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Ground-state energy and geometric magic numbers for homo-atomic metallic clusters

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Abstract

The ground-state energy and geometric magic numbers are derived for large homo-atomic clusters consisting of heavy metallic ions, within the quasi-classical description and the linearized Thomas–Fermi theory. © 2000 Published by Elsevier Science B.V.

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Recently, there was an increasing interest in applying the Thomas–Fermi model to large metallic clusters consisting of heavy ions [1–12][1]. By employing the quasi-classical description we derive here the linearized Thomas–Fermi theory for such clusters, and present the corresponding variational treatment. Within the framework of this theoretical approach we obtain the inter-ionic potentials, and compute the ground-state energy of large metallic clusters and geometric magic numbers.

The highly-elaborate theoretical methods employed nowadays for treating the chemical bond can be conventionally classified as ab initio wavefunctions methods and, respectively, density-functionals methods (see, for instance, Refs. [15,16]). Both share a certain interplay between atomic-like orbitals and molecular-like orbitals, which can be traced back to the origins of the chemical bond theories. The quasi-classical description offers the advantageous starting point of the (quasi-) plane waves as the appropriate form for the molecular-like orbitals, and, in addition, it leads to the linearized Thomas–Fermi theory as a convenient way of getting the main contribution as the zeroth-order approximation, and to treat the quantum corrections as the next-order approximation. The theory we present here provides a clear-cut distinction between the main contributions obtained within the quasi-classical description and the quantum corrections to the metallic bond

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[1] For the Thomas–Fermi model see, for instance [13]; the Thomas–Fermi model has previously been applied to molecules by N.H. March [14]

(and the chemical bond in general); its validity resides in the large number of heavy ions, each contributing a small effective number of electrons to the metallic bond, in comparison with their atomic numbers. The present theoretical approach may also be viewed as a contribution towards bridging the gap between the ab-initio wavefunctions theories and the density-functionals theories.

It is well-known that the electronic single-particle wavefunctions of an atomic aggregate have a partial atomic character; accordingly, not all of the nominal valence electrons z participate in the chemical bond, but only a fraction z^* of effective valence electrons [17]. For heavy metallic ions, i.e. for ions with large atomic numbers $Z \gg 1$, the effective valence charge z^* is comparatively small, as a consequence of the effectiveness of the atomic screening (see, for instance, Refs. [18–22]). Under this circumstance, the electrons participating in the metallic bond of a cluster consisting of a large number $N \gg 1$ of heavy atoms may be viewed as a slightly inhomogeneous liquid of electrons [23,24] moving in a background of point-like ions; such an interacting electron liquid is suitable for a quasi-classical description.

According to the quasi-classical description the electrons in a metallic cluster move in a self-consistent potential φ, which varies slowly in space, except for the neighbourhood of the ionic cores; the equilibrium condition implies the vanishing of the (local) chemical potential, which leads to $k_F^2/2 - \varphi = 0$, where k_F is the Fermi wavevector (the atomic units are used, i.e. the Bohr radius $a_0 = \hbar^2/me^2 = 0.53$ Å for lengths and $e^2/a_0 = 27.2$ eV for energy, where m is the electron mass, $-e$ is the electron charge, and $\hbar$ denotes the Planck's constant). Since the Fermi wavevector k_F has a slow spatial variation, one may substitute $\bar{k}_F k_F$ for k_F^2, and view $\bar{k}_F$ as a variational parameter, constant in space, while transferring all the spatial variation upon the new k_F; such a linearization is valid for those spatial regions where $\bar{k}_F$ is close to k_F (and to the average value k_{Fav} of k_F, see below); this is the case for the electrons participating in the metallic bond in a slightly inhomogeneous electron liquid. Similarly, one may substitute $\bar{k}_F^2 k_F/3\pi^2$ for the electron density $n = k_F^3/3\pi^2$, and making use of $k_F = 2\varphi/\bar{k}_F$, one obtains the self-consistency equation $n = q^2\varphi/4\pi$, where the screening wavevector q is intro-

duced through $q^2 = 8\bar{k}_F/3\pi$. Then, the Poisson's equation reads

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

where z_i^* is the effective-valence charge of the i-th metallic ion located at $\mathbf{r}_i$. The solution to Eq. (1) is a superposition

$$\varphi = \sum_{i=1}^{N} (z_i^*/|\mathbf{r} - \mathbf{r}_i|) e^{-q|\mathbf{r}_i - \mathbf{r}_j|} \qquad (2)$$

