Semiclassical description of electronic supershells in simple metal clusters

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Abstract

A semiclassical approach for calculating shell effects, that has been used in atomic and plasma physics, is applied to describe electronic supershells in metal clusters. Using the spherical jellium model we give the analytical expression for the oscillating part of the binding energy of electrons as an explicit sum of contributions from supershells with quantum numbers $2n_r + l$, $3n_r + l$, $4n_r + l$, ... This expression is written in terms of the classical characteristics of the motion of an electron with the Fermi energy in a self-consistent potential. The conditions under which a new supershell appears and the relative contribution of this shell are studied as a function of the cluster size and form of the potential. Specific calculations are performed for a square well.

1. The electronic structure of atomic clusters has been intensively studied experimentally and theoretically in the last two decades (see, for example, reviews in Refs. [1] and [2]). One general feature of the experimental mass-abundance spectra of $N$-atom clusters is the existence of magic numbers: Clusters with these numbers of atoms are produced more abundantly. As $N$ enlarges, the amplitude of these variations lessens, then in still larger clusters increases once again, and so on, i.e., oscillations with beats occur.

The theoretical reproduction of the beating patterns one can see, for example, in the self-consistent calculations of sodium clusters in Ref. [3], where the spherical jellium model in local density approximation was used. There are two kinds of periodicity in the density of states and in the oscillating part $\delta E_{sh}$ of the binding energy as a function of a cluster radius $R \sim N_e^{1/3}$ ($N_e$ is a number of valence electrons in cluster): the primary shell periodic structure and beat mode with a higher-order period. The similar results were performed in Ref. [4] using the Woods-Saxon potential and in calculations for various metals in Ref. [5] using nearly self-consistent potentials.

For small clusters the interpretation of the numerical results is obvious: the extremum energy cusps occur at $l_{max}$-shell closing and represent the magic
numbers \((l_{\text{max}}\) is a maximum orbital number \(l\) in the cluster). However this law breaks down for \(N_e > 100\).

The theory, explaining quantitatively the beating pattern of the level density for spherical cavity by a superposition of the contributions from closed classical trajectories of electrons, has been developed in the fundamental work of Balian and Bloch \[6\]. The detailed numerical calculations in Ref. \[5\] using more complex spherical cluster potentials reproduce the similar oscillations, one-electron levels \(\varepsilon(n_r, l)\) of the higher angular momentum states bunching in supershells: \(\varepsilon(n_r, l) \simeq \varepsilon(n_r + 1, l - K)\) with pseudoquantum numbers \(K n_r + l\). Here \(n_r\) is a radial quantum number, \(K = 2, 3, 4, \ldots\). The integer number \(K\) under classical treatment (see, for example in Ref.\[7\]) is equal to a ratio of the frequencies in the radial and angular motion of the corresponding closed orbit. At \(K = 2\) pseudoquantum number is the same as a principal quantum number and characterizes the pendulating orbit going through the origin, \(K = 3\) and \(K = 4\) corresponds to the triangular and square orbits, respectively.

One can suppose from here that a periodic-orbit-expansion (or supershell-expansion), obtained for a spherical cavity, is a particular case of the more general expansion for spherical cluster potentials. This conclusion is supported in the recent paper \[8\] where such a generalization was carried out using Woods-Saxon potential by expanding on a parameter \(a/R\) (\(a\) is a surface width) around the known results for a spherical potential well. It is of interest to investigate analytically the origin of supershells and the mechanisms leading to their appearance for a potential of arbitrary form.

In the present paper it is shown that this problem can be solved by a semiclassical method for distinguishing shell effects, previously applied successfully in atomic \[9\],[10], and plasma \[11\],[12] physics on the basis of the Thomas-Fermi (TF) model. Although the TF model and its conventional variants ETF with quantum and exchange corrections (for application to clusters, see, for example, Refs. \[13\] and \[14\]) give only the average dependences of all quantities on the number of particles, a refinement of this model makes it possible to account for the shell structure of the electronic spectrum. This refinement is based on the use of the Bohr-Zommerfeld quantization conditions and on the possibility of performing the sum over quantum numbers analytically, provided that the semiclassity parameter, which for clusters is proportional to \(N_e^{-1/3}\), is small.

