Eur. Phys. J. D **9**, 249–252 (1999)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Electronic states of neutral and ionized alkali clusters calculated on one-particle models

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Received: 31 August 1998 / Received in final form: 18 November 1998

Abstract. We propose a one-electron potential, having a V-shaped valley at the surface, for an alkali cluster. The energy levels calculated by a perturbation method agree with those calculated by a density functional method. From those energy levels, we derive the sum of one-particle energies and clarify its correspondence to the total energy per atom. It is shown that 3/4 of the summed energy levels per atom agree with an oscillatory part of the total energy per atom. By adding another perturbation potential, we obtain the size dependence of ionization energy, which agrees with measured data and the data calculated by a density functional method including self-interaction correction.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 36.40.Wa Charged clusters – 71.24.+q Electronic structure of clusters and nanoparticles

1 Introduction

In recent years, the physics of clusters has been so developed that several kinds of microscopic descriptions of electronic and vibrational properties are given [1–3]. Many researchers have studied electronic states of a cluster as a function of the number of atoms N by several methods: Hartree, Hartree–Fock (HF) and density functional methods (DF) [4–14]. Among them, Ekardt [4] has clarified the utility of a DF method. Including the effect of self-interaction correction (SIC), Ishii *et al.* [13] have calculated the total energy per atom, and the ionization energy of Na_N clusters ($N = 1 \sim 25$). They have shown that a simple DF method underestimates the energy levels and the ionization energy. Recently, Yannouleas and Landman [14] have extended a shell correction method and derived the total energy per atom, the ionization energy, and so on.

Here, we show how one-particle models explain the energy levels, ionization energies, and binding energies of alkali clusters. We propose a model potential which enables us to estimate these quantities.

2 Energy levels for one-particle potentials

Throughout the present report, we assume a cluster to be spherical. At first we consider a square-well potential: $V_{\mathrm{SQ}}(r) = -V_0\theta(R-r)$, where $\theta(x)$ represents a step function and R is the cluster radius defined by $R = a_{\mathrm{B}} r_{\mathrm{S}} N^{1/3}$ in which a_{B} is the Bohr radius, and r_{S} is the radius of a sphere per conduction electron. We find the radial wave function of an electron as

$$\psi_{nl}(r) = \sqrt{2/(C_{nl}^2 R^3)}\big\{j_l(k_{nl}r)\theta(R-r) + [j_l(\xi_{nl})/h_l(\eta_{nl})]\, h_l(q_{nl}r)\theta(r-R)\big\}\,, \tag{1}$$

where ξ_{nl} and η_{nl} are solutions of an eigenvalue equation:

$$\xi_{nl} j_{l+1}(\xi_{nl}) h_l(\eta_{nl}) - \eta_{nl} j_l(\xi_{nl}) h_{l+1}(\eta_{nl}) = 0, \tag{2}$$

with a relation $\xi_{nl}^2 + \eta_{nl}^2 = 2mR^2V_0/\hbar^2$. $j_l(x)$ represents a spherical Bessel function, and $h_l(x)$ represents a spherical Hankel function defined as $h_0(x) = \exp(-x)/x$, $h_1(x) = \exp(-x)(1+x)/x^2$ and so on. C_{nl} represents a normalization constant. Thus we arrive at the energy level as

$$E_{nl}^{(0)} = \hbar^2\xi_{nl}^2/(2mR^2) - V_0\,. \tag{3}$$

To incorporate the effect of a graded potential near the surface, a Wood–Saxon potential has often been considered:

$$V_{\mathrm{WS}}(r) = -\frac{V_0}{1+\exp[(r-R)/d_{\mathrm{WS}}]}\,, \tag{4}$$

where d_{WS} represents the diffusiveness at the surface. A one-particle Schrödinger equation with this Wood–Saxon potential cannot be solved analytically; it has been solved by numerical methods such as the shooting method, Runge–Kutta method, and so forth. In the present report, we calculate energy levels analytically by a perturbation method. By expanding (4) around $r = R$ on the condition that $d_{\mathrm{WS}}/R \ll 1$, we obtain

$$\begin{aligned} V_{\mathrm{WS}}(r) = & -V_0\,[\theta(R-r) - (\pi^2/6)d_{\mathrm{WS}}^2\delta'(r-R) \\ & + O((d_{\mathrm{WS}}/R)^4)]\,, \end{aligned} \tag{5}$$

