ATOMIC CLUSTERS DEPOSITED ON INERT SURFACES

R. A. GHERGHESCU

“Horia Hulubei” National Institute for Physics and Nuclear Engineering, Reactorului 30, RO-077125, P.O.B. MG-6, Măgurele-Bucharest, Romania
Corresponding author: radu@theory.nipne.ro
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Abstract. Possible configurations of deposited atomic clusters are calculated within the macroscopic-microscopic method. The deformation energy is obtained from the liquid drop type term and the shell correction as the microscopic contribution. The two-center shell model, developed for binary processes, is employed to obtain the shell corrections. The equilibrium states are obtained as the minima within the deformation energy on surfaces. The atom number goes up to a few hundreds.

Key words: atomic clusters, shell corrections, single-particle model.

1. INTRODUCTION

In nanotechnology, deposited atomic clusters on surfaces spread on a large scale of applications. Images obtained for colloids on glass surfaces show circular bases with a cone type structure at the top [1–3]. We developed a model which takes into account the quantum structure of the electronic ensemble related to the shape of the corresponding potential well. At present ab initio calculations yield arrangements of atoms in planar and three-dimensional points [4, 5]. We assume a geometry for the deposited cluster in order to select the most appropriate potential to the end of obtaining the electronic level schemes. The coupling between the adsorbate and substrate could generate spheroidal cap like geometrical structures for the deposited atomic clusters. A very similar method to the one we will present considers the shell effects for quantum dot structure using circular shape base and harmonic oscillator levels [6]. The introduction is intended to stress three main ideas as leading points for the following calculations: (1) the spheroidal cap can describe the geometry of atomic clusters on surfaces; (2) the shape configuration must be recovered by the potential quantum well for electrons; (3) energetically favorable patterns of atomic clusters on surfaces are due to minima in the total deformation energy, mainly driven by shell effects. The theory is presented in Sections 2 and 3. Results and applications are presented section 4.

2. THE SHAPE RELATED POTENTIAL

The study refers to atomic clusters for which the change in shape due to the surface influence is the conversion from full spheroid to a spheroidal cap. The defor-
formation energy of the deposited cluster $E_{def}$, due to geometry changes, is considered under the macroscopic-microscopic approach:

$$E_{def} = E_{shell} + E_{macro}$$

where $E_{shell}$ is the microscopic shell correction term and $E_{macro}$ is the liquid drop energy. Our goal is to calculate the total deformation energy for a large range of spheroidal cap shapes and to select the minima within $E_{def}$ in the geometry coordinate space. Minima are mainly due to the shell correction term $E_{shell}$. In order to obtain this microscopic energy, one has to calculate the single-particle energy levels for the free electrons. The level scheme should be the result of the discrete electronic arrangement within a specialized deformed microscopic potential. Such a potential must be completely related to the geometrical configuration of the system it describes. The spheroid semi-axes are $(a,c)$, $z_0$ is the distance from the spheroid center up to the surface contact point along the $c$-axis, which is also the symmetry axis of the shape, and $h$ is the height of the cap. For $z_0=0$ one obtains a semispheroidal cap. The surface is considered inert, thence the potential for the electrons at the plane support (position $z = z_0$), should be infinite.

2.1. THE OSCILLATOR TYPE CUTOFF POTENTIAL

Only axially symmetric shapes are considered. Thus the electrons must be confined within a spheroidal potential, able to describe the surface of the cap. In cylindrical coordinates, a deformed, cutoff oscillator type potential $V_{osc}$ is the most appropriate:

$$V_{osc}(\rho, z) = V(z) + V(\rho)$$

where $V(z)$ and $V(\rho)$ are the components along the symmetry axis Oz and perpendicular to it, respectively. One should comply to the spheroidal shape, hence:

$$V(\rho) = \frac{m_e \omega^2 \rho^2}{2}$$

and

$$V(z) = \begin{cases} \frac{1}{2} m_e \omega^2 z^2, & z \geq z_0 \\ \infty, & z < z_0 \end{cases}$$