2. We furthermore use the expression derived in our future extended publication for the correction to the binding energy of electrons (the atomic units are used):

\[
\delta E = \int_{-\infty}^{\mu} d\mu' \int d\mathbf{r} \delta n(\mathbf{r}, \mu')
\]

(1)

Here \(\delta n(\mathbf{r})\) is the correction to the electronic density, which because of other effects goes beyond the initial model approach (for example, TF or ETF model), \(\mu\) is the chemical potential in the initial model, the correction \(\delta n(\mathbf{r})\) is assumed to be small and is calculated using the initial self-consistent potential.

We are interested in the contribution of the shell correction to the electronic
density of states $\delta n_{sh}(r, \mu)$ or to the number of states:

$$\delta N_{sh}(\mu) = \int d\mathbf{r} \delta n_{sh}(\mathbf{r}, \mu) = N(\mu) - N_{TF}(\mu), \quad (2)$$

where for a cluster with the closing "$l$"-shells

$$N(\mu) = 2 \sum_{n_r,l} (2l + 1) \delta(\mu - \varepsilon_{n_r,l}), \quad (3)$$

and in the semiclassical approach the energy levels $\varepsilon_{n_r,l}$ are determined from the quantization condition

$$S_{cl} = \int d\mathbf{p}_{cl}(r) = \pi \left( n_r + \frac{1}{2} \right) \quad (4)$$

Here $S_{cl} \equiv S_{\varepsilon \lambda}$ and $p_{cl}(r) = \sqrt{2(\varepsilon - U(r)) - (l + 1/2)^2/r^2} \equiv \sqrt{p^2_{cl}(r) - \lambda^2/r^2} \equiv p_{\varepsilon \lambda}$ are, respectively, the classical radial action and momentum of an electron with energy $\varepsilon$ and orbital angular momentum $l$. Simple calculations using the Poisson formula to replace the sums over quantum numbers $n_r$ and $l$ by integrals make it possible to rewrite expression (3) as

$$N(\mu) = \frac{2}{\pi} \sum_{k,s=-\infty}^{\infty} \frac{(-1)^{k+s}}{k} \int_0^\infty d\lambda \lambda \sin(2\pi k \nu_{\varepsilon \lambda}) \cos(2\pi s \lambda) \quad (5)$$

Here $\nu_{\varepsilon \lambda} = S_{\varepsilon \lambda}/\pi$, and $\lambda_{\varepsilon}$ determines the border of the phase area of the classically allowed motion of an electron with an energy $\varepsilon$: $\nu_{\varepsilon \lambda} = 0$. In Eq.(5) the term with $k = s = 0$ gives the TF result $N_{TF}(\mu)$ and according to Eq.(2) the sum (5) without this term is equal to the desired quantity $\delta N_{sh}(\mu)$.

Let’s note now, that the supposed approach is agreed with a general, known from the nuclear physics, concept of separating the total energy of finite sistem as a function of the system size into a smooth part and a fluctuating correction. But here for calculating the last we base the simple expression (1), using initial smooth self-consistent potential or its Woods-Saxon and another fitting.

3. The integral limits and points $\bar{\lambda}$ of stationary phase make the main contribution in the integral over $\lambda$ in Eq.(5). These points are determined from the relation:

$$\left. \frac{\partial \nu_{\varepsilon \lambda}}{\partial \lambda} \right|_{\bar{\lambda}} = -\frac{s}{k}, \quad 0 \leq \lambda \leq \lambda_{\mu} \quad (6)$$

A function $\nu_{\varepsilon \lambda}(\lambda)$ decreases monotonically and for all potentials $U(r)$ that are finite at the origin the slope of the corresponding curve at $\lambda = 0$ is the same

$$\left. \frac{\partial \nu_{\varepsilon \lambda}}{\partial \lambda} \right|_0 = -\frac{1}{2}. \quad (6a)$$