of screened Coulomb potentials, as expected. The potential energy E_{pot} of the electrons in the potential φ can easily be computed now (the intervening integrals are two-centre integrals); adding the Coulomb repulsion $(1/2)\sum_{i \neq j} z_i^* z_j^*/|\mathbf{r}_i - \mathbf{r}_j|$ between the ionic cores one obtains

$$E_{pot} = -\frac{1}{4}q \left[3 \sum_{i=1}^{N} z_i^{*2} + \right.$$
$$\left. + \sum_{i \neq j=1}^{N} z_i^* z_j^* (1 - 2/q|\mathbf{r}_i - \mathbf{r}_j|) e^{-q|\mathbf{r}_i - \mathbf{r}_j|} \right];$$
$$(3)$$

it is worth noting that this potential energy corresponds to effective inter-ionic potentials

$$\Phi_{ij} = -\frac{1}{2} z_i^* z_j^* q (1 - 2/q|\mathbf{r}_i - \mathbf{r}_j|) e^{-q|\mathbf{r}_i - \mathbf{r}_j|}, \qquad (4)$$

which depend on the ions positions through the dimensionless variables $|\mathbf{x}_i - \mathbf{x}_j|$, where $\mathbf{x}_i = q\mathbf{r}_i$. These potentials have a close resemblance to Buckingham potentials [25]; they are slightly attractive at infinite, repulsive at the origin, and have a (negative) minimum value at distances of the order of $1/q$; in addition, they exhibit a slow spatial variation for small q-values, as required by the quasi-classical description of the slightly inhomogeneous electron liquid. The kinetic energy $E_{kin} = Vk_F^5/10\pi^2$ of an electron gas enclosed in a volume V is written as

$$E_{kin} = \frac{1}{10\pi^2} \bar{k}_F^4 \int d\mathbf{r} \cdot k_F$$
$$= (27\pi^2/640) q^4 \sum_{i=1}^{N} z_i^* \qquad (5)$$

for a slightly inhomogeneous electron liquid, and one can see that it does not depend on the inter-atomic distances; it follows that the equilibrium geometric forms of the metallic clusters are obtained by mini-

mizing the potential energy (3) with respect to the dimensionless variables x_i. For homo-atomic clusters this amounts to minimizing $-\sum_{i \neq j} f(|x_i - x_j|)$, where $f(x) = (1 - 2/x)e^{-x}$; this function does not depend on the effective-valence charges z_i^*, i.e. it does not depend on the nature of the chemical species. Once the geometric structures determined for certain equilibrium values X_i of the parameters x_i, the equilibrium energy is obtained as the minimum value of the quasi-classical energy functional $E_q = E_{\text{kin}} + E_{\text{pot}}$ with respect to the variational Thomas–Fermi screening wavevector q; thereafter, the inter-atomic distances are derived from $q|R_i - R_j| = |X_i - X_j|$; in addition, the vibration spectra of the clusters can be derived (as another test, for instance, for the stability of the geometric forms). One can see easily that the equilibrium screening wavevector q is small for small values of the effective valence charges z_i^*, as required by the present quasi-classical description; indeed, the quasi-classical energy functional can be written as $E_q = N(Aq^4/4 - Bq)$, where the coefficients A and B (B depending on N) are determined from (5) and, respectively, (3), and the minimum value $E_q = -3BNq/4$ is reached for $q = (B/A)^{1/3}$; for homo-atomic clusters ($z_i^* = z^*$) $A \sim z^*, B \sim z^{*2}$, and the screening wavevector $q = (B/A)^{1/3}$ goes like $q \sim z^{*1/3}$, which acquires small values for small values of z^* ($z^* \leq 1$); consequently, one can say that under such circumstances the quasi-classical description of a slightly inhomogeneous electron liquid is consistent. It is worth noting here that for large values of N the coefficient B, as determined from (3), has a weak dependence on the number N of atoms in the cluster, as required by the thermodynamic limit. The equations presented above describe the linearized Thomas–Fermi theory and its variational treatment. The linearized Thomas–Fermi theory has also been applied to atoms, where it gives satisfactory results; in particular, it reproduces the leading term $-16Z^{7/3}$ eV to the empirical binding energy of the heavy atoms, when quantum corrections are included [26,27][2]. In addition, it is worth

noting that the virial theorem is not satisfied by the present linearized Thomas–Fermi model ($E_{\text{kin}} = -E_{\text{pot}}/4$ instead of $E_{\text{kin}} = -E_{\text{pot}}/2$); consequently, both the kinetic energy and the potential energy separately are affected by errors, but the quasi-classical energy is correctly given, as a consequence of the quasi-classical description and the variational procedure[3].

