Journal of Theoretical Physics

Ionization potential for 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

Single-particle properties are investigated for large homo-atomic metallic clusters consisting of heavy atoms; the investigation is carried out by means of the self-consistent potential derived within the framework of the quasi-classical description. In particular, a scheme is given for estimating the ionization potentials for such clusters.

The well-known density-functional theory[1] for large metallic clusters consisting of heavy atoms leads to a quasi-classical description and a variational treatment of the linearized Thomas-Fermi model. The metallic cohesion is realized by each i-th atom in the cluster, $i = 1, ...N$ ($N \gg 1$), participating in the metallic bond with a fraction $z_i^* = \alpha z_i$ of its nominal (chemical) valence z_i, the α-factor accounting for the atomic screening and the ionic pseudo-potential. The electrons in such metallic clusters form a slightly inhomogeneous electron liquid interacting with point-like ionic charges z_i^*; this picture is a particularly attractive model for the metallic cohesion. The electron screening derived within such a description is controlled by a screening wavevector q, which is obtained variationally from the energy functional. The quasi-classical motion of the electrons proceeds within the self-consistent potential

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

where $\mathbf{r}_i$ denote the positions of the ions; effective inter-atomic potentials are obtained within this treatment,

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

which resemble Buckingham-like potentials[2] (the distances are expressed in Bohr radii $a_H = \hbar^2/me^2 = 0.53$Å and the energies are given in atomic units $e^2/a_H = 27.2$eV, where $-e$ is the electron charge, m is the electron mass and $\hbar$ denotes the Planck's constant). These effective inter-atomic potentials lead to a potential energy

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

where the function f is given by $f(x) = (1 - 2/x)e^{-x}$; the potential energy given by (3) includes both the electron-ion attraction and the electron-electron repulsion (via screening), as well as the ion-ion Coulomb repulsion. The equilibrium shape of the cluster is obtained by minimizing the

function f with respect to the dimensionless position parameters $x_i = q\mathbf{r}_i$. The quasi-classical energy functional $E_q = E_{kin} + E_{pot}$ is obtained by adding the kinetic energy

$$E_{kin} = \frac{\pi}{5}(3/8)^3 q^6 \int d\mathbf{r} \cdot \varphi = (27\pi^2/640)q^4 \sum_{i=1}^N z_i^* \quad , \tag{4}$$

as derived from the linearized Thomas-Fermi model of the slightly inhomogeneous electron liquid, to the potential energy given above; hence, the variational parameter q is obtained by minimizing this quasi-classical energy; it may be represented as $q \sim 1/a$, where a is the average inter-ionic distance at equilibrium. According to the quasi-classical description the binding energy is given by the minimum value of the equilibrium quasi-classical energy E_q plus the exchange energy

$$E_{ex} = -\frac{1}{2\pi^3}(3\pi/8)^2 q^4 \int d\mathbf{r} \cdot \varphi = -(9/32)q^2 \sum_{i=1}^N z_i^* \quad . \tag{5}$$

The cohesion energies of large homo-atomic metallic clusters of heavy atoms, as well as equilibrium shapes, vibration spectra and geometric magic numbers, have been derived by means of the quasi-classical description of the density-functional theory;[3] the numerical results are in good agreement with those obtained by similar calculations, as well as to experimental data, where available.[4] In particular, the geometric magic numbers obtained for the ground-state of homo-atomic clusters are universal, in the sense that they do not depend on the chemical species. Herein, the single-particle properties of the electrons in metallic clusters are investigated, within the framework of the quasi-classical description. Beforehand, an estimation of the effective-valence charges z_i^* is presented, as based on the theory of the atomic screening.[5]

A similar variational approach can be employed for the linearized Thomas-Fermi model for heavy atoms with atomic numbers $Z \gg 1$.[6] The variational screening wavevector is given by $q = 0.77Z^{1/3}$, while the average of the Fermi wavevector with the self-consistent electron density $n(r) = (q^2/4\pi)Ze^{-qr}/r$ leads to $q = (64Z/9\pi^2)^{1/3} = 0.9Z^{1/3}$; one may adopt a mean value $q = 0.84Z^{1/3}$. On the other hand, the number N_{out} of "outer" electrons, $i.e.$ the electrons lying outside of a sphere of radius R centered on the atomic nucleus, is given by

$$\alpha = N_{out}/Z = 4\pi \int_R^\infty dr \cdot r^2 n(r) = (1 + qR)e^{-qR} \quad ; \tag{6}$$

