The two-centre shell model for the fission of metallic clusters

Armando Vieira, Carlos Fiolhais

Departamento de Física da Universidade de Coimbra, P-3000 Coimbra, Portugal

Received: 10 July 1995/Final version: 4 December 1995

Abstract. We calculate potential energies for charged and neutral jellium clusters which fragment in two pieces, in the framework of the liquid drop model plus Strutinsky shell corrections obtained from the two-centre harmonic oscillator. We consider the symmetric fragmentation of Na_{42}^{++} , Na_{18}^{++} , and Na_{38} . Good agreement is found with results obtained by self-consistent methods, which are much more involved.

PACS: 36.40.Qv; 36.40.Wa

1 Introduction

The preferred decay channel of large charged metal clusters is the evaporation of neutral atoms: the heat of evaporation is lower than the fission barrier. However, when these clusters have less than some critical number of atoms they may undergo fission due to the Coulomb repulsion of the electronic cloud [1–4].

Recently the study of fission processes of this kind has received great attention. In particular, the special stability against fission of clusters with closed electronic shells has been widely recognized [5, 6]. Shell structure dominates the mass spectra of alkaline and other simple metals, due to the fragmentation of initial overcharged clusters in magic fragments. On the other hand, some features of the relative abundance of clusters in mass spectra can be interpreted by the stability of “super-dimers” as, for example, the Na_{38} peak, which is supposed to be a giant molecule formed by two near magic pieces of Na_{19} (similar to the dimer Na_2) [7–9].

The major drawback of the usual theoretical approaches to cluster fission is their requirement in computational effort: that is the case of Molecular Dynamics [10] and Kohn-Sham theory with a deformed positive background [7–9, 11] or even, although to a less extent, of Extended Thomas-Fermi methods [12, 13]. Therefore, the most sophisticated methods are only feasible for small systems.

However, and following the lead of nuclear physics, the fission of metallic clusters can be treated in the simpler framework of the Liquid Drop Model (LDM) [14]. The ground state energy of a cluster is then considered to be an analytical function of the number of valence electrons and a shape dependence of each term of the liquid drop expansion may be assumed. This macroscopic approach is justified microscopically for clusters by self-consistent density-functional methods, as Extended Thomas-Fermi techniques [15]. Quantum fluctuations, also called shell corrections, must be added to the liquid drop energy in order to mimic the more exact quantal results [16–19]. Such corrections are essential for obtaining a realistic value of the barrier height, which controls the probability of a given fragmentation process. Clusters with magic numbers of valence electrons are a more likely outcome, as for instance happens in the processes $\text{Na}_{42}^{++} \rightarrow \text{Na}_{21}^+ + \text{Na}_{21}^+$ and $\text{Na}_{18}^{++} \rightarrow \text{Na}_9^+ + \text{Na}_9^+$.

In the present work we apply the LDM plus shell corrections to evaluate the potential energies describing the symmetric decay of charged and neutral sodium clusters, in the framework of the jellium model.

The jellium model is known to be valid for the density of sodium, i.e., it is a good starting point in the handling of the many-electron problem, either in the bulk or in clusters [6]. For the other simple metals, we can still keep the universality and simplicity of jellium by using the “stabilized jellium” model [20]. In the jellium model, the ionic cores of a metallic cluster are replaced by a constant positive background. Only the valence electrons are explicitly treated by a full quantal method or by some semiclassical approximation. Once the liquid drop constants, calculated within the jellium model, are available, the liquid drop energy of the valence electronic cloud is determined by its geometrical shape. To obtain the liquid drop energy we use Blocki’s parametrization of the cluster shapes [21], which consists basically of two spheres joined by a smooth neck. We emphasize that the LDM is not bound to the jellium model since coefficients pertaining to the stabilized jellium model or even empirical liquid drop coefficients may be used. Our shell corrections are computed using the Strutinsky procedure (following [18])

with the aid of the Two-Centre Shell Model (TCSM) [22–24]: the particles are confined by a double harmonic well which is supposed to take good account of fission configurations.

We are interested in evaluating fission barriers and in comparing them with evaporation energies, which allows us to check the critical number of atoms for fission to take place. This is therefore an extension of our work of [25], where we have used a pure energetic criterium to get information about cluster stability (we have calculated the heats of reaction, i.e., the energy difference between the mother and the daughter clusters).

