

**Metallic Clusters Deposited on Surfaces**

L. C. Cune and M. Apostol

Department of Theoretical Physics, Institute of Atomic Physics,  
Magurele-Bucharest MG-6, POBox MG-35, Romania  
email: apoma@theory.nipne.ro**Abstract**

The quasi-classical theory of matter aggregation is briefly reviewed and the guiding principles of formation of the atomic clusters are discussed. The interaction potential of a metallic ion with a semi-infinite solid exhibiting a free plane surface is derived and atomic clusters deposited on surfaces are constructed. Binding energies, ground-states, magic geometries, isomers, inter-atomic distances, vibration spectra and monolayers are thus obtained, and further developments are outlined.

**1 Introduction**

It is well-known that a large amount of work has been done over the last two decades on the physical and chemical properties of the atomic clusters. In this respect the reader is referred to the comprehensive review articles given in Ref.1 and Ref. 2. Recently, there is an increasing interest in atomic clusters, especially in connection with the progress recorded in the nanosciences. In this context, atomic clusters deposited on surfaces enjoy a particular attention. They bring together the atomic clusters field and the surface physics and chemistry. Such clusters can be viewed as a limiting case of quantum dots of much lower size, which could be called atomic quantum dots. The main source of interest in such nanostructures originates in their unusual properties associated with a functionality on an ultra-miniatural scale. Quantum effects and finite size effects are essential in this respect. However, in spite of the efforts made toward the physical and chemical characterization of such nano-objects, little progress is still recorded in knowing their individual, quantitative properties, the amount of knowledge in the field being rather limited to indirect, macroscopic and phenomenological aspects.[3, 4] The progress in this direction will be brought very likely by an extensive use of refined scanning probe microscopy methods, and other similar techniques.

On the theoretical side, the main task is to understand and predict possible physical and chemical properties of such atomic aggregates, either isolated, or deposited, or with various other environmental constraints, indicate what features might be experimentally testable, and highlight particular functionalities that may lead to technological applications. In this respect, the first main question is the cohesion of the atomic clusters. This is an old problem in quantum chemistry and quantum mechanics, and it has been successfully solved since long for molecules consisting of a rather limited number of atoms. However, major difficulties arise for an increasing number of atoms, originating both in the increasing computational resources required and in the consistency of the conceptual approaches. A direct extension of the quantum-chemistry methods from

molecules to nanostructures is difficult from a practical standpoint, because of the large number of degrees of freedom, though impressive efforts have been made with the so-called ab-initio wavefunction methods.[5] On the other hand, the very large number of degrees of freedom suggests quasi-classical approaches, and such methods, or those derived from them, are generically known as density-functional methods.[6] In both cases certain approximations are involved, or semi-empirical assumptions, whose validity is seldom assessed, and adjustments are often made to get an agreement, when possible, with the experimental data within cca 3 – 5%, an accuracy considered satisfactory. Such computations may frequently be plagued with lack of convergence and instabilities in processing the complex iterative schemes, without ad-hoc control procedures or semi-empirical control parameters. This state of the art of the computational methods for nanostructures requires a re-examination of the basic theoretical concepts and procedures as derived from first principles.

In this sense, the quasi-classical description of matter aggregation has been revisited recently, and a consistent, iterative approach has been devised on this basis for the chemical bond in nanostructures in particular, in two or three steps.[7, 8, 9, 10] This theory is based on the estimation of the order of magnitude of various contributions in a hierarchical scheme, made possible by the quasi-classical description. The approach starts with electron charges distributed in atomic orbitals of the upper valence shell which are allowed to be partly delocalized in extended chemical-bond orbitals. The delocalized charges participating in the chemical bond are input parameters, they being self-consistently determined after carrying the iterative scheme through. This step may be circumvented in some simple cases, where the effective charges can be estimated from the beginning by making use of the atomic screening theory for heavy atoms for instance. This basic aspect of the theory is discussed in Ref. 9 and Ref. 10. The first step in carrying out this computational scheme is the identification of the Hartree term as bringing the main contribution, providing the Thomas-Fermi equations are linearized via a variational parameter related to the electron density. In some simplifying cases, such a variational parameter turns out to play the role of an effective screening wavevector. This procedure, fully based on the consistent quasi-classical description, may ensure cohesion; it was probably suggested for the first time by Schwinger.[11, 12] At this level of computations, the main role is played by the self-consistent potential, and, making use of it, one may estimate the structures of the atomic aggregates, *i.e.* the atom positions and the geometric forms of the nanostructures, compute the binding energy, vibration spectra, stability with respect to the number of atoms, *i.e.* the magic clusters forms and numbers, both for the ground-state and the isomers (*i.e.* clusters whose atoms occupy slightly different positions with respect to each other, and which differ by a small amount of energy in comparison with the ground-state energy). This is already a lot of information which might be tested experimentally. The second step is to compute the so-called quantum corrections by solving Schrodinger's equation for the electron energy levels and wavefunctions, with the self-consistent potential derived in the previous step. The exchange contribution to the Hartree-Fock equations is included in this step. It may be remarked that the exchange term plays in this scheme of computation the role of a quantum correction. Indeed, this is based on its well-known properties of "rigidity" and "non-locality", emphasized probably for the first time by Slater.[13] The quantum corrections lead to the electronic single-particle properties which account for various clusters spectroscopies. Such quantum corrections include the effect of the abrupt variations of the electronic wavefunctions near the ionic cores (including the self-consistent determination of the fractional charges participating in the bond), and their contribution is estimated[7, 9] to cca 17%. At this level, one may also employ the exchange integrals for computing spin-dependent properties, like, for instance, the magnetism of the nanostructures. Similarly, we may estimate now the response of the nanostructures to various external perturbations, including electric polarizability, diamagnetic susceptibility, transport

properties, etc. The next iterative step would bring a second-order correction of the order of  $0.17 \times 17\% \cong 3\%$ , which is estimated as being comparable to the lifetime effects of the quasiparticles. As such effects originate in the Hartree-Fock type of single-particle decomposition of the wavefunction, there is no point in going further on with the accuracy of the computations, unless genuine many-particle wavefunctions are used. However, this is a task which may be left aside for the time being. It is worth noting that this level of accuracy predicted by the present theory coincides with the level of accuracy accepted as being satisfactory on semi-empirical grounds by the current computational methods. It is also worth noting here that this computational scheme described briefly above is valid for large values of the cluster size  $N$  ( $N$  being the number of atoms in the cluster), as it is based on a quasi-classical description. This is precisely the range of the nanostructures, involving a number of atoms from  $N \sim 10 - 20$  up to very large numbers. On the other hand, it differs from the methods currently used for bulk solids, as the latter employ essentially the translational symmetry of the crystals.