where $m_e$ is the mass of the electron. The form of the $V(z)$ potential decides on the shape of the deposited atomic cluster as a spheroidal cap. This potential is a part of a parabolic potential for $z \geq z_0$ (the inside part) and must become infinite for $z \leq z_0$ (the surface position). The potential is finite for $z > z_0$ and has a parabolic behaviour.
in this region, but if infinite for \( z \leq z_0 \). The two frequencies \( \omega_\rho \) and \( \omega_z \) are directly related to the shape of the spheroidal cap through the simple relation:

\[
\frac{\omega_\rho}{\omega_z} = \frac{c}{a}
\]  

and also linked to the corresponding spherical system frequency \( \omega_0 \) by:

\[
\omega_\rho^2 \omega_z = \omega_0^3
\]  

which results from the volume conservation, where the well known equality [7] is applied:

\[
h\omega_0(N) = \frac{13.72}{r_s^2(2N)^{1/3}}
\]  

with the Wigner-Seitz radius \( r_s = 2.17 \) in this work and \( N \) being the number of atoms in the cluster.

When one adds the usual squared angular momentum operator to the cutoff deformed oscillator, one obtains the total Hamiltonian for such cap shapes of atomic clusters. As a consequence, in the corresponding Schroedinger equation:

\[
H \Psi = E \Psi
\]

the Hamiltonian is expressed as:

\[
H = \left[ -\frac{\hbar^2}{2m_0} \Delta + V(\rho) + V(z) + V_{l^2} \right]
\]  

with:

\[
V_{l^2} = -U/h\omega_0(1^2 - < I^2 >)
\]

where the angular momentum interaction strength \( U = 0.04 \). We want the \( I^2 \)-operator to be also shape dependent. For this reason we are using:

\[
I = \nabla V(\rho, z) \times \mathbf{p}
\]

whence the corresponding potential \( V_{l^2} \) reads:

\[
V_{l^2} = \frac{\hbar}{m_0^2\omega_0^3}(\nabla V_{osc}(\rho, z) \times \mathbf{p})(\nabla V_{osc}(\rho, z) \times \mathbf{p})
\]

and the shape dependence is included in the \( \nabla V_{osc} \) term. The further procedure is somehow similar to the classical one with a few exceptions. One solves the oscillator part of the Hamiltonian, which is separable, with the total wave function of the form:

\[
\Psi(\rho, z, \phi) = \Phi_m(\phi) R_{m\rho}^{i\nu}(\rho) Z_{\nu}(z)
\]
The first two normalized components are common knowledge:

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(i m \phi)$$

$$R_{nm}(\rho) = \sqrt{\frac{2\Gamma(n_n + |m| + 1)}{\Gamma(n_n + |m| + 1)}} \exp\left(-\frac{\alpha^2 \rho^2}{2}\right) (\alpha^2 \rho^2)^{|m|/2} L_{n_n}^{|m|}(\alpha^2 \rho^2)$$

where $$\alpha = (m_0 \omega_\rho / \hbar)^{1/2}$$ and $$L(x)$$ is the Laguerre polynomial. Up to now, one can already express the $$\rho$$-direction energy $$E_\rho$$:

$$E_\rho = \hbar \omega_\rho (2n_n + |m| + 1) \quad (14)$$

2.2. WAVE FUNCTION BASIS

On the symmetry axis, the $$z$$-part of the Hamiltonian can be separated. After some variable substitution of the kind $$\zeta = (m_0 \omega_z / \hbar)^{1/2} z = \alpha z$$, one gets the equation along the symmetry axis $$Oz$$ for the semi-parabolic potential:

$$\frac{d^2 Z_\nu}{d\zeta^2} + (\epsilon - \zeta^2) Z_\nu(\zeta) = 0 \quad (15)$$

wherefrom the solutions are:

$$Z_\nu(\zeta) = C_\nu \exp(-\zeta^2 / 2) H_\nu(\zeta), \quad z > 0 \quad (16)$$

The limit $$z = z_0 \neq 0$$ makes all the difference. When $$z_0$$ is different from zero, the usual simple Hermite polynomials are no longer solutions. Instead, the equation is verified for a combination of two hypergeometric functions, which form together the Hermite function $$H_\nu(\zeta)$$, where the quantum number $$\nu$$ is not an integer, but a real number. The normalized solution reads:

$$Z_\nu(\zeta) = \begin{cases} 
C_\nu \exp\left(-\frac{\zeta^2}{2}\right) H_\nu(\zeta), & z \geq z_0 \\
0, & z < z_0 
\end{cases}$$

where $$C_\nu$$ is the normalization constant. The two unknown quantities, $$\nu$$ and $$C_\nu$$, must be searched for. To this end one starts from the limit $$z_0 = 0$$. In this case, which corresponds to the semispheroidal cap, the continuity equation at the surface ($$z = z_0$$):

$$H_\nu(z = 0) = H_{n_z}(0) = 0 \quad (17)$$

yields only odd integer quantum numbers $$n_z = 2k + 1$$, since the wavefunction becomes the Hermite polynomial as a limit situation. As one increases $$z_0$$ (decreases
the height \( h \) of the cap) and comply to the volume conservation, \( n_z \) passes continuously towards real \( \nu \). Thus the search for the quantum numbers \( \nu \) at \( z > 0 \) starts from the corresponding \( n_z = 2k+1 \) at \( z_0 = 0 \). After solving the continuity equation for the \( z \)-function, one obtains the \( \nu \)-quantities at every \( z = z_0 \), by increasing \( z \) in small steps. As \( z_0 \) increases, the cap becomes shorter and thicker (according to the volume conservation). Four corresponding cap shapes are also drawn at different \( z_0 \) values. One can see that the \( z \)-quantum numbers \( \nu \) are always increasing, and all of them start from an odd integer value at \( z_0 = 0 \).

The constant \( C_\nu \) is calculated from the normalization condition which becomes in our particular case:

\[
C_\nu^2 \int_{z_0}^{\infty} e^{-\alpha z^2} H^2_\rho(\alpha z) dz = 1 \tag{18}
\]

We are now in the position of computing the oscillator part of the spheroidal cap energy as:

\[
E_{osc} = \hbar \omega \rho (2n_\rho + |m| + 1) + \hbar \omega z (\nu + 0.5) \tag{19}
\]

The frequency-dependent terms are related to the geometry as:

\[
\hbar \omega \rho = \hbar \omega_0(N) \chi^{-1/3}
\]

\[
\hbar \omega z = \hbar \omega_0(N) \chi^{2/3}.
\]

The calculations have been performed for \( N=20 \) atoms in the cluster. The maximum degeneracy occurs at \( z_0=0 \), which corresponds to the semispherical cap. Then, due to the conversion of \( z \)-quantum numbers from integers to real ones, the oscillator type degeneracy is partially lifted. As one deforms the cap farther from the spherical point, the parabola of maximum degeneracy moves towards larger \( z_0 \)-values. The maximum shift occurs for the maximum spheroidal deformation against spherical cap, for \( \chi=0.84 \). One has to mention that every level in this plot is, on its turn, degenerated due to the \( \rho \)-direction oscillator energy which comprises two integer quantum numbers, \( n_\rho \) and \( m \).

### 2.3. THE SQUARED ANGULAR MOMENTUM POTENTIAL

The \( l^2 \) term is calculated and for its operator the following expression is used:

\[
l^2 = \frac{1}{2}(l^+ l^- + l^- l^+) + l_z^2 \tag{20}
\]

where \( l^+ \) and \( l^- \) are the usual creation and annihilation operators. We are looking for the energy contribution \( E_{l^2} \) due to the \( V_{l^2} \) potential, which follows from the diag-
onalization of the corresponding interaction matrix:

\[ E_{l^2} = \text{diagonal } < \Psi'|V_{l^2}|\Psi > \]

\[ = \frac{\hbar \omega_0}{(m_e \omega_0^2)^2} \sum < \Psi'|1/2(l^+l^- + l^-l^+) + l^2|\Psi > \]