We consider the particular cases of $\text{Na}_{42}^{+} \rightarrow \text{Na}_{21}^{+} + \text{Na}_{21}^{+}$ and $\text{Na}_{18}^{+} \rightarrow \text{Na}_9^{+} + \text{Na}_9^{+}$. The number of atoms 42 lies above the critical number for stability of double charged sodium clusters, which is experimentally known to be 27 [1]. An energy barrier should exist and the evaporation energy should be lower than the barrier height. We compare the output of the LDM with Extended Thomas-Fermi calculations and the LDM plus shell corrections with Kohn-Sham results in the Local Density Approximation (LDA). On the other hand, the number of atoms 18 lies below the critical number. We also consider the symmetric splitting of a neutral cluster: $\text{Na}_{38} \rightarrow \text{Na}_{19} + \text{Na}_{19}$. Although this mother cluster is stable against fission we want to search for the “super-dimer” predicted by Kohn-Sham calculations.

After presenting in the next section the liquid drop formula for charged clusters, spherical or deformed, we describe our choice of the cluster shapes in Sect. 3, the shell correction technique in Sect. 4, the Two-Centre Shell Model in Sect. 5, the fission path in Sect. 6, and our results for the potential energy along the fission path in Sect. 7.

An announcement of some of the present results can be found in [26].

2 Liquid drop energy

Assuming an adiabatic approach to fission dynamics, the potential energy associated with a fragmentation process is given by the sum of the LDM term and the shell corrections:

$$E = E_{\text{LDM}} + E_{\text{SC}}. \quad (1)$$

Let us consider a spherical jellium cluster with N monovalent atoms and a radius $R_0 = r_s N^{1/3}$, with r_s the density parameter of the jellium background. The liquid drop energy of this cluster, up to the order $N^{-1/3}$, is the sum of volume, surface, curvature, and two charge contributions:

$$E_{\text{LDM}} = a_v V + \sigma S + \gamma C - z \left(W + \frac{c}{R_0} \right) + \frac{1}{2} \frac{Q^2}{R_0 + \delta} \quad (2)$$

where a_v , σ , γ , W , c and δ are the liquid drop coefficients, and $V = \frac{4}{3}\pi R_0^3$ is the cluster volume, $S = 4\pi R_0^2$ is the surface, and $C = 2\pi R_0$ is half the surface curvature. The net charge is $Q = -ez$, with e the absolute value of the electronic charge and z the number of excess electrons. The first three terms add up to give the energy of a neutral cluster. The last two terms are contri-

butions due to the charge, as given in [27, 28], which we shall explain below.

For the neutral part we take the following values for the LDM coefficients obtained within the jellium model for the density of sodium $r_s = 3.93$ bohr: $a_v = -8.26 \times 10^{-3}$ eV/bohr³, $\sigma = 2.96 \times 10^{-3}$ eV/bohr², and $\gamma = 9.97 \times 10^{-3}$ eV/bohr. The values of σ and γ were evaluated solving the semi-infinite problem (Lang-Kohn calculation with the Perdew-Wang correlation energy [29]), since they are functionals of the semi-infinite electron density [15]. Instead of the jellium model, we could have considered the stabilized jellium model, whose liquid drop parameters for sodium, excepting the volume term, are approximately the same.

Let us now analyze the charge contributions. The fourth term in the right hand side of (2) is made up of two parts. The first, zW , with W the work function, is the energy needed to remove z electrons from the bulk. For sodium, in the jellium model, we use the value $W = 2.92$ eV, which arises from the above mentioned Lang-Kohn calculation. The second is the first order correction to the chemical potential μ due to the finite size of the cluster: $\mu = -(W + c/R_0)$. We take the value $c = -2.24$ eV obtained by fitting the energies which arise from solving the Euler’s equation with the Thomas-Fermi-Dirac-Gombas-Weizsäcker-4 approximation [30] for several spherical clusters (in fact, this was done at $r_s = 4.00$ and not $r_s = 3.93$ bohr). Seidl and Brack [28] have recently derived an analytical expression for c , which for a given density parametrization of spherical jellium clusters yields $c = -2.28$ eV (again for $r_s = 4.00$ bohr).

