Metallic Clusters

L. C. Cune and M. Apostol
Department of Theoretical Physics, Institute of Atomic Physics,
Magurele-Bucharest MG-6, POBox MG-35, Romania
email:cune@theory.nipne.ro

Abstract

Large metallic clusters of heavy atoms are described within the quasi-classical theory, by means of a variational approach to the linearized Thomas-Fermi model. Effective inter-atomic potentials are derived and equilibrium spatial structures are given; these structures are universal for homo-atomic metallic clusters, in the sense that they are independent of the chemical nature of the atoms. The binding energies, inter-atomic distances, and the vibration spectra are computed as functions of the effective number of "valence" electrons; this effective valence is estimated from the atomic screening. Magic numbers are obtained, corresponding to close spatial packings; these geometric magic numbers are also universal for homo-atomic metallic clusters, in the sense that they do not depend on the atomic species. The quadrupole-deformed electronic potential of a cluster is also derived. The extension of the theory to including ionic or covalent bonds is discussed.

1 Introduction

The molecular-binding or solid-state theories have a limited applicability to atomic clusters; density-functional approaches, for instance, work conveniently for a relatively small number of atomic constituents in a cluster, while jellium-like models are useful for very large metallic clusters;[1] in this respect, the difficulties with the atomic clusters reside in their relatively large, but finite, number of atomic constituents, and in their finite sizes and irregular shapes. The present paper reports upon a direct approach to large metallic clusters of heavy atoms, both homo- and hetero-atomic, which allows one to determine the equilibrium spatial structures, binding energies, inter-atomic distances, clusters shapes and magic numbers, vibration spectra, etc; the equilibrium geometric forms of the homo-atomic clusters are universal within the present theory, in the sense that they are independent of the atomic species; the binding energies and other physical properties are determined as functions of the effective number z^* of the "valence" electrons participating in the metallic bond; this effective valence is an input parameter of the theory, which accounts for the atomic screening (the atoms are identified by the atomic number Z and the nominal valence z); although the binding energies depend on the effective valence z^*, it turns out that the geometric magic numbers for homo-atomic clusters do not, so that the latter may be viewed as being universal too. The method is based upon the quasi-classical description and the statistical character of the electronic single-particle states in a metallic cluster, and consists in the identification of effective inter-atomic potentials; it is a variational approach to a linearized version of the Thomas-Fermi model, appropriate for a slightly inhomogeneous electron gas. A few series M_N of homo-atomic metallic clusters are described herein for illustrative purposes, where M=Na (sodium, $Z = 11$, $z = 1$), Fe (iron, $Z = 26$, $z = 2$) and Ba (barium, $Z = 56$, $z = 2$),

including the isomers. The mass-abundance spectra and the magic numbers are given for such clusters (corresponding to their ground-states); the vibration spectra of the atoms around the equilibrium positions are also computed in some special cases, corresponding to the 13 geometric magic numbers $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$, as well as the inter-atomic distances. These geometric magic numbers appear through quasi-periodic variations between regular and irregular cluster shapes, and, in this respect, the mechanism is related (but not identical) to the electronic-shells mechanism of the deformed potential.[2] The quadrupole-deformed electronic potential of a cluster is also derived within the present theory, and the extension of the theory to including ionic or covalent bonds is discussed.

2 Theory

The theory is a variational approach to a linearized version of the Thomas-Fermi model for atoms.[3] Suppose that we have a collection of N metallic atoms, placed at positions $\mathbf{r}_i$, $i = 1, 2, ...N$, each with a (nominal) valence charge $-z_i e$, where $-e$ is the electron charge; the ionic cores are considered point-like, so that the effective number of "valence" electrons participating in the metallic bond are reduced from the nominal valence z_i to an effective valence z_i^*; these effective valence charges are estimated in the next section, on account of the atomic screening; they acquire relatively small values, so that the interacting electrons moving in the background of such point-like ions may be viewed as a slightly inhomogeneous electron gas.[4] The effective electronic charges are assumed to move in a self-consistent field φ, and for a large cluster, such that the total charge number $z_0 = \sum_{i=1}^{N} z_i^* \gg 1$, they form a slightly inhomogeneous electron gas with a position-dependent Fermi wavevector k_F; under this circumstance, the electrons admit a quasi-classical description according to

$$\hbar^2 k_F^2 / 2m - e\varphi = 0 \quad , \tag{1}$$

where $\hbar$ is Planck's constant and m is the electron mass; we adopt the atomic units, by introducing the Bohr radius $a_H = \hbar^2 / me^2 \simeq 0.53\text{Å}$, and the energy unit $e^2 / a_H \simeq 27.2\text{eV}$ (twice the rydberg 1ry$\simeq 13.6$eV); the potential φ is measured in e/a_H, so that the above equation becomes

$$k_F^2 / 2 - \varphi = 0 \quad ; \tag{2}$$

we note that it corresponds to a neutral cluster, the potential φ (and the chemical potential in the *r.h.s.* of eq. (2)) vanishing at infinite. The self-consistent field φ is given by Poisson's equation

$$\Delta\varphi = -4\pi \sum_{i=1}^{N} z_i^* \delta(\mathbf{r} - \mathbf{r}_i) + 4\pi n \quad , \tag{3}$$

where n is the electronic density; as it is well-known, in the statistical approximation of the Thomas-Fermi model for large clusters ($z_0 \gg 1$) the electrons fill up locally a Fermi sea, so that the electronic density is given by $n = k_F^3 / 3\pi^2$; since k_F is determined by eq. (2) the density n depends on the potential φ, so that the latter is indeed a self-consistent potential, as determined by eqs. (2) and (3).