The above program of computation is being carried out at this moment to a rather limited extent, namely up to the first step in the scheme described above. This gives us results concerning cohesion, structure and related information about nanostructures within an accuracy of cca 17%, as said above. The usefulness of pursuing such a theoretical approach resides in that it is consistently derived from first principles, provides a convergent simple iterative scheme with only two, or three, steps, it is free of any semi-empirical or ad-hoc assumptions or adjustments, and produces meaningful results already in the first step with rather limited computational resources; these results may be used as input data for getting more refined results in the next step. In addition, the computations are restricted at this moment to homo-atomic nanostructures consisting of some simple metallic ions with a model point-like charge distribution. The latter is a simplifying model assumption which does not affect qualitatively the results. The study of more realistic atomic-like orbitals is underway.

The present theory has been tested on computing the binding energy, quantum corrections included, of heavy atoms, which have been used as one of the benchmarks of the present approach. Similarly, the bulk metals have been tackled in the continuum approximation, reproducing in a highly satisfactory manner the cohesion energy, sound velocity, electron-phonon interaction, plasmons and the whole spectrum of results concerning the normal liquid theory for electronic quasi-particles. The emerging overall picture is that of a model metal consisting of screened ionic cores weakly interacting through a two-body potential, very similar to a Wigner metal.[14, 15, 16] Ionization potentials for atomic clusters, as well as electric polarizability and diamagnetic susceptibility have also been computed in a satisfactory agreement with the experimental data. All this information can be found in Ref. 9.

It has also been shown that several results obtained within this theory are in good agreement both with experimental data, where available, and with theoretical results derived by means of different approaches. For instance, we get stable, icosahedral structures in agreement with both theoretical and experimental results for isolated clusters like (iron)  $\text{Fe}_{13}$ , or (palladium)  $\text{Pd}_{13}$ , or (barium)  $\text{Ba}_{45}$ , including inter-atomic distances, binding energies and vibration spectra. A similar agreement was obtained for the iron core of the more complex iron-hydrocarbon cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$ . These results are reported in Ref. 7 and Ref. 8, and are discussed briefly in the next section. It has also been shown that the present theory leads, within certain approximations, to a deformed-harmonic oscillator potential of the Clemenger-Nilson type, which is extensively employed in assessing magic numbers of atomic clusters (see, for instance, Ref. 9). In addition, we derive here the work function for some metals in good agreement with previous computations and experimental data (see Section 3). All this gives support to our computational scheme.

In the present paper we report upon new results concerning metallic clusters deposited on surfaces.

We establish the effective potential of a free surface in the continuum approximation, in perfect agreement with the experimental data concerning the work function, and employ it for constructing metallic clusters deposited on such surfaces. We report upon structural data of such clusters, their geometrical forms, cohesion energy, stability, isomers, magic numbers, and indicate also the way such clusters may diffuse into the bulk. The calculations concerning the electronic structure and the effect of the surface upon the electronic structure of isolated clusters are underway. The results presented here are reliable as they are derived from first principles, are approximate within an accuracy which we know, as discussed above, can be refined quantitatively within the next step of the theory, and offer structures that may be tested experimentally, most directly by scanning probe microscopy.

## 2 Self-consistent potential

Solid atomic aggregates occur through delocalization of the electrons in the upper valence shells. The chemical bond originates in a superposition of atomic-like orbitals and extended orbitals that vary slowly in space. Such a picture is amenable to a quasi-classical description of the Hartree-Fock equations. An atomic aggregate looks like an ensemble of electrons spinning around and the ionic cores left behind.[7] The ionic cores have effective charges  $z_i^*$ , where  $i$  is the label of the ion. These charges are distributed radially-symmetric, as for  $s$ -orbitals, or directionally, as for  $p$ ,  $d$ ,  $f$ -orbitals; several electrons in  $d$ - and  $f$ -orbitals may approximately be viewed as radially-symmetric. In addition, such atomic-orbital charges with spherical symmetry may also be approximated for the beginning by point-like distributions. Most of the metallic ions fall in this class of  $s$ -, or approximately spherical  $d$ ,  $f$ -orbitals. The effective charges may be estimated for atoms sufficiently heavy by making use of the atomic screening theory. For instance, effective charges are  $z^* = 0.44$  for Na (sodium) and  $z^* = 0.57$  for Fe (iron).[7, 8, 9, 10] The point-like charge distribution has a limited validity for  $s$ -orbitals, or for those  $d$ - and  $f$ -orbitals with several electrons, which may be approximately viewed as radially symmetric. In addition, the model assumption of a  $\delta$ -type distribution in the ionic core allows simple calculations, and does not affect qualitatively the results. The approximations involved are comparable with those derived from the general theory as discussed in Introduction.[7, 8, 9, 10]