Within the quasi-classical description the total energy E is obtained by adding the exchange energy E_{ex} to the quasi-classical energy E_q; for a slightly inhomogeneous electron liquid the exchange energy is given by [23,24]

$$E_{\text{ex}} = -\frac{1}{4\pi^3}\bar{k}_{\text{F}}^3 \int dr \cdot k_{\text{F}} = -\frac{9}{32}q^2 \sum_{i=1}^{N} z_i^*, \qquad (6)$$

where $q = (B/A)^{1/3}$ is the equilibrium value of the screening wavevector (as it is well-known, it corresponds to the exchange energy $E_{\text{ex}} = -(1/4\pi^3)Vk_{\text{F}}^4$ of an electron gas confined to a volume V). It is worth noting that the exchange energy given by (6) is not included in the minimization procedure of the quasi-classical energy E_q given by (3) and (5), since the exchange energy is left unchanged for local variations of the electron density within the quasi-classical description, as a consequence of its non-local (quantum) character; however, its value at equilibrium is added to the quasi-classical energy (as a purely quantum contribution); consequently, the total energy can be written[4] as $E = E_q + E_{\text{ex}} = -(3/4) \times NA(B/A)^{2/3}[(B/A)^{2/3} + 20/9\pi^2]$. Moreover, since the electronic single-particle states participat-

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[3] This may be viewed as another indication of the fact that the linearized Thomas–Fermi theory allows for a proper account of the quantum corrections; in this respect, it is distinct from the so-called quasi-classical limit of the non-linear '3/2'-Thomas–Fermi model (where $n \sim \varphi^{3/2}$); in this connection, the reader is referred to the discussion in the second part of the paper by [33] (given in Refs. [26–32]); it seems that the linearized Thomas–Fermi theory is the answer to the low density region that is the domain of chemistry, in Schwinger's terms (loc cit).

[4] Leaving aside the small contribution of the ionic interaction to the potential energy (the inter-ionic potentials Φ_{ij} in (3)) one obtains $B = 3z^{*2}/4$, $q = 0.77z^{*1/3}$ and the energy $E = -N(0.43z^{*7/3} + 0.17z^{*5/3}) = -N(11.78z^{*7/3} + 4.53z^{*5/3})$ eV for homo-atomic clusters.

ing in the metallic bond within the quasi-classical description have a vanishing energy in the atoms separated at infinite, the total energy E given above represents also the binding energy of the cluster. It is worth stressing here that this is so, in spite of the fact that the total energy E obtained here has a formal appearance of a sum of independent contributions of atoms indefinitely separated; yet, one should notice that while such independent-atom contributions (like the kinetic energy (5), or the exchange energy (6), or the ionic 'self-energy' part included in the potential energy (3)) are valid for clusters, they are irrelevant for independent atoms, since the quasi-classical description and the Thomas–Fermi theory are not valid when applied to atoms with small 'atomic numbers' z_i^* ($z_i^* \sim 1$); in this respect the inter-atomic potential Φ_{ij} given by (4) are, in fact, pseudo-potentials.

The minimization of the potential energy given by (3) for homo-atomic metallic clusters is carried out by the usual gradient-method up to $N = 80$, with an error of $10^{-3}\%$ at most (equilibrium forces less than 10^{-4} eV/Å); various geometric forms are obtained for every value of N, which are independent of z^*; their energy is computed as described above, for a physically reasonable range of the effective-valence charge $0 < z^* < 3$; the lowest energy is assigned to the ground-state, while the higher energies are associated with the isomers. It is found that for this range of z^*-values the most stable clusters are those shown in Fig. 1. They correspond to 13 magic numbers $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$ shown in Fig. 2, as obtained from the usual mass-abundance spectrum $D = \ln(I_N^2 / I_{N+1} I_{N-1}) = E(N+1) + E(N-1) - 2E(N)$, where I_N is the Boltzmann statistical weight and $E(N)$ is the ground-state energy of the cluster consisting of N atoms (beyond $N = 80$ the peaks in the mass-abundance spectrum diminish gradually, as the clusters approach the bulk behaviour); it is found that these magic numbers do not depend on z^* for $0 < z^* < 3$. Similar results have also been obtained recently by using model-parameters Morse potentials [34]. Some of the magic numbers in the sequence shown in Fig. 2 have been identified previously, both experimentally and theoretically, and sometimes they are referred to as geometric, or icosahedral, numbers (see, for instance, Refs. [35,36] and references therein, and also Ref. [37]; indeed, the centered icosahedron $N =$

