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NANOELECTRONICS

Self-Capacitance of Nanosized Objects

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Abstract—A method to determine the effective self-capacitance of atomic and molecular objects is proposed. Experimental data and the results of quantum-mechanical computations are used to calculate the self-capacitance of atoms and various molecules. It is demonstrated that the self-capacitance is predominantly determined by the topology of the nanoobject rather than its chemical composition. The notion of the effective self-capacitance makes it possible to establish a relation of the chemical parameters of atoms and molecules and the electric parameters of molecular electronic devices.

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INTRODUCTION

The combinations of classical electronic devices and elements of molecular nanoelectronics can be used for the construction of industrial nanosized electronic units [1, 2]. The most difficult theoretical problem in the analysis of the hybrid electronic devices is related to the simultaneous application of several theoretical approaches that are characterized by physical parameters of different nature. The classical electronic systems are described with the aid of such macroscopic parameters as capacitance, inductance, resistance, and electric current. The quantum description of nanosystems employs microscopic parameters (interatomic distance, sets of allowed quantum states, transparency of tunneling junctions, tunneling matrix elements, etc.). To reach the agreement of the parameters, one can move from microscopic to macroscopic parameters or in the opposite direction. Such approaches correspond to two experimental methods for the creation of hybrid electronic nanodevices that involve the “upward” and “downward” procedures, respectively.

The ab initio calculations based on quantum mechanics, quantum chemistry, and quantum field theory provide the most complete and accurate analysis of the properties of real devices. However, the practical application of the corresponding results for the description of real devices is impeded by the analytical and computational complexity. Such methods are appropriate for the study of several basic (relatively simple) nanoelectronic devices and cannot be used for the characterization of nanoelectronic devices that consist of nanosized elements.

An alternative approach involves the application of macroscopic physical parameters in the analysis of microscopic objects (downward approach). In this case, the classical theory of electronic devices is generalized on quantum objects using additional effective analogs of the classical parameters. The purpose of this work is to demonstrate the applicability of such an approach in the analysis of capacitance using examples of the basic elements of hybrid electronic devices. The main advantage of the method lies in the application of the concepts of the modern circuit technology (see, for example, [3]). The difficulties are related to the absence of the commonly accepted definitions of capacitance and inductance for molecular nanoelements,[1] and the absence of rules for the application of the effective parameters of nanoelements in the circuit technology. The effective parameters do not allow the analysis of fine quantum effects in the ultrasmall electronic units.

In this work, we make an attempt at defining the effective self-capacitance of a single microscopic object (atom, molecule, nanoparticle, quantum dot, etc.) that is weakly chemically bound to electron donors and acceptors. In the analysis of the effective self-capacitance of a single molecule, we employ the notion of capacitance and the rules of its application in the classical electrostatics and electronics.

On the one hand, the notion of the self-capacitance is related to the notion of electric field and its potential energy. The self-capacitance of a perfect insulated conductor C is normally defined as the coefficient of proportionality between charge q and potential φ relative to an infinitely distant point [5].

On the other hand, the same self-capacitance can be defined as the coefficient of proportionality between the squared charge and the electrostatic energy:

$$q^2 = UC. \tag{1}$$

In the approximation $|\mu| \gg q^2/C$, the total energy of an insulated conductor with charge q is given by

$$E(q) = E_0 + \mu q/e + q^2/C, \tag{2}$$

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[1] The notion of resistance for single molecules can be found in [4].

where E_0 is the total internal energy of the neutral conductor, μ is the chemical potential, and e is electron charge. A variation in the total energy of the insulated conductor with a variation in the charge by $\Delta q = ne$ is represented as

$$\Delta E_C(n) = \mu n + e^2 n^2 / C, \qquad (3)$$

where $q/e = n$.

Below, we consider a definition of the effective self-capacitance of a single molecule or an atomic object and employ experimental data and the results of quantum-chemical calculations to analyze the effect of the chemical composition and geometrical shape on the capacitance.

1. A METHOD TO DETERMINE THE EFFECTIVE SELF-CAPACITANCE OF AN ISOLATED NANOSIZED OBJECT

We consider objects (neutral atoms, groups of atoms, molecules, and stable cations and anions) and disregard the effect of variation in charge on the stability of atoms and molecules. A nanoobject is classified as an isolated object when its interaction with the surrounding medium is isotropic and when the interaction energy is no greater than the energy of the dispersion (van der Waals) interactions. To differ between atoms or molecules and cations or anions, we introduce the notion of the charge state of nanoobject. The charge state of nanoobject is determined by the total charge and is similar to the charge state of microscopic conductors in the classical single-electron theory [6].

To determine the electrostatic capacitance, we consider the charging of an insulated macroscopic conductor with a trial charge [5]. Note that the trial charge insignificantly affects the existing distribution of electric fields. We cannot use the trial charge in the case of an isolated atom (molecule), since the minimum possible charge is electron charge e. Even electron charge e is not small for an atom or a nanoparticle consisting of 100–200 atoms. At atomic distances, the electron charge causes variations in the electron density and interatomic distances in molecule and, hence, in the energy of electrostatic interaction.

It is known that the surface electric potential of a conductor is used in electrostatics to determine the capacitance. The notion of the surface potential can hardly be used to characterize a single molecule (atom). The objects with a size of 1–2 nm do not exhibit different surface and internal states, which are typical of macroscopic samples. The electric potential that is generated by a charge on such a nanoobject is distributed over the entire volume, so that the effective capacitance of a molecule (nanoobject) cannot be determined using the potential.

In this section, we define the notion of the effective self-capacitance of a single molecule (nanoobject) using the dependence of the total energy in the ground state on the total charge. Such an approach is based on the analysis of formulas (1)–(3) and the dependence of the electrostatic energy of a system of classical conductors on their charges. The convenience of such a definition lies in the fact that the total energy of a molecule is a scalar quantity that can be determined for quantum microscopic objects with a relatively high accuracy.

The notion of self-capacitance is defined for each conductor in the classical electrostatics on the assumption that the system of conductors is found in the thermodynamic equilibrium with the surrounding medium. Ground state $|\Psi_0\rangle$ of an isolated quantum system serves as an analog of the thermodynamic equilibrium [7]. For the quantum system in the given state, the total energy is one half of the mean potential energy in accordance with the virial theorem:

$$\frac{1}{2}\langle \Psi_0 \mid U \mid \Psi_0 \rangle = \langle \Psi_0 \mid \hat{H} \mid \Psi_0 \rangle. \qquad (4)$$

Relativistic corrections mostly affect inner atomic shells, whereas charging and discharging involve outer shells. Thus, the relativistic corrections can be neglected. For the given state of an isolated molecule (nanoobject), we can determine the minimum effective capacitance using the method that is similar to the method for derivation of formula (2).

2. MODEL OF THE SYSTEM

We consider the object (molecule, nanoparticle, molecular cluster, etc.) as an ensemble of N nuclei with charges Z_α and masses M_α, $\alpha = \overline{1, N}$, and ν electrons and disregard the specific chemical composition and structure of the ensemble. Note that the objects with the number of atoms $N \sim 100$ are interesting for the construction of the elements of the molecular single electronics based on the correlated electron tunneling [1]. For the charging and discharging of such molecules (nanoobjects), variation in the total energy ΔE_{m} is normally significantly greater than the energy of thermal fluctuations even at room temperature ($kT = 0.026$ eV). This circumstance can be used for the creation of the most convenient molecular single-electron devices with a relatively high working temperature [9]. In the framework of the model, we do not consider charging and discharging of molecules (nanoobjects) and assume that the molecule is always found in the ground state.

We introduce the notion of an additional charge of isolated molecule (nanoobject) and consider molecules with the known number of nuclei N and nuclear charges $\{eZ_\alpha\}$. Note that the total number of electrons ν can be varied. We determine the additional charge of molecule (nanoobject) as the difference between the total charge of nuclei and the total charge of electrons in the molecule (nanoobject) [10]:

$$en = e\sum_{\alpha = 1}^{N} Z_\alpha - e\nu. \qquad (5)$$

Here, en is the additional charge of molecule (nanoobject) and n is the charge-state number, which is integer for an isolated molecule (nanoobject) and determines the charge state.

For a nonisolated molecule (open system), the time-averaged additional charge $e\langle n\rangle$ can be fractional [11, 12], since electrons can be delocalized between the given molecule and the neighboring molecule. The charge state is unambiguously determined when the condition for the isolated molecule (nanoobject) (i.e., the absence of contacts with electron donors and acceptors) is satisfied. When such a condition is not satisfied, we consider a distribution over the charge states. For example, the tunneling of electrons takes place when a molecule is placed in the vicinity of a metal electrode. Due to the tunneling, the variance of the additional charge is nonzero $(D_n \neq 0)$. In this work, we consider only isolated molecules.