The quasi-classical description is valid for slow spatial variations of the electronic wavelengths, or, in other words, for a variation of the potential energy over electronic wavelengths much smaller than the kinetic energy; therefore, it requires the potential φ have a weak spatial variation; this is indeed the case over a moderate range of intermediate distances, *i.e.* not very close to, and not
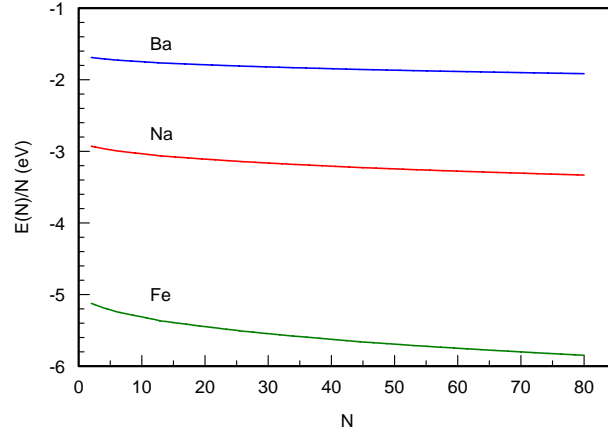
Figure 1: Ground-state energy per atom $E(N)/N$ *vs* cluster size N for Na ($z^* = 0.44$), Fe ($z^* = 0.57$) and Ba ($z^* = 0.34$)

very far from, the atomic nuclei. As it is well-known from the Thomas-Fermi model for an atom with a nuclear charge Z, the quasi-classical approximation is valid for distances much larger than the radius $r_B \sim 1/Z$ of the first Bohr orbit, where the quantum effects are important, and much smaller than distances of the order of unity (*i.e.* the Bohr radius a_H), beyond which the electronic wavelengths increase indefinitely; most part of the electrons in a heavy atom are localized over distances of the order of $r_e \sim Z^{-1/3}$, so that the Thomas-Fermi model is reasonably valid for such atoms, *i.e.* for $Z \gg 1$. Since the large number z_0 of the electrons participating in the metallic bond of a cluster are mostly localized in-between the ionic cores we expect the Thomas-Fermi model to hold also for such a cluster. In addition, since the potential φ varies slowly in space over these in-between regions, the Fermi wavevector k_F has also a weak spatial variation, according to eq. (2), so that we may substitute $\overline{k}_F k_F$ for k_F^2 in eq. (2), and similarly $\overline{k}_F^2 k_F$ for k_F^3 in the electronic density $n = k_F^3/3\pi^2$, where $\overline{k}_F$ is regarded as a variational parameter, constant in space, and the whole spatial dependence is transferred upon the new variable k_F ($\overline{k}_F$ is close to the average k_F, hence the notation); such substitutions are valid over those spatial regions where $\overline{k}_F$ and k_F are comparable in magnitude, *i.e.* for a weak spatial dependence of such quantities; we note that other substitutions, like, for instance, $\overline{k}_F k_F^2$ for k_F^3, would increase the inaccuracy, as higher-order powers of k_F vary stronger than k_F for slight variations of the latter; therefore, we arrive at a linearized version of the Thomas-Fermi model, described by the equations

$$\overline{k}_F k_F/2 - \varphi = 0 \tag{4}$$

and

$$\Delta\varphi = -4\pi \sum_{i=1}^{N} z_i^* \delta(\mathbf{r} - \mathbf{r}_i) + q^2\varphi \quad, \tag{5}$$

where the Thomas-Fermi screening wavevector q has been introduced through

$$q^2 = 8\overline{k}_F/3\pi \quad, \quad n = (q^2/4\pi)\varphi \quad, \tag{6}$$

according to eqs. (2) and (3); according to the above discussion this screening wavevector will be taken as the variational parameter.

The linear Poisson's equation (5) has now a simple analytic solution given by

$$\varphi = \sum_{i=1}^{N} \frac{z_i^*}{|\mathbf{r} - \mathbf{r}_i|} e^{-q|\mathbf{r} - \mathbf{r}_i|} \quad, \tag{7}$$
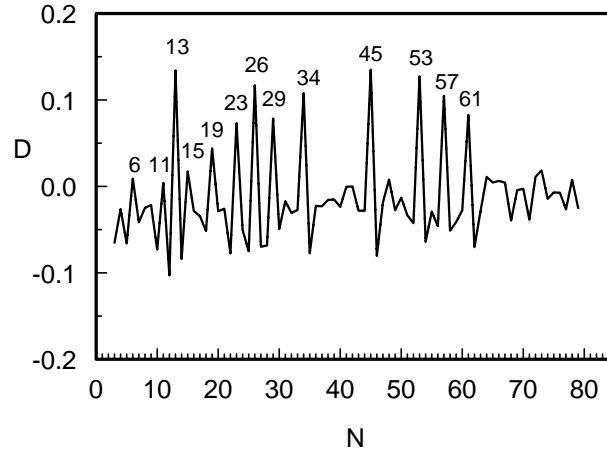
Figure 2: Geometric magic numbers for homo-atomic metallic clusters

i.e. a superposition of screened Coulomb potentials, as expected.

We pass now to the potential energy; it consists of the potential energy of the electrons in the self-consistent field φ (with due care for counting only once the Coulomb repulsion between the electrons) and the Coulomb energy of the ionic cores with poin-like charges z_i^*; the Coulomb repulsion between the ionic cores is given by

$$E_c = \frac{1}{2} \sum_{i \neq j = 1}^{N} z_i^* z_j^* / |\mathbf{r}_i - \mathbf{r}_j| \quad , \tag{8}$$

while the potential energy of the electrons in the self-consistent field φ can be written as

$$E_e = -\int d\mathbf{r} \cdot n(\varphi - \frac{1}{2}\varphi_e) = -\frac{1}{2} \int d\mathbf{r} \cdot n(\varphi + \varphi_c) =$$

$$\tag{9}$$

$$= -\frac{q^2}{8\pi} \int d\mathbf{r} \cdot \varphi(\varphi + \varphi_c) \quad ,$$

where $\varphi_e = \varphi - \varphi_c$ is the electronic part of the field, and

$$\varphi_c = \sum_{i=1}^{N} z_i^* / |\mathbf{r} - \mathbf{r}_i| \tag{10}$$

is the Coulomb field of the ionic cores; the relationship between the electronic density n and the self-consistent field φ as given by eq. (6) has been used in writing up eq. (9).