Under the circumstances given above, within the quasi-classical description, the electrons in an atomic aggregate move in a self-consistent Hartree potential

$$\varphi(\mathbf{r}) = \sum_{i=1}^N \frac{z_i^*}{|\mathbf{r} - \mathbf{R}_i|} e^{-q|\mathbf{r} - \mathbf{R}_i|} , \quad (1)$$

where  $N$  is the number of ions,  $\mathbf{R}_i$  denote their positions and  $q$  is a screening wavevector to be determined variationally. The derivation of this potential is fully discussed in Refs. 7-10. The well-know atomic units are used here, namely the Bohr radius  $a_H = \hbar^2/me^2 = 0.53\text{\AA}$  and twice the rydberg  $e^2/a_H = 27.2\text{eV}$ . According to the general theory,[7, 8, 9, 10] the self-consistency implies the electron density  $n$  being dependent on the potential  $\varphi$  by  $n = (q^2/4\pi)\varphi$ , so that we obtain the potential energy

$$E_{pot} = -\frac{3}{4}q \sum_{i=1}^N z_i^{*2} + \frac{1}{2} \sum_{i \neq j=1}^N \Phi(R_{ij}) \quad (2)$$

of the interacting electrons and ions (electron-electron and ion-ion Coulomb repulsions included),

where

$$\Phi(R_{ij}) = -\frac{1}{2}qz_i^*z_j^*\left(1 - \frac{2}{qR_{ij}}\right)e^{-qR_{ij}} \quad (3)$$

are effective interaction (pseudo-) potentials between ions separated by distance  $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ . The derivation of the potential energy given by (2) can be found in Refs. 7-10. It is worth emphasizing that the effective potentials (3) are spherically symmetric, as expected from a point-like charge distribution in the ionic cores, and are pairwise potentials. In general, many-body contributions to effective ionic potentials, like three- or four-body terms, are difficult to be rigorously justified from first principles, on one hand; on the other hand, in those cases where their derivation is proved, their contribution to the cohesion turns out to be small. In the present theory, the effect of such "correlations effects" is actually taken into account implicitly by the self-consistency of the theory. Indeed, the screening wavevector  $q$ , which is determined variationally, depends on the ions positions, more precisely on the inter-ionic distances  $R_{ij}$ . This is a weak dependence arising from the interacting terms in the potential energy (2), so that we may write the screening wavevector as  $q = q_0 + \delta q(R_{ij})$ , where  $q_0$  includes only the main contribution to the potential energy as expressed by the first term in (2) (this is the ionic self-energy). On the other hand, we may expand the potential (3) in powers of  $\delta q$ , which leads to many-body contributions to the pairwise potential (3), written this time with the screening wavevector  $q_0$ . As one can see, such a formal series expansion is a perturbational scheme, where the higher-body terms bring a small contribution, and the main two-body term (first-order term) is in fact less accurate than the closed formula (3). Another source of many-body contribution resides in the effective charges  $z_i^*$ , and their environment dependence. Such dependence is included in the self-consistent determination of the effective charges, as discussed in Introduction, and the effect of such dependence is of the order of the quantum corrections, as the latter account for the short-scale variations. However, in some cases, like Na and Fe, chosen here for illustrating the theory, the effective charges are satisfactorily estimated from the atomic screening theory, and, consequently such effects are already included. The potential energy given by (2) is minimized with respect to  $\mathbf{R}_i$  (actually  $q\mathbf{R}_i$ ) in order to find the ionic equilibrium positions; this way, we determine the geometric forms of the atomic aggregates, both for their ground-states and isomers. Thereafter, the kinetic energy  $E_{kin} = (27\pi^2/640)q^4 \sum_i z_i^*$  is added, and the quasi-classical energy  $E_q = E_{kin} + E_{pot}$  is minimized with respect to the screening wavevector  $q$ ; finally the exchange energy  $E_{ex} = -(9/32)q^2 \sum_i z_i^*$  is included to obtain the binding energy  $E = E_q + E_{ex}$ . As one can see the exchange interaction is taken into account at this level of computations.

This theoretical approach has been applied to homo-atomic metallic clusters, where geometric magic numbers have been obtained, together with binding energies, inter-atomic distances and vibration spectra (up to  $N \sim 160$ ).[7] Leaving aside the small contribution of the interacting part in the potential energy at equilibrium, the screening wavevector reads approximately  $q \simeq 0.77z^{*1/3}$  in this case, and the average inter-atomic distance may be estimated as  $a = \bar{R}_{ij} \sim 2.73/q$ ; all the same, the binding energy is given by  $E = -N(0.43z^{*7/3} + 0.17z^{*5/3})$ . Similarly, the theory has been used to estimate other, more complex structures, as, for instance, the equilibrium Fe-core structure of the iron-hydrocarbon  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$ -cluster.[8] We emphasize that icosahedral structures of Fe clusters, as  $\text{Fe}_{13}$  for instance, are currently reported in the literature, both experimental and theoretical, and our quantitative results agree satisfactorily with these data, where available.[1, 2, 17, 18] For instance, we obtain  $\simeq -5.3\text{eV}$  a cohesion energy per atom for  $\text{Fe}_{13}$ , which agrees well with  $-5.2\text{eV}$  reported in Ref. 19 by using density-functional methods, and a similar agreement holds also for inter-ionic distances (of cca  $2\text{\AA}$ ; see also Refs. 20-22). The iron-hydrocarbon cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  has been synthesized experimentally,[23] and the structure derived theoretically in Ref. 8 agrees well with the experimental data, including atomic positions in the  $\text{Fe}_{13}$ -core, inter-

atomic distances, core contribution to the binding energy, stability and vibration spectra. Such an agreement is also reported in Ref. 24, with regard to the vibration spectrum as computed by means of the density-functional methods. We may also note here that structures, magic numbers and binding energies have recently been reported for Pd (palladium) clusters up to  $N = 20$  in close agreement with the values obtained by us ( $z_{Pd}^* = 0.40$ , cohesion energy per atom  $\simeq -2.5\text{eV}$  for  $N = 20$ ), by using a theoretical model of an embedded-atom potential.[25] Including more realistic atomic-like charge distribution (instead of the point-like distribution) we expect to get greater inter-atomic distances, but the cohesion energy and other relevant results will not change drastically.

The above theoretical description is to be developed along two directions at least. First, the directional character of the atomic-like orbitals (as well as their radial dependence) must be included in order to obtain, for instance,  $p$ - or  $sp$ -orbitals atomic aggregates (as well as directional  $d$ - and  $f$ -orbitals aggregates). Secondly, the quantum corrections must be included in the quasi-classical treatment, in order to get a more accurate knowledge of the electronic single-particle properties, like energy levels (or bands), ionization potential, chemical affinity, optical properties, polarizability, magnetic properties, etc. An error of cca 17% is estimated without quantum corrections, while including them may lead to an accuracy of up to cca 3%, at most, as discussed in Introduction.[7, 8, 9, 10] Various hetero-atomic aggregates could then be studied with more confidence.