As was mentioned, we use the dependence of the total energy in the ground state on the total charge to determine the effective self-capacitance. To establish such a dependence, we must solve the Schrödinger equation for wave function $\Psi(\{x\}, \{X\}, n)$ for all of the possible charge states:

$$\hat{H}_{\mathrm{m}}\Psi(\{x\}, \{X\}, n) = E_{\mathrm{m}}(n)\Psi(\{x\}, \{X\}, n). \qquad (6)$$

Here, $\{x\}$ and $\{X\}$ are coordinates of electrons and nuclei, respectively, and $\hat{H}_{\mathrm{m}}$ is the Hamiltonian of the molecule given by

$$\hat{H}_{\mathrm{m}} = \hat{T}_e + \hat{T}_N + \hat{U}_{NN} + \hat{U}_{eN} + \hat{U}_{ee}, \qquad (7)$$

where $\hat{T}_e$ is the kinetic energy of electrons, $\hat{T}_N$ is the kinetic energy of nuclei, $\hat{U}_{NN}$ is the energy of the electrostatic repulsion of nuclei, $\hat{U}_{eN}$ is the attraction energy of electrons and nuclei, and $\hat{U}_{ee}$ is the electron–electron repulsion energy.

The analysis of an insulated charged conductor in the classical electrostatics implicitly involves the state with the minimum electrostatic energy. For a quantum object (molecule), the ground state is the state with the minimum potential energy. Note that we can establish one-to-one relations of various charge states only with the ground state of the nanoobject. Therefore, we assume that the molecule occupies the ground state. Below we use notation $|\Psi_0(n)\rangle$ for the wave function of the ground state in charge state n.

For the practical molecular electronics, we need molecules (nanoobjects) that can accept or donate several electrons in the absence of structural damage [13, 14]. A molecule (nanobject) can be found in several charge states but we do not consider the transitions between charge states and the corresponding dynamics. We assume that time interval Δt, after charging or discharging is significantly greater than characteristic time t_{rel} of energy relaxation to the ground state. Thus, the molecule is found in the ground state $|\Psi_0(n)\rangle$ with a relatively high probability at delay time $\Delta t \gg \tau_{\mathrm{rel}}$, relative to the termination of variations in the additional charge.

We consider the total energy of the molecule (nanoobject) in the ground state with allowance for the fact that the total wave function of the molecule is antisymmetric with respect to permutation of electrons and employ the virial theorem [8]. For the ground state of the molecule (nanoobject) in charge state n, the total energy can be represented in terms of the mean potential energy:

$$\begin{aligned} E_0(n) = \frac{1}{2}\langle U_0(n)\rangle &= \frac{1}{4}\sum_{\alpha \neq \beta}^{N}\left\langle\frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}\right\rangle_n \\ &- \frac{\nu}{2}\sum_{\alpha = 1}^{N}\left\langle\frac{Z_\alpha e^2}{r_{\alpha e}}\right\rangle_n + \frac{\nu(\nu - 1)}{4}\left\langle\frac{e^2}{r_{ee}}\right\rangle_n, \end{aligned} \qquad (8)$$

where $\langle Z_\alpha e^2/r_{\alpha e}\rangle_n$ is the mean potential energy of the interaction of nuclei α and β, $\langle Z_\alpha e^2/r_{\alpha e}\rangle_n$ is the mean potential energy of the interaction of electron with nucleus α, $\langle e^2/r_{ee}\rangle_n$ is the mean potential energy of the interaction of two electrons in the molecule.

In accordance with the results from [6], we determine the charge energy as the difference of the total energy in the state with the nonzero additional charge ($en \neq 0$), and the total energy in the charge state ($en = 0$):

$$\begin{aligned} E_C(n) &= E_0(n) - E_0(0) \\ &= \frac{1}{4}\sum_{\alpha \neq \beta}^{N} Z_\alpha Z_\beta e^2\left(\left\langle\frac{1}{r_{\alpha\beta}}\right\rangle_n - \left\langle\frac{1}{r_{\alpha\beta}}\right\rangle_0\right) \\ &- \sum_{\alpha = 1}^{N} Z_\alpha e^2\left(\frac{\nu_0 + n}{2}\left\langle\frac{1}{r_{\alpha e}}\right\rangle_n - \frac{\nu_0}{2}\left\langle\frac{1}{r_{\alpha e}}\right\rangle_0\right) \\ &+ e^2\left(\frac{(\nu_0 + n)(\nu_0 + n - 1)}{4}\left\langle\frac{1}{r_{ee}}\right\rangle_n - \frac{\nu_0(\nu_0 - 1)}{4}\left\langle\frac{1}{r_{ee}}\right\rangle_0\right). \end{aligned} \qquad (9)$$

Here, the number of electrons in the neutral molecule is $\nu_0 = \sum_{\alpha = 1}^{N} Z_\alpha$.

Note that the difference of charge energies calculated for two neighboring charge states is equal to the corresponding ionization potential or the electron affinity:

$$\begin{aligned} &E_C(1) = I_1, \\ &E_C(2) - E_C(1) = I_2, \\ &\ldots, \\ &E_C(-1) = -A_1, \\ &E_C(-1) - E_C(-2) = A_2, \\ &\ldots. \end{aligned} \tag{10}$$

Here, I_i is the ionization potential of the ith atom or molecule and A_j is the affinity with respect to the jth electron.

Note that expression (9) is written in terms of n, and n^2 and that the structure of the expression with respect to variable n, is similar to the structure of expression (3), which characterizes a variation in the energy of a single macroscopic conductor that is charged with charge q. On the assumption that matrix elements $\langle 1/r_{\alpha\beta}\rangle_n$, $\langle 1/r_{\alpha e}\rangle_n$, and $\langle 1/r_{ee}\rangle_n$ in expression (9) are independent of n,, the structure of the resulting expression for $E_C(n)$ fully coincides with the structure of the expression for a variation in the total energy of an insulated conductor (expression (3)):

$$\begin{aligned} E_C(n) &\approx \frac{1}{4}\left\langle\frac{e^2}{r_{ee}}\right\rangle n^2 \\ &+\left(\frac{2\nu_0 - 1}{4}\left\langle\frac{e^2}{r_{ee}}\right\rangle - \sum_{\alpha=1}^{N}\frac{1}{2}\left\langle\frac{Z_\alpha e^2}{r_{\alpha e}}\right\rangle\right)n. \end{aligned} \tag{11}$$

In general, quantities $\langle 1/r_{\alpha\beta}\rangle_n$, $\langle 1/r_{\alpha e}\rangle_n$, and $\langle 1/r_{ee}\rangle_n$ depend on n. However, we demonstrate below that the dependence is weak (section 5).

The similarity of expressions (3) and (11) makes it possible to introduce the notion of the effective capacitance of molecule, which is similar to the self-capacitance of conductor. Moreover, such an approach also makes it possible to introduce the notion of capacitance at the microscopic level for semiconductors and insulators (in addition to conductors). Note that the analysis of the experimental data from [15] or the results of numerical calculations can be used to prove the validity of the above statement, since the exact analytical solution of the Schrödinger equation for atoms and molecules with more than one electron is not available.

3. EFFECTIVE SELF-CAPACITANCE OF A SINGLE ATOM

The above notion of charge energy $E_C(n)$ can be used for any isolated object including purely quantum objects (single atoms and molecules) and larger objects (up to large nanoparticles). Methodologically, the most interesting and useful analysis employs the properties of charge energy of single atoms, since the characteristics of such objects are studied in various charge states and extensive experimental data on the ionization potentials and electron affinity are available. Atoms represent the main structural elements of complex objects. Therefore, we start the investigation of the effective capacitance of nanoobjects from the determination of the effective capacitance of a single atom.

The experimental data on the ionization potential from [16] show that single atoms exhibit charge states with additional charges $q = 0\ldots + eZ$, where eZ is the charge of nucleus. In addition, most atoms allow the state with a single electron (i.e., with a charge of $-e$,), which is proven by experimental data on the electron affinity A [17]. At the same time, the state with two additional electrons (i.e., with an additional charge of $-2e$,) is energetically disadvantageous.

For clearness, we use the following notation for the kth affinity:

$$A_k = I_{k-1}. \tag{12}$$

Such a notation makes it possible to interpret the first affinity A_1 as the zero potential of atomic ionization from the charge state with subscript -1 (one excess electron) to the zero state, which is convenient for the analysis of variations in the charge state.

The experimental data on the ionization potentials from [16] show that all of the ionization potentials with numbers k linearly depend on the number provided that the electrons from one subshell are removed in the course of ionization:

$$I_k \approx b_1 k + b_0. \tag{13}$$

Here, b_1 and b_0 are the coefficients of linear regression.