where a prime over $\delta(r-R)$ means a derivative with respect to r. Regarding the second term as a perturbation, we obtain the perturbed energy to first order in $(d_{\mathrm{WS}}/R)^2$ as

$$\begin{aligned} \delta E_{nl}^{\mathrm{WS}(1)} = & -\frac{2\pi^2 V_0}{3C_{nl}^2}\left(\frac{d_{\mathrm{WS}}}{R}\right)^2 j_l(\xi_{nl}) \\ & \times [(l+1)j_l(\xi_{nl}) - \xi_{nl}j_{l+l}(\xi_{nl})]\ . \end{aligned} \tag{6}$$

In the case of a simple one-particle model, exchange correlation and Coulomb correlation between electrons have not been considered. For electrons in a square well with a finite depth, the electron density has the maximum – coming from Friedel oscillations – just inside the surface. At that region, electrons having parallel spins avoid one another because of the Pauli exclusion principle, and electrons having antiparallel spins avoid one another because of Coulomb repulsion. Thus electrons at that region tend to suppress the density obtained by a one-electron model, and eventually the positive background of jellium attracts electrons there. To incorporate these factors, we consider a potential having a V-shaped valley at the surface:

$$\begin{aligned} V_{\mathrm{V}}(r) = & V_{\mathrm{SQ}}(r) \qquad\qquad (7) \\ & -p_{\mathrm{V}}V_0\left\{e^{(r-R)/d_{\mathrm{V}}}\theta(R-r) + e^{-(r-R)/d_{\mathrm{V}}}\theta(r-R)\right\} \\ = & V_{\mathrm{SQ}}(r) - 2p_{\mathrm{V}}V_0\left[d_{\mathrm{V}}\delta(r-R) + O((d_{\mathrm{V}}/R)^3)\right]\ , \end{aligned}$$

where $-p_{\mathrm{V}}V_0$ is the additional depth to $-V_0$, and d_{V} is the diffusiveness. The second line of (7) shows an expanded form around $r = R$, with the condition that $d_{\mathrm{V}}/R \ll 1$. The perturbed energy to first order in (d_{V}/R) is written as

$$\delta E_{nl}^{\mathrm{V}(1)} = -\frac{2p_{\mathrm{V}}V_0}{C_{nl}^2}\left[\frac{2d_{\mathrm{V}}}{R}j_l^2(\xi_{nl}) + O((d_{\mathrm{V}}/R)^3)\right]\ . \tag{8}$$

Though it seems that $\delta E_{nl}^{\mathrm{V}(1)}$ depends on both p_{V} and d_{V}, it depends only on a product $p_{\mathrm{V}}d_{\mathrm{V}}$ as far as $d_{\mathrm{V}}/R \ll 1$. Thus $\delta E_{nl}^{\mathrm{V}(1)}$ for a deep and narrow valley can be the same as that for a shallow and broad valley.

Figure 1 shows profiles of these potentials for a Na_{20} cluster with parameters $V_0 = 6.0$ eV, $r_{\mathrm{S}} = 4.0$, and $d_{\mathrm{WS}} = d_{\mathrm{V}} = 0.25$ Å. Expansion parameters are estimated as $d_{\mathrm{WS}}/R = d_{\mathrm{V}}/R = 0.044$. A dashed-dotted curve shows the potential obtained by Ekardt [4]. A dashed curve shows the V-shaped potential $V_{\mathrm{V}}(r)$. Throughout the paper, we set $p_{\mathrm{V}}d_{\mathrm{V}} = 0.125$ Å for Na clusters.

Figure 2 shows the energy levels of occupied states: $E_{nl} = E_{nl}^{(0)} + \delta E_{nl}^{\mathrm{WS}(1)}$ and $E_{nl} = E_{nl}^{(0)} + \delta E_{nl}^{\mathrm{V}(1)}$. Our energy diagram agrees well with that calculated by Ekardt [4]. With the increase in energy, energy levels with a Wood–Saxon potential $V_{\mathrm{WS}}(r)$ start to deviate from other energy levels. The reason is that the $V_{\mathrm{WS}}(r)$ has a slightly raised region inside the surface, whereas the Ekardt's potential has a descending profile there. This comes from exchange and Coulomb correlations between electrons mentioned above.