Until then, the present theory can be employed to get a description of metallic surfaces or interfaces, or metallic clusters deposited on such surfaces, or atomic aggregates with various others geometric constraints.

### 3 Metallic Surface

The summation over ions in (1) can be restricted to half a space, as for a semi-infinite solid with a free plane surface perpendicular to, say, the  $x$ -direction at  $x = 0$ . Such a surface is shown in Fig. 1. In the continuum approximation we obtain the self-consistent potential

$$\begin{aligned} \varphi(x) &= \frac{4\pi z^*}{q^2 a^3} \left(1 - \frac{1}{2} e^{qx}\right), \quad x < 0, \\ \varphi(x) &= \frac{2\pi z^*}{q^2 a^3} e^{-qx}, \quad x > 0, \end{aligned} \tag{4}$$

where  $z^*$  is the average effective charge and  $a$  denotes the average inter-atomic distance.

When compared to the bulk contribution  $\varphi = 4\pi z^*/q^2 a^3$  one can see that a dipolar potential  $\delta\varphi$  occurs at the surface, which gives rise to a spill over of the electrons and a surface charge double layer. The electron density  $n = (q^2/4\pi)\varphi$  is shown in Fig. 2, and the total charge density is plotted in Fig. 3 *vs*  $x$ .

The work function of the solid as computed from (4) is  $\varphi$ , as expected. The interaction energy  $-(1/2) \int dx \cdot \delta\varphi \delta n$  associated with the electronic double layer (per unit area) is  $-\pi z^{*2}/2q^3 a^6$ , and it acts like an additional uncertainty in the quasi-particle energy giving rise to boundary (finite-size) lifetime; it also leads to a weak relaxation of the ionic positions at the surface.

It is worth noting that the surface potential (4) and the corresponding surface charge distribution has been suggested long time ago on semi-empirical grounds[26] (see also Ref. 27), and used for computing work function of metals. The screening wavevector given in Ref. 26 and Ref. 27 for Na is  $1.27\text{\AA}^{-1}$  corresponding to a work function  $2.9\text{eV}$  as compared with the experimental  $2.4\text{eV}$ .

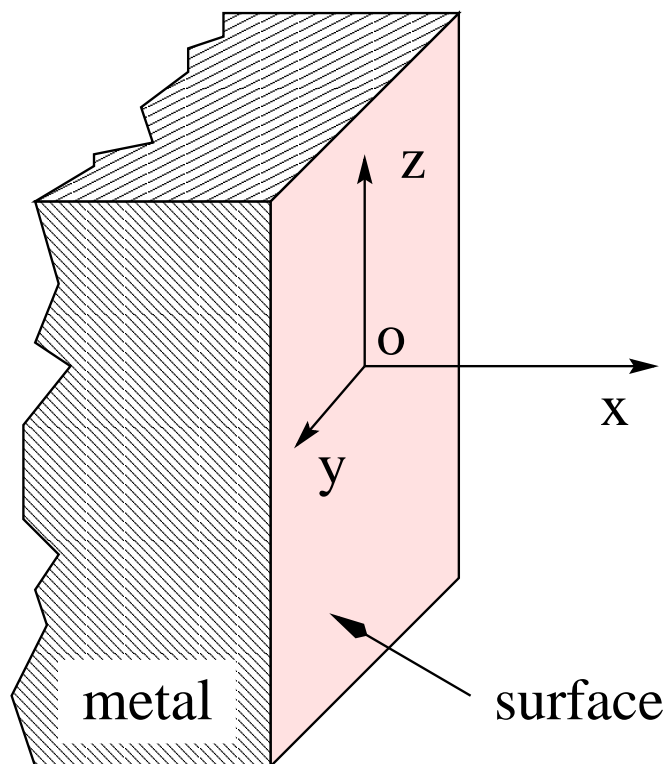


Figure 1: A free plane surface of a semi-infinite solid

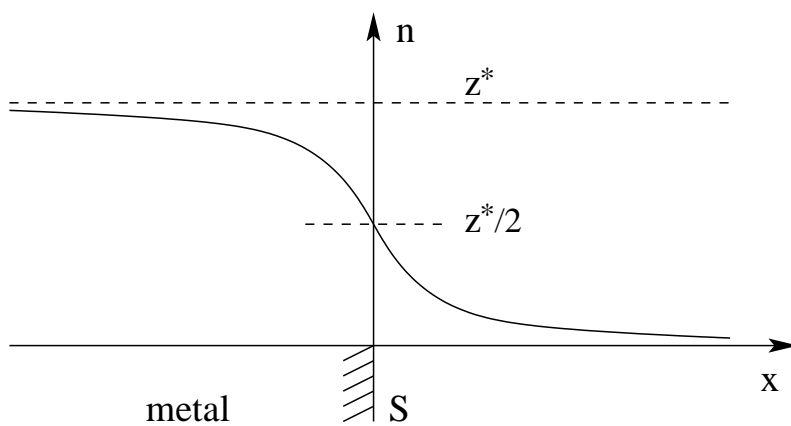


Figure 2: Electron density at the surface

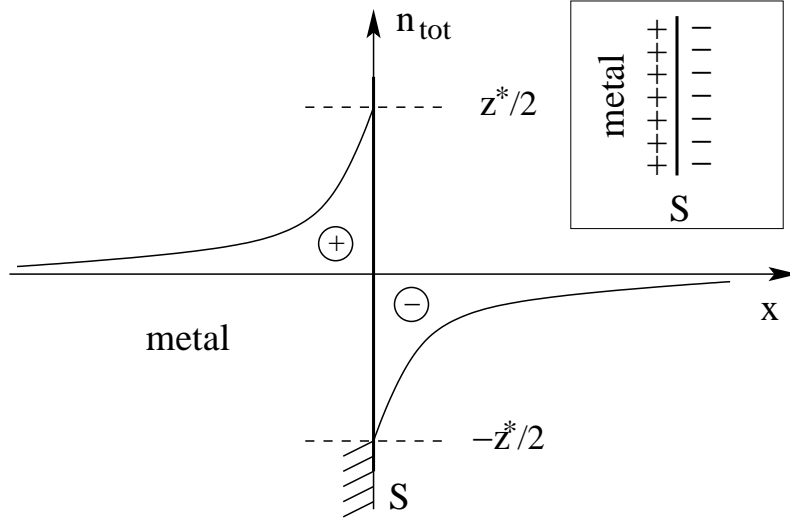


Figure 3: Charge distribution at the surface by-layer

We obtain a screening wavevector  $q = 1.17\text{\AA}^{-1}$  from our theory ( $q = 0.77z^{*1/3}$ ), leading to a 2.7eV work function, which is closer to the experimental value. A similar agreement holds also for other metals.