Owing to the linearity of the dependences of the ionization potentials and electron affinity on the number within a single shell, it is suffice to know only two values to be able to accurately determine all of the remaining ionization potentials and affinities within a single subshell or a single shell. For example, the first ionization potential and the first affinity can be used to represent all of the remaining ionization potentials and affinities of the given shell:

$$\begin{aligned} I_k &= I_1 k - A_1(k-1), \text{ where } k \geq 1, \\ A_k &= A_1 k - I_1(k-1), \text{ where } k \geq 1. \end{aligned} \tag{14}$$

Figures 1 and 2 demonstrate the experimental data on the ionization potentials of the Cl, Cr, Mn, Fe, and Co atoms. We choose these atoms, since extensive experimental data are available (see, for example, [16]). Figure 1 shows the ionization potentials of the Cl atom. We present the ionization potentials that correspond to the electrons removed from the 1s, 2s, 2p, 3s, and 3p shells. Figure 2 shows the ionization potentials of the Cr, Mn, Fe, and Co atoms. It is seen that coefficients a_1 and a_0 exhibit stepwise variations for the transition from one electron shell to another in the

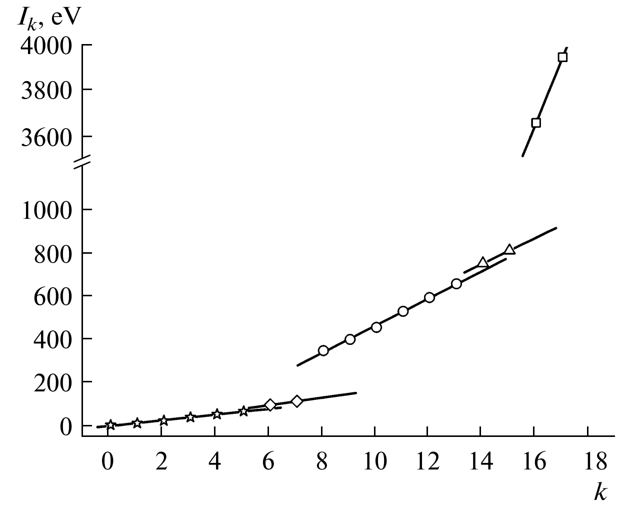

Fig. 1. Plots of ionization potential I_k of the Cl atom vs. ionization order k for (stars) $3p$, (diamonds) $3s$, (circles) $2p$, and (squares) $2s$ electrons and the regression lines for the corresponding electron shells.

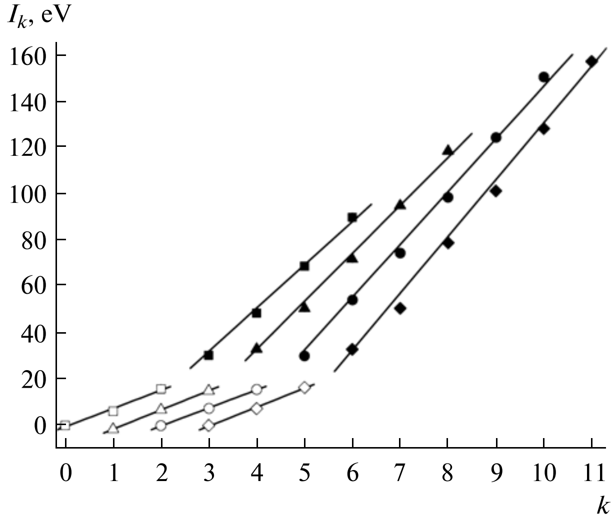

Fig. 2. Plots of ionization potential I_k vs. ionization order k for (squares) Cr, (triangles) Mn, (circles) Fe, and (diamonds) Co atoms. Open and closed symbols correspond to the ionization potentials of the $4s$ and $3d$ electrons, respectively. For clearness, the ionization potentials of the Mn, Fe, and Co atoms are shifted to the right-hand side by 1, 2 and 3 units, respectively. The regression lines are plotted for the electron shells of atoms.

course of the atomic ionization. Note that the jumps of the potentials are insignificant when we consider the transitions between electron subshells within a single electron shell.

Note the features of the dependences of the ionization potentials and electron affinity on the number of charge state (Figs. 1 and 2). Based on such curves, we can approximate the dependences of the charge energy on the number of charge state for all of the atoms from the Mendeleev table using sets of parabolas (quadratic polynomials) that intersect or appear tangent to each other. Each parabola corresponds to a shell or subshell. Thus, the assumption on the quadratic dependence of the charge energy on the number of charge state for atoms is in agreement with the experimental data.

The experimental data are used in [15] to demonstrate that, at a fixed nuclear charge, the dependence of the total atomic energy on the number of electrons can be approximated as

$$E_0(n) = a_4 n^4 + a_3 n^3 + a_2 n^2 + a_1 n + E_0(0), \qquad (15)$$

where $E_0(0)$ is the total energy of neutral atom and n is the integer number of the charge state of atom. It is also demonstrated that, normally, coefficients a_4 and a_3 are significantly less than coefficients a_2 and a_1:

$$a_4, a_3 \ll a_2, a_1. \qquad (16)$$

The above data show that the second-order polynomials are sufficient for a relatively accurate approximation of the dependence of the charge energy on the charge state. Below, we calculate the effective capacitance using the polynomial regression of the second order. If the ionization potentials and electron affinity of a single atom depend on the charge energy E_C, in accordance with expression (10), the coefficients of the polynomial regression of the total atomic energy with respect to the number of charge state can be determined from the experimental data on the first ionization potential I_1 and electron affinity A of the atom with charge Z. Simple calculations yield the following expressions for the expansion coefficients:

$$\begin{aligned} a_2 &\approx \frac{I_1 - A_1}{2} = b_1/2, \\ a_1 &\approx \frac{I_1 + A_1}{2} = b_1/2 + b_0. \end{aligned} \qquad (17)$$

The linear dependences of the ionization potentials and electron affinity on the number of charge state (Figs. 1 and 2) are typical of all atoms. In this work, we study the dependence of the charge energy on the number of charge state for several atoms that satisfy expression (15). Based on the similarity of expression (3) for the total energy of the classical conductor and formula (11) for the charge energy of atom, which was derived with the aid of the virial theorem, we define the notion of the effective self-capacitance of atom using coefficient a_2. Note that linear term $a_1 n$ in expressions (11) and (15) is an analog of the Gibbs energy for the processes of charging and discharging in macroscopic systems.

The effective self-capacitance of atom can be defined as

$$C_{\text{eff}} = \frac{e^2}{a_2} = \frac{2e^2}{I_1 - A_1}. \qquad (18)$$

Using expression (13), we represent this equality as

$$C_{\text{eff}} = \frac{2e^2}{b_1}. \tag{19}$$

This expression is more convenient than expression (18) for the practical determination of the effective self-capacitance of a single atom. We can obtain coefficient b_1 of the linear regression of the ionization potential versus number (degree) of ionization for the outer electron shell and, hence, the effective capacitance of atom using the data on any two ionization potentials that correspond to the given electron subshell.

Formula (18) shows that the effective capacitance of atom increases with decreasing difference between the ionization potential of atom and electron affinity. The formula makes it possible to calculate the effective self-capacitance of a single atom in the quantum approximation.

At the same time, we can estimate the self-capacitance of atom based on the classical model of a perfectly conducting sphere, which is used for the interpretation of the experimental results on one-electron structures (see, for example, [18]). The interest in the comparison of different methods for the calculation of the effective capacitance is related to the fact that the capacitance in classical physics depends on the size of the conductor. However, the above energy method for the determination of the effective capacitance of a nanoobject does not lead to the explicit dependence on the spatial parameters.

It is known from [5] that the self-capacitance of a conducting macroscopic sphere is given by

$$C_{\text{sph}} = 4\pi\varepsilon_0 r, \tag{20}$$

where r is the radius of sphere and $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1} is the electric constant. The radius of atom is a conditional quantity. We assume that the radius of atom is the radius of a sphere that contains the main part of the electron density. It is demonstrated in [19] that the atomic electron density in the ground state can be approximated as

$$\rho \sim \exp\left(-2\sqrt{\frac{I_1 r}{Ry\, a_0}}\right), \tag{21}$$

where $Ry = 13.6$ eV is Rydberg and a_0 is the radius of the first Bohr orbit. Using expression (21), we estimate the size of atom as

$$\langle r \rangle \sim a_0\sqrt{\frac{Ry}{I_1}}. \tag{22}$$

Formally substituting expression (22) in formula (20), we estimate the effective capacitance of atom based on the model of a perfectly conducting sphere:

$$C_{\text{sph}} \sim 4\pi\varepsilon_0 a_0\sqrt{\frac{Ry}{I_1}}. \tag{23}$$

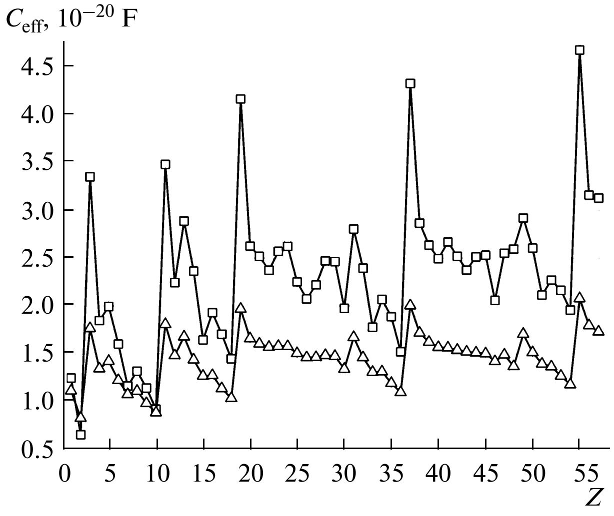

Fig. 3. Plots of the effective self-capacitances of single atoms vs. the number in the periodic table of elements calculated using (squares) expression (18) and (triangles) classical expression (23) for the capacitance of sphere. For clearness, we also plot the corresponding connecting lines.