Making use of the field φ given by (7), and using eq. (10), the integration in (9) is straightforward (the intervening integrals are two-centre integrals); adding the Coulomb repulsion between the ionic cores as given by (8) we obtain the potential energy

$$E_{pot} = E_e + E_c = -\frac{1}{4}q[3\sum_{i=1}^{N} z_i^{*2} +$$

$$\tag{11}$$

$$+ \sum_{i \neq j = 1}^{N} z_i^* z_j^* \left(1 - 2/q|\mathbf{r}_i - \mathbf{r}_j|\right) e^{-q|\mathbf{r}_i - \mathbf{r}_j|}] \quad ;$$
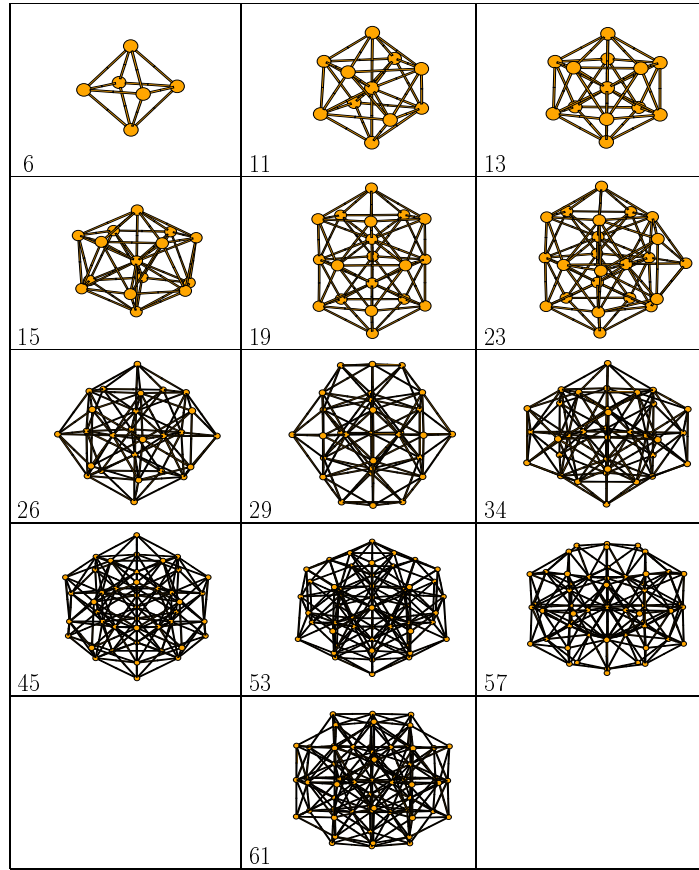
Figure 3: Magic homo-atomic metallic clusters

it is worth noting that this potential energy depends on the inter-atomic positions only through the dimensionless variables $|\mathbf{x}_i - \mathbf{x}_j|$, where $\mathbf{x}_i = q\mathbf{r}_i$.

According to the linearization procedure, the kinetic energy $E_{kin} = V k_F^5/10\pi^2$ of an electron gas enclosed in a volume V is written as

$$E_{kin} = \frac{1}{10\pi^2}\bar{k}_F^4 \int d\mathbf{r} \cdot k_F = \frac{\pi}{5}(3/8)^3 q^6 \int d\mathbf{r} \cdot \varphi \tag{12}$$

for a slightly inhomogeneous electron gas; making use of the potential φ given by (7) we obtain

$$E_{kin} = (27\pi^2/640)q^4 \sum_{i=1}^{N} z_i^* \quad, \tag{13}$$

and we note that, formally, it is the sum of the kinetic energies of N independent atoms, and does not depend on the inter-atomic distances. Within the quasi-classical description the total energy must be corrected by the exchange contribution; the exchange energy is a quantum correction (in this respect the potential energy given above is the direct (or Hartree) contribution), and for an electron gas confined to a volume V it is given by $E_{ex} = -(1/4\pi^3)V k_F^4$; according to the linearization procedure it can be written as

$$E_{ex} = -\frac{1}{4\pi^3}\bar{k}_F^3 \int d\mathbf{r} \cdot k_F = -\frac{1}{2\pi^3}\bar{k}_F^2 \int d\mathbf{r} \cdot \varphi \quad, \tag{14}$$

for a slightly inhomogeneous electron gas; making use of eqs. (6) and (7) we obtain

$$E_{ex} = -\frac{9}{32}q^2 \sum_{i=1}^{N} z_i^* \quad , \tag{15}$$

we note again that it corresponds formally to a collection of N independent atoms, and does not depend on the inter-atomic distances. It is worth emphasizing that the exchange energy corresponds to a slightly inhomogeneous electron gas within the quasi-classical description, in which case it has the form given by (15); as such, small local density variations, like those involved by the variations of q, do not bring any appreciable change in the exchange energy, in spite of its formal dependence on q; this dependence is valid only for the extended (quasi-) plane waves of the quasi-classical description, and any local density variation in this picture leaves the exchange energy practically unchanged, as a consequence of the non-local character of the exchange energy; consequently, within the quasi-classical description, E_{ex} is not included in the energy functional whose minima lead to the equilibrium energy of the cluster, but its value given by (15) is simply added to the equilibrium value of the total energy.
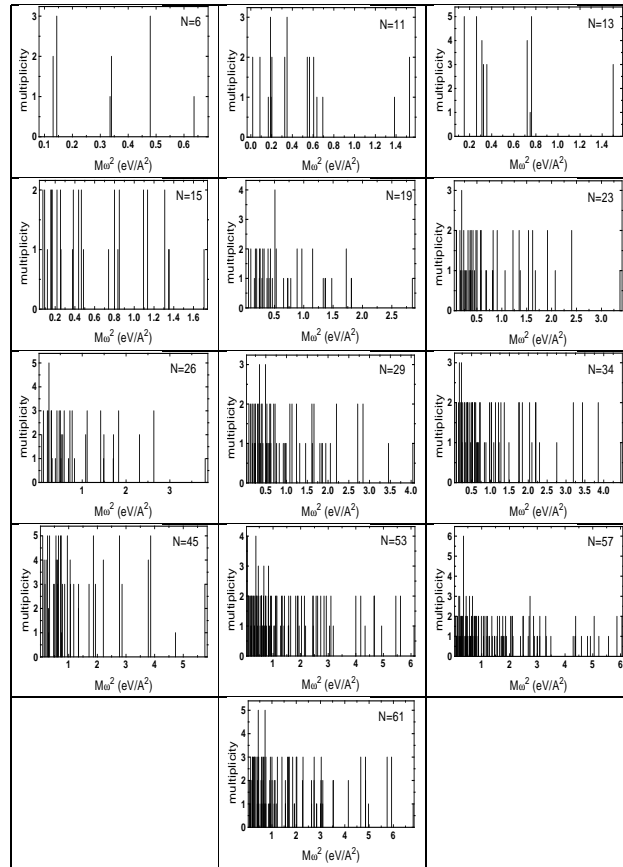

