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Hemispheroidal atomic clusters on planar surfaces

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ABSTRACT

The surface influence on deposited atomic clusters is accounted for as a change in the geometry of the free cluster from spheroidal to semispheroidal (oblate and prolate) shapes. The energy levels for the electrons are calculated using a deformed oscillator quantum well plus squared angular momentum half-cut by an infinite wall located at the surface. The level scheme is used to compute the shell corrections, to which a macroscopic liquid drop energy is added. Clear minima of the total deformation energy are obtained for semispheroids at the same deformation, within a range of atom number from 2 to 100. These minima are interpreted as stable structures of various magic numbers for deposited atomic clusters.

1. Introduction

The study of metal clusters on surfaces provides useful informations for nanotechnological applications like electronic devices, catalysis processes or sensor fabrications among others [1–4]. Therefore the ability to design and fabricate elements at submicron dimensions comprises a deep knowledge towards the enhancement of the stability of these microsystems. Such efforts upon investigating the growth and stability of self-organized nanoscale clusters on different surfaces are theoretically and experimentally underway. No matter which approach is used, the goals include the need to determine the nature of the structure formed on the surface and the degree of its stability.

There is a direct interdependence between the electronic structure of the atomic cluster and the shape of the potential well. This is verified by the maxima of experimental cluster abundance spectra which manifest themselves at shell closing atom numbers. For a start approximation the ionic structure could be overlooked and electrons may be considered to be nearly free and confined in a potential well [5]. The choice of the most appropriate quantum well should result in matching the experiment with the total energy values of the deposited cluster. As for the corresponding shapes, ab initio calculations produce structures of atoms arranged in planar and three-dimensional fixed points [6,7]. These exact constructions are, for the sake of simplicity, modelled in more compact spherical and spheroidal shapes [5], like, for example, in the Clemenger–Nilsson model [8]. As a result, the peaks in the abundance spectra are reasonably obtained. This convenient shape correspondence is used in the present work. Our procedure assigns an appropriate, simplified geometry for the deposited cluster, close to the ones obtained by ab initio calculations and to obtain the microscopic potential able to provide the electronic level scheme for the adsorbed metallic cluster. The various external conditions, like the surface, influence the characteristics of the potential well. In order to reproduce the deformation of the system, the well must comply to the shape parameters, while keeping the volume of the cluster constant. Only soft landed atomic clusters onto the surface are considered. The supported clusters are separated enough so that they do not coalesce with each other.

Based on published literature, one shall try to discern what are the geometrical modifications induced by the surface upon the cluster. The method of local density approximation using energy-density functional has been used to calculate the total energy in the ultimate jellium model (UJM) for clusters on insulating surfaces [9]. Shell effects are also deduced in a macroscopic–microscopic type computation. The very useful result is that the planar shapes on surface have axial symmetry, which is also true for quantum dots. An even more directly related study to the present work has been done for Na clusters on NaCl surfaces [10]. Besides planar clusters, BD isomers are calculated. Shapes are decided as a balance between the attraction from the substrate and the cluster surface tension plus shell energy. The 3D-cluster isomer is treated like a stable soft-landed drop. The interface energy induce a larger area of contact with the substrate, then the cluster extends in the vertical direction in a pear-shaped axially

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symmetric construction. The circular contact area obtained for $N=6$, 8, 12 and 24, together with the crude but workable approximation of a spherical segment for the 3D isomers on the surface, is a decisive boost for the choice of our single-particle potential. If five Na ions on the surface plus the sixth on top [11] is an *exact* structure for soft landing Na_6 cluster on Ar(0 0 1) surface, then it is reasonable to approximate such structure (the same kind of approximation like in Ref. [5]) with a hemispheroidal geometry. In fact the last three cited papers lead to such a choice of parametrization. A very expressive display of the shape of a cluster on surface is presented in a study of Be cluster on Be(0 0 1) substrate [12]. The wetting region is circular, then the adsorbate develops on vertical direction, decreasing the number of atoms as one approaches the top. A simulated many-body potential has been used. The main two features are stressed again, as being important for the present work: the contact layer is the largest one, being the layer wetting the substrate and the shape narrows toward the upper layers, forming an axially symmetric structure.

The main starting point resulting from the above calculations is that the coupling between the adsorbate and substrate could generate hemispheroidal like geometrical structures for the deposited atomic clusters. A circular base contour of self-consistent densities for quasi-two-dimensional (slightly thicker than or just a monolayer) cluster is also obtained using the ultimate jellium model [13]. Another approach, similar to the one we use here, calculates the shell effects for quantum dot structure using circular shapes and harmonic oscillator levels [14]. The level spacing is directly related to the geometry of the dot via the base radius. It is exactly what the present work shall try to achieve: relate a geometry dependent potential to the level spacing so that at the end, the HOMO-LUMO gaps provide magicity for deposited clusters.