On the other hand, the potential energy can be estimated from (2) and (3) for a semi-infinite solid; in the continuum approximation we obtain

$$E_{pot} = -\frac{3}{4}qz^{*2}N + \frac{\pi z^{*2}}{2q^3a^6}A, \quad (5)$$

where  $A$  is the area of the cross-section; therefore, the potential energy (5) includes a surface contribution  $(\pi z^{*2}/2q^3a^6)A$ , beside the bulk contribution given by the first term (the interacting part vanishes in the bulk continuum limit); the surface tension of the solid is  $\sigma = (\pi z^{*2}/2q^3a^6)$ , and it agrees with the double layer energy given above.

Similarly, we can estimate the interaction potential between a semi-infinite solid and an ion with an effective charge  $z_0^*$  placed at distance  $x$  from the surface; indeed, making use of (2) and (3), we obtain

$$E_{pot} = E_s - \frac{3}{4}qz_0^{*2} - \frac{\pi z^* z_0^*}{qa^3}xe^{-q|x|}, \quad (6)$$

where  $E_s$  is the potential energy of the solid as given by (5); the second term in (6) is the self-energy of the added atom and the third term represents the interaction potential of the atom with the semi-infinite solid; it is shown in Fig. 4.

This interaction potential exhibits a potential barrier just beneath the surface, and has an attractive part above; the latter is responsible of adsorbing additional atoms on the surface, and of stabilizing deposited atomic clusters.

Now it is easy to write down the potential energy of an ensemble of  $N$  atoms of effective charges  $z_i^*$  deposited on the surface; it reads

$$E_{pot} = E_s - \frac{3}{4}q \sum_{i=1}^N z_i^{*2} + \frac{1}{2} \sum_{i \neq j=1}^N \Phi(R_{ij}) - \frac{\pi z^*}{qa^3} \sum_{i=1}^N z_i^* X_i e^{-q|X_i|}, \quad (7)$$

where the potentials  $\Phi(R_{ij})$  are given by (3) and  $X_i$  is the  $x$ -coordinate of  $\mathbf{R}_i$ . It is worth noting that the screening wavevector  $q$  is the one corresponding to the solid, as the latter prevails upon



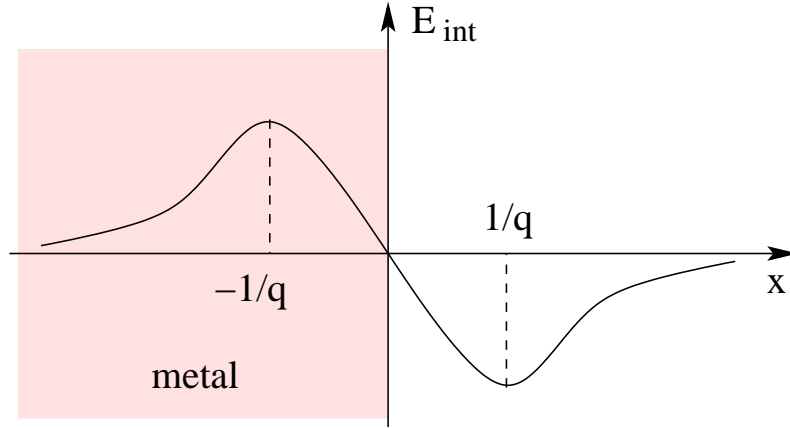


Figure 4: Interaction potential between an atom and a semi-infinite solid

the deposited cluster in the thermodynamic limit. In this respect the deposited clusters differ from the isolated clusters, which have their own screening wavevector as it results from the minimization of their quasi-classical energy. The binding energy of a deposited cluster is given by  $E = E_q + E_{ex}$ , where the quasi-classical energy is  $E_q = (27\pi^2/640)q^4 \sum_i z_i^* + E_{pot} - E_s$ , and the exchange energy is given by  $E_{ex} = -(9/32)q^2 \sum_i z_i^*$ ; the potential energy given by (7) is minimized with respect to the ionic positions  $\mathbf{R}_i$ . It is worth noting that an interaction energy

$$E_{int} = -\frac{\pi z^*}{qa^3} \sum_{i=1}^N z_i^* X_i e^{-q|X_i|} \quad (8)$$

can be defined from (7), between the deposited cluster and the solid, which may serve as a measure of the energy needed to separate the cluster off the surface (the difference in the cluster energy must be added, arising from its own screening wavevector corresponding to the cluster relaxation). One can also notice that the interaction energy (8) for the halves of a solid compensates exactly the surface energies of the two faces, as given by (5). If two distinct solids are put in contact there is a diffusion of one into another across the interface, according to the tunneling through the interaction potentials given by (8). Finally, we note that the continuum approximation is not necessary, and we can treat the cluster deposition by preserving the discrete summations over fixed ionic positions in solid; we have adopted the continuum approximation here for the sake of the simplicity; the errors introduced on this occasion refer to the few atomic layers in the vicinity of the surface, and of course to the matching problem of the lattice constants.

## 4 Clusters Deposited on Surface

The main problem of depositing atomic clusters on a surface is the minimization of the potential energy (7) with respect to the ionic positions  $\mathbf{R}_i$  (in fact with respect to  $q\mathbf{R}_i$ ).

