4\pi V_0})^{1/3}$ and $\beta = \frac{d}{c}$

In this way we arrive at an equation for $R$ which is of the same form as the one appearing in studies of nuclei or hypernuclei on the basis of the rigid-core model (see ref. 11,12,18 and references therein). The difference is that, in the present case, the parameter $r_0$ becomes $r_0'$ and depends on the particle number. Furthermore, instead of $N_c = N - 1$,N appears now in the equation. The third order equation (8) can be solved exactly [18,19] and

one gets the following expression for the potential radius as a function of the number of particles:

$$R = \frac{1}{2^{1/3}} r_0' N^{1/3} \left\{ \left[ 1 + [1 + \frac{4}{27} (\frac{\pi a}{r_0' N^{1/3}})^6]^{1/2} \right]^{1/3} + \right.$$

$$\left. + \left[ 1 - [1 + \frac{4}{27} (\frac{\pi a}{r_0' N^{1/3}})^6]^{1/2} \right]^{1/3} \right\} \qquad (9a)$$

From this expression we may derive the following expansion by taking also into account that $r_0'$ depends upon $N$.

$$R = r_0 N^{1/3} \left\{ 1 - \frac{1}{3} (\frac{\pi a}{r_0})^2 N^{-2/3} + \frac{\beta}{3} N^{-1} + \frac{\beta}{3^2} (\frac{\pi a}{r_0})^2 N^{-5/3} + \right.$$

$$\left. \frac{1}{3^4} [(\frac{\pi a}{r_0})^6 - 9\beta^2] N^{-2} - ... \right\} \qquad (9b)$$

We also note that the explicit dependence of the potential r.m.s. radius on the particle number follows from expressions (4) and (9a). Furthermore, the leading terms in an expansion of $< r^2 >^{1/2}$ in powers of the particle number are easily derived. The result is:

$$< r^2 >_{SF}^{1/2} = (\frac{3}{5})^{1/2} r_0 N^{1/3} \left\{ 1 + \frac{5}{6} (\frac{\pi a}{r_0})^2 N^{-2/3} + \frac{\beta}{3} N^{-1} - \frac{7}{24} (\frac{\pi a}{r_0})^4 N^{-4/3} - \right.$$

$$\left. \frac{5\beta}{9} (\frac{\pi a}{r_0})^2 N^{-5/3} + ... \right\} \qquad (10)$$

It is clear that in this generalized case, apart from the parameters $V_0$, $r_0$ and $a$, there is an additional parameter $\beta$. By using these parameters as fitting parameters we get the following best fit values: $V_0 = 6.03eV$, $r_0 = 2.295\mathring{A}$, $a = 0.781\mathring{A}$ and $\beta = 10.49$. In this case a marked improvement in the quality of the fit is observed in comparison to the one obtained with the simple expression $R = r_0 N^{1/3}$.

A very similar quality of the fit is obtained if $R$ is taken to be of the form

$$R = r_0 N^{1/3} + b \qquad (11)$$

The best fit values in the latter case are: $V_0 = 6.03eV$, $r_0 = 2.10\mathring{A}$, $b = 1.09\mathring{A}$, $a = 0.78\mathring{A}$.
The expansion in this case of the potential r.m.s. in powers of the particle number is:

$$< r^2 >_{S.F.}^{1/2} = (\frac{3}{5})^{1/2} r_0 N^{1/3} \left\{ 1 + \frac{b}{r_0} N^{-1/3} + \frac{7}{6}(\frac{\pi a}{r_0})^2 N^{-2/3} - \frac{7b}{6r_0}(\frac{\pi a}{r_0})^2 N^{-1} + \right.$$

$$\left. + \left[ \frac{7b^2}{6r_0^2} - \frac{49}{72}(\frac{\pi a}{r_0})^2 \right] (\frac{\pi a}{r_0})^2 N^{-4/3} + ... \right\} \qquad (12)$$

It is seen that in this case the leading $N$-depedent term of the expansion in curly brackets is proportional to $N^{-1/3}$ ,while in the previous case it was proportional to $N^{-2/3}$.

Another least squares fitting procedure we attempted aimed to consider the average values of the potential depths $V_0$ and of the diffuseness parameters $\overline{a}$ ($\overline{V}_0 = 6.05eV$, $\overline{a} = 0.79\mathring{A}$). The parameters in $R$ (expression (11)) were determined by least squares fitting of the expression of $< r^2 >_{SF}$ to the corresponding values obtained by the fitting of the symmetrized W-S potential to the values of $V_{eff}(r)$ for individual clusters. The best fit values in this case are: $r_0 = 2.16\mathring{A}$, $b = 0.795\mathring{A}$.

It should be noted that the best fit values depend on the clusters considered. Thus, if among the values of $N$ only those with $N \geq 90$ are included in the fitting, the best fit values in the first of the above mentioned fitting procedures, with expression (11) for $R$, become: $V_0 = 6.01eV$, $r_0 = 2.28\mathring{A}$, $b = 0.114\mathring{A}$ and $a = 0.87\mathring{A}$. The improvement in the quality of the fitting, compared to the one in which the expression $R = r_0 N^{1/3}$ is used becomes now much smaller.

From our analysis we have realized that the fitting of $V_{eff}(r)$ by a (symmetrized) Woods-Saxon potential is on the whole fairly satisfactory in most cases(see e.g. figures 2 and 3). All these results were obtained with the above mentioned "global fitting" and expression (11) for $R$. In certain cases the fitting is improved if the "Wine-bottle" symmetrized Woods-Saxon potential is used. Different choices of $w$ for the individual clusters seem, however, necessary in many cases.It should be noted that in general the latter potential does not give an improved fitting at least in the "global fitting" procedures.

In fig. 4 and 5 we have plotted the Woods-Saxon potential and the wine-bottle potential (denoted by 1 in each figure) of ref. 10 used by Nishioka et

al [2] (see their fig. 1). In the same figures symmetrized Woods-Saxon and Wine-Bottle symmetrized Woods-Saxon potentials, obtained in this work are shown. It is seen that there is in both cases a marked difference in the surface region.

Finally, in fig. 6 the variation of the radius of the (symmetrized) Woods-Saxon potential with respect to $N^{1/3}$ is shown. The best fit values used are those of the above mentioned "global least squares fitting" and are given after expression (11). The functional dependence of $R$ on $N^{1/3}$ is apparent.

Regarding the "wine-bottle" symmetrized Woods-Saxon potential, the adjustable parameters in the overall fitting were $V_0, a, r_0, \beta$ and $w$ and their corresponding best fit values: $V_0 = 5.882eV$, $r_0 = 2.054\mathring{A}$, $a = 0.836\mathring{A}$, $\beta = 1.21$ and $w = 0.134$.

In the case of the "wine-bottle" symmetrized Woods-Saxon potential, it is more difficult to establish the dependence of the potential radius $R$ on the particle number. This matter is discussed in the appendix. If the expansion of $R$ derived there is used, the following expression for the r.m.s. radius of the potential may be derived:

$$< r^2 >^{1/2}_{W.B.} = (\frac{3}{7})^{1/2}(\frac{7+5w}{5+3w})^{1/2}(\frac{5}{5+3w})^{1/3} r_0 N^{1/3}$$

$$\left\{1 + \frac{1}{6}(\frac{5}{5+3w})^{1/3}(\frac{13w^2+52w+35}{7+5w})(\frac{\pi a}{r_0})^2 N^{-2/3} + \frac{\beta}{3}N^{-1} + ...\right\} \quad (13)$$

If on the other hand, the expression (11) for $R$ is used, we obtain:

$$< r^2 >^{1/2}_{W.B.} = (\frac{3}{7})^{1/2}(\frac{7+5w}{5+3w})^{1/2} r_0 N^{1/3} \left\{1 + (\frac{b}{r_0})N^{-1/3} + \right.$$

$$\frac{5(33w^2+90w+49)a^2\pi^2}{6(7+5w)(5+3w)r_0^2}N^{-2/3} -$$

$$\left. - \frac{5(33w^2+90w+49)a^2\pi^2 b}{6(7+5w)(5+3w)r_0^3}N^{-1} + ...\right\} \quad (14)$$

In fig. 7 the plot: $R = f(N^{1/3})$, obtained with the best fit values of the "global fitting" is shown. Moreover, by using these best fit values we plotted some "Wine-bottle" potentials, which are compared to the ones by Ekardt

Ref [7]. The results show that for some of Ekardt's potentials the "Wine-bottle" potential is a rather good approximation as in the case $Na_{198}$ (Fig. 8b), while for others, such as for $Na_{90}$, this is not the case (Fig. 9).