according to the theory of the atomic screening this is the factor by which the nominal valence z has to be reduced in order to get the effective number $z^* = \alpha z$ of electrons participating in the metallic bond. For practical purposes one may take, together with the mean value $q = 0.84Z^{1/3}$ of the screening wavevector given above, the radius $R = 1$ ($i.e.$ one Bohr radius a_H), as suggested for the "atomic radius" by the quasi-classical theory of the Thomas-Fermi atomic model. Making use of these values one obtains, for instance, $z_{Na}^* = 0.44$ for sodium (Na, $Z = 11, z = 1$), $z_K^* = 0.34$ for potassium (K, $Z = 19, z = 1$), $z_{Fe}^* = 0.57$ for iron (Fe, $Z = 26, z = 2$), $z_{Ag}^* = 0.19$ for silver (Ag, $Z = 47, z = 1$), $z_{Ba}^* = 0.34$ for barium (Ba, $Z = 56, z = 2$), etc; as expected from a quasi-classical treatment the results are not reliable for small values of the atomic number Z (like sodium, for instance), and the formula used above in (6) for the atomic-screening factor is affected by large errors for very large values of Z (like barium); the estimation of the effective-valence charge z^* amounts in fact to determining realistic ionic pseudo-potentials, and, in this respect, the approximate atomic-screening formula (6) resembles a well-known psudo-potential,[7] which is known to give satisfactory results. According to the quasi-classical description the effective-valence charge z^* is the content of plane waves in the atomic-like orbitals corresponding to the cluster wavefunction, such that, for each atom, z^* electrons move quasi-freely in the cluster and

participate in the metallic bond, while $z - z^* = (1-\alpha)z$ electrons remain in the individual atomic-like orbitals; $z^*/z = \alpha$ may therefore be viewed as the effective, or "renormalized", occupancy of the single-particle electron orbitals in such clusters. However, the determination of this effective occupancy α remain the main problem of the present approach, and, in most cases, it can only be taken as a model parameter.

The single-particle properties are obtained by solving the Schrodinger's equation for electrons moving in the self-consistent potential φ given by (1); these single-particle properties are the next-order corrections to the starting quasi-classical picture. Indeed, according to the quasi-classical description only the slowly-varying part of the potential φ is relevant, so that one may expand the Fourier representation

$$\varphi = \frac{1}{2\pi^2} \sum_{i=1}^{N} \int d\mathbf{k} \frac{z_i^*}{k^2 + q^2} e^{i\mathbf{k}\boldsymbol{\rho}_i} \tag{7}$$

of the self-consistent potential given by (1) in powers of $\mathbf{k}\boldsymbol{\rho}_i \ll 1$, and perform the $\mathbf{k}$-integration up to a cutoff K; one obtains

$$\varphi(r) = \beta_0 \sum_i z_i^* - \beta_1 \sum_i z_i^* \rho_i^2 - \beta_2 \sum_i z_i^* \rho_i^4 ..., \tag{8}$$

where the coefficients $\beta_{0,1,2}$ are given by

$$\beta_0 = \frac{2}{\pi} q(\beta - \arctan\beta) \quad ,$$

$$\beta_1 = \frac{1}{3\pi} q^3(\beta^3/3 - \beta + \arctan\beta) \quad , \tag{9}$$

$$\beta_2 = -\frac{1}{35\pi} q^5(\beta^5/5 - \beta^3/3 + \beta - \arctan\beta] \quad ,$$

and $\beta = K/q$. Up to the quadrupole contributions the potential given by (8) can be rewritten as

$$\varphi(r) = \varphi_0 - \varphi_x x^2 - \varphi_y y^2 - \varphi_y z^2 \quad , \tag{10}$$

the coefficients being given by $\varphi_0 = \beta_0 z_0 - \beta_1 Q, \varphi_a = \beta_1 z_0 + 2\beta_2(Q + 2Q_a), a = x, y, z$, where $z_0 = \sum_{i=1}^{N} z_i^*$ is the total charge of the cluster, $Q = \sum_{i=1}^{N} z_i^* r_i^2$ denotes the quadrupole moment, and Q_a are the components of the quadrupole moment $(Q_x = \sum_{i=1}^{N} z_i^* x_i^2, Q_x = \sum_{i=1}^{N} z_i^* y_i^2, Q_x = \sum_{i=1}^{N} z_i^* z_i^2)$. The potential given by (10) is the quadrupole-deformed potential employed frequently for describing the single-particle properties of the metallic clusters;[8] one can see that in the long-wavelength limit $\beta \to 0$ the above potential has indeed a slow spatial variation, and consequently it brings only small corrections to the plane-waves picture of the quasi-classical description.