Initially, we give positions  $\mathbf{R}_i$  randomly distributed in space and let the ions move step by step along the forces until a local equilibrium is reached (corresponding to forces less than  $10^{-4} \text{eV}/\text{\AA}$ ); this equilibrium is checked by computing the corresponding vibration spectra. For each number  $N$  of atoms the procedure is repeated for a few hundreds times, in order to get the ground-state and the isomers; the latter are clusters higher in energy with slightly different ionic positions. This procedure has been applied to Fe-clusters ( $z^* = 0.57$ ) deposited on Na-surface ( $z^* = 0.44$ ) up to  $N = 100$ . The original ionic positions are randomly distributed in space both below and above

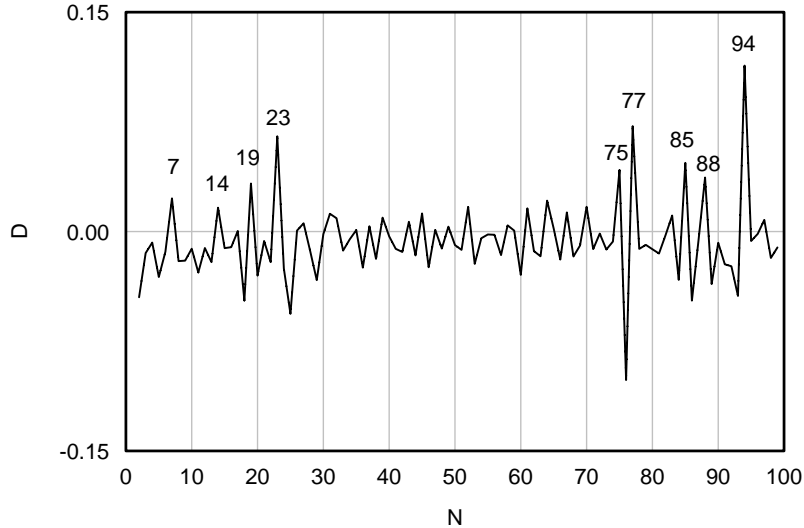


Figure 5: Ground-state abundance spectrum and magic clusters deposited on surfaces

the surface of the solid; we find that equilibrium positions are reached mostly above the surface, as for deposited clusters. The binding energies  $E(N)$  have been computed for the ground-state of these clusters as indicated before, and abundance spectra  $D = \ln(I_N^2/I_{N+1}I_{N-1}) = E(N+1) + E(N-1) - 2E(N)$  have been obtained, where  $I_N$  is Boltzmann's statistical weight.

Such an abundance spectrum  $D$  is shown in Fig. 5; these spectra depend weakly on the nature of the clusters and of the substrate. Magic clusters deposited on surface are to be noted in Fig. 5, as, for instance, those corresponding to  $N = 7, 14, 19, 23, 75, 77, 85, 88, 94\dots$ ; they acquire highly symmetric forms, as shown in Fig. 6. The rather structureless island between  $N = 23$  and  $N = 75$  is intriguing in Fig. 5. As a general rule, for small values of  $N$  the atoms are adsorbed on the surface as a monolayer, forming up more-or-less regular polygons. On increasing the number of atoms, they distribute themselves both horizontally and vertically, giving rise to multilayer structures, with various, intricate geometries, and sometimes beautiful symmetries, as those corresponding for instance to  $N = 23, 77, 94$ .

It is worth noting that their binding energies are higher in comparison with their monolayer (two-dimensional) versions (which are isomers), *i.e.* growing up vertically helps stabilizing the clusters; such a comparison is shown in Fig. 7. In general, there is a competition between the two directions of growth, horizontal and vertical, and it is difficult to predict which would prevail for a given number of atoms.

Bound states can also be obtained for clusters deposited on surfaces with parts pervading beneath the surface, as shown in Fig. 8. Indeed, the first two pictures in Fig. 8 shown a 50-atoms cluster diffusing into solid, while the last picture in Fig. 8 exhibits a 100-atoms cluster developing an interface with the solid. These states are isomeric, and, in some cases, atoms may escape into the solid where they acquire free positions, *i.e.* they are no more bound to the cluster. Similar formations can be obtained for a large variety of situations, including both geometric constraints, like a deposition surface, and dynamic constraints, like applying external forces.[3, 28]

As regards the comparison of the present structural results with experimental data concerning homo-metallic clusters deposited on surfaces, or incipiently diffusing into metals just beneath the surface, we are not aware of distinct, clear-cut experimental results yet, amenable to such a comparison. Direct observations have been reported to our knowledge for Si (silicon) and Ga (gallium) clusters deposited on Si-surfaces by electron scanning microscopy, indicating the existence of stable, abundant structures and corresponding magic numbers. It is relevant in this context the