Figure 4: Vibration spectra for magic Fe-clusters ($z^* = 0.57$)

The potential energy given by (11) can be expressed (up to a constant) in terms of two-particle

effective inter-atomic potentials

$$\Phi_{ij} = -\frac{1}{2} z_i^* z_j^* q \left(1 - 2/q|\mathbf{r}_i - \mathbf{r}_j|\right) e^{-q|\mathbf{r}_i - \mathbf{r}_j|} \quad , \tag{16}$$

which have a close resemblance to Buckingham's potentials; [5] they are slightly attractive (and vanish) at large distances, are repulsive at short distances, and have a (negative) minimum value at intermediate distances; one can also see easily that they exhibit a smooth spatial variation over large distances for small values of q, and the equilibrium inter-atomic distances are of the order of $\sim 1/q$. In addition, we note that for indefinitely large inter-atomic separations the potential energy given by (11) reduces formally to a sum of independent-atoms contributions; however, while such contributions are valid for a cluster, they are irrelevant for independent, neutral atoms (since the Thomas-Fermi model is not applicable for small z_i^* values of "atomic numbers"). In the same way, the effective potentials Φ_{ij} given by (16) are valid around the equilibrium atomic positions in a cluster, and they are not appropriate for either a too close or a too far pair of atoms; for this reason they may be called pseudo-potentials.

The potential energy E_{pot} given by (11) will be minimized with respect to $\mathbf{r}_i$, in fact with respect to $\mathbf{x}_i = q\mathbf{r}_i$, in order to find the equilibrium-positions parameters $\mathbf{X}_i = q\mathbf{R}_i$ of the atoms; the solutions are not unique, in general, as corresponding to local minima of the potential energy, thus describing both the ground-state and the isomers of a cluster; we note that for homo-atomic clusters (where the effective charges z_i^* are the same for all the atoms, $z_i^* = z^*$) the equilibrium-positions parameters $\mathbf{X}_i$ are independent of the effective charges, *i.e.* the clusters shapes are universal; they are given by the minimum values of the function $\sum_{i \neq j} f(|\mathbf{x}_i - \mathbf{x}_j|)$, where $f(x) = (1 - 2/x)e^{-x}$. The energy is determined by minimizing the quasi-classical energy $E_q = E_{kin} + E_{pot}$ as given by (11) and (13) with respect to the variational parameter q; according to the discussion made above the exchange energy E_{ex} given by (15) is not included in the energy functional E_q which gives the equilibrium; however, the value of the exchange energy at equilibrium is added to the total energy $E = E_q + E_{ex}$. Introducing the notations

$$
\begin{aligned}
A &= (27\pi^2/160) \sum_{i=1}^{N} z_i^* \quad , \\
\\
B &= \frac{1}{4} \left[3 \sum_{i=1}^{N} z_i^{*2} + \sum_{i \neq j=1}^{N} z_i^* z_j^* f(|\mathbf{X}_i - \mathbf{X}_j|) \right] \quad ,
\end{aligned}
\tag{17}
$$

(where the function f has been defined above), the quasi-classical energy reads $E_q = Aq^4/4 - Bq$, and the minimum value is reached for a screening wavevector $q = (B/A)^{1/3}$; therefore, the total energy can be written as

$$E = -\frac{3}{4} A(B/A)^{2/3} \left[(B/A)^{2/3} + 20/9\pi^2 \right] \quad . \tag{18}$$

One may check that the variational screening wavevector $q = (B/A)^{1/3}$ is associated with a $\bar{k}_F$-value, according to (6), which is close to the average value of the Fermi wavevector, as expected; this indicates that the quasi-classical approximation is valid for metallic clusters, as it holds also for heavy atoms. The reason is that in both cases the self-consistent potential varies slowly over the relevant length scales (determined by the electronic wavelengths) in comparison with the electronic kinetic energies; for atoms this is due to the large values of the atomic numbers Z, while in the case of metallic clusters this originates in the small values of the effective charges

z_i^*, the large values of the number N of atomic constituents, and to an extended spatial range of distances available for the electronic motion, as for a slightly inhomogeneous electron gas; the later condition is also due to the high values of the atomic number Z of the atomic constituents, as we shall see below.
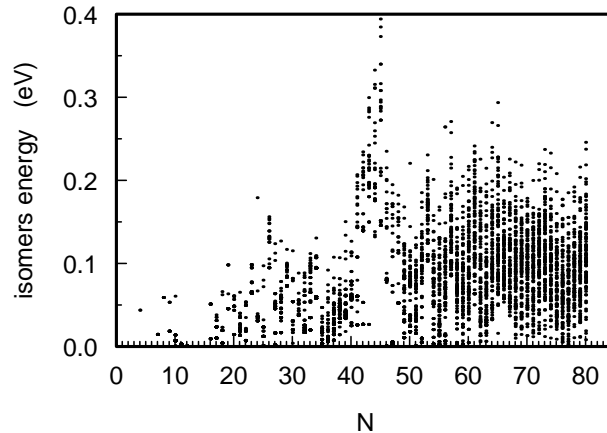