Figure 3 demonstrates the dependence of the effective self-capacitance of a single atom on the atomic number that is calculated using formula (18), the experimental data on the ionization potential and electron affinity, and formula (23). For several atoms, the charge states with one excess electron ($n = -1$) are unstable and the data on the electron affinity are missing. The corresponding electron affinities were numerically calculated. Squares denote the effective capacitances that are obtained using the model of a perfectly conducting sphere.

Figure 3 shows that the effective capacitances of most atoms range from 1×10^{-20} to 3×10^{-20} F. For most atoms of metals and semiconductors that are used in micro- and nanoelectronics, the effective capacitance is $C_{\text{eff}} \sim 2.5 \times 10^{-20}$ F. We observe a tendency towards an increase in the effective self-capacitance of atoms with increasing nuclear charge of the element from the shells with smaller principal quantum numbers to the shells with larger principal quantum numbers proportionally to $Z^{1/3}$. The atoms of alkali metals and inert gases exhibit the largest and smallest effective capacitances, respectively. In the framework of the above model, the helium atom has the minimum effective capacitance $C_{\text{eff He}} \sim 6.5 \times 10^{-21}$ F.

In addition, the capacitance that is calculated with the aid of the classical model for the capacitance of sphere whose radius corresponds to the size of atom is approximately two times less than the effective capacitance that is calculated using quantum formula (18). Such a difference can be due to the fact that the atomic radius in the classical theory is the distance from the nucleus to the last filled electron shell whereas, in a

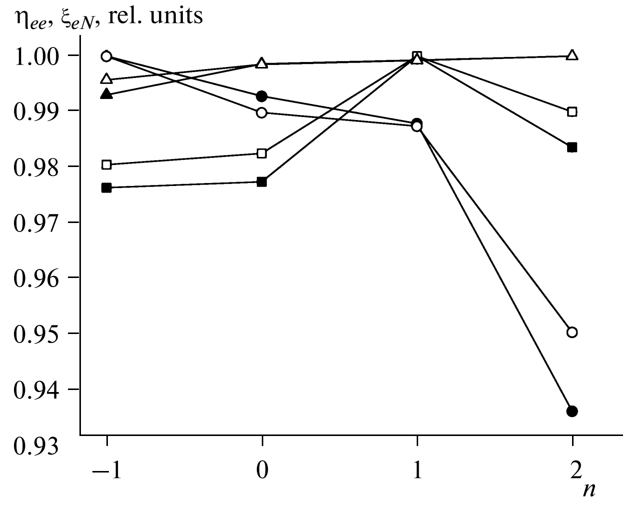

Fig. 4. Plots of the relative specific energies (in relative units) of (open symbols) the electron–nuclear interaction η_{eN} and (closed symbols) electron–electron interaction ξ_{ee} vs. number of charge state n for (squares) carboran molecule $C_2B_{10}H_{12}$, (triangles) fullerene C_{60}, and (circles) the thallium derivative of the carboran cluster 1,7-$(CH_3)_2$-1,2-$C_2B_{10}H_9Tl(OCOCF_3)_2$. For clearness, we also plot the corresponding connecting lines.

real atom, the distribution of electron density differs from zero at relatively large distances.

Note the following feature of the curves in Fig. 3. The effective capacitance is greater for the atoms that have unpaired electrons (e.g., atoms of alkali metals). This effect can be interpreted using the Hund rule, in accordance with which the system with the maximum spin has the minimum energy for the given electron configuration. Normally, the ionization potential (electron affinity) of the atom with unpaired electron is greater (less) than the ionization potential (electron affinity) of the atom whose nuclear charge differs by unity.

Thus, we demonstrate the quadratic dependence of the charge energy of isolated atoms on the additional charge using the classical expression for the charge energy.

4. EFFECTIVE SELF-CAPACITANCE OF SINGLE MOLECULES

In this section, we generalize the above regularities obtained for single atoms on single molecules. Note that the characteristics of molecules in various charge states were studied in less details (in comparison with the atomic characteristics). The key feature that makes it possible to introduce the effective self-capacitance of atoms is the quadratic dependence of the charge energy on the charge. To determine such a dependence and to generalize the above definition of the effective capacitance on molecular objects, we consider several examples. We restrict consideration to relatively simple molecules with characteristic structures or the molecules that are used in the experimental works on molecular optoelectronics [9].

Expression (9) shows that the charge energy of molecule is represented as the second-order polynomial in terms of n when the coefficients in this expression are independent of or weakly depend on n. For the specification of this dependence, we theoretically calculate the coefficients of the quadratic regression. Note that the weakness or the absence of the dependence of the coefficients on n is not proven by the ab initio calculations but the experimental data on the ionization potential from [16] and the numerical calculations of the quantities $\langle 1/r_{\alpha\beta}\rangle_n$, $\langle 1/r_{\alpha e}\rangle_n$, and $\langle 1/r_{ee}\rangle_n$ using the methods of quantum chemistry provide the supporting evidence. By way of example, Fig. 4 demonstrates the dependences of the relative specific energies of the electron–nuclear and electron–electron interaction

$$\eta_{eN} = \frac{|\langle 1/r_{\alpha e}\rangle_n|}{|\langle 1/r_{\alpha e}\rangle_n|_{\max}}, \quad \xi_{ee} = \frac{|\langle 1/r_{ee}\rangle_n|}{|\langle 1/r_{ee}\rangle_n|_{\max}} \tag{24}$$

for several molecules that were used for the creation of molecular optoelectronic devices [20]. The curves are calculated using the method of the density functional [7] and the GAMESS software package [21].

Figure 4 shows that the deviation of the specific energies of the electron–nuclear and electron–electron interaction from a certain constant level is several percents for a small range of the charge states. This circumstance indicates the validity of the assumption on the independence of the matrix elements on the number of charge state. The authors assume that the deviation is predominantly related to the insufficient accuracy of the existing numerical methods for the calculation of the total energy in various charge states of molecules (e.g., neutral and ionized molecule). Below, we assume that the matrix elements are independent of n.

Our calculations and the analysis of published works indicate that, for most isolated molecules, the curve of the charge energy versus the number of charge state is similar to the curve for atoms (expression (15)). Note that the dependence is closer to the quadratic dependence for larger molecules and, in the limiting case of macroscopically large conductors, we obtain a parabola. In addition, for most molecules, the dependence of the ionization potential on the number (degree) of ionization is linear with a relatively high accuracy. As in the case of atoms, the dependence is given by expression (13). As in the case of single atoms, we define the effective capacitance of a single molecule using the first ionization potential and the first electron affinity (formula (18)). We interpret the terms that are proportional to n^2, and n, as analogs of the electrostatic energy in macroscopic objects and the Gibbs energy, respectively.

Table 1. Coefficients of the linear regression for the dependences of ionization potential I_k on number k (13), numbers of atoms in molecule N, and the effective self-capacitances C_{eff} for several molecules. The data result from the numerical calculations using the theory of the density functional from [7]. Quantities Δb_i are the standard errors of linear regression

Molecule	b_1, eV	Δb_1, eV	b_0, eV	Δb_0, eV	N	C_{eff}, 10^{-20} F
CN	10.5	0.6	3.8	0.7	2	1.5
CO_2	12.7	0.5	0.3	0.6	3	1.3
BCl_3	9.2	1.1	1.1	1.4	4	1.7
$Cr(CO)_6$	7.0	0.6	1.0	0.7	13	2.3
$PtCl_3C_2H_4$	5.1	0.2	4.9	0.2	10	3.1
$B_{12}H_{12}$	5.1	0.7	5.8	0.9	24	3.1
Fe(Dicarbollide)$_2$	4.9	0.2	4.8	0.2	45	3.3
TDCC	1.5	0.1	3.4	0.1	44	1.1

Note: TDCC is 1,7-$(CH_3)_2$-1,2-$C_2B_{10}H_9Tl(OCOCF_3)_2$.

The maximum negative charge of the molecule is a critical parameter of molecules and clusters in nanoelectronic devices, since the experiments from [16] show that the maximum positive charge is greater than the maximum negative charge. We can determine the charge for each molecule using the dependence of the charge energy on the number of charge state. Such a dependence exhibits a minimum, and all of the energy states lying on the left-hand side of the minimum are energetically disadvantageous. The condition for the minimum of the charge energy is written as

$$\frac{dE_C(\xi)}{d\xi} \approx (I_1 - A_1)\xi + \frac{I_1 + A_1}{2} = 0, \tag{25}$$

where we introduce continuous variable ξ instead of discrete variable n. Using this equation, we derive the following expression for the maximum possible additional charge of an isolated anion:

$$n_{\max} \approx -\left[\frac{I_1 + A_1}{2(I_1 - A_1)}\right] = -\left[\frac{1}{2} + \frac{b_0}{b_1}\right]. \tag{26}$$

Here, $[x]$ is the integer part of x. In the limiting case of the macroscopic conductors, the expression is represented as

$$n_{\max} \approx -\left[\frac{CW}{e^2}\right], \tag{27}$$

where $[\xi]$ is the integer part of ξ, and $W = (I_1 + A_1)/2$ is the work function of electron for the surface of conductor.