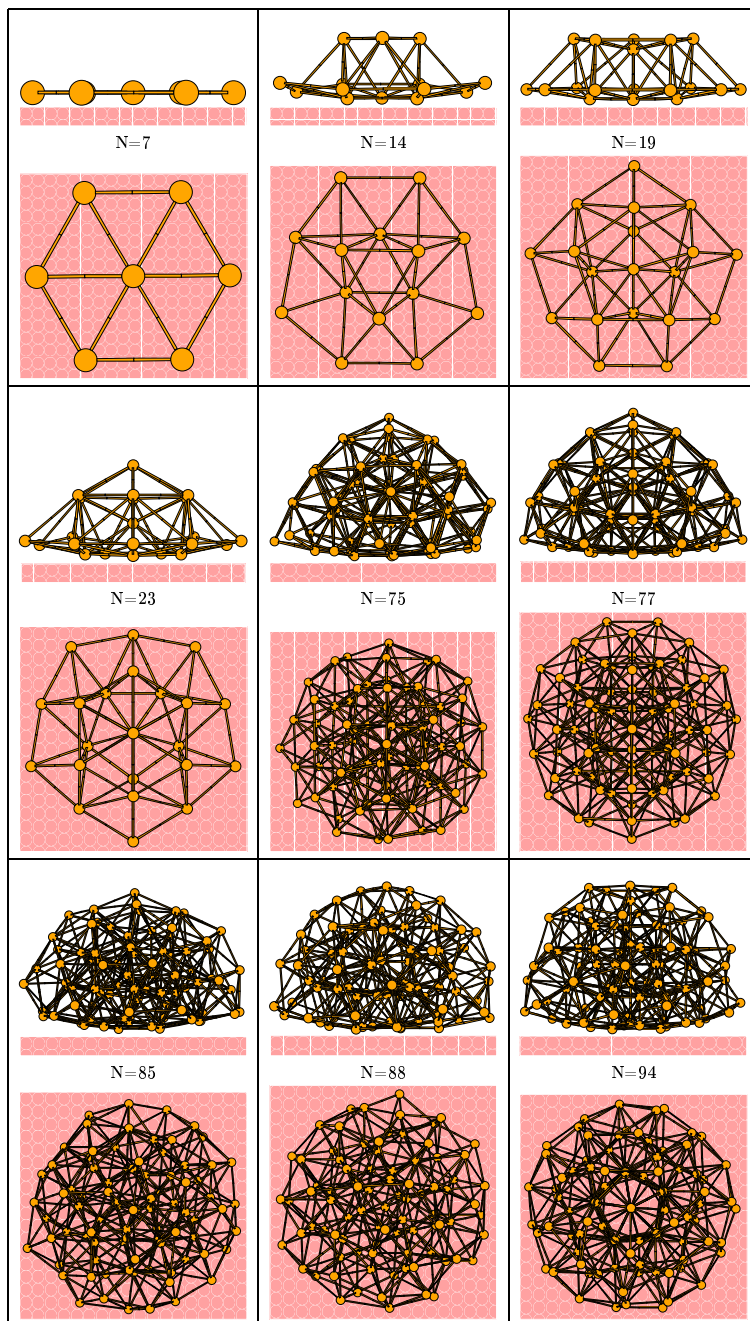


Figure 6: Magic clusters deposited on a surface

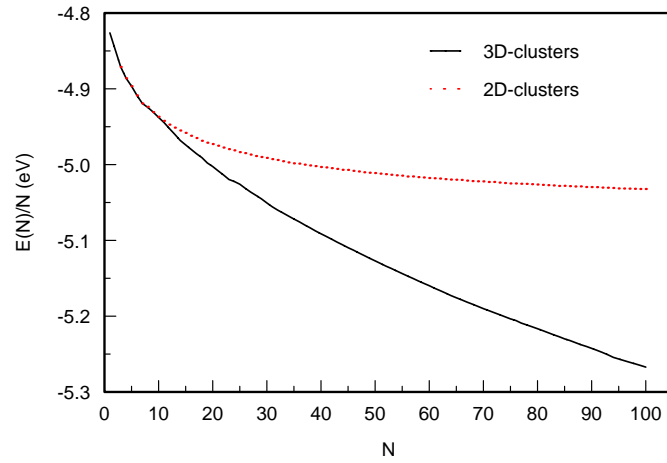


Figure 7: Ground-state energy per atom for Fe-clusters (3D, solid line) deposited on Na-surface vs number of atoms, as compared with monolayer cluster energy (2D, dashed line)

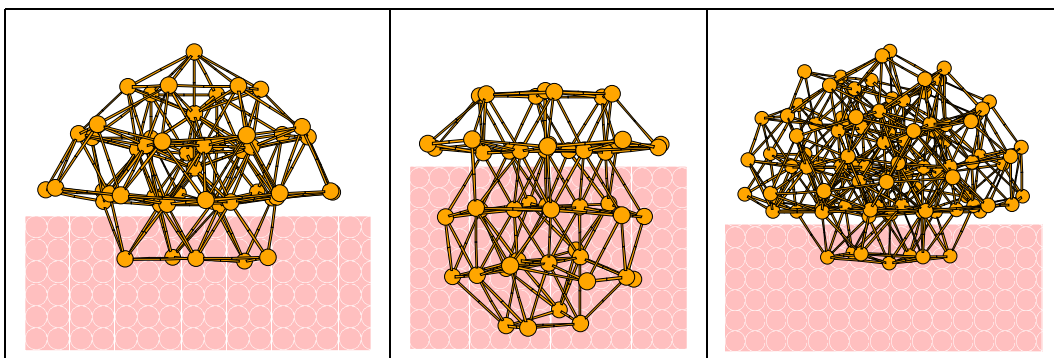


Figure 8: A 50-atoms cluster diffusing into solid (first two pictures), a 100-atoms one developing an interface with the solid (last picture)

following excerpt from Ref. 28:

”Although speculations about the existence of magic clusters on surfaces were raised in a paper in 1992, which was based on a study of the Pt/Pt(111) surface using He scattering,[29] no SCM (*surface magic clusters, our note*) were found in the later scanning tunneling microscopy (STM) study of this surface.[30] The first demonstration of such clusters exhibiting enhanced stability and abundance had to wait for several years until SCM were directly observed on the  $\sqrt{3} \times \sqrt{3}R30^\circ$ -reconstructed Ga/Si(111) surface.[31, 32] Soon after this work, Si islands with magic numbers of unit cells on the Si(111)  $7 \times 7$  surface were reported.[33] This was then followed by the observation of a type of Si magic cluster on Si(111).[34]”

The study of Si, or Ga clusters, and others alike, requires the inclusion of the directional character of the atomic-like orbitals. Such an investigation is underway.

## 5 Concluding Remarks

In conclusion, we may say that interaction potentials can be identified in the quasi-classical description of atomic aggregation, between atoms and semi-infinite solids, which allow to analyze the deposition of the atomic clusters on surfaces. At the present level of computations the geometric forms of deposited metallic clusters are obtained, as well as binding energies, inter-atomic distances and vibration spectra. Magic clusters are identified, deposited on surfaces, exhibiting, in general, high symmetries, both horizontally and vertically. Increasing the number of atoms they may intrude beneath the surface, giving thus the possibility of building up interfaces, and contacts, between two solids. Further investigations are pursued into extending the theory to directional chemical bonds and electronic single-particle properties, and to increase the degree of accuracy of the results.