13 is an outstanding structure, according to its symmetry and stability, and several intertwinned icosahedra may also be identified in other highly-symmetric structures shown in Fig. 1, as, for instance, in the remarkable body corresponding to $N = 45$; the 'perfection' of these bodies seems to reside in a 'space economy' principle, the atoms trying to pack together as tightly as possible, in multiple, closed, spatial shells.

For numerical values of the energy (and the inter-ionic distances) one needs the values of the effective valence z^*. As a first approximation, such values can be estimated from the atomic screening theory [18–22]. As noted above, the linearized Thomas–Fermi theory works well for heavy atoms, where one obtains [26–32] an electron density $n = q^2 Z e^{-qr} / 4\pi r = q^2 \varphi / 4\pi$ and a (variational) screening wavevector $q = 0.77 Z^{1/3}$; the atomic binding energy obtained within this theory is $E = -16.34 Z^{7/3}$ eV (including the quantum corrections), which is in an excellent agreement with the empirical atomic binding energy [26–32] $E \simeq -16 Z^{7/3}$ eV. The linearized Thomas–Fermi theory is valid as long as the variational Fermi wavevector $\bar{k}_F = (3\pi/8) q^2$ derived before is close to the average Fermi wavevector k_{Fav} given by

$$k_{Fav} = \frac{1}{Z} \int dr \cdot k_F n = \frac{4}{3\pi^2 Z} \int dr \cdot \varphi^2$$

$$= \frac{8Z}{3\pi q_{av}} = \frac{3\pi}{8} q_{av}^2 ; \qquad (7)$$

hence, one obtains $q_{av} = (64/9\pi^2)^{1/3} Z^{1/3} \simeq 0.9 Z^{1/3}$. The discrepancy with respect to the variational screening wavevector $q = 0.77 Z^{1/3}$ (cca 17%) originates in the abrupt variation of the self-consistent potential φ and the electron density n close to the atomic nucleus, where quantum corrections are needed; as one can see, such quantum corrections are indeed small in comparison with the main quasi-classical contribution. Similar estimations hold also for clusters, and one may say that the potential energy derived above with the variational screening wavevector q is affected by an error of cca 17%; correspondingly, the geometric forms of the clusters are affected by the same error; however, such an
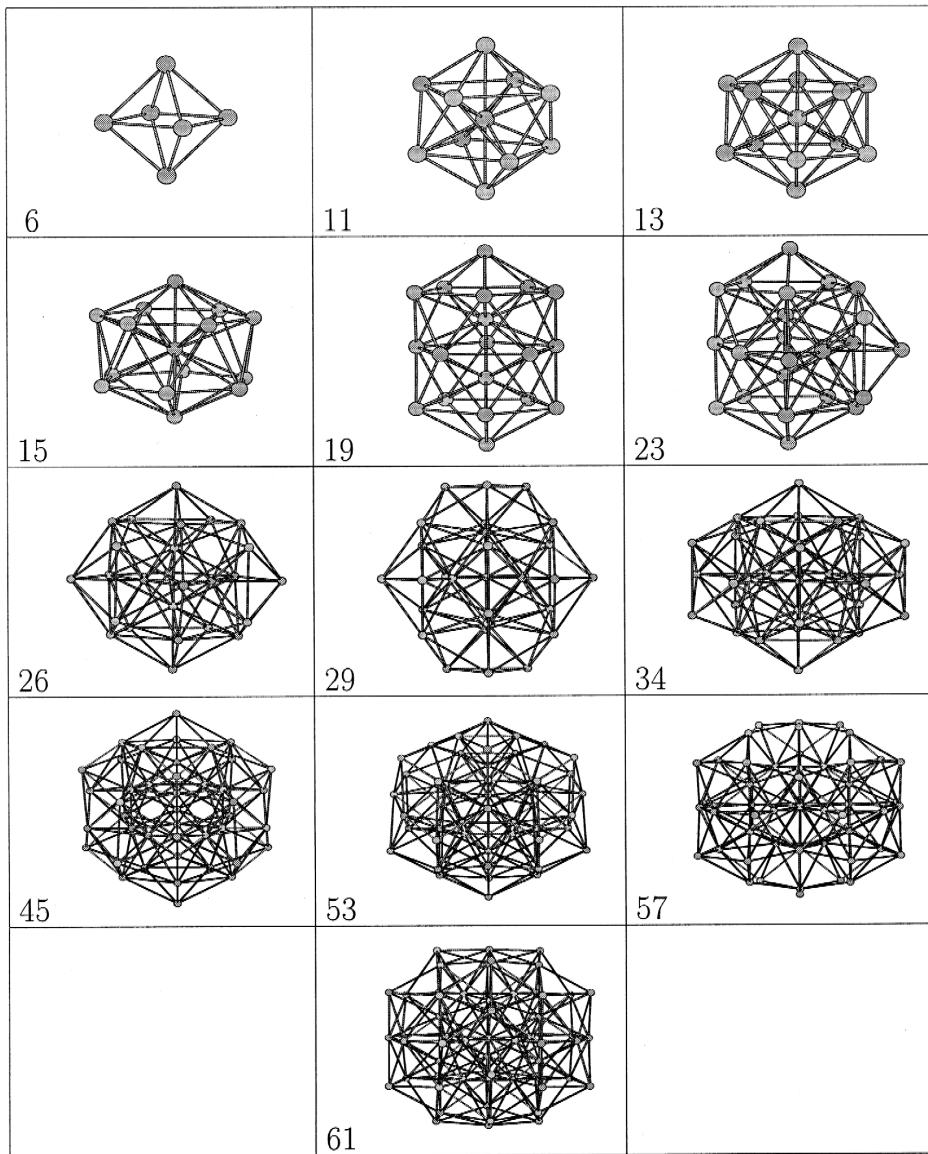
Fig. 1. Magic homo-atomic metallic clusters.