The deformation dependence is included in these operators through the frequencies \( \omega_\rho \) and \( \omega_z \) as follows:

\[ l^+ = -e^{i\phi} \left( \frac{\partial V_{osc}}{\partial \rho} \frac{\partial}{\partial z} - \frac{\partial V_{osc}}{\partial z} \frac{\partial}{\partial \rho} - \frac{i}{\rho} \frac{\partial V_{osc}}{\partial \varphi} \right) \]

\[ = -e^{i\phi} \left( m_e \omega_\rho^2 \frac{\partial}{\partial z} - m_e \omega_z^2 \frac{\partial}{\partial \rho} - \frac{i}{\rho} m_e \omega_z^2 \frac{\partial}{\partial \varphi} \right) \]

\[ l^- = e^{-i\phi} \left( \frac{\partial V_{osc}}{\partial \rho} \frac{\partial}{\partial z} - \frac{\partial V_{osc}}{\partial z} \frac{\partial}{\partial \rho} + \frac{i}{\rho} \frac{\partial V_{osc}}{\partial \varphi} \right) \]

\[ = e^{-i\phi} \left( m_e \omega_\rho^2 \frac{\partial}{\partial z} - m_e \omega_z^2 \frac{\partial}{\partial \rho} + \frac{i}{\rho} m_e \omega_z^2 \frac{\partial}{\partial \varphi} \right) \]

\[ l_z = -i \frac{\partial V_{osc}}{\partial \rho} \frac{\partial}{\partial \rho} = -im_e \omega_\rho^2 \frac{\partial}{\partial \varphi} \]

One shall also use the completion relation:

\[ < \Psi|1^+1^-|\Psi >_{\infty} = \sum < \Psi'|1^+|\Psi'' >_{\infty} < \Psi''|1^-|\Psi >_{\infty} \]

\[ < \Psi|1^-1^+|\Psi >_{\infty} = \sum < \Psi'|1^-|\Psi'' >_{\infty} < \Psi''|1^+|\Psi >_{\infty} \]

\[ < \Psi|^2_z|\Psi >_{\infty} = (m_e \omega_z^2)^2 \sum \sum < \Psi''|l'' >_{\infty} < \Psi''|l'' >_{\infty} \]

In the appendix the detailed formulae for the straightforward calculation of these matrix elements are given. Finally we obtain the total matrix interaction elements. After diagonalization, the energy level for every possible deformed spheroidal cap are calculated as:

\[ E = E_{osc} + E_{l^2} \]

When the \( l^2 \)-term has been added, only the double degeneracy due to spin-up spin-down remains. The general remark is that there is a level depression, towards lower energy values, as the deformation increases. This is due mainly to the \( z \)-direction dependent terms, since the \( \hbar \omega_z \) decreases with increasing the \( z \)-axis, c.
Note that only half of the usual levels are present, since only the odd quantum numbers \( n_z \) are allowed as a starting point of semispheroidal shape.

### 3. INFLUENCE OF THE ENERGY LEVELS - SHELL CORRECTIONS

As the energy levels for the electrons are obtained, one can calculate the microscopic part of the potential. The shell correction energy \( E_{\text{shell}} \) is obtained as the difference between the sum of the level energies \( E_i \) and a continuous term \( \tilde{U} \), calculated by the smearing level procedure:

\[
E_{\text{shell}} = \sum E_i - \tilde{U} \quad (22)
\]

