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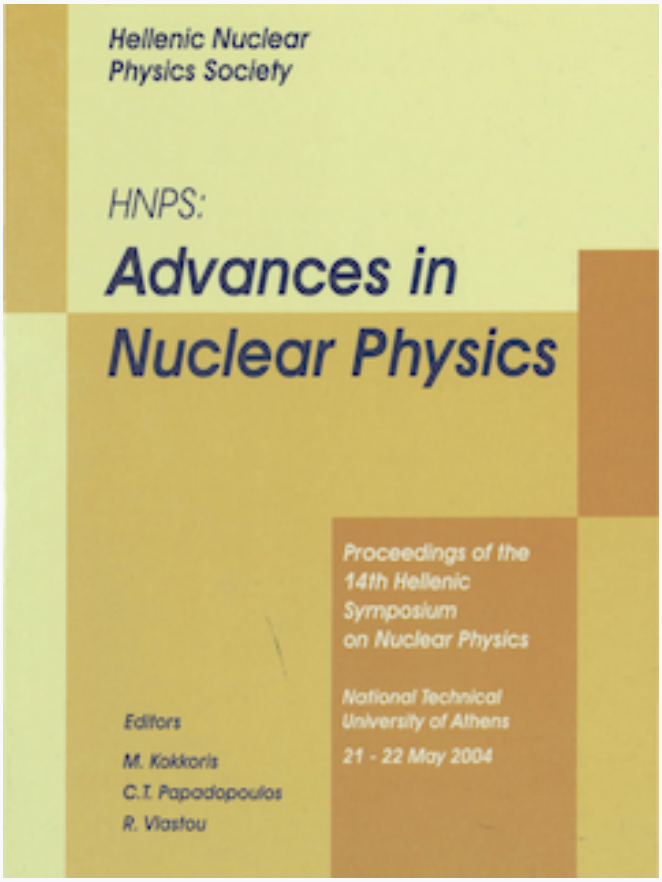

A Simplified Analytic Treatment of Shell-Effects in Metal Clusters

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A Simplified Analytic Treatment of Shell-Effects in Metal Clusters

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Abstract

A simplified treatment of shell-effects in metal clusters, such as those of Na, is considered. This treatment is carried out by means of an approximate scheme based on the spherical harmonic oscillator jellium model and its advantage is that it suggests the possibility quantities of physical interest to be calculated analytically. As a result, the variation of these quantities with the number of the valence electrons of the atoms in the cluster could be given explicitly in certain cases.

Key words: Metal clusters, Na clusters, Harmonic oscillator jellium model, ionization potential.

1 Introduction

It has been emphasized in the Physics of Atomic and Molecular clusters, that "A prominent and much celebrated feature of simple metal clusters is the occurrence of magic numbers and their interpretation in terms of quantal shells"[1]. Extensive theoretical work has been undertaken to study this interesting feature of metal clusters and various approaches, such as the local density approximation, were applied [2-4].

The aim of this report is to describe a simplified treatment of shell-effects in metal clusters and specifically those of Na clusters. This treatment is approximate and is based on the spherical harmonic oscillator (HO) jellium model [5].

Attempt is made to derive approximate analytic expressions of quantities of physical interest which show explicitly their dependence on the particle num-

ber, which is the number of the valence electrons of the atoms in the jellium model for the metal cluster considered. We denote this number by N.

We focus our attention to the estimates of the energy per particle E/N and to the ionization potential (IP). In deriving the approximate expression, for these quantities, use is made of the expression of the oscillator energy level spacing $\hbar\omega$in terms of N [6] and in particular of an appropriate expression derived recently [7] by means of a Fermi distribution for the average electronic density. The approximate expression for E/N and IP are given in the section 2, while the third section is devoted to some numerical,results and comments.

2 The approximate analytic expression for E/N and IP.

The starting point of our investigation is the expressions of the harmonic oscillator energy level spacing$\hbar\omega$. This quantity has received attention in the past (see e.g. refs [6]) and more recently in ref [7].

In that reference a Fermi (F) distribution

$$\rho_F(r) = \rho_0/[1 + \exp[(r - c)/a]] \tag{1}$$

or a symmetrized Fermi (SF) one (see ref.[8]) was used.

The expression for $\hbar\omega = \hbar\omega_F$ resulted by calculating in the HO jellium model the average (over all occupied cluster shells) mean-square radius $\overline{< r^2 >_{K+\upsilon}}$and equating it with the mean-square radius of the Fermi (or SF) distribution $< r^2 >_F$:

$$\overline{< r^2 >_{K+\upsilon}} =< r^2 >_F= \frac{3}{5}c^2[1 + (\frac{7}{3})(\frac{\pi a}{c})^2] \tag{2}$$

The latter expression for $< r^2 >_F$isessentially exact (that is if the usually negligible exponential terms are omitted).It is noted that the "half-way" radius c of the distribution is given explicitly in terms of the particle number N (see formula (4) of [7]).

Also, in formula (2), K is the serial number of the highest completely filled cluster shell (K=n_{max}+ 1, n being the HO quantum number: n=2n_r+l =0, 1, 2...).