Using expression (27), we estimate $n_{\max}$ for conductors with the macroscopic size $r_{\text{cond}} \sim 1$ cm. The self-capacitance of such conductors is $C_{\text{cond}} \sim 10^{-12}$ F and the maximum number of additional electrons is about 10^7. For the conductors from the conventional single-electron devices, we have $C_{\text{single}} = 10^{-16}$–$10^{-15}$ F [6] and the maximum number of additional electrons is 10^4–10^5.

Thus the above method for the calculation of the effective capacitance is reduced to the calculation of two or more ionization potentials and electron affinity or the corresponding experimental measurements. The ionization potentials and electron affinity must be substituted in formula (18) or formula (19) for the calculation of the effective self-capacitance of molecule. Note that the ionization potential and electron affinity must be linear functions of the number, otherwise formulas (18) and (19) incorrectly estimate the effective capacitance of molecule.

5. CALCULATIONS OF THE EFFECTIVE SELF-CAPACITANCES OF SEVERAL MOLECULES

By way of example, we calculate the effective self-capacitances of several molecules. We choose the examples to briefly illustrate the main regularities that follow from the calculations of the effective self-capacitances and to perform the comparison with the classical electrostatics. Note that the dependences of the effective capacitance of molecule on its sizes, number of atoms, geometrical structure, and chemical composition are important for designing of molecular single-electron devices.

Figures 5 and 6 demonstrate the dependences of the ionization potential on its number (degree) for several molecules. It is seen that the ionization potential almost linearly depends on the number.

Table 1 presents the coefficients of linear regression and the calculated effective capacitance. Note that the molecules were arbitrarily chosen with allowance for characteristic sizes and regardless of the linearity of the dependence. The maximum size is limited only by computational resources. Figures 5 and 6 show that the slope of curve decreases with increasing number of atoms N in the molecule. Thus, the effective capacitance of molecule increases with increasing number of atoms. Note that the effective capacitance is not proportional to the number of atoms in the molecule. Moreover, a greater number of atoms does not correspond to a greater effective self-capacitance (Table 1) owing to a relatively complicated relation of the num-

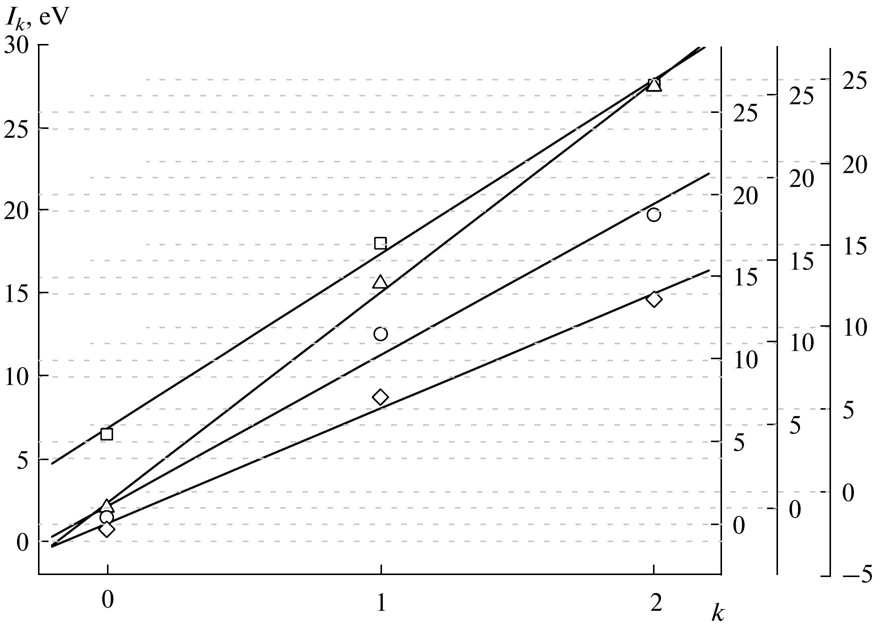

Fig. 5. Plots of ionization potential I_k vs. ionization order k for (squares) CN, (triangles) CO_2, (circles) BCl_3, and (diamonds) $Cr(CO)_6$ molecules. For clearness, the squares, triangles, and circles are shifted upwards by 3, 2, and 1 eV, respectively. The regression lines for the corresponding molecules are presented.

ber of atoms and the characteristic size. Such a relationship completely depends on the molecular topology. For the interpretation of such results, we employ the classical electrostatics, in which the capacitance is proportional to the size. Similarly, the molecules with the maximum characteristic size exhibit the maximum effective capacitance. For the molecules with different chemical compositions and numbers of atoms, the effective self-capacitances can be equal. By way of example, consider the calculated capacitances of the $PtCl_3C_2H_4$ and $B_{12}H_{12}$. molecules. The above assumption that relationship (11) is satisfied with a relatively high accuracy for molecules is proven by the results for an arbitrary set of molecules.

A more detailed analysis of the relation between the size of molecule and the effective capacitance employs homoatomic highly symmetric molecules whose structure is close to the spherical structure (e.g., fullerenes [22], which are important for the creation of nanoelectronic structures).

We can also consider the relation of size and capacitance for heteroatomic compounds. However, in this case, it is more difficult to choose substances with similar topologies and different numbers of atoms due to diversity of heteroatomic compounds. The study in this work shows that the topology rather than the chemical composition determines the effective capacitance of a single molecule. Therefore, we analyze the dependence of the effective capacitance on the topology of homoatomic molecules with relatively simple shapes. The same analysis can be performed for various types of heteroatomic molecules with different topologies.

Table 2 shows the coefficients of linear regression and the calculated effective self-capacitances of the carbon atom and the C_{60}, C_{70}, and C_{180}molecules. It is seen that the effective self-capacitance increases with increasing number of atoms in the molecule.

However, the calculated effective capacitances of the C_{60} and C_{70} molecules are less than the effective capacitance of a single carbon atom multiplied by the number of atoms in the corresponding fullerene:

$$C_{\mathrm{eff}\ C_N} \leqslant NC_{\mathrm{eff}\ C}. \tag{28}$$

Therefore, the effective capacitance of molecule cannot be calculated as a sum of the effective capacitances of atoms. We must accurately take into account the spatial configuration of molecule, which substantially affects the total and charge energies and, hence, the self-capacitance. It is demonstrated in [23] that the dependence of the ionization potential and electron affinity on the characteristic size of fullerenes can be obtained using the model of a conducting sphere:

$$\begin{aligned} I_1 &\approx W + \frac{e^2}{4\pi\varepsilon_0 R}, \\ A_1 &\approx W - \frac{e^2}{4\pi\varepsilon_0 R}. \end{aligned} \tag{29}$$

Here, R is the radius of the sphere that coincides with the surface of fullerene and W is the work function for graphite. Substituting these quantities in expression (18), we find that the effective self-capacitance of fullerenes

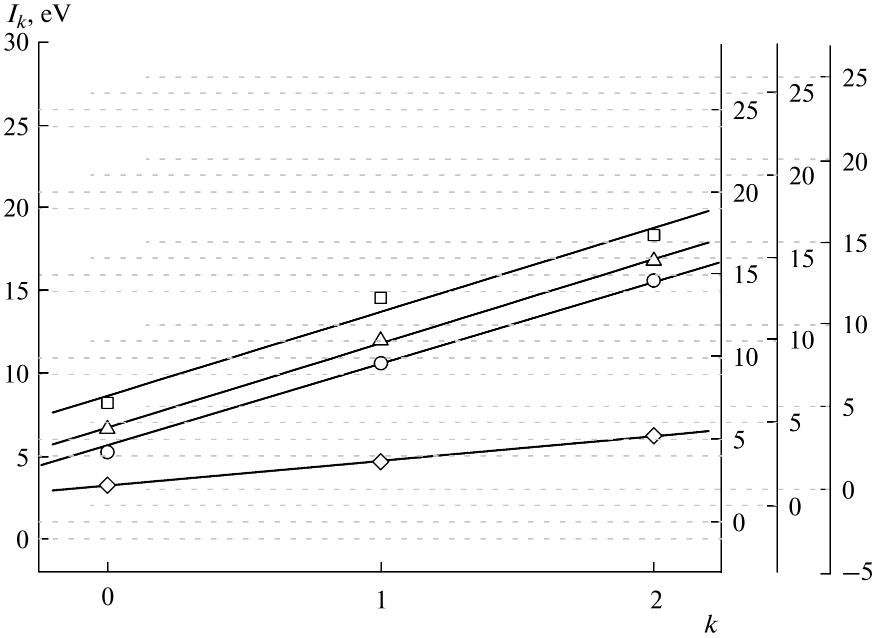

Fig. 6. Plots of ionization potential I_k vs. ionization order k for (squares) $B_{12}H_{12}$, (triangles) $PtCl_3C_2H_4$, (circles) Fe(Dicarbollide)$_2$, and (diamonds) 1,7-$(CH_3)_2$-1,2-$C_2B_{10}H_9Tl(OCOCF_3)_2$ molecules. For clearness, the squares, triangles, and circles are shifted upwards by 3, 2, and 1 eV, respectively. The regression lines for the corresponding molecules are presented.