We also performed three least squares fittings to $< r^2 >_{W.B.}$:

a) For the $V_0, a, w$ we used the average values $\overline{V_0} = 5.841eV, \overline{a} = 0.8778\mathring{A}$ and $\overline{w} = 0.2643$ while for the radius $R$ we used the expression $R = r_0 N_c^{1/3} + b$, $N_c = N - 1$, where the fitting parameters were $r_0$ and $b$. We found $r_0 = 2.115\mathring{A}$ and $b = 0.6953\mathring{A}$.

b)For $V_0$, $a$, $w$, we used the same values as above, but for $R$ the expression was $R = r_0 N^{1/3} + b$. The fitting parameters were $r_0$ and $b$ and their best fit values: $r_0 = 2.140\mathring{A}$ and $b = 0.5428\mathring{A}$.

c)We used $V_0 = \overline{V}_0$, $a = \overline{a}$ and the formula $R = r_0 N^{1/3} + b$ for the radius and we treated $r_0$, $b$ and $w$ as adjustable parameters. The best fit values are: $r_0 = 2.157\mathring{A}, b = 0.268\mathring{A}, w = 0.510$.

The best quality of the fit among the above three cases was obtained with the last set of values. Using these values we plotted the corresponding potential for some clusters. It is obvious that for some of them the results are rather good e.g. $Na_{198}$ (Fig. 10) but for others, such as $Na_{90}$, this is not the case (Fig. 11).

Additional fittings were performed with the "Wine-Bottle" symmetrized Woods-Saxon potential using only the larger clusters ($N \geq 90$) in the global fitting of the potential values. Among the several possibilities which were tried, the one with $R = r_0 N^{1/3} + b$ gave the best quality of the fitting. The best fit values were $V_0 = 6.027eV$, $r_0 = 1.965\mathring{A}$, $a = 0.859\mathring{A}$, $w = 0.102$ and $b = 1.641\mathring{A}$.

## 5. The dependence of energy quantities on the number of the particles.

In this section we give numerical results for energy quantities, such as the single-particle energies for the ground and the first excited state, the average level spacing and the lowest energy level spacing and we discuss their variation with the particle number. In obtaining these results the symmetrized Woods-Saxon potential was used and its parameters were determined either by fitting to individual clusters or by means of the "global fitting" (cases I

and II respectively) using expression (9a) for the potential radius $R$. The corresponding values for $R$ are those displayed in table 1.

In table 2 the ground-state ($1s$) single-particle energies calculated by Ekardt [7] for a number of neutral sodium clusters with $8 \leq N \leq 198$ are displayed, along with the values obtained by numerical solution of the Schrödinger equation with the symmetrized Woods-Saxon potential in cases I and II (see above and table 1) for the determination of the parameters. In the same table the $E_{1s}$ energies calculated with the analytic expression

$$E_{1s} = -V_0 + C_{s_1} N^{-2/3} + C_{s_2} N^{-1} \tag{15}$$

are displayed. The parameters $C_{s_1} = 7.556eV$ and $C_{s_2} = -3.295eV$ were determined by least squares fitting to the values of case II. $V_0$ is the potential depth parameter ($V_0 = 6.031eV$). The variation of $E_{1s}$ with the particle number $N$ is shown in Fig. 12.

The energy values of the first excited state ($1p$) are displayed in table 3 and the corresponding plots are in figure 13.

The analytic expression in this case is

$$E_{1p} = -V_0 + C_{p_1} N^{-2/3} + C_{p_2} N^{-1} \tag{16}$$

The values of the parameters are: $C_{p_1} = 16.059eV$ and $C_{p_2} = 10.388eV$. Finally,in tables 4 and 5 and Figs. 14 and 15 respectively, the corresponding results are given for the average spacing of the single particle levels of each neutral sodium cluster $\Delta E_{av}$ and for the lowest energy level spacing (LELS):$|E_{1p} - E_{1s}|$ of each cluster. The corresponding analytic expression is:

$$|E_{1p} - E_{1s}| = 8.503N^{-2/3} - 7.093N^{-1} \tag{17}$$

It is seen, on the basis of the previously mentioned results that there is in general very good agreement between the energy values obtained by Ekardt [7] and those obtained with the symmetrized Woods-Saxon potential, in both cases, I and II. It is also seen that although fluctuations of these quantities with the number of atoms $N$ are observed, the average trend of each of these quantities is as expected.Furthermore, the analytic expressions(15),(16),(17) give good results.

We also note that by using the "Wine-Bottle" potential,for certain clusters, such as $Na_{20}$, $Na_{106}$ and $Na_{198}$ for which this potential approximates rather

well the corresponding Ekardt's potential,the ground state single-particle energies are fairly close to those obtained with the symmetrized Woods-Saxon potential. Note that the larger the cluster the smaller the difference.

We finally performed calculations of the ground state single-particle energies using the Woods-Saxon potential (with the parameters $V_0 = 6.031eV$, $r_0 = 2.295\ AA$, $a = 0.781\ AA$, $\beta = 10.49$). The reason for these additional calculations of the ground state energy is that for the usual Woods-Saxon potential (which, except for the light clusters, coincides with the symmetrized one) an approximate closed form analytic expression can be given in terms of the potential parameters. This is the following [18, 20]:

$$E_{1s} = -V_0 + \frac{\hbar^2\pi^2}{2m_e}\frac{1}{R^2}\left[\frac{1}{(1+S^{-1})^2}\right] \tag{18}$$

where

$$S^{-1} = \left[1 - 2a\ \tilde{K_0}\ [\gamma + \Psi(1 + a\ \tilde{K_0})]\right]/(\tilde{K_0}\ R) \tag{19}$$

In this expression $\tilde{K_0} = (\frac{2m_e V_0}{\hbar^2})^{1/2}$, while the function $\Psi$ is the logarithmic derivative of the $\Gamma$ function.This may also be given in the terms of the following expansion:[21]

$$\Psi(1 + a\ \tilde{K_0}) = -\gamma + \sum_{n=1}^{\infty}(-1)^{n+1} j(n+1)(a\ \tilde{K_0})^n\ , \quad a\ \tilde{K_0} < 1 \tag{20}$$

where $j(n+1)$, $n = 1, 2, ...$ is Riemann's zeta functions and $\gamma$ Euler's constant.($\gamma$=0.577). If the complex expression (9a) of $R$ is used and its expansion (9b) in terms of the particle number we arrive after some algebra at the following expansion of $E_{1s}$:

$$E_{1s} = -V_0 + \frac{\hbar^2\pi^2}{2m_e}\left\{r_0^{-2}N^{-\frac{2}{3}} - 2r_0^{-2}(\tilde{S}^{-1})N^{-1} + \left[\frac{2}{3}(\frac{\pi a}{r_0})^2 + 3(\tilde{S}^{-1})^2\right] r_0^{-2}N^{-\frac{4}{3}} - \right.$$

$$\left.\left[\frac{2\beta}{3}r_0^{-2} + 2(\frac{\pi a}{r_0})^2\ \tilde{S}^{-1}\ r_0^{-2} + 4(\tilde{S}^{-1})^3 r_0^{-2}\right] N^{-\frac{5}{3}} + ...\right\} \tag{21a}$$

where

$$\tilde{S}^{-1} = r_0^{-1}\left[\tilde{K_0}^{-1} - 2a\left[\gamma + \Psi(1 + a\ \tilde{K_0})\right]\right]$$