error is related to atomic arrangements on a short-scale length, and it does not affect the overall forms of the clusters; in addition, the atomic positions on such short-scale lengths may be corrected by appropriately including the quantum contributions. Part of such contributions may be taken into account in estimating the effective valence z^*, by using a mean screening wavevector $q = (0.77 + 0.9)Z^{1/3}/2 =$ $0.84Z^{1/3}$ in the atomic screening theory. Indeed, one may estimate easily the number of outer electrons N_{out} lying outside of a sphere of radius R around the atomic nucleus; making use of the electron density $n = q^2 Z e^{-qr}/4\pi r$ the number of the outer electrons is given by $N_{out} = Z(1 + qR)e^{-qR}$; the effective-valence charge may then be taken as $z^* = z(1 + qR)e^{-qR}$, where z is the nominal valence. Taking the
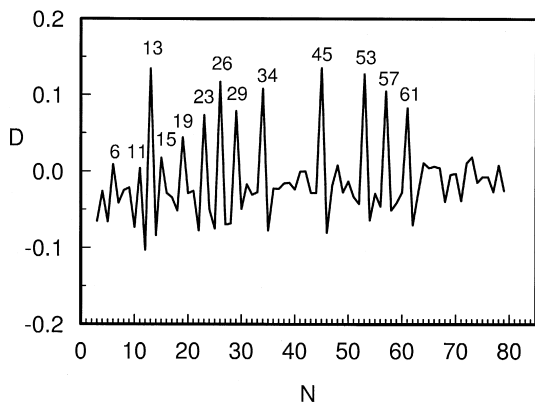
Fig. 2. Ground-state mass-abundance spectrum and geometric magic numbers.