is well described using the classical formula for the capacitance of a charged sphere whose size is equal to the size of fullerene:

$$C_{\text{eff}} = \frac{2e^2}{I_1 - A_1} \approx 4\pi\varepsilon_0 R. \qquad (30)$$

In accordance with the conformity principle [24], the effective self-capacitance of molecule that is determined at the microscopic level (see expression (18)) must be determined by the classical expression for the self-capacitance of conductor when the size of molecule increases to the macroscopic level due to an increase in the number of atoms. To verify this statement, we calculate the effective self-capacitances of homoatomic cyclic carbon compounds[2] and fullerenes that contain from 1 to 180 atoms. The limitations on the number of atoms are determined by the available experimental data and the computational facilities. Figure 7 demonstrates the effective capacitances of the cyclic carbon compounds and fullerenes that are calculated using formula (18). The data for calculations are from either the experimental works [23, 25–28] or the original quantum-chemical calculations. We perform calculations only for compounds whose existence is proven in experiments.

When the number of atoms in the homoatomic molecule increases, the electron affinity and ionization potential tend to the work function of the macroscopic sample that consists of the same atoms. Thus, the difference between the ionization potential of molecule and its electron affinity decreases with increasing number of atoms, so that the effective self-capacitance increases in accordance with expression (18). Figure 7 demonstrates an increase in the effective self-capacitance of homoatomic carbon compounds. The nonmonotonic increase in the effective self-capacitance of carbon compounds can be due to the fact that several fullerenes do not exhibit the equilibrium spatial structure in which all of the atomic nuclei are located on a spherical surface. Therefore, such molecules can be elongated in a certain direction. The resulting capacitances are greater than the capacitances that correspond to spherical shapes. The solid line in Fig. 7 is plotted using the allometric regression based on the equation $C_{\text{eff}} = a + bN^D$ with the coefficients $a = 1.3 \times 10^{-20}$ F, $b = 2.3 \times 10^{-21}$ F, and $D = 0.56$.

The knowledge of the maximum possible number of additional electrons that can be transferred to a neutral molecule is important for designing of molecular electronic devices. Figure 8 shows the dependence of this quantity for cyclic carbon compounds and fullerenes on the number of atoms that is calculated using formula (27).

The molecules with the number of atoms of no greater than 72 can accommodate no greater than one electron. The molecules with the number of atoms of no less than 92 can accommodate up to three electrons.

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[2] In the calculations, we employ the cyclic compounds with numbers of atoms of no greater than 20, since the fullerenes with such numbers of atoms are unavailable [22].

Table 2. Coefficients of the linear regression for the dependence of ionization potentials I_k on number k for the carbon atoms and the C_{60}, C_{70}, and C_{180} molecules. Quantities Δb_i are the standard errors of linear regression

Molecule	b_1, eV	Δb_1, eV	b_0, eV	Δb_0, eV	d, Å	C_{eff}, 10^{-20} F
C	12.2	0.5	–0.3	0.7	–	1.3
C_{60}	4.0	0.1	3.1	0.3	6.9	4.0
C_{70}	3.7	0.1	3.4	0.3	7.8	4.3
C_{180}	2.9	0.1	4.5	0.4	11.3	5.5

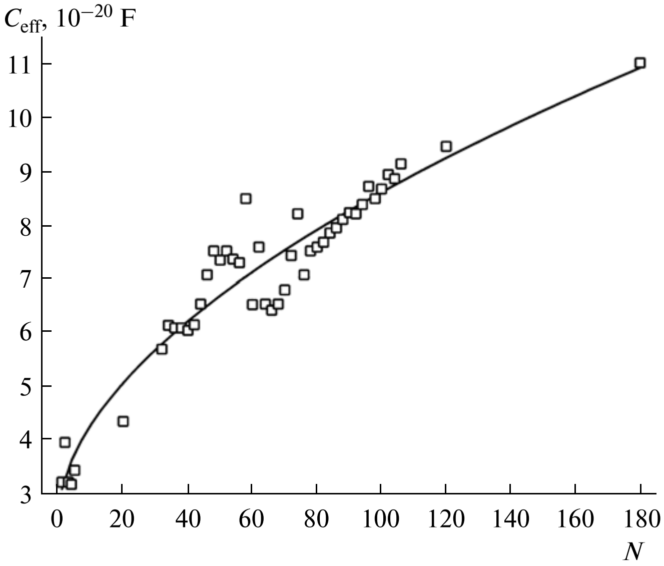

Fig. 7. Plot of effective self-capacitance C_{eff} of cyclic carbon compounds and fullerenes vs. number of atoms N: (squares) calculated capacitances and (solid line) the allometric regression of the calculated effective self-capacitances.

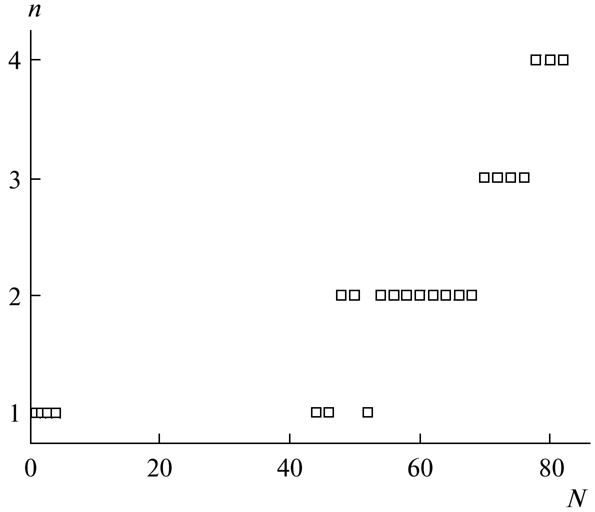

Fig. 8. Plot of the maximum number of additional electrons n_{max} that can be transferred to cyclic carbon compounds and fullerenes vs. number of atoms N.

The fullerene molecules are hollow, and their capacitances are determined by the surface properties. For comparison, we also calculate the effective self-capacitances of the spherical clusters consisting of closely packed atoms. The electronic properties of such clusters are determined by both surface and inner atoms. Figure 9 shows the plot of the effective self-capacitance of iron clusters. In the calculations, we employ the ionization potentials and electron affinities from [29, 30]. For the given effective capacitances of the iron clusters, we calculate the regression curve $y = ax^b$. The calculations yield the following regression coefficients and standard deviations:

$$\begin{aligned} a &= 2.3\times10^{-20}, \quad \Delta a = 1\times10^{-21}, \\ b &= 0.27, \qquad\quad \Delta b = 0.01. \end{aligned} \tag{31}$$

Note that b is close to 1/3, so that the effective capacitance of the iron clusters is proportional to the cubic root of the number of atoms:

$$C_{\text{eff}} \sim N^{1/3}. \tag{32}$$

The characteristic size of incomplete clusters is proportional to $N^{1/3}$, so that the effective capacitance can be estimated using the classical expression for the capacitance of a sphere with the corresponding radius.

With allowance for the interest in such structures due to the development and study of the nanoelectronic systems [31], we calculate the effective self-capacitances of linear chains and plane cyclic nanostructures that consist of various metal atoms. As distinct from the fullerenes, whose atoms form a closed surface, and from iron clusters, which represent 3D objects, the homoatomic chains consist of atoms that are located on a curved or straight line. Using this example, we demonstrate variations in the effective self-capacitance of the linear molecule with an increase in the number of atoms for several types of atoms. We do not consider the stability of such structures. The effective self-capacitances of the linear atomic chains and cycles were calculated with the aid of the GAMESS software package [21].