The last term in (2) is the classical electrostatic energy, obtained under the assumption that the metal cluster is a perfect conductor, i.e., that all its charge lies on the surface. This assumption is consistent with the calculations of the static polarizability of a jellium sphere [31]. A small spill-out effect due to the accumulation of excess charge on a radial centroid is included. The distance $R_0 + \delta$ is the radius of the charge centroid, with $\delta = 0.9$ bohr [20].

The LDM formula (2) may be generalized to account for the deformed clusters with the same volume as a spherical cluster:

$$E_{\text{LDM}} = a_v V + \sigma S + \gamma C - z \left(W + \frac{c}{C/2\pi} \right) + a_{\text{Coul}} Q^2. \quad (3)$$

Here, the surface $S = \int dA$ refers to the deformed shape and $C = \frac{1}{4} \int [(R_{\min})^{-1} + (R_{\max})^{-1}] dA$, with $R_{\min}$ and $R_{\max}$ the principal radii of curvature at a point of the surface, is half the mean curvature. Both these quantities must be evaluated numerically. In the size correction to the chemical potential, we have replaced R_0 by $C/2\pi$, since this gives the right asymptotic behavior for the initial ($C = 2\pi R_0$) and the final system ($C^{-1} = (2\pi R_1)^{-1} + (2\pi R_2)^{-1}$), and interpolates smoothly between these two limits. This is an ad-hoc recipe since, as discussed in [28], the generalization of the LDM term containing c from spherical to deformed charged systems is unknown. We note that the contribution arising from that term is, in general, small in comparison with the other terms in (3).

needed to describe a wide variety of deformed shapes. The shapes we consider consist of two spheres connected smoothly by a quadratic portion of a surface of revolution [21], as displayed in Fig. 1. The shape parameters ρ and λ are defined by:

$$\rho = \frac{d}{2R}, \quad \lambda = \frac{l}{R}, \quad (4)$$

where R is the radius of the two spheres, d is the centre to centre distance between them and l is the thickness of the lens-shaped piece of the sphere that lies within the matching quadratic surface. When the fragments start to separate, λ is a measure of the degree of opening of the neck through which the fragments communicate. For splitted shapes, the neck parameter λ is a measure of the bulging of the separating fragments. As λ increases, the neck concavity disappears and the shapes become convex everywhere. For $\lambda = 1$ a sphere is obtained, while for $\lambda = 0$ two

Fig. 1. Cluster shapes for symmetric fission (Blocki's parametrization). Above, the Two-Center Shell Model potential (TCSM)

$$\tilde{g}(\varepsilon) = \frac{1}{\gamma\sqrt{\pi}} \sum_{i=1}^{\infty} e^{-u_i^2} \sum_{m=0}^M c_m H_m(u_i), \quad (6)$$

where $u_i(\varepsilon) = \frac{\varepsilon - \varepsilon_F}{\gamma}$, and H_m are the Hermite polynomials of order m . The scaling factor γ , which has the dimensions of an energy, has been introduced to control the range over which the Gaussian weighting function is nonzero. The expansion coefficients are $c_m = (-1)^{m/2}/(2^m(m/2)!)$, for even m and 0 for odd m . The shell correction order is defined by the number M . The average total energy is just

$$\tilde{E} = \int_{-\infty}^{\tilde{\varepsilon}_F} \varepsilon \tilde{g}(\varepsilon) d\varepsilon, \quad (7)$$

where the average Fermi energy $\tilde{\varepsilon}_F$ is determined by the condition $\tilde{n}(\tilde{\varepsilon}_F) = N$.

The shell correction is the difference between the sum of the spectrum energies and the average energy:

$$E_{SC} = \sum_{n=1}^N \varepsilon_n - \tilde{E}. \quad (8)$$

Because neither the smoothing range γ nor the shell correction order M represent physical quantities, they must be chosen so that the shell correction is independent of them. The values $\gamma = 1.5 \omega_0$ and $M = 6$ seem to be, in our case, a good choice (ω_0 is defined below Eq. (10)). The shell correction technique we have described only makes sense, in principle, for large enough clusters, since it is based on the idea of averaging out an energy spectrum.

There are other methods for obtaining the shell corrections (see [38–43] for applications of the shell correction method to metal clusters) but the one we use here offers the advantage of simplicity.