radius $R = 1$ as for neutral atoms, and using $q = 0.84Z^{1/3}$, one obtains, for instance, an effective charge $z^* = 0.57$ for Fe (iron, $Z = 26$, $z = 2$), and the corresponding ground-state energy per atom $E(N)/N$ is plotted vs. N in Fig. 3. The energies in Fig. 3 agree satisfactorily with other calculations, as, for instance, with the density-functional calculations corresponding to $N = 13$ ($E(N)/N \simeq -5.2$ eV), as well as the inter-atomic distances, which are of the order of $2\,\text{Å}$ [38] (see also Refs. [39–41]). Similar results are obtained for other metallic clusters, with an appropriate estimation of the effective-valence charge z^*. For instance, the ground-state energy per atom for Na-clusters (sodium, $Z = 11$, $z = 1$, $z^* = 0.44$) is $E(N)/N \simeq -3$ eV, as an average, and, similarly, $E(N)/N \simeq -2$ eV for Ba-clusters (barium, $Z = 56$, $z = 2$, $z^* = 0.34$). Such numerical estimations agree qualitatively with similar numerical results obtained by means of other theoretical approaches. In this respect, it is worth mentioning the large amount of work devoted to metallic clusters, by employing both ab-initio calculations, molecular dynamics, density functionals, or jellium-like models; numerical data, where available, can be found in Refs. [42–50] and in the review papers in Refs. [35–37]. It is worth noting that the estimation given here for z^*, as based on the Thomas–Fermi atomic screening, underestimates, in general, both the energies and the inter-atomic distances (the packing is too tight); in addition, it introduces rather large errors for very heavy metallic ions (like Ba, for

instance), where the tail of the outer electrons is short; and, of course, it is not appropriate for very light ions (like lithium, Li). One may also note that such an estimation is very similar, in fact, with a particular case of Ashcroft's ionic pseudo-potential [51,52], and a further investigation in this direction may lead to better estimations for z^*.

The single-particle properties, as well as the next-order corrections to the energy are given, in principle, by solving the Schrödinger's equation for electrons in the potential φ given by (2). According to the quasi-classical description of the slightly inhomogeneous electron liquid [23,24], such corrections, though small, are of interest for single-electron properties, like ionization potentials, lowest-energy excitations, response functions, etc. It is worth noting in this respect the fractional occupancy $\alpha = z^*/z$ (on the average) of the metallic-like single-particle orbitals predicted by the quasi-classical description, as a consequence of electron interaction with the ionic cores (leading to a 'strongly-renormalized' Hartree–Fock quasi-particles) [53]. One can also check easily that the long-range part of the potential φ given by (2) leads to a quadrupole-deformed potential of a spatial harmonic oscillator, whose shell-effects have previously been discussed [54]. Such an investigation within the framework of the linearized Thomas–Fermi model is left for a forthcoming publication. We limit ourselves here to note that the potential energy (3) has also many local minima with respect to the ionic positions, which give isomers, i.e. clus-
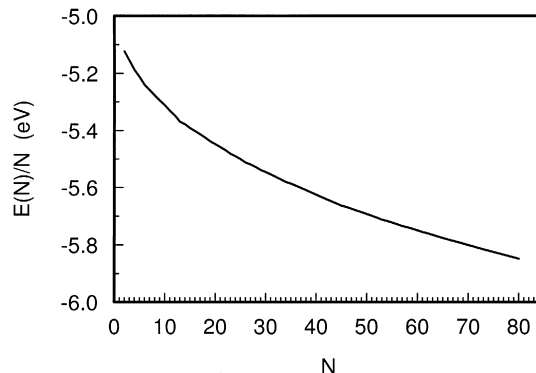

Fig. 3. Ground-state energy per atom $E(N)/N$ for Fe-clusters ($z^* = 0.57$) plotted vs. cluster size N.

ters of the same size N, but with distinct forms and higher energies; in principle, the isomers are produced experimentally, and the abundance spectra are given in this case by the free energy, instead of the ground-state energy, thus leading to statistical magic numbers, which are distinct from the geometric magic numbers derived here; averages over such statistical ensembles may correspond, in some cases, to slow-varying self-consistent potentials, as those including only the long-wavelength contributions, for instance; where such potentials apply one obtains another set of magic numbers, which may be termed electronic magic numbers, as due to the electronic-shell effects; usually, they are given, for instance, by the well-known quadrupole-deformed potential of the spatial harmonic oscillator, as remarked above.

In conclusion, one may say that geometric forms and magic numbers are derived herein for homo-atomic metallic clusters within the quasi-classical description and the linearized Thomas–Fermi theory. The results are valid for large clusters consisting of heavy atoms, and the numerical results for energies and inter-atomic distances depend on the input parameters z_i^* of the effective-valence charges. The present theory can straightforwardly be applied to hetero-atomic metallic clusters, and it may also be extended to metallic clusters containing a small number of non-metallic inclusions, like a few ionic, or even covalent, bonds, or a few number of light metallic ions. Moreover, the theory can also be extended to include spatially-extended charge distributions around the ions, allowing thereby for directional and local effects in the chemical bond.

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