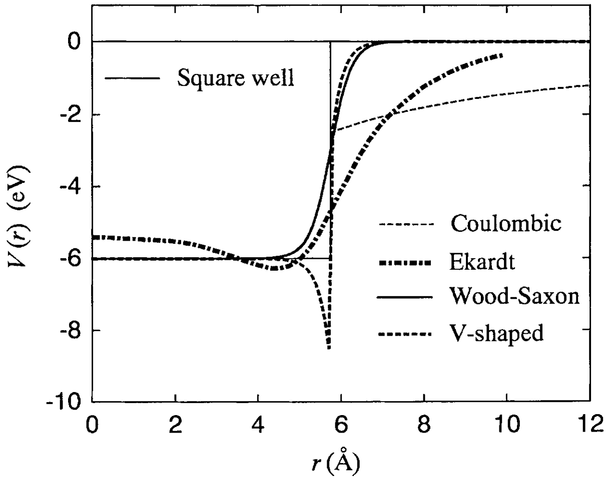

Fig. 1. One-electron potentials.

In the case of unoccupied states, it can be shown that energy levels for $V_{\mathrm{WS}}(r)$ are higher than those for $V_{\mathrm{V}}(r)$, because an electron having a high angular momentum tends to be affected by the potential modulation near the surface. Hereafter, we use $V_{\mathrm{V}}(r)$ as a one-electron potential. Analytical expressions of (6) and (8) enable us to check the accuracy of calculations. In most cases, ratios d_{WS}/R and d_{V}/R are a few percent and ensure our estimation of energy levels.

3 Energy levels of an ionized cluster

We apply the present treatment to the energy levels of an ionized cluster. For an ionized cluster with a positive charge Ze, we introduce an additional potential coming from the Coulomb interaction:

$$\delta V_Z(r) = -\frac{Ze^2}{R}\theta(R-r) - \frac{(Z+1)e^2}{r}\theta(r-R)\,. \tag{9}$$

In total, the depth of the potential inside a cluster becomes $-(V_0 + Ze^2/R)$. From the perturbation outside the surface, we have an additional energy

$$\delta E_{nl}^{\mathrm{Z}(1)} = -\frac{2Ze^2}{\hbar^2 RC_{nl}^2\eta_{nl}^2}\left[\frac{j_1(\xi_{nl})}{h_l(\eta_{nl})}\right]^2\int_{\eta_{nl}}^{\infty} xh_l^2(x)\mathrm{d}x\,, \tag{10}$$

For the sake of rapid convergence, we carry out Romberg integration of (10). Figure 3 shows the energy levels of a Na_{60}^{+1} cluster. Our diagram agrees with that calculated by Ekardt [4]. The greatest difference, 0.1 eV, appears at the $1d$-level. Comparing with a neutral Na_{60} cluster, one sees that the energy levels are shifted by the same amount, which is the trend that Ekardt has shown [4]. This means that a Coulombic potential does not affect the mutual energy levels of the occupied states.

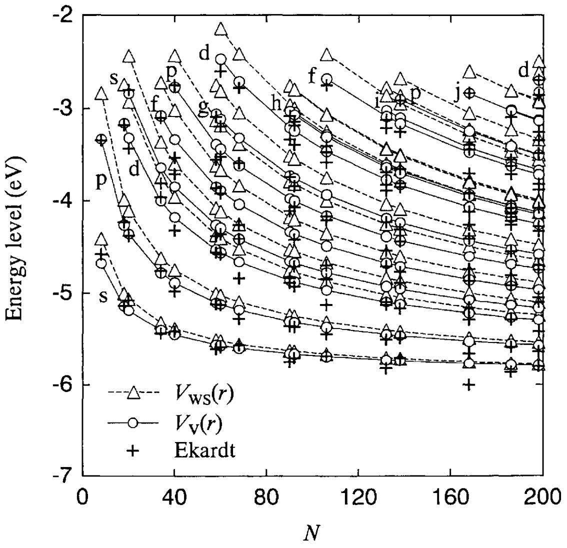

Fig. 2. Energy levels of Na_N clusters with $r_{\rm S} = 4.0$. Labels show angular momenta. Triangles show the data calculated for a Wood–Saxon potential, and circles show the data calculated for a V-shaped potential.