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## References

- [1] de Heer, W. A. (1993) The physics of simple metal clusters: experimental aspects and simple models, *Revs. Mod. Phys.* **65**, 611-676.
- [2] Brack, M. (1993) The physics of simple metal clusters: self-consistent jellium model and semi-classical approaches, *Revs. Mod. Phys.* **65**, 677-732.
- [3] Meiwes-Broer, K.-H. (ed) (2000) *Metal Clusters at Surfaces: Structure, Quantum Properties, Physical Chemistry (Cluster Physics)*, Springer.
- [4] Binns, C. (2001) Nanoclusters deposited on surfaces, *Surf. Sc. Rep.* **44**, 1-49.
- [5] Pople, J. A. (1999) Nobel Lecture: Quantum chemical models, *Revs. Mod. Phys.* **71**, 1267-1274.
- [6] Kohn, W. (1999) Nobel Lecture: Electronic structure of matter-wave functions and density functionals, *Revs. Mod. Phys.* **71**, 1253-1266.

- [7] Cune, L. C. and Apostol, M. (2000) Ground-state energy and geometric magic numbers for homo-atomic metallic clusters, *Phys. Lett.* **A273**, 117-124.
- [8] Cune, L. C. and Apostol, M. (2001) Iron-hydrocarbon cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$ , *Chem. Phys. Lett.* **344**, 287-291.
- [9] Cune, L. C. and Apostol, M. (2000) *Metallic Binding*, apoma, Magurele-Bucharest.
- [10] Cune, L. C. and Apostol, M. (2002) Atomic Clusters: Chemical Bond in Condensed Matter, in Graja, A., Bulka, B. R. and Kajzar, F. (eds) *Molecular Low-Dimensional and Nanostructured Materials for Advanced Applications*, Kluwer Academic Publishers, Dordrecht, pp 221-231.
- [11] Schwinger, J. (1980) Thomas-Fermi model: The leading correction, *Phys. Rev.* **A22**, 1827-1832.
- [12] Schwinger, J. (1981) Thomas-Fermi model: The second correction, *Phys. Rev.* **A24**, 2353-2361.
- [13] Slater, J. C. (1979) *The Calculations of Molecular Orbitals*, Wiley, NY.
- [14] Wigner, E. and Seitz, F. (1933) On the Constitution of Metallic Sodium, *Phys. Rev.* **43**, 804-810.
- [15] Wigner, E. and Seitz, F. (1934) On the Constitution of Metallic Sodium. II, *Phys. Rev.* **46**, 509-524.
- [16] Wigner, E. (1934) On the Interaction of Electrons in Metals, *Phys. Rev.* **46**, 1002-1011.
- [17] Doye, J. P. K. and Wales, D. J. (1997) Structural consequences of the range of the interatomic potential: a menagerie of clusters, *J. Chem. Soc., Faraday Trans.* **93**, 4233-4244.
- [18] D. Rayane, P. Melinon, B. Tribollet, B. Chabaud, A. Hoareau and M. Broyer, *J. Chem. Phys.* **91** 3100 (1989).
- [19] Dunlap, B. I. (1990) Symmetry and cluster magnetism, *Phys. Rev.* **A41**, 5691-5694.
- [20] Castro, M. and Salahub, D. R. (1993) Theoretical study of the structure and binding of iron clusters:  $\text{Fe}_n$  ( $n \leq 5$ ), *Phys. Rev.* **B47**, 10955-10958.
- [21] Christensen, O. B. and Cohen, M. L. (1993) Ground-state properties of small iron clusters, *Phys. Rev.* **B47**, 13643-13647.
- [22] Wang, Q., Sun, Q., Sakurai, M., Yu, J. Z., Gu, B. L., Sumiyama, K. and Kawazoe, Y. (1999) Geometry and electronic structure of magic iron oxide clusters, *Phys. Rev.* **B59**, 12672-12677.
- [23] Huisken, F., Kohn, B., Alexandrescu, R. and Morjan, I. (2000) Reactions of iron clusters with oxygen and ethylene: Observation of particularly stable species, *J. Chem. Phys.* **113**, 6579-6584.
- [24] Knickelbein, M. B., Koretsky, G. M., Jackson, K. A., Pederson, M. R. and Haznal, Z. (1998) Hydrogenated and deuterated iron clusters: Infrared spectra and density functional calculations, *J. Chem. Phys.* **109**, 10692-10700.
- [25] Karabacak, M., Ozcelik, S. and Guvench, Z. B. (2002) Structures and energetics of  $\text{Pd}_n$  ( $n = 2 - 20$ ) clusters using an embedded-atom model potential, *Surf. Science* **C507-510**, 636-642.

- [26] Smith, J. R. (1969) Self-Consistent Many-Electron Theory of Electron Work Functions and Surface Potential Characteristics for Selected Metals, *Phys. Rev.* **181**, 522-529.
- [27] Jones, W. and March, N. H. (1973) *Theoretical Solid-State Physics*, Wiley-Interscience, London, vol. II, p. 1062 and *ff.*
- [28] Wang, Y. L. and Lai, M. Y. (2001) Formation of surface magic clusters: a pathway to monodispersed nanostructures on surfaces, *J. Phys.: Condens. Matter* **13**, R589-R618.
- [29] Rosenfeld, G., Becker, A. F., Poelsema, B., Verheij, L. K. and Comsa, G. (1992) Magic clusters in two dimensions?, *Phys. Rev. Lett.* **69**, 917-920.
- [30] Michely, T., Hohage, M., Esch, S. and Comsa, G. (1996) The effect of surface reconstruction on the growth mode in homoepitaxy, *Surf. Sci. Lett.* **349**, L89-L94.
- [31] Lai, M. Y. and Wang, Y. L. (1998) Direct Observation of Two Dimensional Magic Clusters, *Phys. Rev. Lett.* **81**, 164-167.
- [32] Lai, M. Y. and Wang, Y. L. (1999) Gallium-induced nanostructures on Si(111): From magic clusters to incommensurate structures, *Phys. Rev.* **B60**, 1764-1770.
- [33] Voigtlander, B., Kastner, M. and Smilauer, P. (1998) Magic Islands in Si/Si(111) Homoepitaxy, *Phys. Rev. Lett.* **81**, 858-861.
- [34] Hwang, I.-S., Ho, M.-S. and Tsong, T. T. (1999) Dynamic Behavior of Si Magic Clusters on Si(111) Surfaces, *Phys. Rev. Lett.* **83**, 120-123.