Figure 5: Isomer table for Fe-clusters ($z^* = 0.57$; accuracy less than 10^{-2}eV)

The total energy given by (18) is valid for electrons participating in the metallic bond of a cluster, and it can not be used for isolated atoms, *i.e.* for an infinite inter-atomic separation; though E has a non-vanishing value in this latter case (corresponding to $B \rightarrow (3/4) \sum_i z_i^{*2}$), this limiting value does not correspond to neutral atoms, since the present Thomas-Fermi theory is not valid for small z_i^* values of the "atomic numbers", as noted above. In fact, the electronic states participating in the metalic bond have a vanishing energy in the isolated atoms, within the quasi-classical description (the Fermi sea is filled up to a vanishing energy level for neutral atoms, as well as for neutral clusters); consequently, the energy corresponding to isolated atoms may be taken as being equal to zero in the present theory, which shows that the total energy given by (18) is in fact the binding energy of the cluster.

At this point it is worthwhile estimating the equilibrium value of the screening wavevector q, as derived by the procedure described above. First, we assume an average effective charge z^* instead of z_i^* (as for homo-atomic clusters); then, we note that the potential energy given by (11) is practically proportional to the number N of the atoms in the cluster for large values of N (since the summation over j in (11) for any fixed i is finite, and depends weakly on N, especially for large N); the potential energy goes then like $E_{pot} \sim -qNz^{*2}$, while the kinetic energy given by (13) behaves like $E_{kin} \sim q^4Nz^*$; the equilibrium is reached for $q \sim z^{*1/3}$, and the average inter-atomic distance at equilibrium is of the order of $1/q$. The radial electron density $\sim r^2n$ around an ion has a maximum value at distances $r \sim 1/q$, for the screened Coulomb potential $(z^*/r)e^{-qr}$ contained in (7) for each ion (the electronic density is proportional to the self-consistent field, according to (6)); it folows that the electrons participating in the metallic bond are indeed localized mostly in-between the ions, where the self-consistent field has a weak spatial variation; in fact, as noted above, the quasi-classical description holds for an atom with the atomic number $Z \gg 1$ for distances $r_e \sim 1/Z^{1/3}$, where most of the electrons are localized in a heavy atom; hence, by comparing the volumes corresponding to these regions, and using $r \sim 1/q \sim z^{*-1/3}$, one may infere that the quasi-classical description presented here for a cluster holds for the binding electrons since $(r_e/r)^3 \sim z^*/Z \ll 1$, *i.e.* it holds for heavy atoms which participate in the metallic

bond with a small number of "valence" electrons. As known, the quasi-classical picture breaks down for heavy atoms at distances of the order of the radius $r_B \sim 1/Z$ of the first Bohr orbit, so that, comparing again the corresponding volumes available for the electronic motion, one can see that the condition $(r_B/r)^3 = (1/Z^2)(z^*/Z) \ll 1$ is satisfied. All these conditions break down for light atoms, and, in this respect, one may say that the theory developed here exhibits a limited range of applicability for clusters consisting of light atoms (like lithium, for instance), or for those parts of a cluster containing light atoms; however, if the number of the light atoms participating in a cluster is much smaller than the number of the rest of the atoms, which are heavy atoms, then the quasi-classical approximation is again applicable; in general, the quasi-classical description may be viewed as being satisfactory providing the number of electrons for which it works is much larger than the number of electrons for which it does not; this is the basic principle for extending the use of the present theory of metallic binding to atomic clusters containing also a small number of local ionic, or even covalent, bonds

It is also worth noting here that the virial theorem is not satisfied in the present theory, as indicated by the q-dependence of the various contributions to the energy; indeed, making use of the above estimations we obtain $E_{kin} = -(1/4)E_{pot}$, instead of $E_{kin} = -(1/2)E_{pot}$, as required by the virial theorem; this originates, as expected, in the linearization procedure, and it means that both the kinetic and the potential energy are separately affected by errors in the present treatment; however, we expect the total energy be close to the right one, as a consequence of the quasi-classical description, statistical behaviour, and the variational procedure, as presented above. For instance, we have checked out that the present linear Thomas-Fermi model model is able to reproduce correctly the leading $-16Z^{7/3}$eV-term to the empirical binding energy of the heavy atoms, when quantum corrections are included.[6] Indeed, it is worth emphasizing here that, in principle, the results should be corrected for the quantum behaviour of the electrons at very close distances to the atomic nuclei (comparable with the radius r_B of the first Bohr orbit), where the self-consistent field has a strong spatial variation; however, contrary to the atoms, these corrections are already included for clusters, by using the effective valence z^*; in addition, such corrections are irrelevant, to a large extent, for the binding energy, since they affect equally the independent atoms separated at infinite.

To end this section, we may note again that the theory presented above is a density-functional theory[4] for an ensemble of electrons which form a slightly inomogeneous gas in the presence of point-like ionic cores.

3 Effective Valence Charge

The effective valence charges z_i^* must be considered, in principle, as input parameters of the present theory. We give here an estimation of such effective valence charges, on account of the atomic screening. Within the ionic cores the electronic states corresponding to the nominal valence electrons have a different regime, in comparison with the spatial region from the outside of the ionic cores; inside the cores these eletronic states start to feel gradually the screened charge of the atomic nucleus, and their character changes gradually toward that of atomic orbitals; consequently, within a point-like model of ionic cores the effective number of valence electrons participating in the metallic bond is diminished, as an effect of the atomic screening. This is equivalent in fact to determining the content of plane waves, specific to the electrons participating in the metallic binding within the quasi-classical description, in the atomic-like orbital corresponding to the cluster atoms. The variational treatment given above for the linearized Thomas-Fermi model can