If expression (11) is used for $R$, the following expansion of $E_{1s}$ in terms of $N$ arises:

$$E_{1s} = -V_0 + \frac{\hbar^2\pi^2}{2m_e}\left\{r_0^{-2}N^{-2/3} - 2\left[br_0^{-1} + \tilde{S}^{-1}\right]r_0^{-2}N^{-1} + \right.$$

$$3\left[b^2r_0^{-2} + 2br_0^{-1}\,\tilde{S}^{-1} + (\tilde{S}^{-1})^2\right]r_0^{-2}N^{-4/3} -$$

$$\left. 4\left[b^3r_0^{-3} + 3b^2r_0^{-2}\,\tilde{S^{-1}} + 3br_0{}^{-1}(\tilde{S^{-1}})^2 + (\tilde{S^{-1}})^3\right]r_0{}^{-2}N^{-5/3} + ...\right\} \qquad (21b)$$

It is seen from the above expressions that the ground state single-particle energy eigenvalue depends more strongly on the potential depth $V_0$ and the potential radius parameter $r_0$ and more weakly on the diffuseness parameter a and the other parameters b and $\beta$ appearing in the expression of $R$.The heavier the cluster the weaker the influence of the latter parameters.In particular the parameter $\beta$ does not appear at all in the first four terms of the corresponding expansion.

It is also clear from the above expressions that the leading terms depending on $N$ are of the order $N^{-2/3}$ and $N^{-1}$. This corroborates the validity of expression (15) used earlier.

The numerical results obtained with expression (18) and the first three terms of expression (21a), along with the Ekardt's values and those with the numerical solution of the Schrödinger equation are presented in Table 6. It is seen that the above analytic expressions give in most cases satisfactory results.

## 6. Summary and conclusions

In this paper an attempt was made to investigate in some detail the variation of quantities related to the radial extension of the electronic potential and of energy quantities reffered to the single particle electronic states of neutral sodium clusters with the number of atoms.This was done by considering the effective potentials obtained by Ekardt[7] and parametrizing them by means of (Symmetrized) Woods-Saxon and "Wine bottle" Symmetrized Woods-Saxon potentials.Two main least-squares fitting procedures were used,although other possibilities were also considered:

i)"Global least squares fitting," in which the analytic expressions of the above potentials were fitted to potential values of all the clusters considered

by Ekardt ($8 \leq N \leq 198$),treating $V_0$, a and the other parameters as fitting parameters.

ii)"Fitting to the mean-square radii $< r^2 >$ of the above potentials".In this case, the average values of $V_0$, a : $\bar{V}_0$ and $\bar{a}$ for the clusters considered were used. The other parameters were determined by least-squares fittings of the analytic expressions of $< r^2 >$(for each of the two potentials) to the values of $< r^2 >$ obtained by using as parameters those resulting by fitting for each individual cluster the analytic expression (2) or (5) to values of the effective potential.

It was found on the basis of the above treatments that in certain cases the fitting is fairly satisfactory,while in others this is not the case.

The depedence of the potential radius $R$ of the Symmetrized Woods-Saxon or the "Wine-bottle" Symmetrized Woods-Saxon potential on the particle number $N$ was established on the basis of the observation that the volume integral of these potentials,which can be derived analytically,varies with $N$ like $cN + d$.This led to rather complex analytic expressions for$R$ and also for the r.m.s.radius$< r^2 >^{1/2}$ of the potential.Expansions of these quantities in powers of $N$ were derived for each of those potentials. It was found that additional correction terms to the standard expression $R = r_0 N^{1/3}$ for the Symmetrized Woods-Saxon potential which are, of the order $N^{-1/3}$, $N^{-2/3}$ or higher appear now in $R$(see expression (9b)). Analogous comments hold for the "Wine-bottle" Symmetrized Woods-Saxon potential and for the r.m.s.radii of the potentials.It seems worth while to point out that with the above expressions for $R$ or with an expression of the form $R = r_0 N^{1/3} + b$ a marked improvement in the quality of the fitting is observed and therefore these expressions seem more appropriate to use in practice, than the one $R = r_0 N^{1/3}$, which is commonly used. To our knowledge, this is pointed out for the first time , pertaining to atomic clusters.It should be noted,however, that the observed improvement becomes very small if the analysis is confined only to the heavier clusters ($N \geq 90$).

Another variation with the particle number $N$ which was examined was that of the energy of the lower electronic states,of the corresponding lowest energy level spacing and of the average level spacing.It was found that Ekardt's results can be reproduced quite satisfactorily by the corresponding results obtained with the numerical solutions of the Schrödinger equation with the (Symmetrized) Woods-Saxon and the"Wine-bottle"Symmetrized Woods-Saxon potential(using parameters either by fitting to individual clus-

ters or those of the "global fitting"). Furthermore, it was realized that the same conclusion holds if the simple analytic expressions (15) and (16), for the energies of $1s$ and $1p$ states respectively, are used. Finally, a closed form analytic expression for the $E_{1s}$ state in terms of the potential parameters was considered(expression (18)) for the Woods-Saxon potential with good results.The leading terms of the expansion of this expression in powers of $N$ (with either of the expressions for $R$) provide also justification for the use of the expression(15).


## Acknowledgements

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## APPENDIX

In this appendix, we outline the derivation of the expression for the Wine-bottle potential radius R as a function of the number of particles $N$. This is based on the observation that the volume integral (6) varies with $N$, like $cN+d$ , as was also found for the symmetrized Woods-Saxon one. The relevant expression is, however, more complex, since the equation which follows from (6) is now of fourth order:

$$(5+3w)R^4 + 5a^2\pi^2(1+2w)R^2 - 5r_0'^3 NR + 7a^4\pi^4 w = 0 \qquad (A.1)$$

The $r_0'$ is given by the same expression as in the symmetrized Woods-Saxon potential. The above equation may be transformed into a third-order one. Thus,the solution of (A.1) is given by the following expression:

$$R = \frac{1}{2}\left[\sqrt{\psi_1 - a_2} + \sqrt{-a_2 - \psi_1 + 2\sqrt{\psi_1^2 - 4a_4}}\right] \qquad (A.2)$$

where

$$\psi_1 = (P + \sqrt{Q^3 + P^2})^{1/3} + (P - \sqrt{Q^3 + P^2})^{1/3} + \frac{5a^2\pi^2(1+2w)}{3(5+3w)} \qquad (A.3)$$

and

$$P = \frac{25r_0'^6 N^2}{2(5+3w)^2}\left[1 - \frac{10a^6\pi^6(1312w^3 + 2976w^2 + 1110w - 25)}{675(5+3w)r_0'^6 N^2}\right] \qquad (A.4)$$

$$Q = -\frac{a^4\pi^4(352w^2 + 520w + 25)}{9(5+3w)^2} \qquad (A.5)$$

$$a_2 = \frac{5a^2\pi^2(1+2w)}{5+3w} \qquad a_4 = \frac{7a^4\pi^4 w}{5+3w} \qquad (A.6)$$

From the above expression of $R$, the following expansion may arise:

$$R = (\frac{5}{5+3w})^{1/3} r_0 N^{1/3}\left\{1 - (1/3)(\frac{5}{5+3w})^{1/3}(1+2w)(\frac{a^2\pi^2}{r_0^2})N^{-2/3} + \frac{\beta}{3}N^{-1}\right.$$

$$\left. -\frac{1}{144}(\frac{5}{5+3w})^{-4/3}\frac{2924w^2 + 4940w - 25 + 8L}{(5+3w)^2}(\frac{a^4\pi^4}{r_0^4})N^{-4/3} + \right.$$

$$+\frac{\beta}{9}(\frac{5}{5+3w})^{1/3}(1+2w)(\frac{a^2\pi^2}{r_0^2})N^{-5/3}+...\Big\} \qquad (A.7)$$

where

$$L=(\frac{9^3(1312w^3+2976w^2+1110w-25)^2-25(352w^2+520w+25)^3}{25})^{1/3} \qquad (A.8)$$

It should be also noted that there is a marked dependence of the parameter $w$ on $N : w = w(N)$. We may also note that the first four or five terms of this expansion give quite accurate values of $R$ in the cases we have investigated.