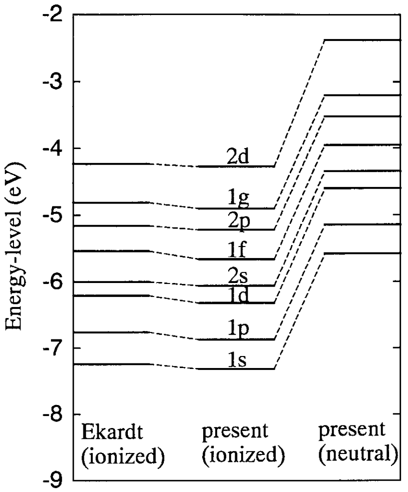

Fig. 3. Energy levels of a neutral Na_{60} cluster and an ionized Na_{60}^{+1} cluster.

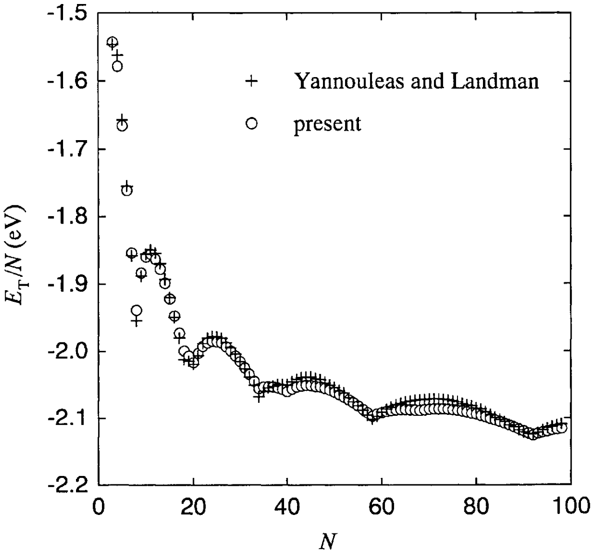

Fig. 4. Total energy per atom of Na_N clusters.

4 Total energy per atom

Several researchers have calculated the total energy per atom, which reflects the stability of clusters. Here we clarify the relation between the total energy and the summed one-particle energies. We define the sum as follows:

$$E_{\rm S}(N) = \sum_{\sigma} \sum_{nl} (2l+1) E_{nl} \theta(E_{\rm F} - E_{nl}) , \qquad (11)$$

where σ represents the spin state, $E_{\rm F}$ means the Fermi energy and $E_{nl} = E_{nl}^{(0)} + \delta E_{nl}^{\rm V(1)}$. Because our profile of $E_{\rm S}(N)/N$ is similar to that calculated by Ekardt [4] and Yannouleas and Landman [14], we use the least squares method to fit our data to theirs. Assuming the total energy per atom to be expressed as

$$E_{\rm T}(N)/N = \alpha[E_{\rm S}(N)/N] + \beta , \qquad (12)$$

we obtain $\alpha = 0.758$ and $\beta = 0.839$ eV. Our calculated result, shown in Fig. 4, traces their data well in a wide range of N. It should be noted that the value 0.758 is very close to 3/4, which has been proposed by Clemenger [15] to explain the binding energy of electrons in a modified harmonic potential. Since the potential has a different profile from our potential, it is concluded that the oscillatory part of $E_{\rm T}(N)/N$ can be estimated by 3/4 of $E_{\rm S}(N)/N$.

5 Ionization energy

In the above sections, it is shown that our results agree with those calculated by a DF method [4] without SIC. Ishii *et al.* [13] have shown that such a simple DF method underestimates the ionization energy and that SIC supplies the lack of it. Considering this situation, we superpose an additional term to the potential $V_{\rm V}(r)$ of (7). Because the effect is thought to be great near the surface, we take it to be of the same type as $V_{\rm V}(r)$ but with a different coefficient, and the diffusiveness:

$$\delta V_{\rm CR}(r) = -2 p_{\rm CR} V_0 [d_{\rm CR} \delta(r - R) + O((d_{\rm CR}/R)^3)] . \qquad (13)$$

Another reason for choosing this type of potential is that we need to avoid the increase in the number of fitting parameters. In this sense, our model is favorable. We calculate the highest occupied energy levels for both Na and K clusters. Figure 5 shows the results of Na clusters with $p_{\rm CR} d_{\rm CR} = 0.8$ Å. Zigzag sequences of circles reflect processes of filling vacant states with electrons. For example, a sequence of 2 circles from $N = 19$ to 20 shows the filling process of the 2s-state with 2 electrons. A sequence of 14 circles from $N = 21$ to 34 shows the filling process of

