THE STUDY OF SILVER NANOPARTICLES IN BASIS OF SLATER FUNCTIONS

Abstract. The electronic structure of the silver nanoparticles were investigated by semi-empirical Wolfsberg – Helmholz method. This is a variant of the molecular orbitals method. Molecular orbitals are represented as a linear combination of valence atomic orbitals of the atoms of the nanoparticle. As the atomic orbitals used 5s-, $5p_y$-, $5p_z$- and $5p_x$- Slater atomic orbitals of silver atoms. The exponential parameters of Slater functions were calculated and the analytic expression of the basis functions were defined. The numerical values of the unknown coefficients of the linear combination were calculated by solution of equations of molecular orbitals method. Calculations were carried out the authors' own computer program. The orbital energies, potential ionization, the total electronic energy and effective charge of atoms of silver nanoparticles were calculated. The results indicate that the silver nanoparticle are soft, electrophile and stabile semi-conductive material.
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1. The used method

The silver nanoparticles have a wide range of applications due to their properties. These nanoparticles are used in the preparation of different transmitters, in electronics, for diagnostics of various diseases in medicine, in the chemical processes as a catalysts and its application fields are expanding[1]. The study of electronic structure of the nanoparticles by quantum mechanics methods has a great importance [2, 3]. It is obvious that the structure and properties of nanoparticles is determined by the sizes and the number of atoms in nanoparticles. The size of nanoparticles which is consists of the same N atoms is given at the following formula [4].

$$D = \sqrt[3]{\frac{6MN}{\pi\rho N_A}} \qquad (1)$$

Where N - number of atoms, M - molar mass, ρ - material density and N_A–Avagadro number. The calculated size of silver nanoparticles, which consist of N=16 atoms by the formula (1) is obtained $D \approx 0{,}8$ nm. The theoritical visual model of nanoparticles Ag_{16} was constracted and the cartesian coordinaties of atoms were calculated in molecular coordinate system(Fig. 1).

In this work the electronic structure of the Ag_{16} silver nanoparticles were investigated by semi-empirical Wolfsberg - Helmholz (WH) method. It is known that the WH method is a simple semi- empirical variant of the molecular orbital(MO) method[5- 10]. In MO the state of the electron is described with one electron wave function so-called molecular orbital. Molecular orbitals are represented as a linear combination of valence atomic orbital of the atoms of the nanoparticles. Molecular orbitals U_i are multicenter functions. Thus, the distances of electron from a variety nucleus of atoms included into their expression. There are various ways to construct molecular orbitals. One of them is MO LCAO approximation. In this approximation the molecular orbitals are written as linear combinations of valence atomic orbitals of atoms:

$$U_i = \sum_{q=1}^{m} C_{qi}\chi_q \qquad (2)$$

where, C_{qi} - the unknown coefficients, χ_q - atom orbitals given as basis functions. In this work as basis functions the real Slater type atomic orbitals (STO's) were used. It is well-known that the calculation of multicenter matrix elements over exponential type orbitals (ETO's) has great importance for accurate evaluation of problems in quantum chemistry and physics[11-12]. Among the ETO's commonly used are the Gaussian type orbitals (GTO's) and STO's. The STO's represent the real situation for the electron density in valence region, but are not so good nearer to the nucleus. Many calculation over the years have been carried out with STO's[13-20]:

$$\chi_q \equiv \chi_{nlm}(\xi,\vec{r}) = \frac{(2\xi)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} r^{n-1} e^{-\xi r} S_{lm}(\theta,\varphi) \qquad (3)$$

where $S_{lm}(\theta,\varphi)$ - are real spherical harmonical functions [21]. The quantity ξ was calculated by formula given in[22].

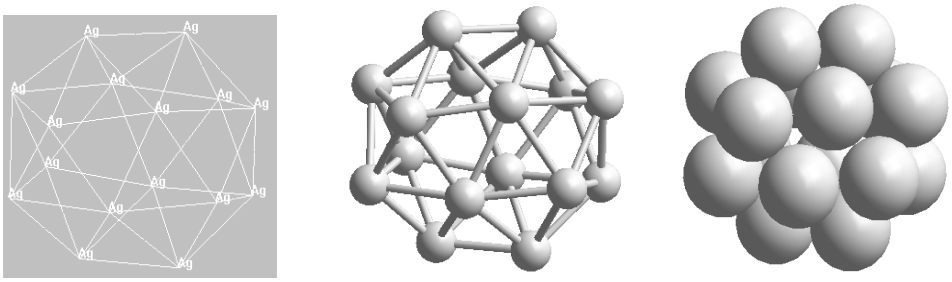

Fig 1. Theoritical visual model of silver nanoparticle

Usually in quantum mechanics calculations of electronic structure molecules satisfied considering only the atomic orbitals of valence electrons. For the creation of molecular orbitals of silver nanoparticles are taken 4 valence atomic orbitals 5s, $5p_y$, $5p_z$, $5p_x$ from each silver atoms. Thus 64 Slater's atomic orbitals were used. The analytic expressions of atomic orbitals are considered as follow:

$$\chi_{5s}(1{,}992739,\, r) = \frac{0{,}5269031}{\sqrt{\pi}} \cdot r^4 e^{-1{,}992739 r} \qquad (4)$$

$$\chi_{5p_x}(2{,}065968,\, r) = \frac{1{,}112997}{\sqrt{\pi}} \cdot r^4 e^{-2{,}065968 r} \sin\theta\cos\varphi \qquad (5)$$

$$\chi_{5p_y}(2{,}065968,\, r) = \frac{1{,}112997}{\sqrt{\pi}} \cdot r^4 e^{-2{,}065968 r} \sin\theta\sin\varphi \qquad (6)$$

$$\chi_{5p_z}(2{,}065968,\, r) = \frac{1{,}112997}{\sqrt{\pi}} \cdot r^4 e^{-2{,}065968 r} \cos\theta \qquad (7)$$

In the expressions of (4) – (7) r, θ, φ are spherical coordinates of electron. Based on the formula (2) 64 molecular orbital are established. The nanoparticle which was created from 16 silver atoms has $16*1=16$ valence electrons. They fill 8 low energetic levels. The unknown coefficients C_{qi} are found by solving the following system of equations[9]:

$$\sum_q (H_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0 \qquad (8)$$

There the following definitions are introduced:

$$H_{pq} = \int \chi_p^* \hat{H}_{ef} \chi_q dV \qquad (9)$$

$$S_{pq} = \int \chi_p^* \chi_q dV \qquad (10)$$

S_{pq} - are the overlap integrals between atomic orbitals χ_p and χ_q. $\hat{H}_{ef}$ is effective Hamilton operator for the one electron independently moving from other electrons in some effective field in molecule:

$$\hat{H}_{ef} = -\frac{1}{2}\nabla^2 + U(r) \qquad (11)$$

The quantity Hpq are matrix elements of effective Hamiltonian (11), for one electron moving in a molecule in some effective field independent from other Thus, for solution of system of equations(8), i.e. for determinations of the orbitals energies ε_i and corresponding sets of coefficients Cqi, one must know numerical Hpq and Spq values. However, Hpq values can not be calculated exactly because the explicit expression for the operator is unknown. So need to estimate them by varios ways, one of which based quantium chemical semi-empirical VH method. Accoding VH method each diagonal matrix elements Hpq are guessed equal to potential of ionization accoding valence state of the given atoms.The non-diagonal elements are defined by a ratio[6, 7]:

$$H_{pq} = 0.5 \cdot K \cdot S_{pq}(H_{pp} + H_{qq}) \qquad (12)$$

where the meaning of coeficient K is established theoretical from the condition of minimum of energy or from comparision with experimental data. As seen from (8) and (12) expression for the implementation quantum mechanical calculating by VH method it is important to know the value of overlap integrals in molecular coordination system[23]. In this work for the calculation of overlap integrals in basis of STO's the expressions from [24-28] were used. On the basis of these expressions for the calculating overlap integrals the quantum numbers n, ℓ, m, ξ - exponential parameters of atomic orbitals and the cartesian coordinates of atoms should be included. The calcultions indicate that analitical expressions and the created computer program for overlap integral are usable for any of quantum numbers n, ℓ, m. In order to calculate of H_{pq} matrix elements we use the following value of potential ionization of 5s and 5p valences state of silver atoms:

$(5s \mid Ag \mid 5s)$ = -0.789736 *a.u.*

$(5p \mid Ag \mid 5p)$ = -0.278332 *a.u.*

By knowing the value of H_{pq} and S_{pq} matrix elements and solving the system equations (11) we can find the value of ε_i orbital energies, $E = \sum_i \varepsilon_i$ total electronic energy, Ip potential ionization and C_{qi} coefficients in the VH approach. The numerical values of coefficients C_{qi} allow one to determine the effective charge q_a (in a.u.) of an atom A in the molecule according to the MO LCAO method by the formula [28].

$$q_A = n_A^o - \sum_i n_i \sum_{q \in A} |C_{qi}|^2 \qquad (12)$$

where n_A^o is the positive charge of the nuclear core of atom *A* (for the silver atoms n_A^o=1), n_i is the number of electrons in the i-th molecular orbitals. Summation for i is performed over the occupied molecular orbitals. We designed software for computations and determined the numerical values of Cqi, orbital energies ε_i, total energy E, potential ionization Ip and effective charge of atoms in VH approach.