Making use of a potential φ as the one given by (10) the single-particle hamiltonian reads

$$H = -\frac{1}{2}\Delta + \frac{1}{2}\omega_0^2[(\xi_x x)^2 + (\xi_y y)^2 + (\xi_z z)^2] - \varphi_0 \quad , \tag{11}$$

where $\omega_0^2 = 2\beta_1 z_0 + 4\beta_2 Q$ and

$$\xi_a^2 = 1 + \frac{4\beta_2 Q_a}{\beta_1 z_0 + 2\beta_2 Q} \quad , \quad a = x, y, z \; ; \tag{12}$$

it corresponds to a quadrupole-deformed harmonic-oscillator hamiltonian of frequency ω_0 and deformation parameters ξ_a. The eigenvalues of the hamiltonian (11) are given by

$$E(n_x, n_y, n_z) = \omega_0[(n_x + \frac{1}{2})\xi_x + (n_y + \frac{1}{2})\xi_y + (n_y + \frac{1}{2})\xi_z] - \varphi_0 \quad , \tag{13}$$

where n_x, n_y, n_z denote harmonic-oscillator quantum numbers; the corresponding single-particle wavefunctions can be written as

$$\psi_{n_x,n_y,n_z}(x, y, z) = N_{n_x,n_y,n_z} \cdot \exp\{-\tfrac{1}{2}\omega_0[\xi_x x^2 + \xi_y y^2 + \xi_z z^2]\}\cdot$$
$$\cdot H_{n_x}((\xi_x\omega_0)^{1/2}x) \cdot H_{n_y}((\xi_y\omega_0)^{1/2}y) \cdot H_{n_z}((\xi_z\omega_0)^{1/2}z) \quad , \tag{14}$$

were the normalization factor N_{n_x,n_y,n_z} is given by

$$N_{n_x,n_y,n_z} = (\pi\sqrt{\pi}2^{n_x+n_y+n_z}n_x!n_y!n_z!)^{-1/2} \quad . \tag{15}$$

Thereby one obtains the single-particle picture of the Hartree-Fock quasi-particles derived within the quasi-classical description; each energy level is occupied by α electrons, the remaining $1 - \alpha$ being localized on the original atomic-like orbitals; the quasi-particles obtained in this way look like strongly "renormalized" quasi-particles of the slightly inhomogeneous electron liquid, with an effective occupancy α; the "renormalization" factor α is estimated by using the atomic screening theory as indicated in (6). Denoting by E_0 the highest-occupied level given by (13) one may write down immediately the cluster ionization potential as

$$E_{ion} = -\alpha E_0 + (1 - \alpha)E_a \quad , \tag{16}$$

where E_a is the atomic ionization potential.

The single-particle picture described above depends on the cutoff parameter $\beta = K/q$. In order to illustrate the above calculations with numerical estimations one may make further simplifications of the quadrupole-deformed potential φ given by (10). First, one may note that the cutoff parameter β can be written as

$$\beta \sim \frac{a}{R} \simeq \frac{1}{N^{1/3}} \quad , \tag{17}$$

where a is the average inter-atomic distance, R denotes the cluster radius, and N is the number of atoms in the cluster (cluster's size); in the limit of validity of the quasi-classical description $N \gg 1$ one can see that $\beta \ll 1$, and, consequently, the $\beta_{0,1,2}$-parameters given by (9) can be written as

$$\beta_0 \simeq \frac{2}{3\pi}q\beta^3 \quad , \quad \beta_1 \simeq \frac{1}{15\pi}q^3\beta^5 \quad , \quad \beta_2 \simeq -\frac{1}{245\pi}q^5\beta^7 \quad ; \tag{18}$$

so that $\beta_2 \ll \beta_1 \ll \beta_0$; limiting oneself to the leading non-trivial contributions one obtains $\varphi_0 \simeq \beta_0 z_0$ and $\varphi_x = \varphi_y = \varphi_z \simeq \beta_1 z_0$, so that the self-consistent potential φ becomes the isotropic harmonic-oscillator potential, $\varphi = \varphi_0 - (1/2)\omega_0^2 r^2$, where the frequency ω_0 is given by $\omega_0^2 = 2\varphi_1 \simeq 2\beta_1 z_0$; therefore, the energy levels can be written as $E_n = \omega_0(n+3/2) - \varphi_0$, and the corresponding degeneracy is $g_n = (n+1)(n+2)$ (spin included). Under these circumstances the highest-occupied energy level E_0 reads $E_0 = (2q^3\beta^5 z_0/15\pi)^{1/2}(n_0+3/2) - 2q\beta^3 z_0/3\pi$, where n_0 is the corresponding quantum number; since $n_0 \sim N^{1/3}$ for large N, one can see immediately that E_0 is vanishing in this limit, in comparison with contributions of the order of φ_0. Consequently, one may neglect E_0 in the ionization potential (16), thus obtaining