also be applied to a heavy atom of atomic number Z ($Z \gg 1$). It is easy to see that the screened Coulomb potential gives an electron density $n = (q^2/4\pi)Ze^{-qr}/r$ according to (6), the screening wavevector is given by $q = 0.77Z^{1/3}$, and the leading contribution to energy is $E = -11.8Z^{7/3}$eV (as noted above, the quantum corrections to this energy lead to $E = -16Z^{7/3}$eV, in agreement with empirical data); the exchange energy goes like $Z^{5/3}$, and it is the next-order correction to the binding energy (a similar dependence on the effective average charge z^* holds for clusters too, where, in contrast to the atomic binding energy, the exchange energy does contribute). Within this model, one can estimate easily the number N_{out} of "outer" electrons in an atom, $i.e.$ the electrons lying outside of a sphere of radius R centered on the atomic nucleus; it is given by

$$\alpha = N_{out}/Z =$$

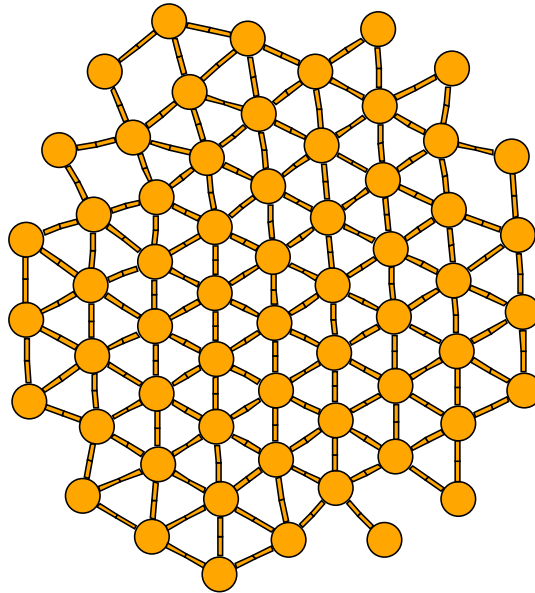$$= 4\pi \int_R^\infty dr \cdot r^2 n(r) = (1 + qR)e^{-qR} \; ;$$

(19)

Figure 6: A hexagonal atomic sheet obtained as a saddle-point of the potential energy given by (11)

this screening factor reduces the number of (nominal) valence electrons in the point-like approximation for the ionic cores, so that one may write $z_i^* = \alpha z_i$; one can see, that the effective valence charge accounts for the atomic screening (through the atomic screening wavevector $q = 0.77Z^{1/3}$), and depends on the chemical nature of the atoms (through Z); in addition, it involves also the "radius" R of the atom, or of the ionic core, and, in this respect, it amounts to a simplified version of the atomic (ionic) pseudo-potentials; in fact, the estimation given here is very similar to a particular case of a well-known pseudo-potential,[7] which is known to give satisfactory results; while its relation to the screening factor may be traced back to the screening lengths in the theory of the atomic structure.[8]

For practical estimations we adopt the radius $R = 1$ ($i.e.$ one Bohr radius a_H), which corresponds approximately to a neutral atom; one can check easily that the screening wavevector for an atom, as derived from the average Fermi wavevector is given by $q = (64Z/9\pi^2)^{1/3} = 0.9Z^{1/3}$, which is close

to the variational screening wavevector $q = 0.77Z^{1/3}$; consequently, we may take a mean value $q = 0.84Z^{1/3}$ in (19). Making use of (19) and of these parameters values we obtain an effective valence $z^* = 0.44$ for Na ($Z = 11$, $z = 1$), $z^* = 0.57$ for Fe ($Z = 26$, $z = 2$) and $z^* = 0.34$ for Ba ($Z = 56$, $z = 2$); these effective valences are used in the results reported below. The actual values of the atomic screening parameter qR in (19) could be slightly larger than $0.84Z^{1/3}$, but the variations do not have an appreciable qualitative effect; the numerical values of the binding energy are more affected, in view of the $z^{*7/3}$- and $z^{*5/3}$-dependence, but, as noted above, the cluster shapes are universal for homo-atomic clusters; similarly, the magic numbers turn out to be independent of z^* for any reasonable range of this parameter (we have checked it for $0 < z^* < 3$); such an estimation based on the atomic screening is, however, not perfectly adequate, and it may underestimate both the binding energy and the inter-atomic distances (the clusters might be too tightly packed within the present calculations); in addition, such an estimation is less accurate for very heavy atoms (very high atomic numbers Z), since the screening-tail of their electronic densities is small, and the errors affect it more significantly.

4   Results: Homo-Atomic Metallic Clusters

The equilibrium inter-atomic distances are obtained by minimizing first the potential energy E_{pot} given by (11) with respect to the parameters $\mathbf{x}_i = q\mathbf{r}_i$; the equilibrium values $\mathbf{X}_i = q\mathbf{R}_i$ of these parameters give the cluster shapes; as noted above, these values do not depend on the chemical nature of the atoms for homo-atomic clusters, *i.e.* the geometric forms obtained for such clusters are universal. We start with an arbitrary spatial configuration of N point-like atoms and compute the forces acting upon the atoms; then, the positions are changed in successive steps in the direction of the forces, and the process stops for all the forces smaller than 0.2meV/Å; this is the usual gradient-method, and it implies an overall accuracy of less than $10^{-3}\%$ within the present procedure. The parameter q is then computed by minimizing $E_q = E_{kin} + E_{pot}$ as given by (11) and (13), for fixed values of the structure parameters $\mathbf{X}_i$, and the total (binding) energy (18) is obtained, as described in the previous section; the equilibrium positions are finally obtained from $\mathbf{R}_i = \mathbf{X}_i/q$; various isomers are also obtained this way, corresponding to local minima of the potential energy, *i.e.* clusters with the same N but of different shapes and energies; after a reasonable number of shape determinations (cca 100) for each N (up to $N = 80$) we identify the cluster ground-state as that corresponding to the lowest energy obtained. This energy per atom, denoted $E(N)/N$, is plotted in Fig.1 *vs* N for $z_i^* = z^* = 0.44$ (Na), $z_i^* = z^* = 0.57$ (Fe) and $z_i^* = z^* = 0.34$ (Ba); one can see that it has a relatively weak dependence on N for large N. The mass-abundance spectra are computed as usually from $D = \ln(I_N^2/I_{N-1}I_{N+1}) = E(N+1)+E(N-1)-2E(N)$, where I_N is proportional to the Boltzmann statistical weights; these spectra do not depend significantly on z^*, so that only one of them is given in Fig.2, corresponding to $z^* = 0.57$. One can see 13 magic numbers $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$ in Fig.2, which are preserved for any value of z^* in the physically reasonable range $0 < z^* < 3$ (for N larger than 80 the peaks in the mass spectra diminish gradually, as the clusters approach the bulk behaviour). These magic numbers correspond to well-packed spatial structures of clusters with high symmetries; these universal cluster structures are given in Fig.3, and the corresponding vibration spectra for $z^* = 0.57$ are given in Fig.4.