The sum goes up to the Fermi level in order to obtain the specific level density. The \( \tilde{U} \) energy is obtained by smoothing the level density \( g(\epsilon) \) and calculating a new continuous level distribution \( \tilde{g}(\epsilon) \), which is computed by averaging the real sequence of levels over a finite energy interval \( \gamma \) (here \( \gamma = 1.2 \ h\omega_0 \)):

\[
\tilde{g}(\epsilon) = \frac{1}{\gamma} \int_{-\infty}^{\infty} \zeta \left( \frac{\epsilon - \epsilon'}{\gamma} \right) g(\epsilon')d\epsilon'
\]

\[
= \frac{1}{\gamma} \sum_{i=1}^{\infty} \zeta \left( \frac{\epsilon - \epsilon_i}{\gamma} \right)
\]

where \( \epsilon_i \) are the energy levels. The smoothing functions have the form:

\[
\zeta(x) = \frac{1}{\sqrt{\pi}} \exp \left( -x^2 \right) \sum_{k=0}^{m} a_{2k} H_{2k}(x) \quad (23)
\]

where \( H_n(x) \) are the Hermite polynomials. The maximum degree \( m=3 \) is taken such that \( d\tilde{U}/d\gamma = \text{constant} \) (the plateau condition). The exponential term allows only the levels close to the Fermi energy to count. The density of the smoothed distribution of levels \( g(\epsilon) \) is used to calculate the smoothed part of the initial difference \( d\tilde{U} \)

\[
\tilde{U} = h\omega = \int_{\infty}^{\tilde{\lambda}} \tilde{g}(\epsilon)\epsilon d\epsilon \quad (24)
\]

The Fermi level \( \tilde{\lambda} \) for the smoothed distribution is calculated from the conservation of the total number of delocalized valence electrons \( N_e \):

\[
N_e = 2 \int_{\infty}^{\tilde{\lambda}} \tilde{g}(\epsilon)\epsilon d\epsilon \quad (25)
\]
4. THE CHARGED LIQUID DROP ENERGY

The macroscopic part of the deformation energy is obtained from the liquid drop model of the atom $E_{\text{macro}}$. It is mainly composed from the surface and the curvature energies. Its calculation starts with the equation of the surface shape in cylindrical coordinates:

\[
\rho^2(z) = \begin{cases} 
(a/c)^2(c^2 - z^2), & z \geq z_0 \\
0, & z < z_0
\end{cases}
\]  

(26)

In order to work with putative quantities, we adopt the definition of the deformation parameter $\delta$ [7, 8] as:

\[
a = \left(\frac{2 - \delta^2}{2 + \delta}\right)^{1/3}R, \quad c = \left(\frac{2 + \delta^2}{2 - \delta}\right)^{2/3}R
\]

(27)

where $a$ and $c$ are the semiaxes of the prolate deformed cap, and $R$ is the equivalent radius of the spherical shape with the same number of atoms (same volume). The eccentricity of the spheroidal cap is also expressed as:

\[
e^2(z) = 1 - (a/c)^2
\]

(28)

One shall express the macroscopic deformation energy $E_{\text{macro}}$ with respect to the semispherical shape of the atomic cluster:

\[
E_{\text{macro}} = E^0_s(B_s - 1) + E^0_c(B_c - 1)
\]

(29)

where $B_s = E_s/E^0_s$, $B_c = E_c/E^0_c$. $E_s$ and $E_c$ are the surface and the curvature energies. For a semisphere we have:

\[
E^0_s = 3\pi R^2_s\sigma
\]

\[
E^0_c = 2\pi R_s\gamma_c
\]

where $R_s$ is the radius of the semipheroid circular base, given by $R_s = r_s(2N)^{1/3}$, and $N$ is the number of atoms. The value of surface tension $\sigma$ and curvature $\gamma_c$ coefficients correspond to the typical relations $4\pi r^2_s\sigma=0.541$ eV and $4\pi r_s\gamma_c=0.514$ eV respectively. In this way the scaled deformation dependent terms read:

\[
B_s = \frac{S}{3\pi R^2_s} = \frac{a^2}{3} + \frac{2}{3} \int_0^c dz \rho \sqrt{1 + \left(\frac{d\rho}{dz}\right)^2}
\]