In the calculations of the molecular chains, we assume that each chain or cycle consists of identical atoms that are located on a straight line. The interatomic distance that corresponds to the minimum total energy is determined for each charge state. In the calculation of the effective capacitance of rings con-

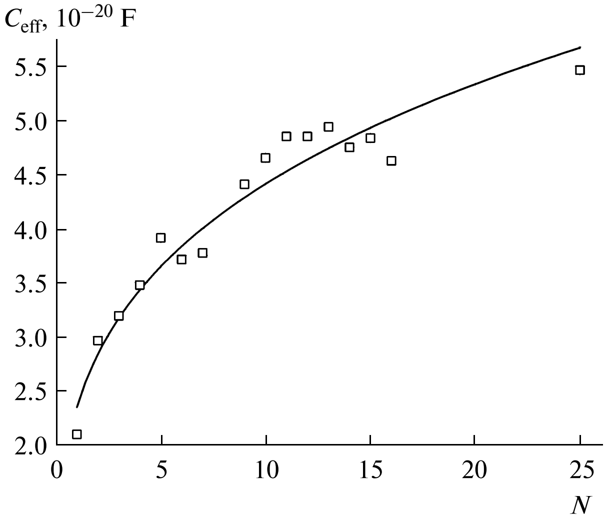

Fig. 9. Plot of effective self-capacitance C_{eff} of iron clusters vs. number of atoms N: (squares) calculated capacitances and (solid line) the regression of the calculated data using the function $y = ax^b$. For the calculations, we employ the experimental data from [29, 30].

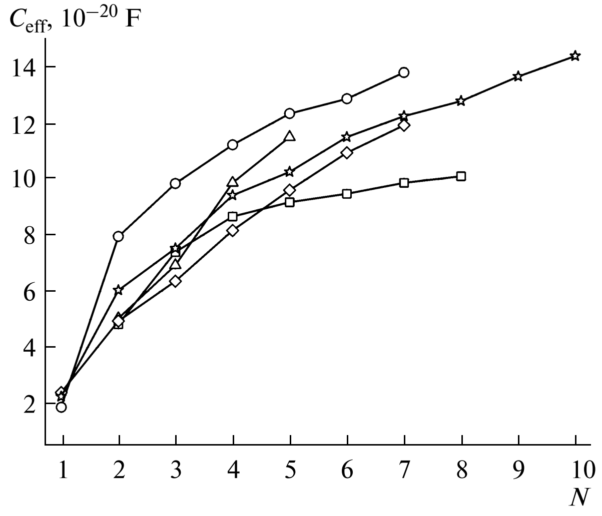

Fig. 10. Plots of effective self-capacitance C_{eff} of linear atomic chains vs. number of atoms N for (squares) Co, (triangles) Fe, (circles) Mg, (diamonds) Ni, and (stars) Si atoms. For clearness, we also plot the corresponding connecting lines.

sisting of identical atoms, we use the angles between the atomic valence bonds $\varphi = (N-2)\pi/N$. The distance between the neighboring atoms in the molecular ring that is constant for all of the pairs is determined from the calculations for each of the charge states. We choose the atoms that can form linear chains and cycles, based on the data from [32].

Figure 10 shows the calculated effective self-capacitances of the molecular chains with different numbers of different atoms. Starting from three atoms, the dependence of the effective capacitance on the number of atoms in the chain is close to linear in accordance with the classical theory, in which the capacitance of rod depends only on the length (see, for example, [33]). Using the linear regression for the dependence of the effective self-capacitance of the molecular chain with a number of atoms of greater than three on the length, we approximate the effective capacitance as

$$C_{\text{eff}}(N) = C_1 N + C_0. \quad (33)$$

Table 3 presents the coefficients of the linear regression of the effective capacitance for several linear molecular chains. The comparison of the data from Table 3 and Fig. 3 shows that coefficient C_0 in expression (33) is nonzero for the atoms under study and appears greater than the effective capacitances of single atoms in the chain. When the number of atoms in the chain increases by one, the effective capacitance increases by C_1, which is less than the effective self-capacitance of the added atom.

Thus, the effective self-capacitance of the molecule cannot be determined as a sum of the atomic capacitances. The total energy of the molecule depends on the chemical bonds, and the corresponding contribution must be taken into account in the calculations of the effective capacitance of molecule.

Figure 11 demonstrates the calculated effective self-capacitances of the homoatomic cycles and also illustrates the linear (starting from three atoms) dependence on the number of atoms. For macroscopic conductors, the capacitance is independent of the chemical composition (see, for example, [5]) and depends only on the size. Therefore, we can assume the validity of the corresponding linear dependence for the hypothetical macroscopic atomic cycles. The cycles under study consist of the atoms with identical properties, so that the edge effects are absent. Therefore, the dependence of the effective self-capacitance on the number of atoms in the ring is well approximated using a linear dependence staring from three atoms in the ring. As in the case of the linear chains, the dependence of the effective capacitance of the molecular cycle on the number of atoms can be approximated using linear function (33).

Table 3. Coefficients of the linear regression for effective self-capacitances C_{eff} of the Si_N, Ni_N, Mg_N, Fe_N, and Co_N molecular chains

Atom	C_1, 10^{-20} F	C_0, 10^{-20} F
Si	0.8	6.3
Ni	1.4	2.5
Mg	1.0	7.2
Fe	2.2	5.2
Co	0.3	7.6

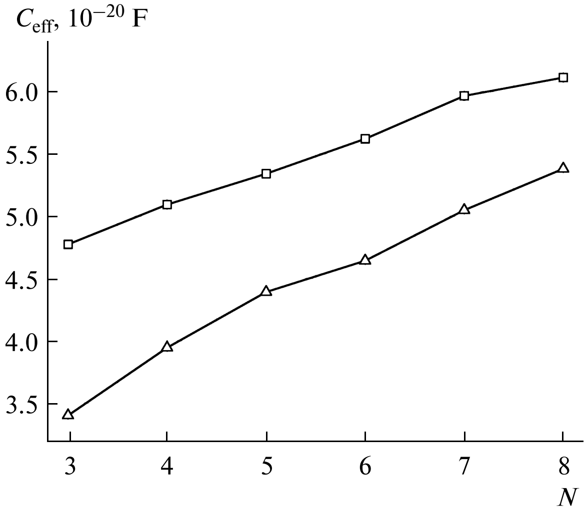

Fig. 11. Plots of effective self-capacitance C_{eff} of atomic rings vs. number of atoms N for (squares) Mg and (triangles) Ni atoms. For clearness, we also plot the corresponding connecting lines.

Table 4 presents the coefficients of the linear regression for the Mg_N and Ni_N. molecular cycles.

The results for the linear chains and the cycles of the Ni and Mg atoms show that the capacitances of chains are slightly greater than the capacitances of cycles in agreement with the classical predictions on the dependence of the capacitance on the topology of the object [33]. At the same numbers of atoms in the chain and ring, the capacitance of the chain consisting of identical atoms is always greater than the capacitance of the ring consisting of the same atoms in accordance with the classical theory from [5], which shows that the capacitance of a thin rod is greater than the capacitance of the ring with the same length.

Thus, we calculated the effective capacitances of the molecules of three types (chains, closely packed clusters, and the molecules in which the atoms form hollow nanospheres or nanoellipsoids). It is demonstrated that the effective self-capacitance of the nanoobject is always determined by the spatial configuration, size, and shape. The resulting relationship of the effective capacitance and the size of nanoobject is similar to the relationship of the size and capacitance of the conductor in classical electrostatics [5, 33]. This means that the above concept of the effective capacitance is in agreement with the notion of the classical capacitance.

Table 4. Coefficients of the linear regression for effective self-capacitances C_{eff} of the Mg_N and Ni_N atomic cycles

Atom	C_1, 10^{-20} F	C_0, 10^{-20} F
Mg	0.5	8.0
Ni	0.8	4.7

6. DISCUSSION

The proposed method for the determination of the effective self-capacitance can be used in the analysis of single molecules, atoms, nanoparticles, and any nanosized objects. The proposed definition remains valid for all possible types of nanoobjects with different chemical and physical properties (the objects can have different chemical compositions and can exhibit dielectric, conductor, or semiconductor properties). We considered the features of the effective capacitances of atoms and molecules.

Expressions (8) and (9) are valid for both single isolated atoms and molecules and isolated macroscopic objects. This circumstance allows the application of the method for the determination of the effective self-capacitance in the study of macroscopic objects. However, accurate measurements of the ionization potential and electron affinity are needed. For example, the self-capacitance of a conducting sphere with a diameter of 1 cm is about 1 pF, so that the difference between the ionization potential and electron affinity is about 10^{-7} eV in accordance with formula (18).

The application of the proposed method for the determination of the capacitance necessitates the measurement of the ionization potential and electron affinity with an accuracy of seven digits after decimal point, which is hardly possible in a real experiment. The accuracy of the modern experiments on the measurement of ionization potential and electron affinity is $\Delta E \sim 0.1$ eV [16]. The maximum size of the microscopic objects that allows the application of the proposed method for the calculation of the effective self-capacitance is $\Delta r \sim \dfrac{e^2}{4\pi\varepsilon_0 \Delta E} \approx 15$ nm. Such a size corresponds to the existing electronic nanodevices [34] and the mean sizes of nanoparticles that are widely used at present. The above value indicates that the proposed method is appropriate and helpful for the calculations of the self-capacitance of ultimately small elements in the absence of alternative approaches.

The calculations of the effective self-capacitances of various microscopic objects show that an increase in the number of atoms leads to an increase in the effective capacitance, which asymptotically tends to the value that is calculated using the classical electrostatic formulas. This means that the above notion of the effective self-capacitance of microscopic objects satisfies the Bohr complementarity principle.