The value of the derivative at $\lambda = \lambda_{\mu}$

$$\left. \frac{\partial \nu_{\varepsilon \lambda}}{\partial \lambda} \right|_{\lambda_{\mu}} \equiv -\nu'_{\mu} \quad (6b)$$

Here $\nu_{\varepsilon \lambda} = S_{\varepsilon \lambda}/\pi$, and $\lambda_{\varepsilon}$ determines the border of the phase area of the classically allowed motion of an electron with an energy $\varepsilon$: $\nu_{\varepsilon \lambda} = 0$. In Eq.(5) the term with $k = s = 0$ gives the TF result $N_{TF}(\mu)$ and according to Eq.(2) the sum (5) without this term is equal to the desired quantity $\delta N_{sh}(\mu)$.

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depends strongly on the form of the potential. For an oscillator \( \nu_\mu' = 1/2 \), for a square well \( \nu_\mu' = 0 \), and for the Woods-Saxon potential the value of \( \nu_\mu' \) varies with increasing \( N \), vanishing in the limit of a very large number of atoms.

On this basis it follows that the relation (6) distinguishes in the sum over \( k \) the leading terms

\[
k = (2 + j)s, \quad \left. \frac{\partial \nu_\mu \lambda}{\partial \lambda} \right|_{\tilde{\lambda}_j} = -\frac{1}{2 + j},
\]

\[
j = 0, 1, \ldots j_{\text{max}}, \quad j_{\text{max}} = \left[ \frac{1}{\nu_\mu'} - 2 \right]
\]

The terms \( k = 2s(j = 0) \) must be studied separately, since in this case the point of stationary phase \( \tilde{\lambda} = 0 \) is also the lower limit of integration. As a result we obtain

\[
\delta N_{sh} = \sum_{s=1}^{\infty} (-1)^s \left( \frac{\cos(2\pi s^2\nu_\mu 0)}{\delta_\mu(0)} - \frac{\lambda_\mu \cos(2\pi s\lambda_\mu)}{0.5 - \nu_\mu'} \right)
\]

\[
- \sum_{j=1}^{j_{\text{max}}} 4\sqrt{s} \cdot j \cdot (-1)^j \cdot s \cos \left[ 2\pi s \left( (2 + j)\nu_\mu \tilde{\lambda}_j + \tilde{\lambda}_j \right) - \frac{\pi}{4} \right]
\]

(8)

Here

\[
\delta_l^{(j)} \equiv \left. \frac{\partial^2 \nu_\mu \lambda}{\partial \lambda^2} \right|_{\tilde{\lambda}_j}.
\]

Substituting expression (8) into Eq.(1) and integrating by parts to separate the terms which are of leading order in the semiclassicity parameter give a semiclassical formula for the shell correction to the binding energy of electrons in a cluster

\[
\delta E_{sh} = \sum_{s=1}^{\infty} \left( \frac{-1)^s}{(\pi s)^3} \left( \frac{\sin(2\pi s^2\nu_\mu 0)}{\delta_\mu(0)} - \frac{\lambda_\mu \sin(2\pi s\lambda_\mu)}{(0.5 - \nu_\mu')(\partial \nu_\mu / \partial \mu)} \right) - \sum_{j=1}^{j_{\text{max}}} 4\sqrt{s} \cdot j \cdot (-1)^j \cdot s \sin \left[ 2\pi s \left( (2 + j)\nu_\mu \tilde{\lambda}_j + \tilde{\lambda}_j \right) - \frac{\pi}{4} \right] \right) \frac{1}{(2 + j)^{5/2}}
\]

(9)

as an sum of contributions from supershells with quantum numbers \( n_j = Kn_\nu + l, \quad K = 2 + j, \) the quantization on the Fermi level being substantial. In Eqs.(8) and (9) the symbol \( j \) numerates a kind of the electronic orbit: \( j = 0 \) corresponds to the linear pendulating orbit, the terms \( j \geq 1 \) \((K \geq 3)\) are connected with the planar regular polygons, \( K \) being the number of their vertices. The integer value \( s \) is equal to a number of periods that the electronic trajectory \((j, s)\)
includes, so the sum over $s$ is the trajectory length-expansion for a $j$-orbit (compare with the orbits $(\lambda, \nu)$ in Ref. [5]).