(30)
and

\[ B_c = \frac{K}{2\pi R_s} = \frac{1}{2\pi R_s} \int k dS \]

\[ = R_s \int_0^c k \rho \sqrt{1 + \left(\frac{d\rho}{dz}\right)^2} \, dz \]

where \( k \) is the local curvature:

\[ k = 0.5(R_1^{-1} + R_2^{-1}) \quad (31) \]

with \( R_1 = R_0 \rho \sqrt{1 + (d\rho/dz)^2} \) and \( R_2 = -R_0 [1 + (d\rho/dz)^2]^{3/2} / (d^2\rho/dz^2) \). After some calculation, the final results, ready for computation are expressed as:

\[ B_s(\text{prolate}) = \frac{a}{3} \left(2a + \frac{c}{e} \arcsin e\right) \quad (32) \]

and

\[ B_c(\text{prolate}) = \frac{c}{2} + \frac{a^2}{4ce} \ln \left|\frac{1+e}{1-e}\right| \quad (33) \]

5. RESULTS

Calculations are made for atomic clusters with \( N=70 \) and \( N=200 \). Five values of the semiaxis ratio have been accounted for: \( \chi=1, 0.96, 0.92, 0.88 \) and 0.84. As \( z_0 \) increases, the cap becomes more flat, the circular base of the shape becomes larger and the height shorter, according to the volume conservation condition. Consequently, one expects five different evolutions, one for each semiaxis ratio, for the shell corrections, macroscopic and total deformation energy.

The \( N=20 \) cluster presents a deep minima in the shell corrections at \( z_0=0 \). The \( \chi=0.96 \) also displays a minimum for hemispheroidal shape. A shallow minimum is observed for \( \chi=0.88 \) around \( z_0=0.7 \, \text{Å} \). Then, as one increases \( z_0 \) and the cap becomes more flat for the same semiaxis ratio, the shell corrections are smoothly decreasing.

The macroscopic energy has a smooth behaviour with increasing \( z_0 \). Another minimum is observable for hemispheroidal cap shape at \( \chi=0.96 \), next to the spherical one. The other curves are insignificantly increasing with \( z_0 \), as the macroscopic behaviour is dominant. The shape for the deepest minimum is also marked at \( z_0=0 \). Consequently, a deposited cluster with \( N=70 \) has good chances to undertake a semi-spherical shape as an equilibrium configuration.

The heaviest atomic cluster, \( N=200 \) has been studied for the same values of the semiaxis ratios and the same cap heights. The spherical cap displays an energetically
decreasing trend, towards larger surface contact base a more flat shapes. A small minimum is visible for \( \chi=0.96 \), whereas the \( \chi=0.88 \) behaviour is slowly increasing. The other two evolutions, \( \chi=0.92 \) and 0.84 are more or less constant. The values are obviously much higher than for the lighter mass clusters. The total deformation energy for \( N=200 \) shows a dominant trend for the macroscopic part. The minima at \( z_0=0 \) for the other visible spheroidal deformation of the cap does not compulsory mean that a semispheroidal cap having the corresponding semiaxis ratio can be found. One would suggest the continuation of the calculation beyond semispheroidal shape, towards higher cap configurations.

6. CONCLUSIONS

The present work developed a specialized macroscopic-microscopic method applicable to spheroidal cap shapes, typical for some of the deposited atomic clusters. The method has been used to calculate the deformation energy for such shapes in order to detect minima within the deformation energy. The core of the method is the single-particle model, capable to provide the transition of the electron level scheme from semispheroids up to thicker and flater spheroidal caps. The level schemes, used as input data, provide the shell corrections which determine eventual minima within the total energy. Such minima have been found at semiaxis ratios \( \chi=0.92 \) and 0.84, for a more flat cap than the semispheroid. For \( N=70 \) a semisphere provide the lower minimum in the deformation energy. The heavier cluster on the surface studied in this work, \( N=200 \), displays a shallow minimum at a very flat spherical cap configuration. However, the behaviour of other spheroidal deformations suggest the need to continue the calculations towards larger height caps, beyond the height of the semispheroids.

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