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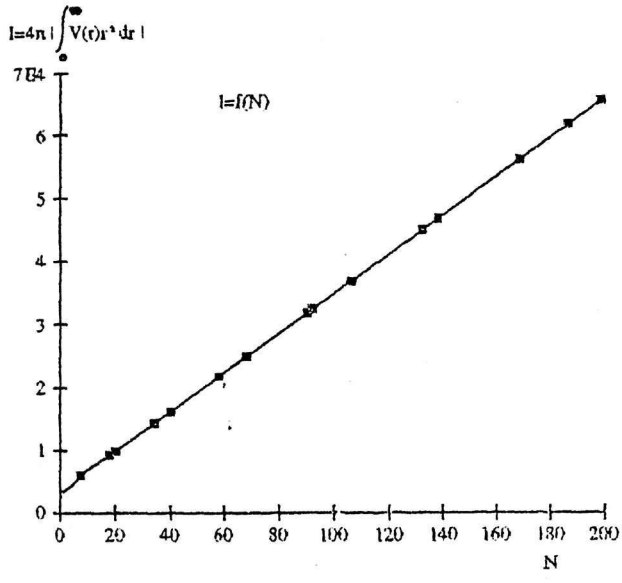



**Fig. 1.** The volume integral of the Symmetrized Woods-Saxon potential as a function of the number of particles $N$.The potential parameters of each cluster were determined by least squares fitting of expression (2) to corresponding values of $V_{eff}$ of ref[7].

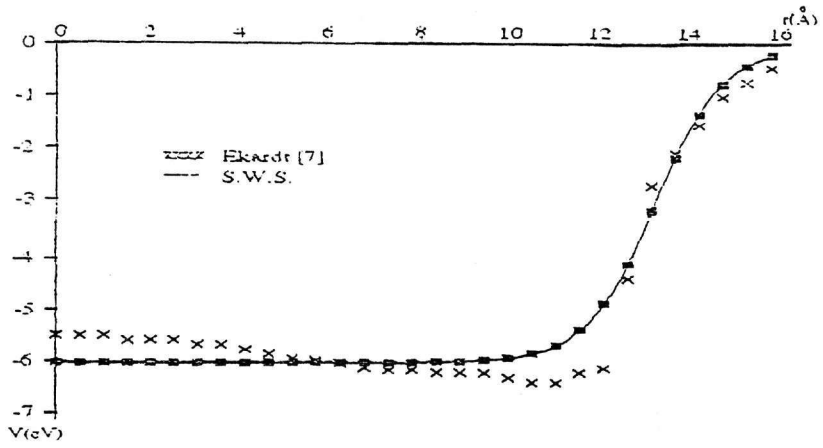



**Fig. 2.** The $V_{eff}(r)$ of Ekardt [7] for $N = 198$(denoted by (x) points) and the corresponding symmetrized Woods-Saxon one (solid line) plotted with the best fit values of the "global fitting" and $R = r_0 N^{1/3} + b$.

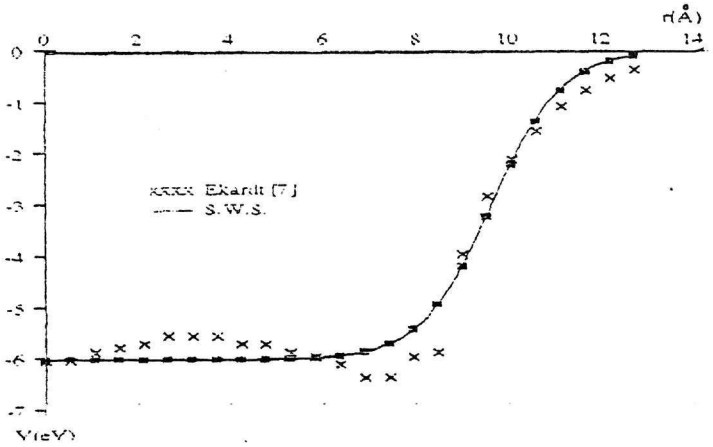



Fig. 3.The $V_{eff}(r)$ of Ekardt [7] for $N = 68$ (denoted by (x) points) and the corresponding symmetrized Woods-Saxon one (solid line) plotted with the best fit values of the "global fitting" and $R = r_0 N^{1/3} + b$.

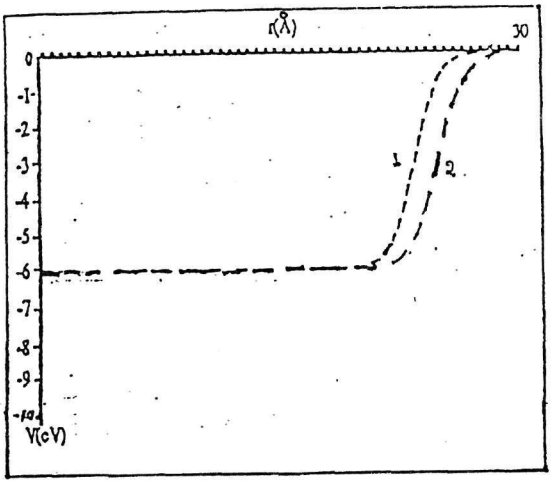



**Fig. 4.** The Woods Saxon potential (No 1) with the parameters of ref [2] for the cluster with N=1000 and the corresponding symmetrized Woods-Saxon potential of this work (No 2) using the expression $R = r_0 N^{1/3} + b$ and the best fit values: $V_0 = 6.014eV, r_0 = 2.28\mathring{A}$ and $b = 0.114\mathring{A}, a = 0.87\mathring{A}$.

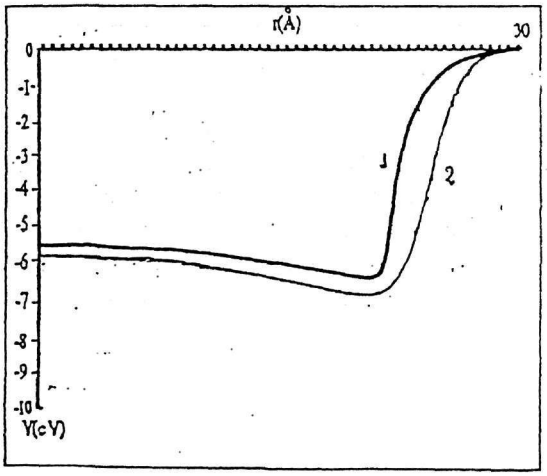



**Fig. 5.** The wine-bottle-potential (No 1) for $N = 1000$ obtained with the method of ref. [10] and used in ref. [2] and the "Wine-bottle" symmetrized Woods-Saxon potential (No 2) of this work using the expression $R = r_0 N^{1/3} + b$ and the best fit values: $V_0 = 6.03eV, r_0 = 1.97\mathring{A}, b = 1.64\mathring{A}, a = 0.86\mathring{A}, w = 0.102,$.