The vibration spectra are computed as usually from the characteristic roots ω of the equations of motion

$$\det\left(\omega^2 M_i \delta_{ij}\delta_{\alpha\beta} - D_{ij}^{\alpha\beta}\right) = 0 \tag{20}$$

in the harmonic-approximation, where M_i is the mass of the i-th atom in the cluster, and the
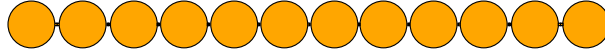
Figure 7: An atomic chain obtained as an unstable aggregate in the present theory

dynamic matrix matrix is $D_{ij}^{\alpha\beta} = \partial^2 E_{pot}/\partial R_{i\alpha}\partial R_{j\beta}$; the polarizations labels α and β correspond to the cartesian coordinates of the position vectors $\mathbf{R}_i$. One can see in Fig.3 only one of the well-known Plato's "perfect" polyhedra, namely the octahedron ($N = 6$), which, however, is not inscriptible; the tetrahedron $N = 4$, though obtained as a ground-state, might however be affected by significant errors; two other Plato's "perfect" polyhedra, namely the hexahedron (the cube) $N = 8$ and the dodecahedron $N = 20$ are distorted, while the icosahedron $N = 12$ is more stable when centered, *i.e.* for $N = 13$; they are not obtained as cluster ground-states, but as isomers. In turn, other perfect forms are obtained, like the centered icosahedron $N = 13$ which is quite a "perfect" body, judging after its symmetries and inter-atomic distances, or highly-symmetric magic clusters corresponding to $N = 11, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$; the principle of such magic packings seems to be a "space economy", the atoms trying to accomodate as close as possible to each other; such a close packing is realized by certain complete spatial shells, made of interpenetrating, highly-symmetric polyhedra, as, for instance, in the case of the remarkable magic cluster $N = 45$, where several inter-twinned icosahedra may be identified. As long as the number of atoms is not sufficient to complete such a shell, the clusters are not magic, their shapes are more irregular, and their energy is higher than the energy of their neighbouring magic clusters. Therefore, the magic clusters appear in the present theory through a close spatial packing in successive complete shells, as dictated by the inter-atomic potentials (given by (16)), and not as a direct consequence of a periodic filling up of electronic shells; on the contrary, the latter itself is a consequence of the magic, geometric shapes of the clusters, as the corresponding deformed potential of the electrons gets more symmetric, and increases the degeneracy of the electronic energy levels, for highly-symmetric clusters.[2]

The relationship between the geometric and the electronic magic numbers originates in the presence of the isomers; such an isomer table is given in Fig.5 (for $z^* = 0.57$), where the isomer energies are plotted with respect to the ground-state energies; if the temperature is high enough in the Boltzmann weights of the mass-abundance spectra, then more and more isomers may be excited, and the magic numbers change correspondingly; they are no more geometric numbers, associated with the ground-state, but they are statistical in character now, associated with the free energy; the electrons move now in a self-consistent potential which is more and more symmetric, as corresponding to the statistical average; this potential, as derived in the end section, is that of a (quadrupole- deformed) three-dimensional oscillator, which predicts the well-known electronic magic numbers (like, for instance, $N = 2, 8, 20, ...$ for small deformations).[2],[9] The isomer statistics obtained by the present procedure is rather poor (as corresponding only to 100 determinations for each cluster size N) to attempt any relevant determination of statistical magic numbers for various temperatures; however, such a determination made for Na-clusters at 10^3K indicates magic numbers like $N = 7, 17, 21, 28, 33$ which are close to magic numbers corresponding to certain deformations in a quadrupole-deformed potential.[2]

We note that the energies given in Fig.1 are relatively close to numerical results obtained by other calculations, and this is true also for inter-atomic distances; for instance, the energy per atom for Fe_{13} is approximately $\simeq -5.2$eV, and the inter-atomic distances are of the order of 2Å, in a relatively good agreement with density-functional results.[10] Similarly, the numerical results

derived here compare relatively well with other calculations where available (see, for instance, Refs. 1, 2), the main source of errors in the present calculations being the determination of the effective-valence charge parameters.