5 The two-centre shell model

In order to evaluate the shell corrections we need a single-particle potential which describes the physical

situation under consideration. The TCSM, whose potential is shown in Fig. 1, is known to be adequate for describing the fission process, having been extensively used in nuclear physics. The equipotential surfaces are formed by two spherical pieces, stuck to each other, but the density shapes may be described by the above mentioned Blocki's parametrization. Different shell models may be used to generate the energy spectrum to be averaged, for instance the free particle in a deformed box, which has been adopted in [32]. However, this model not only is a drastic approximation to electronic confinement but is also more time demanding from the computational viewpoint.

The energy spectrum given by the symmetric TCSM can be found analytically

$$E_{n_x, n_\rho, m} = \hbar\omega \left(n_x + 2n_\rho + |m| + \frac{3}{2} \right), \quad (9)$$

where the frequency of the harmonic oscillator,

$$\omega = \omega_0 \frac{R_0}{R_{eq}}, \quad (10)$$

was chosen so that the Fermi energy, ε_F , is kept constant. The frequency of the spherical oscillator is $\hbar\omega_0 = \varepsilon_F (\frac{3}{2}N)^{-1/3}$, and R_{eq} is the radius of the equipotential surface corresponding to the energy ε_F . The quantities $n_x, n_\rho = 0, 1, 2, \dots$ and $m = 0, \pm 1, \pm 2, \dots$, are quantum numbers for the longitudinal, radial and azimuthal directions, respectively.

The solutions of the Schrödinger equation along the x direction, $\psi_{n_x}(\sqrt{2\omega}(x - \frac{d}{2}))$, are parabolic cylindrical functions characterized by the quantum numbers n_x . These numbers are determined numerically from the condition of continuity of ψ_{n_x} and its first derivative at the point $x = 0$:

$$\begin{aligned} \psi_{n_x} \left(-\sqrt{2\omega} \frac{d}{2} \right) &= 0, \\ \psi'_{n_x} \left(-\sqrt{2\omega} \frac{d}{2} \right) &= 0. \end{aligned} \quad (11)$$

In order to check the validity of the shell correction method, we start by comparing its results with LDA Kohn-Sham calculations of spherical jellium clusters (with the Perdew-Wang correlation energy). We consider neutral, single and double positively charged clusters of sodium.

Figure 2 shows the very good agreement of the LDM plus shell correction energies with the quantal ones. The shell structure is well reproduced with the simple harmonic oscillator up to $N = 42$. A small discrepancy occurs in the region around $N = 34$ (neutral case), where the cluster closes the $1f$ shell in the Kohn-Sham description, whereas in the harmonic oscillator that only happens for $N = 40$. We also show results for very small clusters, keeping the same shell correction parameters, γ and M , since, remarkably enough, they still compare rather well with the quantal energies.

Fig. 2. LDM and LDM plus Strutinsky shell correction (LDM + SC) energy of spherical jellium clusters of sodium, with charges 0, +1 and +2, in comparison with Kohn-Sham results (KS) in the LDA approximation

6 The fission path

The LDM energy refers to the electronic density, which does not necessarily follow the jellium positive background. We can select as we like the ionic background but, in a self-consistent treatment, the electrons are free to adjust themselves to that background. In what follows, we will always refer to density shapes and not to jellium shapes. The jellium shapes could be two spheres stuck to each other or could simply coincide with the electronic density shape.

In order to allow for full freedom of the cluster shapes, we should evaluate the energy landscape in the (ρ, λ) parameter space and trace a fission path $\lambda(\rho)$ according to some criterium. A good choice is to follow the steepest descent path in the energy landscape including shell corrections, starting from a saddle point configuration. However, since we use here a single parameter shell model, we prefer to consider the path we describe in the following.

For the symmetric decay of Na_{42}^{++} , we found that the saddle point is located at $(\rho = 1.32, \lambda = 0.24)$ (point 4 of Fig. 3), very close to the fission line, i.e., line which separates connected from disconnected shapes in the (ρ, λ) plane, given by the equation $\lambda = 1 - 1/\rho$. We choose the path to start with the horizontal line 1-2, given by $\lambda = 1$, since the neck is not expected to form at the very beginning of the fission process [10]. We note that the steepest descent path on the LDM potential energy landscape coincides with that straight line. After point 2, we impose the development of a neck and that the path follows the fastest variation of the neck up to the saddle point and further down to the final configuration made up of two spheres (this path has been used in [13] for the jellium background). The LDM energy increases before the saddle point and decreases afterwards, so that there is an energy barrier. Any other path would lead to the same barrier height differing only in its shape (that is the case of

Fig. 3. Plane (ρ, λ) for the family of fission shapes. The region below the line of two intersecting spheres, $\lambda = 1 - \rho$, is forbidden. The fission line, $\lambda = 1 - 1/\rho$, is indicated by a dashed line. The line 1-2-3-4-5 is the chosen path for the symmetric fragmentation of Na_{42}^{++} . The correspondent sequence of shapes is displayed above

a straight line, used by some authors [34, 36]). After point 5, the system consists of two separated spheres, being the path given by the line $\lambda = 0$.