The shell correction energy proved to be a very decisive term in nuclear physics [15], where it provides the total energy minima due to complete occupation of a bunch of close energies in the nucleon level scheme (closed shells). The shell correction energy has been carefully calculated for metal-clusters having triaxially deformations [16], starting from an anisotropic three-dimensional modified harmonic-oscillator potential. We consider our work as being inspired and closely related to the above mentioned publication, since: first, one allows for the Nilsson-type potential to be a valuable, verified tool in describing the deformed electronic shells in metal clusters and second, we use the same potential, but with a cut off at the middle of the spheroid. When combined with the macroscopic liquid-drop term, one obtains the total deformation energy. Since the theoretical results agree very well with experimental ones for copper and sodium clusters in Ref. [16], we are confident that our similar approach for the specific deformation we take into account can produce good results. However, our calculations are somewhat simpler than Ref. [17], where the entropy of the electrons and thermal effects are also taken into account, besides the triaxial deformations. In the future, the dependence on temperature for deposited clusters shall be considered.

Experiments sustain our choice for hemispheroidal shapes, assigned to describe deposited atomic clusters on surfaces. Shapes visible in topographic images of Au colloids deposited on glass clearly display a larger circular base topping narrower [18]. Silver clusters produced by controlled condensation in nanopits on graphite surface are visualized and STM topographs show semispheroidal shapes [19]. Also the images of Ag nanopucks on Pb quantum islands reveal shapes with approximately spherical base, a higher peak in the middle and diffuse borders [20].

We conclude the introduction by assuming that: (1) a hemispheroidal shape is a good approximation for the configuration of at least some atomic clusters deposited on surfaces; (2) the hemispheroid must be reproduced in the expression for the potential quantum well; (3) energetically favourable patterns of atoms on a cluster surface are due to large HOMO-LUMO gaps within the level scheme for certain numbers of atoms—free electrons, in the deposited cluster, which manifest themselves through the shell effects. The choice of the simple microscopic potential and the results from solving the corresponding Schroedinger equation are presented in Section 2. Since the macroscopic–microscopic method is employed to calculate the total deformation energy of the cluster, the liquid drop part will be briefly treated in Section 3. Section 4 is devoted to the numerical results about magicity on surfaces and discussions.

2. Hemispheroidal microscopic potential

One assumes soft landing alkali clusters, so that the changes are considered as small perturbations of the shape. According to the *hierarchical* model for Na clusters [21,11], the total energy of the adsorbate-support system can be expressed as the sum of the involved terms:

$$E_{total}=E_{cluster}+E_{surface}+E_{coupling} \tag{1}$$

where $E_{cluster}$ is the energy of the supported cluster, $E_{surface}$ is the substrate energy and $E_{coupling}$ assigns for the coupling between the two interacting systems. We are treating the first term here, $E_{cluster}$, considered as the deformation energy of the adsorbate when its geometry changes from the one of a free cluster to a supported one. The atomic cluster energy is the sum of the microscopic shell correction E_{shell} and the macroscopic, liquid drop type energy, E_{macro}:

$$E_{cluster}=E_{shell}+E_{macro} \tag{2}$$

In this way the minima of the pure deformation energy of the deposited cluster will provide the stable structures corresponding to certain atom numbers.

In order to obtain the microscopic term, the deformed single-particle level scheme must be calculated for shapes appropriate to the deposited cluster. To reach this goal, a specialized microscopic potential must be chosen. As mentioned before, the hemispheroidal electronic structure calculations are used in searching for geometries of clusters and estimating their stabilities. If one considers the surface as inert, the potential at the plane support must be infinite for electrons. On the other hand, a potential which describes an axially symmetric hemispheroid could be expressed in cylindrical coordinates with Oz the symmetry axis, as a spheroidal oscillator one. Then the total microscopic potential is the sum of the components along the two directions:

$$V_{osc}(\rho,z)=V(z)+V(\rho) \tag{3}$$

where

$$V(\rho)=\frac{m_0\omega_\rho^2\rho^2}{2} \tag{4}$$

and

$$V(z)=\begin{cases}\dfrac{1}{2}m_0\omega_z^2z^2, & z\geq 0\\ \infty, & z<0\end{cases} \tag{5}$$

where m_0 is the electron mass and the two frequencies are determined by the semiaxis ratio of the hemispheroid. Fig. 1 shows the planar variation of such a potential along the symmetry axis Oz. Due to volume conservation and considering ω_0 the spherical system frequency, we have

$$\omega_\rho^2\omega_z=\omega_0^3 \tag{6}$$

and if one considers equipotentiality on the cluster surface, we have the geometrical influence on the microscopic potential as