$$E_{ion} \simeq (1 - \alpha)E_a \quad , \tag{19}$$

i.e. the atomic ionization potential properly "renormalized" by the metallic bond. For a uniform distribution of atoms in the cluster one obtains straightforwardly from (7) $\varphi \simeq 4\pi z^*/a^3 q^2$, which is a constant potential, and represents the main contribution within the quasi-classical description. In other words, the quantum corrections for large metallic clusters are very small, as expected. For a spherical cluster of radius R with a uniform distribution of atoms one obtains directly from (1)

$$\varphi = \frac{4\pi z^*}{a^3 q^2}(1 - Fe^{-qR}) \quad , \tag{20}$$

where

$$F = (1 + qR)\frac{\sinh qr}{qr}, \quad r < R \quad ; \tag{21}$$

for $r > R$ the potential is given by $\varphi = (4\pi z^*/a^3 q^2)(\cosh qr - \sinh qr/qr)e^{-qr}$; hence, one can obtian the electron density $n(r) = (q^2/4\pi)\varphi(r)$. One can see again that the surface (or finite-size) effects are indeed very small for large clusters. Under the same assumptions one can also compute the potential energy given by (3), surface correction included; the result of such a computation is

$$E_{pot} = -\frac{3}{4}qNz^{*2}\left[1 - \frac{2\pi}{(aq)^3}\frac{1}{qR}\right] \quad , \tag{22}$$

whence the surface tension $\sigma = \pi z^{*2}/2a^6 q^3$.

The main contribution to the ionization potential of the metallic clusters as given by (19) does not depend on the size, or the shape, of the cluster, but it is given solely by the chemical nature of the atomic constituents of the cluster and the "renormalization" factor α. Making use of (19) and the factor α estimated before for various metallic ions, one obtains $E_{ion}(\text{Na}) = 2.88\text{eV}$ for sodium ($\alpha = 0.44, E_a(\text{Na}) = 5.14\text{eV}$),[9] $E_{ion}(\text{K}) = 2.86\text{eV}$ for potassium ($\alpha = 0.34, E_a(\text{K}) = 4.34\text{eV}$), $E_{ion}(\text{Fe}) = 5.67\text{eV}$ for iron ($\alpha = 0.28, E_a(\text{Fe}) = 7.87\text{eV}$), $E_{ion}(\text{Ag}) = 6.13\text{eV}$ for silver ($\alpha = 0.19, E_a(\text{Ag}) = 7.57\text{eV}$), $E_{ion}(\text{Ba}) = 4.32\text{eV}$ for barium ($\alpha = 0.17, E_a(\text{Ba}) = 5.21\text{eV}$); these values compare well with the experimental values[4] 3.5eV (Na), 2.8eV (K), 5.5eV (Ag).

References

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136** B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140** A1113 (1965).

[2] R. A. Buckingham, Trans. Faraday Soc. **54** 453 (1958).

[3] L. C. Cune and M. Apostol, J. Theor. Phys. **49** 1 (2000); *ibid* **50** 1 (2000).

[4] For a review on atomic clusters properties see, for instance, W. A. de Heer, Revs. Mod. Phys. **65** 611 (1993), and M. Brack, *ibid* **65** 677 (1993); for geometric magic numbers derived with model-parameters inter-atomic potentials see, for example, J. P. K. Doye and D. J. Wales, J. Chem. Soc., Faraday Trans., **93** 4233 (1997).

[5] See, for instance, J. C. Slater, *Quantum Theory of Atomic Structure*, McGraw-Hill, NY (1960).

[6] L. C. Cune and M. Apostol, J. Theor. Phys. **45** 1 (1999); the Thomas-Fermi model has previously been applied to molecules by N. H. March, Proc. Cambr. Phil. Soc. **48** 665 (1952), and more recently to the fullerene molecule by D. Clougherty and X. Zhu, Phys. Rev. **A56** 632 (1997).

[7] N. W. Ashcroft, Phys. Lett. **23** 48 (1966); N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Holt, Rinehart and Winston, NY (1976).

[8] K. Clemenger Phys. Rev. **B32** 1359 (1985).

[9] The atomic ionization potentials are taken from J. Emsley, *The Elements*, Clarendon, Oxford (1991).