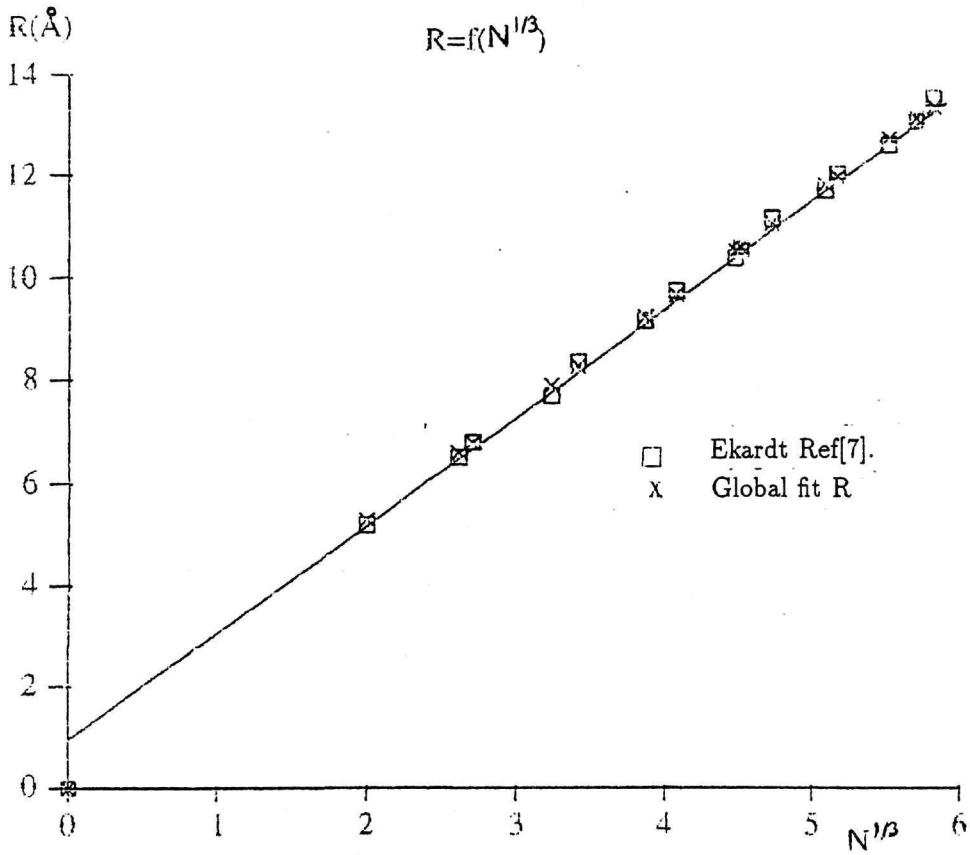



**Fig. 6.** The variation of the radius $R$ of the Symmetrized Woods-Saxon potential with respect to the cubic root of the particle number $N$. The values of $R$ obtained by performing least squares fitting of $V_{SF}(r)$ to the $V_{eff}(r)$ of Ekardt[7] for individual clusters are denoted by □, while those values obtained by a "global least squares fitting" using the expression $R = r_0 N^{1/3} + b$ are denoted by ×.

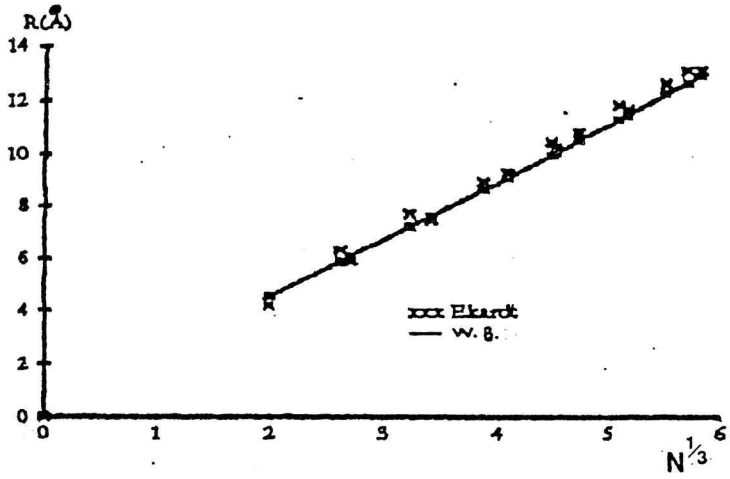
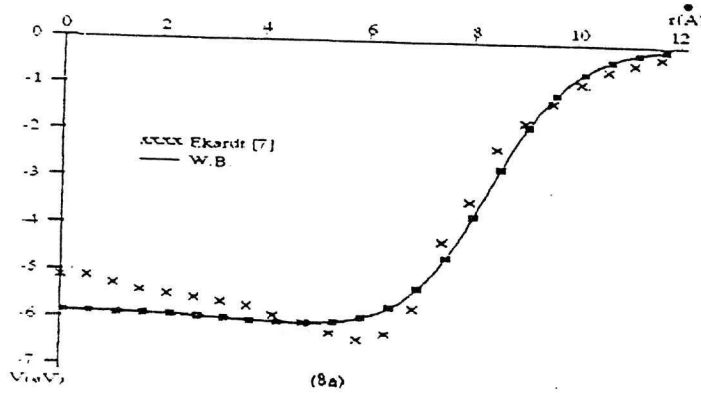



Fig. 7. Plot of $R = f(N^{1/3})$ with parameters obtained by a "global fitting" of the values of the "Wine-bottle" potentials to the values of Ekardt's [7] potentials.



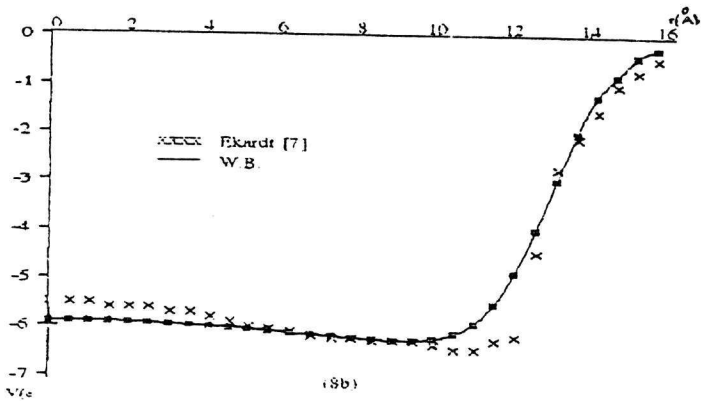




**Fig. 8.** The plotts $V_{eff}(r)$ of Ekardt for $N = 40$ and $N = 198$ sodium atoms (denoted by (x) points) and the corresponding "Wine Bottle" potential (solid line) obtained using the expression A2 for the radius $R$ and the best fit values $V_0 = 5.882eV, r_0 = 2.054\mathring{A}, a = 0.836\mathring{A}, \beta = 1.21$ and $w = 0.134$