5   Discussion and Concluding Remarks

The application of the present theory to large hetero-atomic metallic clusters consisting of heavy atoms is straightforward from the above presentation; metallic clusters consisting of light atoms, or including light atoms, raise problems as regards the applicability of the quasi-classical description, as noted before. However, for large enough clusters such problems may be overcome by an accurate determination of the effective valence charges of the light atoms (which itself is yet another problem). The present theory of a slightly inhomogeneous electron gas may, in principle, be applied to including both ionic and covalent bonds in metallic clusters, providing the conditions discussed here are fulfilled. However, two types of difficulties appear in such an enterprise; one is related to the accurate determination of the effective valence charges, while the other pertains to the directional character of the covalent bonds. As it is well-known, the ionic bond is realized by a charge transfer, like, for instance, between a metal ion and oxygen, and the equilibrium is reached by the interplay between the electron affinity of the oxygen, ionization energy of the metal, and the Coulomb interaction associated with the charge transfer;[11] usually, $z_O = 2$ electrons are accepted by oxygen in such a transfer. Both the metal (M) cation and the oxygen (O) anion participate in the ionic bond with an effective valence z_M^* and, respectively, z_O^*, and attempts can be made to determine these effective charges by various methods. For instance, one may use the Thomas-Fermi atomic screening theory as before for metals (though the metal cation environment is different in the presence of the oxygen anion than in the presence of metal ions); the atomic-screening formula given by (19) may also be used as a qualitative estimation for oxygen, though the oxygen atomic number $Z = 6$ is rather small for ensuring a satisfactory validity for the Thomas-Fermi screening; in addition, we must allow for the angular dependence of the valence p-orbitals of the oxygen anion, which contribute an average factor $\overline{\cos^2 \theta} = 1/3$ (or $(1/2)\overline{\sin^2 \theta}$) for each orbital; consequently, one obtains $z_O^* = (1/3)z_O(1 + 0.84Z_O^{1/3})\exp(-0.84Z_O^{1/3}) = 0.36$ as a tentative estimate for the effective valence charge of the oxygen. A similar estimation may be attempted for covalent bonds too; however, the covalent bonds are directional, and further errors are introduced by approximating them with spherically-symmetric metal-like orbitals. Nevertheless, it is interesting to note that cluster shapes predicted by covalent-bond theories are usually reproduced within the present theory, like, for instance, the (unstable) hexagonal arrangement in the atomic sheet shown in Fig. 6, which is very suggestive for a graphite sheet (and might tentatively be taken as a precursor form for the fullerene molecule); however, such formations appear as isomers, *i.e.* their energy is higher than the energy of other, more compact, forms, or are unstable. In general, as noted above, ionic or covalent bonds may be introduced in metallic clusters within the present theory with the reserve discussed here, providing their number is much smaller than the number of metallic bonds; appreciable distortions may be expected, however, in the local surrounding of these non-metallic bonds, in regard to both their size and shape.

It is perhaps worth noting here also that the gradient-method employed in the present theory for getting the equilibrium shapes of the atomic clusters yields frequently exotic atomic arrangements, like, for instance, the unstable atomic chain shown in Fig.7, or the two separate clusters in quasi-equilibrium positions, shown in Fig.8; the force acting between these two cluster fragments are weaker than the accuracy with which we have run the minimization-energy program. An open
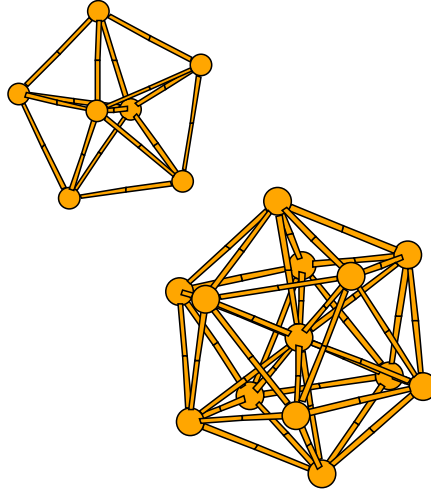
Figure 8: Two atomic fragments in quasi-equilibrium given by the gradient-method for the potential energy (11)

problem is the extension of this theory to bulk metals; for a very large number of atomic constituents there are indications of forming up central structures in such clusters, with an incipient translation symmetry, as well as fragments of symmetric polyhedra on the cluster facets.

Finally, we derive the average electronic potential in the present theory, which may serve for computing the electronic single-particle energy levels, as discussed before; since the electrons are localized mainly in-between the ionic cores where the self-consistent field potential φ given by (7) has a weak spatial variation, one may expand this potential in powers of $\mathbf{k}\boldsymbol{\rho}_i \ll 1$, where the wavevector $\mathbf{k}$ denotes the Fourier components, and $\boldsymbol{\rho}_i = \mathbf{r} - \mathbf{r}_i$; in addition, such an expansion is even more appropriate for a statistical ensemble of clusters, where the small geometric irregularities are averaged out, and the ensemble represents a highly-symmetric cluster; from (7) one may write

$$\varphi = \frac{1}{2\pi^2} \sum_{i=1}^{N} z_i^* \int d\mathbf{k} \frac{1}{k^2 + q^2} e^{i\mathbf{k}\boldsymbol{\rho}_i} \quad , \tag{21}$$

and performing the expansion up to the 4-th power in $\mathbf{k}\boldsymbol{\rho}_i$, and integrating over k up to an upper bound K, one obtains

$$\varphi = \varphi_0 - (\varphi_1 + \varphi_2 \cos^2 \theta) r^2 \quad , \tag{22}$$

where θ is the azimuthal angle of $\mathbf{r}$; this is the well-known quadrupole-deformed potential employed frequently in describing the electron energy levels in atomic clusters;[9] the coefficients $\varphi_{0,1,2}$ are given by

$$\varphi_0 = \frac{2}{3\pi} q\alpha^3 z_0 \quad , \quad \varphi_1 = \frac{1}{15\pi} q^3 \alpha^5 z_0 \quad ,$$

$$\varphi_2 = \frac{1}{2100\pi} q^5 \alpha^7 Q \quad , \tag{23}$$

for $\alpha = K/q \ll 1$, where $Q = \sum_{i=1}^{N} z_i^* r_i^2$ is the (average) quadrupole momentum (and $z_0 = \sum_{i=1}^{N} z_i^*$ is the total charge). As noted before, this potential is relevant for the statistical ensemble of cluster isomers. One can see that q, z_0 and Q are determined in the present theory for a given cluster, while $\alpha < 1$ is a parameter (for $\alpha \sim 1$ the above coefficients $\varphi_{0,1,2}$ in (23) have a different expression, as resulting from the expansion of φ); one may use the above quadrupole-deformed potential for estimating the lowest-energy spectrum of a metallic cluster, ionization potential including; the latter can also be obtained from the chemical potential of the cluster cation, by solving, for instance, the cluster cation problem within the quasi-classical description; this may serve to fixing up the value of the α-parameter, and, thereby, the lowest-energy spectrum. All this part concerning the electronic properties of the metallic clusters is, however, beyond the scope of the present paper, and it is left for a forthcoming investigation.

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