The above described path agrees roughly with the quantum mechanical density shape obtained from the TCSM, with a neck developing slowly in the early phases of fragmentation and very quickly in a later stage.

Since the system Na_{18}^{++} has a higher fissibility parameter, $x = Q^2/(16\pi\sigma R_0^3)$, than Na_{42}^{++} ($x = 0.59$ in comparison with $x = 0.29$), we expect that the saddle point for the binary fission of Na_{18}^{++} to be located before the fission line. We have found that point at $(\rho = 1.36, \lambda = 0.28)$.

To describe the fragmentation of Na_{38} we have used the same path as for Na_{42}^{++} . Our path for this neutral system does not go through the point $\rho = \lambda = 0$ of Fig. 3 (two intersecting spheres) corresponding to the least LDM energy along the fission line since a smooth fission shape is physically more realistic and agrees better with the TSCM. There is no energy barrier for the fragmentation of a neutral liquid drop cluster.

7 Results

Figure 4 shows the total LDM energy of the system $\text{Na}_{42}^{++} \rightarrow \text{Na}_{21}^+ + \text{Na}_{21}^+$, along the path defined in the previous section, and its decomposition in various components (surface, curvature, and charge terms). There is an energy barrier of 1.7 eV, which arises from the competition between the surface and the charge terms. The maximum of the barrier occurs at the saddle point 4 of Fig. 4, where the center to center distance between the two fragments is $d = 28$ bohr. This distance is a little bigger than $2R$, meaning that, if we model the ionic background by two jellium spheres, the maximum occurs after the separation of the pieces [12, 13]. This fact is explained by the

Fig. 4. LDM energy for the reaction $\text{Na}_{42}^{++} \rightarrow \text{Na}_{21}^+ + \text{Na}_{21}^+$ and its decomposition in surface (Surf), curvature (Curv) and charge contributions, along the path shown in Fig. 3. The charge contribution includes all charge dependent terms of (3). The shell correction (SC) is also shown. In the inset, a "blow-up" of the curvature energy. The following LDM parameters were used: $a_s = 0.56$ eV, $a_c = 0.24$ eV, $W = 2.92$ eV, $c = -2.24$ eV, and $\delta = 0.9$ bohr. ($a_s = 4\pi r_s^2 \sigma$ and $a_c = 2\pi r_s^2 \gamma$). Note that the volume term is not included. $\bullet$ --- $\bullet$, SC; —, LDM; ----, Surf; ----, Curv; ----, Charge

gluing effect of the electronic cloud between the two jellium spheres when they are already disconnected.

The contribution of the curvature is not very significant. It increases smoothly along the chosen path up to the point 5, being constant after that (see inset in Fig. 4). The present work justifies therefore the neglect of curvature for systems of similar or bigger size [32].

The results obtained for the same system in Extended Thomas-Fermi calculations by Garcias et al. [13] allow for a fair comparison with our LDM potential energy. For that purpose we must, however, use LDM parameters corresponding to the same density functional (kinetic and correlation energies). We have arrived at the values $\sigma = 5.5 \times 10^{-3}$ eV/bohr² and $\gamma = 1.8 \times 10^{-2}$ eV/bohr, solving, with a variational ansatz, the semi-infinite jellium problem, with the Weizsäcker parameter $\beta = 0.5$ in the kinetic energy functional and the Wigner formula for the correlation energy (the new σ and γ are close to those of [44]). We find our barrier to have approximately the same shape but to be 15% higher, as shown in Fig. 5. The difference may be explained by the approximation of the constant potential we have used for evaluating the classical electrostatic energy, an approximation which is relaxed in a self-consistent calculation.