The number K is given in terms of N andυ, the number of the (cluster) valence

electrons as follows:

$$K+1=\left(\frac{3}{2}\right)^{\frac{1}{3}}(N-\upsilon)^{\frac{1}{3}}$$

$$\left\{\left[1+\left[1-\frac{4}{27}\left[3\left(N-\upsilon\right)\right]^{-2}\right]^{\frac{1}{2}}\right]^{\frac{1}{3}}+\left[1-\left[1-\frac{4}{27}\left[3\left(N-\upsilon\right)\right]^{-2}\right]^{\frac{1}{2}}\right]^{\frac{1}{3}}\right\}$$

$$=3^{1}/3N^{1}/3[1+\frac{1}{3^{5}/3}N^{-2}/3-\frac{\upsilon}{3}N^{-1}+\frac{\upsilon}{3^{8}/3}N^{-5}/3-\frac{1}{3^{2}}(\upsilon^{2}+\frac{1}{3^{4}})N^{-2}+...](3)$$

and the final expression for $\hbar\omega_F$ is [7]:

$$\hbar\omega_F=\frac{5\hbar^2}{3m_ec^2}\frac{1}{4N}[1+\frac{7}{3}(\frac{\pi a}{c})^2]^{-1}[(K+1)(3N+\upsilon)+2\upsilon] \tag{4}$$

In terms of $\hbar\omega_F$, the HO model expression for E/N :

$$\frac{E}{N}=-V_0+\frac{1}{N}\sum_{i=1}^{N}\left(n_i+\frac{3}{2}\right)\hbar\omega \tag{5}$$

becomes, by suitable application of the virial theorem, the following:

$$\frac{E}{N}=-V_0+\frac{1}{4N}[(K+1)(3N+\upsilon)+2\upsilon]\hbar\omega_F \tag{6}$$

This is the expression of the energy per electron in the framework of the simple model considered, namely the HO jellium model for the metal cluster.

Using (3) for $\hbar\omega_F$the expression for the total energy becomes

$$E=-V_0N+\frac{1}{4}[(K+1)(3N+\upsilon)+2\upsilon]\frac{5\hbar^2}{3m_ec^2}\frac{1}{4N}$$

$$[1+\frac{7}{3}(\frac{\pi a}{c})^2]^{-1}[(K+1)(3N+\upsilon)+2\upsilon] \tag{7}$$

Pertaining to the ionization potential, an estimate of IP should be obtained by means of the approximate expression:

$$IP=E(N-1)-E(N)=-\frac{\Delta E}{\Delta N} \tag{8}$$

which could be further elaborated taking into account expression (6). The resulting formulae would be, however, complicated.

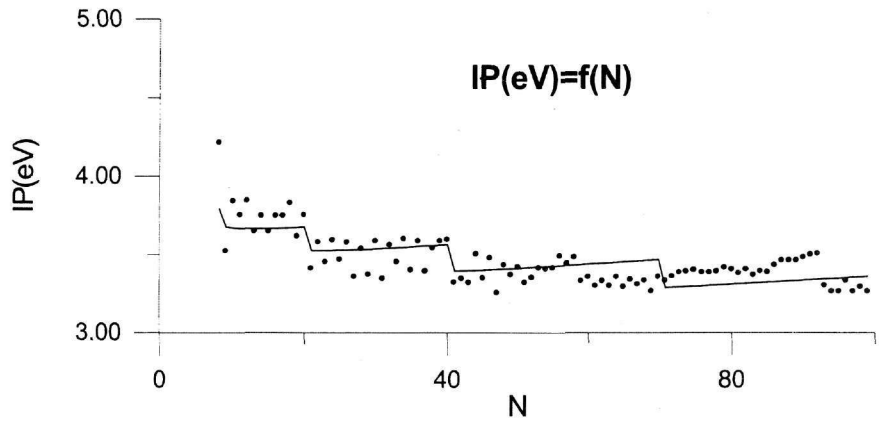

Fig. 1. The variation of IP with N, the number of valence electrons of the atoms in the jellium model for sodium clusters. The solid line shows the theoretical values, while the solid circles are the experimental values obtained by Omer (quoted by de Heer, Ref. [9]).

3 Numerical results and comments.

It would be appropriate to comment first that due to the single particle nature of the model we would not expect expression (6) for the total energy to lead to satisfactory results.

As regards the ionization potential, however, expression (7) for IP should lead to reasonable estimates provided that the parameters involved are suitably determined. In view of this remark we considered the experimental values of IP for sodium clusters which are quoted in ref. [9] and we fitted the theoretical results on the basis of expression (7) to the experimental values taking V_0, r_0, and α as adjustable parameters. The best fit values of these parameters turn out to be $V_{0=}3.950$eV, $r_{0=}3.945\overset{0}{\text{A}}$ and $\alpha=4.601\overset{0}{\text{A}}$.

The theoretical curve obtained with these values, along with the experimental points, is depicted in Fig.1. The shell-effects manifested by the discontinuities at the magic numbers are apparent in this figure.

In conclusion, we should mention that the simplified and approximate approach discussed, in spite of its limitations, appears to have a number of worth-mentioning features, such as:

1. It is neither classical nor semi-classical, but a completely quantum mechanical approach and thus able to show up shell-effects.

2. It has certain analytic advantages.

3. Expressions such as that of the cluster energy E may be seen (from expression (6) and some further assumptions) to have the structure:

$$E = E_{average} + E_{shell}$$

In other words it splits in two terms: $E_{average}$ and E_{shell}. The first one determines the average (smooth) behaviour of E with N, while the second is the "shell correction". Thus, shell-effects spring out naturally from the theoretical treatment and one does not have to introduce them "ad-hoc", as an additional correction to the liquid-drop model energy.

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