The effective self-capacitance of a microscopic object is determined by its size and shape. The greater the difference between the shape of the object and the spherical shape, the greater the effective capacitance at the same number of atoms. For the spherical molecules, the proposed method yields the capacitance that coincides with result of the classical calculations (see, for example, formula (30)).

The isolated character of the molecular objects under study is a model simplification with respect to the real experimental scenario. On the one hand, the simplification makes it possible to unambiguously define the notion of the effective capacitance. On the other hand, an absolutely isolated molecular object is impossible in a real experiment. In the framework of the proposed approach to the determination of the effective self-capacitance, we stress the absence of the effective exchange of electrons between the molecular object and the surrounding medium, which leads to a relatively small variance of the total molecular charge. Such a condition is satisfied when the resistance of the tunneling barrier between the molecule and electron reservoir is significantly greater than the unit quantum resistance $R_{\text{tun}} \gg R_{\text{q}} = \pi\hbar/2e^2$ [6]. Thus, we obtain the necessary condition for the observation of single-electron effects. Hence, the above results can be used in the analysis of the parameters of such nanosystems in the absence of specific assumptions.

When the condition is not satisfied, molecular objects are involved in the electron and energy exchange with the environment. The objects cannot be classified as isolated in the above definition and the corresponding analysis must be based on the formalism of density matrix. In this case, we must take into account that the total charge of the microscopic object becomes a time-averaged quantity and, hence, can be noninteger in terms of electron charge e.. Charge energy $E_C(n)$ of such nanoobjects is the function of continuous index ξ of charge state.

The analysis of this function shows that the electric properties of molecular objects are closely related to the chemical properties. It is known from [7] that the first derivative of the total energy of a nonisolated microscopic object with respect to charge is equal to the chemical potential of this nanoobject. Owing to the fact that the charge energy is equal to the total energy accurate to a constant, the first derivative of the charge energy with respect to the number of charge state is also equal to the chemical potential:

$$\frac{\partial E_C(\xi)}{\partial \xi} = \frac{\delta E_C(\xi)}{\delta \rho(\xi)} = \mu = -\chi \approx -\frac{I_1 + A_1}{2}. \qquad (34)$$

For atoms and molecules, this derivative is also equal to the Mulliken electronegativity with opposite sign [7]. The second derivative of the charge energy of a nonisolated molecule or atom is equal to the doubled chemical hardness and is inversely proportional to the chemical softness of molecule [35]:

$$\frac{1}{2}\frac{\partial^2 E_C(\xi)}{\partial \xi^2} = 2\eta = \frac{1}{\sigma} \approx I_1 - A_1, \qquad (35)$$

where η is the chemical hardness of molecule and σ is the chemical softness.

Thus, the capacitance of a nonisolated molecule is determined as the quantity that is inversely proportional to the chemical hardness and is proportional to the chemical softness. The charging and discharging of nonisolated atoms and molecules are determined by the chemical potential and the chemical hardness. This circumstance makes it possible to reveal the close relationship of the chemical properties of microscopic objects that determine their behavior in chemical reactions and the effective electrostatic properties that determine their behavior and possible applications in nanoelectronic devices with atomic or molecular sizes.

In particular, the chemical hardness of atoms increases with increasing number of group and decreases with increasing number of period [35]. Therefore, the effective self-capacitance of atoms must decrease with increasing number of group and must increase with increasing number of period. Formula (18), which determines the effective self-capacitance of atoms is valid in the absence of additional conditions provided that the charge states of atom are chosen in such a way that the ionization of electrons occurs from a single electron shell of atom. The helium atom exhibits the maximum hardness [35], and, hence, its effective self-capacitance serves as the minimum possible self-capacitance of atomic objects ($C_{\text{He}} \approx 6.5 \times 10^{-21}$ F). The effective capacitances of most atoms range from 1×10^{-20} to 3×10^{-20} F. Single atoms of alkali metals exhibit the maximum effective self-capacitances. Such chemically soft atoms have the maximum self-capacitance and a relatively high chemical activity due to the flexibility of the outer part of electron cloud. The softness of the outer part of the electron cloud is manifested in the stronger delocalization of valence electrons and, hence, a greater volume of the electron cloud. This circumstance leads to an increase in the effective self-capacitance.

Chemically hard atoms (e.g., atoms of inert gases) exhibit the maximum hardness of the outer part of electron cloud and, hence, a relatively low chemical activity, a smaller size of atom, and a smaller self-capacitance.

The principle of maximum hardness is known in chemistry [35]. In accordance with this principle, the structure of the molecule corresponds to the maximum hardness. The state with the minimum self-capacitance is energetically advantageous. Apparently, such a tendency is related to the minimization of the surface energy, sizes, and effective self-capacitance. It is also known that the energy excitation of molecules leads to an increase in the softness and to an increase in the capacitance in accordance with the above method. The excitation can be interpreted as the excitation of any degree of freedom (electronic, vibrational, or rotational). Thus, we can expect that the effective self-capacitance of molecular objects that are involved in the energy exchange with the thermostat is greater than the capacitance of isolated objects. Hence, the effective self-capacitance of a single microscopic object given by formula (18) is the lower estimate for the self-capacitance of a nonisolated microscopic object.

The analysis of experimental works makes it possible to determine the regularity in accordance with which the self-capacitance of molecule that is found from the measured I–V characteristic (see, for example [9, 36]) appears greater than the capacitance of an isolated microscopic object given by expression (18). This fact proves that the molecules that exhibit variations in charge are not found in the ground state.

The analysis of molecules with different shapes indicates that the effective self-capacitances differently depend on the total number of atoms. For linear molecules, the effective self-capacitance is proportional to the number of atoms in the molecule. For the molecules whose atoms form a certain surface, the self-capacitance is proportional to $N^{1/2}$. For the molecules, whose atoms are closely packed in a certain volume, the capacitance is proportional to $N^{1/3}$. For all of the remaining scenarios, the dependence of the capacitance on the number of atoms is a combination of the above dependences. In general, we have

$$C \sim N^{1/m}, \tag{36}$$

where m is the dimension of molecule (nanoobject). The number of atoms in the nanoobject and their properties and topology unambiguously determine the properties of electron cloud with respect to the charging and discharging and, hence, the effective self-capacitance of the object.

The effective self-capacitance of a molecular object is related to the number of additional electrons that can be transferred to the neutral molecular object. The method for the estimation of the maximum possible additional electron charge also directly follows from the quadratic dependence of the total energy of molecular object on the charge.

Thus, we specify the notion of capacitance of atomic and molecular objects and study the properties of this parameter. However, we disregard several problems that necessitate additional study. In particular, we plan to analyze the stability of the spatial configuration with respect to charging and discharging of molecular objects. The notion of capacitance is physically meaningful only for stable spatial configurations of molecular objects in which the number of atoms remains constant and the configuration is reversible with respect to charging and discharging. The structural stability of a molecular object depends on its properties and on the method for charging and discharging.

In addition, we must thoroughly take into account the isomers of molecular objects, since the presence of isomers impedes the determination of the ground state. Local and global minima of the total energy correspond to different isomers. The isomerization can take place in the course of charging and discharging.

CONCLUSIONS

It is demonstrated that the notion of capacitance must be specified for atomic-size objects for the adequate analysis of charge transfer in nanoelectronic systems, and a method for such a specification is proposed. The analysis of experimental and calculated data for a large number of atomic and molecular objects yields the quadratic dependence of the total energy of a microscopic object on the number of electrons. Such a quadratic dependence makes it possible to determine the effective self-capacitance using the coefficient of the quadratic term in the above dependence of the total energy. We derive a formula for the calculation of the effective self-capacitance of a single isolated atomic-size nanoobject using two values of the ionization potential or the values of the ionization potential and electron affinity.

Based on the proposed method, we determine the effective self-capacitances of atoms. The method for the determination of the electric capacitance is valid for the recharging process that involves a single electron shell. In addition, the calculated effective self-capacitances prove the intuitive assumption that the capacitance is predominantly determined by the valence electrons. The results for atoms allow the analysis of the dependence of the effective self-capacitance on the size, shape, and topology of more complicated objects (molecules, nanoparticles, quantum dots, etc.).

The dependence of the effective self-capacitance on the shape of molecule is qualitatively similar to the classical dependence. For one group with respect to shape and topology, the capacitance is proportional to the size of the microscopic object at a relatively large number of atoms. The dependence of the self-capacitance on the number of atoms is determined by the dimension of the nanoobject. For 1D objects, the self-capacitance linearly increases with an increase in the number of atoms. For the 2D (3D) objects, the capacitance is proportional to the square (cubic) root of the number of atoms in the molecule.

The proposed method for the determination of the self-capacitance of nanoobjects and the results of calculations make it possible to consider such objects as conventional elements in the course of designing and analysis of working parameters of nanoelectronic devices. Such an approach allows the prediction and study of the circuit parameters of molecular nanoelectronic units with the aid of the conventional methods of microelectronics in the absence of specific quantum techniques.

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