Since the reaction we are studying has one magic mother and two magic daughter clusters, shell corrections should play a major role in setting the shape of the fission barrier. These corrections are small in comparison with the LDM terms but are relevant when compared with the barrier height. Figure 6 shows the potential energy including the shell corrections. The energy barrier has about the same height as in the pure LDM case (it is now 1.5 eV),

Fig. 5. LDM energy for the reaction $\text{Na}_{42}^{++} \rightarrow \text{Na}_{21}^{+} + \text{Na}_{21}^{+}$, using the following LDM coefficients: $a_r = -8.85 \times 10^{-3}$ eV, $a_s = 1.10$ eV, $a_c = 0.44$ eV, $W = 3.01$ eV, $c = -2.24$ eV, and $\delta = 0.9$ bohr, in comparison with the energy obtained by Garcia et al. in [13]. The two curves have been adjusted for $d = 0$ to allow for a comparison of the barrier height

Fig. 6. LDM plus shell correction (LDM + SC) energy for the reaction $\text{Na}_{42}^{++} \rightarrow \text{Na}_{21}^{+} + \text{Na}_{21}^{+}$, using the same LDM coefficients as in Fig. 5, in comparison with the pure LDM energy. The horizontal lines represent the final states

being its maximum located at the same distance $d = 28$ bohr (that is due to the constant value of the shell corrections in the saddle region). The Kohn-Sham calculations of [11] show a lower barrier (0.4 eV). The difference should be related to the fact that our Strutinsky result for Na_{42}^{++} underestimates the quantal energy by 0.9 eV. We find a metastable molecular state at $d = 18$ bohr, which does not appear in Ref. [11] but is typical of a quantal description of fission.

Figure 7 represents the LDM energy for the symmetric fission of Na_{18}^{++} as well as the total energy including shell

Fig. 7. LDM plus shell correction (LDM + SC) energy for the reaction $\text{Na}_{18}^{++} \rightarrow \text{Na}_9^{+} + \text{Na}_9^{+}$, using the same LDM coefficients as in Fig. 5, in comparison with the LDM result. The horizontal lines represent the final states

Fig. 8. LDM plus shell correction (LDM + SC) energy for the reaction $\text{Na}_{38} \rightarrow \text{Na}_{19} + \text{Na}_{19}$, using the same LDM coefficients as in Fig. 5, in comparison with the potential energy obtained by Engel et al. in [7]

corrections. In the framework of our method, this cluster is clearly unstable against fission, although we still observe a small barrier of 0.3 eV. There is an energy minimum for $d = 12$ bohr as a consequence of shell effects.

We have also studied the symmetrical fragmentation of Na_{38} since different authors [7–9] have treated this process using the Kohn-Sham formalism. The comparison with the self-consistent results should allow for an additional assessment of the present method. Figure 8 shows our result in comparison with that of Engel et al. [8]. The agreement between the two calculations is good.

Table 1. Heat of evaporation and heat of reaction, in eV, obtained with the Strutinsky method in comparison with the Kohn-Sham method within the LDA approximation (in brackets). In the case of the heat of evaporation, the energy of the atom has been calculated with the Kohn-Sham method

Reaction	Heat of evaporation	Heat of reaction
$\text{Na}_{42}^{++} \rightarrow 2\text{Na}_{21}^{+}$	1.28 (1.10)	0.25 (- 0.45)
$\text{Na}_{18}^{++} \rightarrow 2\text{Na}_9^{+}$	1.25 (1.19)	- 2.05 (- 2.05)
$\text{Na}_{38} \rightarrow 2\text{Na}_{19}$	1.25 (0.95)	1.83 (1.28)

The energy bump at $d = 10$ bohr and the pouch at $d = 15$ bohr, both due to shell oscillations, are correctly reproduced by our much simpler calculation. The $(\text{Na}_{19})_2$ molecule corresponds to the local minimum at $d = 15$ bohr of the potential energy.

Table 1 provides information on the heats of evaporation and reaction for the symmetric decays of Na_{42}^{++} , Na_{18}^{++} and Na_{38} . For Na_{42}^{++} and Na_{38} the agreement between the Kohn-Sham and the Strutinsky results is good for the heat of evaporation but only qualitative for the heat of reaction. The difference of about 0.6 eV for the heat of reaction in these systems is again due to the failure of the harmonic shell correction for clusters with $N = 40$ (the tiny discrepancy of Fig. 2 in the energy per particle between the Kohn-Sham and Strutinsky results is amplified when it is multiplied by the number of particles).