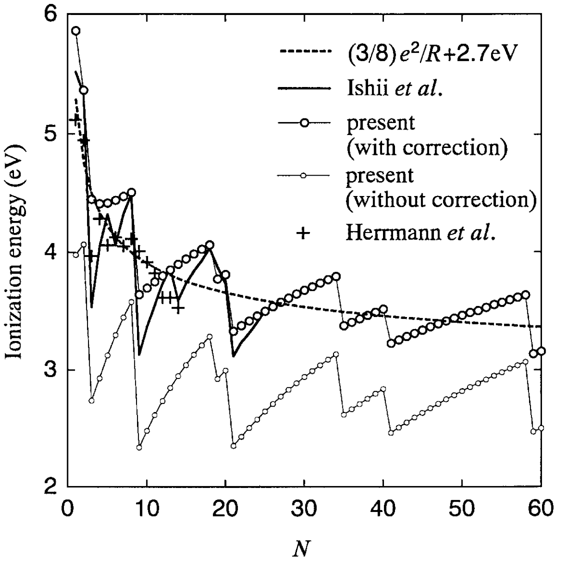

Fig. 5. Ionization energy of Na_N clusters.

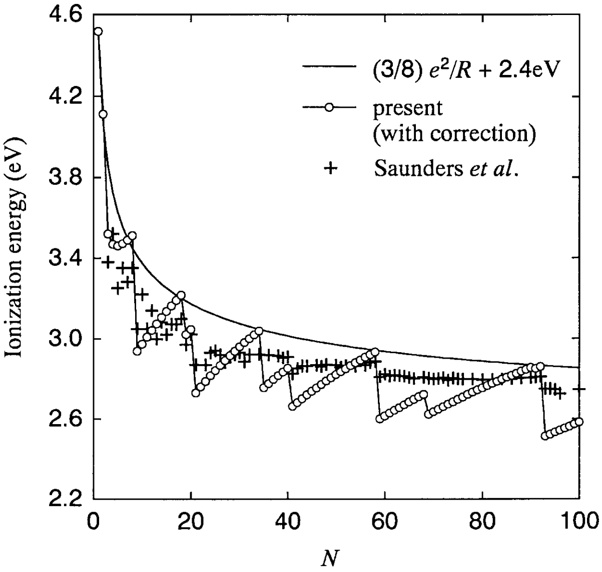

Fig. 6. Ionization energy of K_N clusters. The bulk ionization energy is 2.4 eV.

the $1f$-state with 14 electrons. Thus the number of circles in a certain sequence shows the degeneracy of the highest energy level. The dashed curve shows a classical result, including an image charge effect [16] in which 2.7 eV is the bulk ionization energy. The lower sequence of open circles shows the result without the correction $\delta V_{\mathrm{CR}}(r)$. As has been pointed out by Ishii *et al.* [13], the ionization energy is underestimated. If we include the correction potential $\delta V_{\mathrm{CR}}(r)$, the calculated values become closer to experimental data [17] and those of Ishii *et al.* [13]. It should be noted that our calculation is based on a spherical cluster, which gives an oscillatory profile connecting only neighboring magic numbers. Between magic numbers, oscillations appearing in their data come mainly from shape deformations. Clemenger [15] has considered the effect of shape deformations for a modified harmonic potential.

Figure 6 shows the ionization energy of K clusters; we choose $r_{\mathrm{S}} = 4.86$ and $V_0 = 4.5$ eV, estimating from the calculated data by Chou *et al.* [18]. Since the surface diffusiveness is thought to be larger than that of Na clusters, we set a product $p_{\mathrm{CR}}d_{\mathrm{CR}}$ for K clusters to be $(4.86/3.93) \times 0.8$ Å. In the same way as Na clusters, the size dependence of ionization energy agrees with the experimental data of Saunders *et al.* [19].

6 Conclusion

Though our shell model is phenomenological and simple, we show that a one-particle potential having a V-shaped valley at the surface works well to explain electronic states of alkali clusters: energy levels, total energy per atom, and energy levels of ionized clusters. Our shell model has the advantage over other models, because it gives analytical expressions of energy levels, and it is applicable to a large cluster having more than 1000 atoms. Moreover, it can be easily extended to include the effect of shape deformations.

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