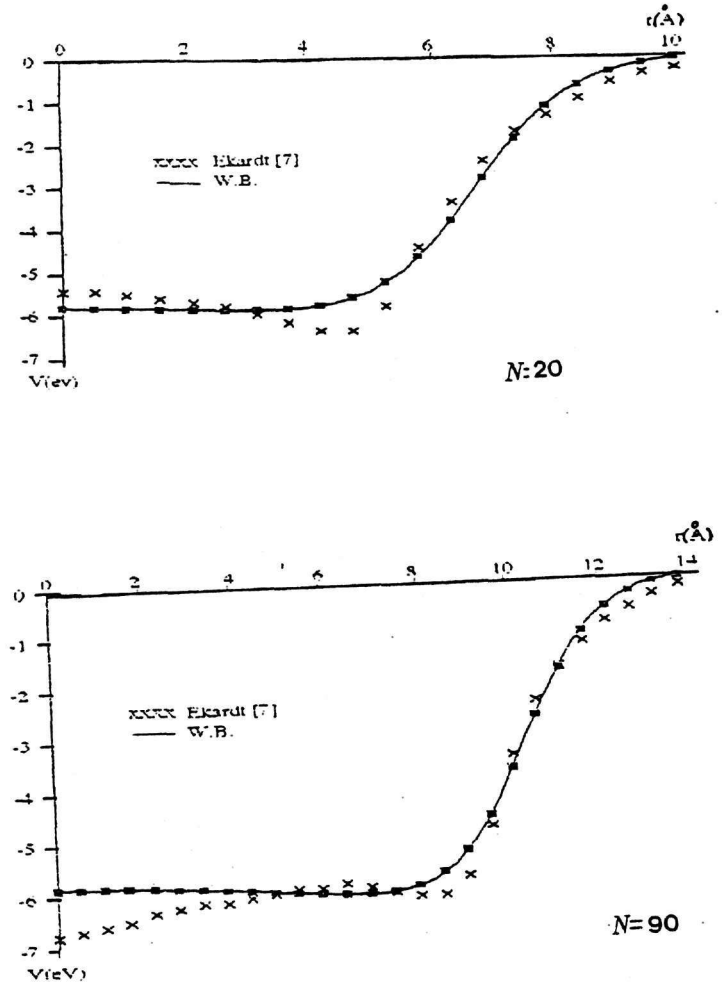



**Fig.9.** The plots $V_{eff}(r)$ of Ekardt for $N = 20$ and $N = 90$ sodium atoms (denoted by (x) points) and the corrresponding "Wine bottle" potential (solid line) obtained using the expression for the radius $R = r_0 N^{1/3} + b$ and the best fit values of the "global fitting". $V_0 = 5.882eV, r_0 = 2.054\mathring{A}, a = 0.836\mathring{A}, b = 1.09\mathring{A}$ and $w = 0.131$.

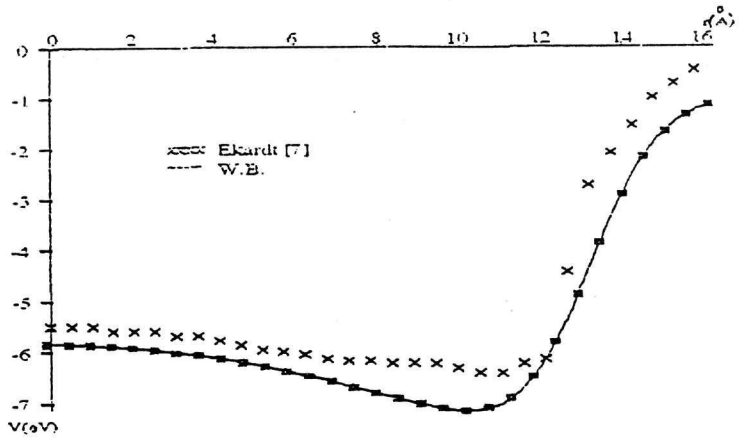



**Fig.10.** The plot of Ekardt potential for the $Na_{198}$ cluster denoted by $(x)$ points and the corresponding "Wine bottle" potential (solid line), which is obtained with parameters determined by least squares fitting of $< r^2 >_{W.B.}$ (see text).

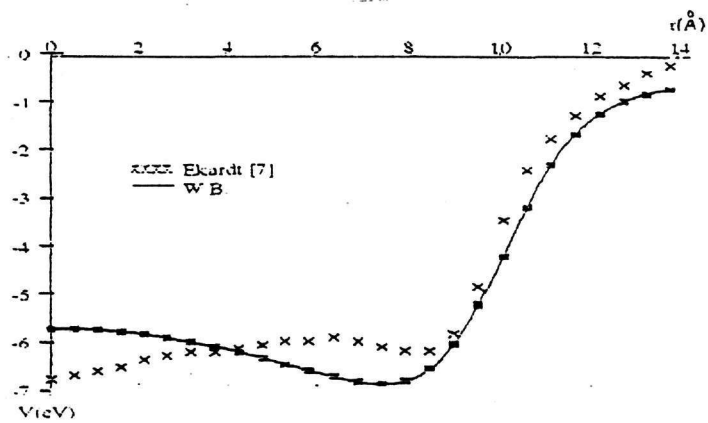



**Fig.11.** The plot of Ekardt potential for the $Na_{90}$ cluster denoted by $(x)$ points and the corresponding "Wine bottle" potential (solid line), which is obtained with parameters determined by least squares fitting of $< r^2 >_{W.B.}$ (see text).

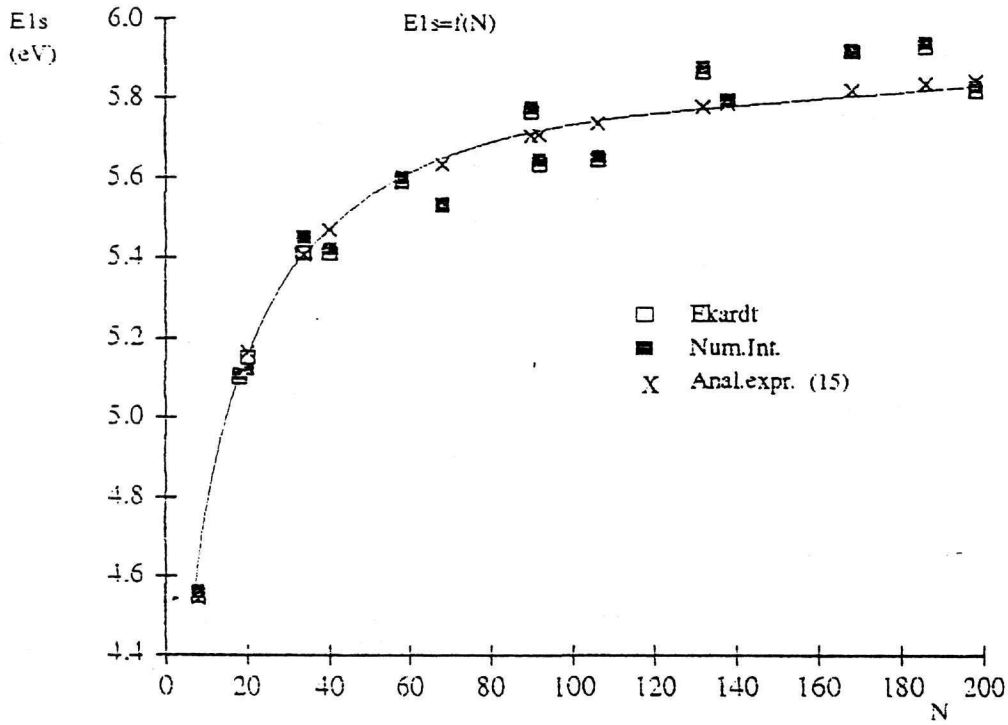



**Fig. 12.** The ground state single particle energy $E_1$, as a function of the number of atoms $N$ in the neutral cluster.

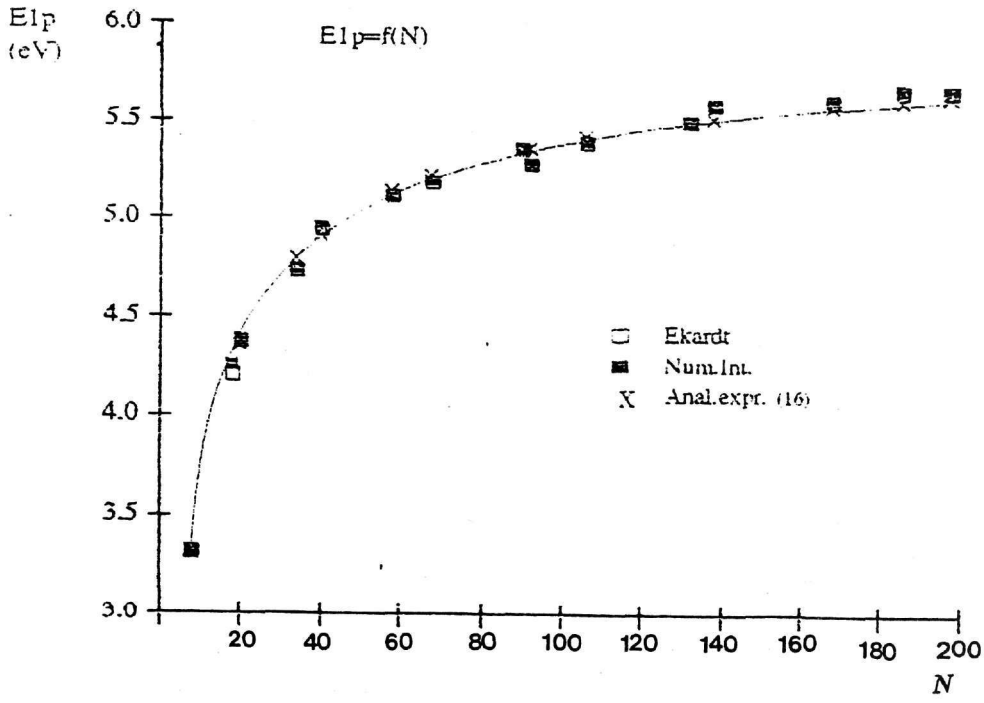



**Fig.13.** The single particle energies of the $1p-$state, as a function of the number of atoms $N$ in the neutral cluster.