The cluster Na_{42}^{++} prefers to decay by evaporation and not by fission since the corresponding heat (1.3 eV) is lower than the fission barrier (1.5 eV). The united system lies above the threshold for fission so that the criterium for predicting fission based on the heat of reaction may, indeed, be misleading.

In contrast with Na_{42}^{++} , the evaporation energy of Na_{18}^{++} (1.3 eV) is much higher than the barrier (0.3 eV). In this case, both the heat of evaporation and the heat of reaction in the Kohn-Sham approach are correctly reproduced by the shell correction method. The negative value for the heat of reaction means that fission may, in principle, take place.

8 Conclusions

In spite of the big differences in the system structure and energy scale, the fission of metallic clusters displays striking similarities with the fission of atomic nuclei. In both cases, fission is determined by the competition between surface and Coulomb terms. However, the Coulomb term in atomic clusters is due to the surface charge while in nuclei is due to the volume charge. In cluster physics, we may charge a system independently of its size. Small clusters with enough charge fragment while, in nuclear physics, fission is peculiar of heavy systems.

Shell effects play a major role in shaping fission barriers, changing drastically the liquid drop scenario. These effects are in principle given by a full quantal method.

Inspired by nuclear physics, we have used a method to evaluate potential energies of fragmenting systems which is simple (conceptually and in computational effort) but incorporates shell effects with an accuracy which seems to be good enough for most practical purposes, even for small clusters. In particular, the version of the Strutinsky method we use seems suitable for undertaking systematic studies of cluster fission. This conclusion is corroborated by related work of Yannouleas and Landman [38–40] and Reimann, Brack, Hansen, and Frauendorf [42, 43].

Finally, let us describe some extensions of the present investigation. We have used a schematic double harmonic well, with a cusp at the origin. It is more convenient to include a neck parameter in the TCSM, so that the Blocki's shapes taken in the LDM and the TCSM shapes have similar degrees of freedom. Furthermore, our oscillator model overestimates the shell corrections giving too much degeneracy to the one-electron energy levels. This defect can be corrected by using a more realistic potential in the tail region as, for instance, a Woods-Saxon shape.

We have only considered the symmetric splitting of the charged clusters, yielding magic fragments. However, asymmetric splittings are known from experiment to be, in general, more probable than symmetric ones. Therefore, further refinements of our method should include, besides an improved shell model, a generalization to asymmetric reactions, which is straightforward. An ellipsoidal deformation of the fragments could also be considered.

After this work was completed, we were informed of a work where Yannouleas and Landman also use the shell correction method with the TCSM for describing the fission process of sodium clusters [45]. Their results compare well with ours in the case of spherical Na_{18}^{++} , but incorporate some of the above mentioned refinements.

We thank Matthias Brack, Luis Carlos Balbás, Angel Mañanes and John Perdew for useful discussions. This work has been partially supported by the Commission of the European Communities under Science contract No. ERB4002PL-910205. A. Vieira was supported by a grant from JNICT, Portugal.

References

- Bréchnignac, C., Cahuzac, Ph., Carlier, F., Frutos, M.: Phys. Rev. Lett. **64**, 2893 (1990)
- Näher, U., Frank, S., Malinowski, N., Zimmermann, U., Martin, T.P.: Z. Phys. **D31**, 191 (1984)
- Näher, U., Gochlich, H., Lange, T., Martin, T.P.: Phys. Rev. **B68**, 3416 (1992)
- Alonso, J.A., Barranco, M., Garcías, F., López, J.M.: Comm. At. Mol. Phys. (in press)
- de Heer, W.: Rev. Mod. Phys. **65**, 611 (1993)
- Brack, M.: Rev. Mod. Phys. **65**, 677 (1993)
- Saito, S., Ohnishi, S.: Phys. Rev. Lett. **59**, 190 (1987)
- Engel, E., Schmitt, U.R., Lüdde, H.-J., Toepfer, A., Wüst, E., Dreizler, R.M., Knospe, O., Schmidt, R., Chattopadhyay, P.: Phys. Rev. **B48**, 1862 (1993)
- Knospe, O., Schmitt, R., Engel, E., Schmitt, U.R., Dreizler, R.M.: Phys. Lett. **A183**, 332 (1993)
- Barnett, R.N., Landman, U., Rajagopal, G.: Phys. Rev. Lett. **67**, 3058 (1991)
- Garcías, F., Alonso, J.A., Barranco, M., López, J.M., Mañanes, A., Németh, J.: Z. Phys. **D31**, 275 (1994)