4. The proposed simple method makes it possible for any spherical potential to determine the period and amplitude of oscillations associated with each supershell and to estimate their relative role in beating occurrence. The results of such an analysis for a square well potential:

$$ U(r) = \begin{cases} -2\varepsilon_F, & r \leq R \\ 0, & r > R \end{cases}, \quad R = r_s N_e^{1/3}, \quad \varepsilon_F = \frac{1}{2r_s^2} \left( \frac{9\pi}{4} \right)^{2/3}, \quad \mu = -\varepsilon_F $$

are displayed in Fig.1. Let’s note that even though we start with the expression (3) for a cluster with the closing “$T$”-shells our results for $N_e > 100$ check well with the results of the complete calculations in Ref. [5]. Fig.1 shows, that the first period ($N_e^{1/3} < 7$) of the beats is determined by terms with $j = 0, 1, 2$, the term with $j = 0$ contributing little. The account for term with $j = 3$ ($K = 5$) is needed to describe well the second period ($N_e^{1/3} \leq 13$). Adding a term with $j = 4$ ($K = 6$) is sufficient to describe the behavior of $\delta E_{sh}$ in the entire range under study. This means that the actual value $j_{\text{max}}$ is less that determined from Eq.(7) and corresponds to the filled states, for which

$$ \nu_\mu \lambda_j \geq \frac{1}{2}. $$

5. For spherical potential we give the analytical expression for the oscillating part of the binding energy of electrons as an explicit sum of contributions from the leading periodic orbits (supershells). We show that a number of the leading orbits in the expansion depends strongly on the form of the potential and is determined by the value of derivative (6b)(see Eq.(7)). The more soft potentials will be dealt in detail in our extended publication where among other things small clusters and finite temperatures will be analyzed.

![Figure 1](image-url)  

Figure 1: a) – Shell energy correction $\delta E_{sh}$ as a function of $N_e^{1/3}$. The unit of energy is the Fermi energy $\varepsilon_F$.  

b-f) – Comparasion of a truncated supershell-expansions.
References

[1] W. A. de Heer, Rev.Mod.Phys.65, 612 (1993)
[2] M. Brack, Rev.Mod.Phys.65, 677 (1993)
[3] O. Genzken and M. Brack, Phys.Rev.Lett 76, 3286 (1991)
[4] H. Nishioka, K. Hansen and B. R. Mottelson, Phys.Rev. B42, 9377 (1990)
[5] K. Clemenger, Phys.Rev. B44, 12991 (1991)
[6] R. Balian and C. Bloch, Ann.Phys. 69, 76 (1971)
[7] S. Bjørnholm, in "Nuclear Physics Concepts in Atomic Cluster Physics" (Springer, 1992), pp.26-38
[8] E. Koch, Phys.Rev. B58, 2329 (1998)[cond-mat/9803309]
[9] D. A. Kirzhnits, Yu. E. Lozovik and G. V. Shpatakovskaya, Usp. Fiz. Nauk 111, 3 (1975) [Sov. Phys. Usp. 18, 649 (1976)]
[10] B. G. Englert, "Semiclassical Theory of Atoms". Lecture Notes in Physics, 300 (Springer, 1988)
[11] G. V. Shpatakovskaya, Teplofiz. Vysok. Temp. 23, 42 (1985) [Sov. Phys. High. Temp. 23, 36 (1985)]
[12] E. A. Kuzmenkov and G. V. Shpatakovskaya, Int. J. Thermophys., 13, 315 (1992)
[13] V. Kresin, Phys.Rev. B38, 3741 (1988)
[14] M. Membrado and A. F. Pacheco, Phys.Rev. B41, 5643 (1990)
[15] V. M. Strutinsky, Nucl.Phys. A122, 1 (1968)
[16] C. Yannouleas and Uzi Landman, Phys.Rev. B48, 8376 (1993)
[17] D. A. Kirzhnits and G. V. Shpatakovskaya, Zh.Eksp.Teor.Fiz. 62, 2082 (1972) [Sov.Phys.- JETP, 35, 1088 (1972)]