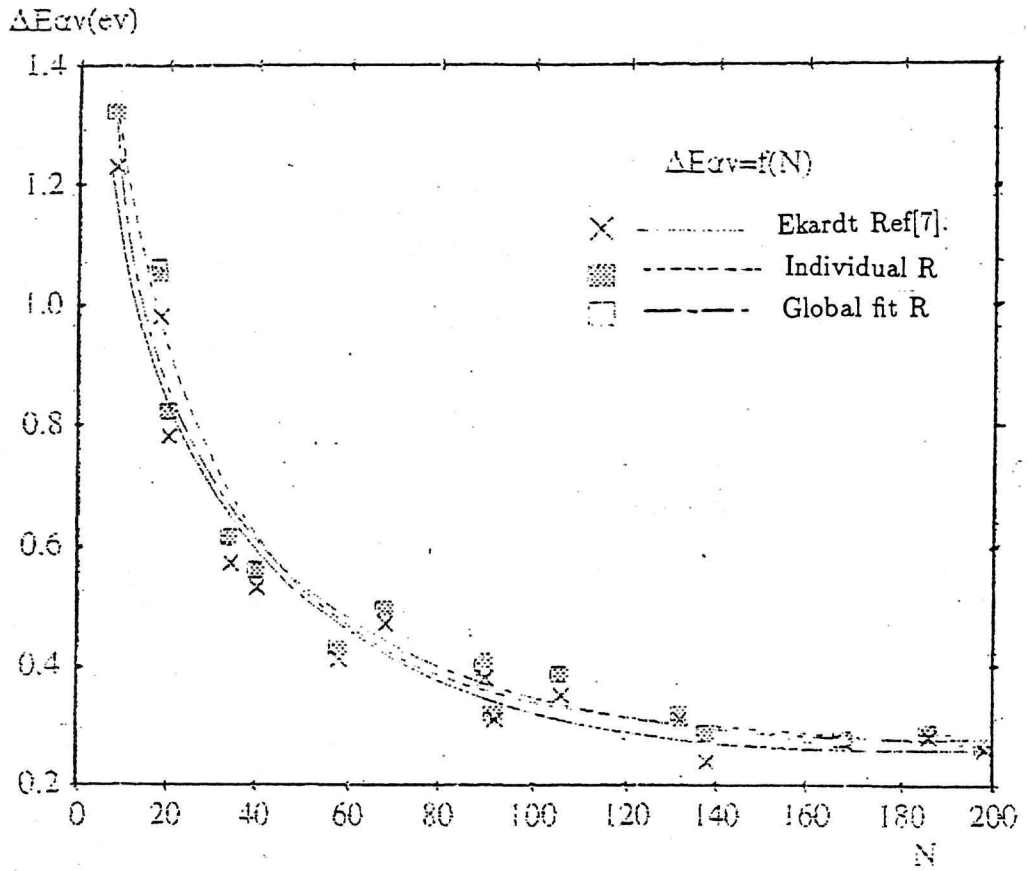



Fig.14. The average energy level spacing, as a function of the number of atoms $N$ in the neutral $Na$ clusters.

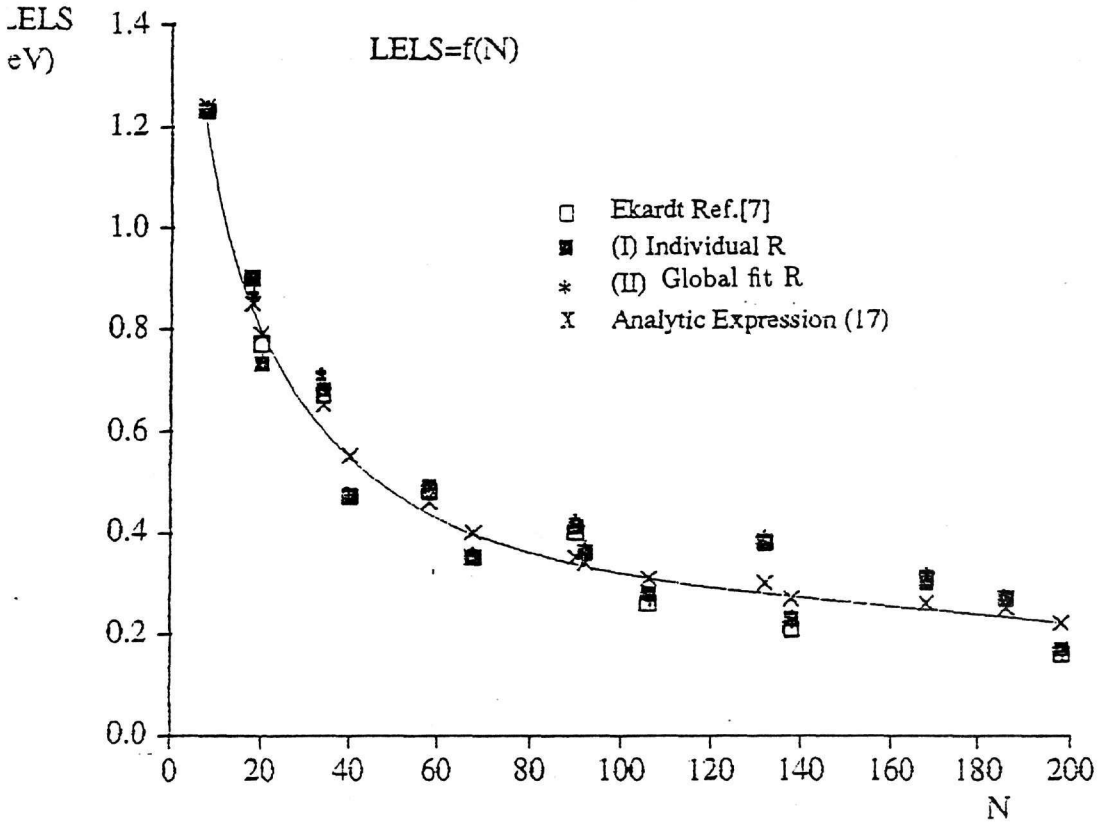



Fig.15. The lowest energies level spacing as a function of the number of atoms $N$ in the cluster.

| SYMMETRISED WOODS-SAXON POTENTIAL | | |
|---|---|---|
| N | Case I Individual R (Å) | Case II Global fit R. (Å) |
| 8 | 5.199 | 5.290 |
| 18 | 6.508 | 6.593 |
| 20 | 6.790 | 6.790 |
| 34 | 7.703 | 7.893 |
| 40 | 8.352 | 8.271 |
| 58 | 9.158 | 9.218 |
| 68 | 9.738 | 9.661 |
| 90 | 10.367 | 10.500 |
| 92 | 10.522 | 10.570 |
| 106 | 11.120 | 11.028 |
| 132 | 11.670 | 11.782 |
| 138 | 11.988 | 11.942 |
| 168 | 12.561 | 12.677 |
| 186 | 13.031 | 13.077 |
| 198 | 13.477 | 13.205 |

**Table 1.** The values of the Symmetrized Woods-Saxon potential radius $R$ determined by fitting to individual clusters (case I: Individual $R$) or by a "global fitting" (case II: global fit $R$) using the expression (9a) for $R$ and $V_0, r_0, a, \beta$ as adjustable parameters.