12. López, J.M., Alonso, J.A., Garcias, F., Barranco, M.: *Ann. Phys. (Leipzig)* **1**, 270 (1992)
13. Garcias, F., Mañanes A., López, J.M., Alonso, J.A., Barranco, M.: *Phys. Rev. B* **51**, 1897 (1995)
14. Saunders, W.A.: *Phys. Rev. B* **46**, 7028 (1992)
15. Fiolhais, C., Perdew, J.P.: *Phys. Rev. B* **45**, 6207 (1992)
16. Strutinsky, V.M.: *Nucl. Phys. A* **95**, 420 (1967)
17. Strutinsky, V.M.: *Nucl. Phys. A* **122**, 1 (1968)
18. Nix, J.R.: *Ann. Rev. Nucl. Sci.* **22**, 65 (1972)
19. Brack, M., Damgaard, J., Jensen, A.S., Pauli, H.C., Strutinsky, V.M., Wong, C.Y.: *Rev. Mod. Phys.* **44**, 320 (1972)
20. Perdew, J.P., Tran, H.Q., Smith, E.: *Phys. Rev. B* **42**, 11627 (1990)
21. Blocki, J.: *J. Phys.* **45** C6, 489 (1984)
22. Holzer, P., Mosel, U., Greiner, W.: *Nucl. Phys. A* **138**, 241 (1969)
23. Scharnweber, D., Greiner, W., Mosel, U.: *Nucl. Phys. A* **164**, 257 (1971)
24. Maruhn, J., Greiner, W.: *Z. Phys.* **251**, 431 (1972)
25. Vieira, A., Brajczewska, M., Fiolhais, C.: *Int. J. Quant. Chem.* **56**, 239 (1995)
26. Fiolhais, C., Vieira, A.: In: *Collective motions in nuclear dynamics. Proc. of the Predeal International Summer School*. Raduta, A. (ed.). Singapore: World Scientific 1996
27. Perdew, J.P.: In: *Condensed matter theories*, Vol. 4, p. 145, Keller, J. (ed.). New York: Plenum Press 1989
28. Seidl, M., Brack, M.: *Ann. Phys.* **245**, 275 (1996)
29. Perdew, J.P., Wang, Y.: *Phys. Rev. B* **45**, 13244 (1992)
30. Engel, E., Perdew, J.P.: *Phys. Rev. B* **43**, 1331 (1991)
31. Beck, D.: *Phys. Rev. B* **30**, 6935 (1984)
32. Koizumi, H., Sugano, S., Ishii, Y.: *Z. Phys. D* **28**, 223 (1993)
33. Sugano, S., Tamura, A., Ishii, Y.: *Z. Phys. D* **12**, 213 (1989)
34. Nakamura, M., Ishii, Y., Tamura, A., Sugano, S.: *Phys. Rev. A* **42**, 2267 (1990)
35. Koizumi, H., Sugano, S.: *Phys. Rev. B* **51**, R886 (1995)
36. Sugano, S.: *Microcluster physics*. Berlin, Heidelberg, New York: Springer 1991
37. Brajczewska, M., Fiolhais, C., Perdew, J.P.: *Int. J. Quant. Chem.* **27**, 249 (1993)
38. Yannouleas, C., Landman, U.: *Chem. Phys. Lett.* **210**, 437 (1993)
39. Yannouleas, C., Landman, U.: *Phys. Rev. B* **48**, 8376 (1993)
40. Yannouleas, C., Landman, U.: *Phys. Rev. B* **51**, 1902 (1995)
41. Frauendorf, S., Pashkevich, V.: *Z. Phys. D* **26**, S98 (1993)
42. Reimann, S.M., Brack, M., Hansen, K.: *Z. Phys. D* **28**, 235 (1993)
43. Reimann, S.M., Frauendorf, S., Brack, M.: *Z. Phys. D* **34**, 125 (1995)
44. Mañanes, A., Membrado, M., Pacheco, A.F., Sañudo, J., Balbás, L.C.: *Int. J. Quant. Chem.* **52**, 767 (1994)
45. Yannouleas, C., Landman, U.: in: *Large clusters of atoms and molecules. Proc. of the NATO ASI, Erice, June 19–22 (1995)* (in press)