1s-LEVEL (eV)

| N | Ekardt Ref.[7] | Case I Individual R | Case II Global fit R | Analytic expression (15) |
|---|---|---|---|---|
| 8 | -4.55 | -4.56 | -4.56 | -4.55 |
| 18 | -5.10 | -5.10 | -5.11 | -5.11 |
| 20 | -5.15 | -5.12 | -5.12 | -5.17 |
| 34 | -5.41 | -5.44 | -5.45 | -5.41 |
| 40 | -5.41 | -5.42 | -5.42 | -5.46 |
| 58 | -5.59 | -5.60 | -5.60 | -5.58 |
| 68 | -5.53 | -5.53 | -5.53 | -5.62 |
| 90 | -5.76 | -5.76 | -5.77 | -5.69 |
| 92 | -5.63 | -5.64 | -5.64 | -5.69 |
| 106 | -5.64 | -5.67 | -5.65 | -5.72 |
| 132 | -5.86 | -5.87 | -5.87 | -5.76 |
| 138 | -5.79 | -5.80 | -5.79 | -5.77 |
| 168 | -5.91 | -5.90 | -5.91 | -5.80 |
| 186 | -5.92 | -5.92 | -5.93 | -5.82 |
| 198 | -5.81 | -5.83 | -5.82 | -5.83 |

**Table 2.** The ground state ($1s$) single particle energies for neutral sodium clusters calculated in ref. [7] along with those obtained through numerical integration of the Schrödinger equation using the symmetrized Woods- Saxon potential (cases I and II, as in table 1). In the last column the same energy values obtained with the analytic expression (15) are also displayed.

1p-LEVEL (eV)

| N | Ekardt Ref.[7] | Case I | Case II | Analytic |
|---|---|---|---|---|
| | | Individual R | Global fit R | expression (16) |
| 8 | -3.32 | -3.33 | -3.32 | -3.31 |
| 18 | -4.21 | -4.20 | -4.26 | -4.27 |
| 20 | -4.38 | -4.39 | -4.39 | -4.37 |
| 34 | -4.74 | -4.76 | -4.75 | -4.80 |
| 40 | -4.94 | -4.95 | -4.95 | -4.92 |
| 58 | -5.11 | -5.11 | -5.11 | -5.13 |
| 68 | -5.18 | -5.19 | -5.19 | -5.22 |
| 90 | -5.35 | -5.36 | -5.36 | -5.35 |
| 92 | -5.27 | -5.28 | -5.28 | -5.35 |
| 106 | -5.38 | -5.39 | -5.39 | -5.41 |
| 132 | -5.49 | -5.49 | -5.49 | -5.49 |
| 138 | -5.58 | -5.57 | -5.57 | -5.51 |
| 168 | -5.60 | -5.60 | -5.60 | -5.57 |
| 186 | -5.65 | -5.65 | -5.66 | -5.59 |
| 198 | -5.65 | -5.66 | -5.65 | -5.61 |

Table 3. The single particle energies of the $1p$–state for neutral sodium clusters (see table 2). The analytic expression (16) has now been used.

AVERAGE SPACING (eV)

| N | Ekardt Ref(7) | Case I | Case II |
|---|---|---|---|
| | | Individual R | Global fit R |
| 8 | 1.23 | 1.23 | 1.23 |
| 18 | 0.98 | 0.98 | 0.99 |
| 20 | 0.78 | 0.77 | 0.77 |
| 34 | 0.57 | 0.58 | 0.58 |
| 40 | 0.53 | 0.53 | 0.53 |
| 58 | 0.41 | 0.41 | 0.41 |
| 68 | 0.47 | 0.47 | 0.47 |
| 90 | 0.38 | 0.39 | 0.38 |
| 92 | 0.31 | 0.31 | 0.31 |
| 106 | 0.35 | 0.37 | 0.37 |
| 132 | 0.31 | 0.31 | 0.31 |
| 138 | 0.24 | 0.28 | 0.28 |
| 168 | 0.27 | 0.27 | 0.27 |
| 186 | 0.28 | 0.28 | 0.28 |
| 198 | 0.26 | 0.26 | 0.26 |

Table 4. The average energy level spacing $\Delta E(av)$ for neutral sodium clusters (see table 2).

LELS (eV)

| N | Ekardt Ref.[7] | Case I | Case II | Analytic |
|---|---|---|---|---|
| | | Individual R | Global fit R | expression (17) |
| 8 | 1.23 | 1.23 | 1.24 | 1.24 |
| 18 | 0.89 | 0.90 | 0.85 | 0.84 |
| 20 | 0.77 | 0.73 | 0.73 | 0.80 |
| 34 | 0.67 | 0.68 | 0.70 | 0.61 |
| 40 | 0.47 | 0.47 | 0.47 | 0.54 |
| 58 | 0.48 | 0.49 | 0.49 | 0.45 |
| 68 | 0.35 | 0.34 | 0.34 | 0.40 |
| 90 | 0.41 | 0.40 | 0.41 | 0.34 |
| 92 | 0.36 | 0.36 | 0.36 | 0.34 |
| 106 | 0.26 | 0.28 | 0.26 | 0.31 |
| 132 | 0.37 | 0.38 | 0.38 | 0.27 |
| 138 | 0.21 | 0.23 | 0.22 | 0.26 |
| 168 | 0.31 | 0.30 | 0.31 | 0.23 |
| 186 | 0.27 | 0.27 | 0.27 | 0.23 |
| 198 | 0.16 | 0.17 | 0.17 | 0.22 |

**Table 5.** The energy level spacing between $1p$ and $1s$ states (lowest energy level spacing:LELS) for sodium clusters (see table 2). The analytic expression (17) has now been used.

WOODS-SAXON POTENTIAL

1s - LEVEL (eV)

| N | Ekardt Ref.[7] | Numerical Integration | Expression (18) | 3 first terms of expansion (21a) | Analytic expression (15) |
|---|---|---|---|---|---|
| 8 | -4.55 | -4.82 | -4.94 | -5.15 | -4.55 |
| 18 | -5.10 | -5.32 | -5.30 | -5.36 | -5.11 |
| 20 | -5.15 | -5.40 | -5.34 | -5.39 | -5.17 |
| 34 | -5.41 | -5.52 | -5.50 | -5.53 | -5.41 |
| 40 | -5.41 | -5.55 | -5.55 | -5.56 | -5.46 |
| 58 | -5.59 | -5.64 | -5.64 | -5.65 | -5.58 |
| 68 | -5.53 | -5.65 | -5.67 | -5.68 | -5.62 |
| 90 | -5.76 | -5.71 | -5.72 | -5.73 | -5.69 |
| 92 | -5.63 | -5.72 | -5.73 | -5.74 | -5.69 |
| 106 | -5.64 | -5.71 | -5.75 | -5.76 | -5.72 |
| 132 | -5.86 | -5.80 | -5.78 | -5.79 | -5.76 |
| 138 | -5.79 | -5.82 | -5.79 | -5.80 | -5.77 |
| 168 | -5.91 | -5.89 | -5.82 | -5.82 | -5.80 |
| 186 | -5.92 | -5.90 | -5.83 | -5.84 | -5.82 |
| 198 | -5.81 | -5.88 | -5.84 | -5.84 | -5.83 |

**Table 6.** The ground state ($1s$) single particle energies for neutral sodium clusters, calculated in ref. [7], along with those obtained by the numerical solution of the Schrödinger equation using the Woods-Saxon potential. Also the same energies obtained by means of the analytic expressions (18) (21a) and (15) are given.