2. The computer calculations for silver Ag_{16} nanoparticles by the Wolfsberg-Helmholz method

Total electronic energy E = -15.027638 a.u.
Potential ionization I_p = 19.771964 eV
Orbital energies (a.u.)

-1.170832	-1.083916	-1.066290	-1.014616	-0.837913	-0.831932	-0.781719	-0.726601
-0.684174	-0.557607	-0.541771	-0.493868	-0.490898	-0.483505	-0.461802	-0.395196
-0.361529	-0.341670	-0.338956	-0.338876	-0.327527	-0.317396	-0.316707	-0.312671
-0.312071	-0.306468	-0.303170	-0.294944	-0.281399	-0.281077	-0.272556	-0.268143
-0.255869	-0.244131	-0.214240	-0.204089	-0.137771	-0.127481	-0.073974	-0.070470
-0.064365	0.002556	0.005128	0.058071	0.060850	0.067135	0.185937	0.190002
0.337688	0.381342	0.462554	0.536640	0.614872	0.627916	0.640551	0.752829
0.868786	0.971381	1.008168	1.097059	1.144841	1.261422	1.311763	1.379747

EFFECTIVE CHARGES OF ATOMS AND COORDINATES

N0	Z Atom	Charge	Coordinates (a.u.)		
			x	y	z
1	47	0.257275	-5.03929687	-2.098277136	-2.31674846
2	47	0.257295	2.705200717	5.273547414	-0.180223252
3	47	0.257286	5.637206455	1.525236358	1.028937388
4	47	0.387377	2.580667716	1.011740873	-3.033484071
5	47	0.262163	4.730458807	-3.028967623	-0.790397164
6	47	0.280563	4.183666335	-2.054019733	4.15955342
7	47	0.387397	1.118094702	2.002600264	3.409842076
8	47	0.262116	-2.124922285	5.152529305	1.055620331
9	47	0.280535	-0.680717416	4.908508873	-3.803207622
10	47	0.387392	-3.602329655	0.378247732	1.940352661
11	47	0.262127	-0.723179579	-2.423045597	5.077885093
12	47	0.280534	1.53649913	-5.728612544	1.960251485
13	47	0.387382	-0.096300482	-3.392645561	-2.31674846
14	47	0.262172	-1.882432532	0.299653991	-5.343051569

15	47	0.280542	-5.03929687	2.873953328	-2.31674846
16	47	0.257269	-3.303337069	-4.700449944	1.468166606

3. Interpretation of results for silver Ag_{16} nanoparticles

Starting from the lowest energy level the 16 valence electrons of Ag_{16} nanoparticles are placed in levels two by two. The energy of the highest level which occupied by electrons, equal to the value of potential ionization with negative sign. $I_p = -\varepsilon_8 =$ -19.7719938 eV. The value of band gap can be calculated as the difference the energy lowest unoccupied molecular orbital $\varepsilon_{LUMO} = \varepsilon_9 =$ -18.61748619eV and the energy of the highest occupied molecular orbitals $\varepsilon_{HUMO} = \varepsilon_8$. $\varepsilon_{LUMO} - \varepsilon_{HUMO} =$ 1.154508 eV. It indicates that Ag_{16} nanoparticles are semi-conductors. Strength can be calculated as $\eta = \frac{1}{2}(\varepsilon_{LUMO} - \varepsilon_{HUMO})$ = 0.577254 eV. Thus, $\eta < 1eV$ and Ag_{16} nanoparticles are considered soft material. The energy of the lowest unoccupied molecular orbital is negative sign Ag_{16} nanoparticles are electrophilic. The stability of Ag_{16} nanoparticles can be expressed by the formula $\Delta E(Ag_{16}) = E_{Ag_{16}} - 8 \cdot E_{Ag_2}$. Here, $\Delta E(Ag_{16})$ is the parameter which identified the stability of Ag_{16} nanoparticles. If the $\Delta E(Ag_{16}) > 0$ material is not stable, but if $\Delta E(Ag_{16}) < 0$ material is considered stable. $E_{Ag_{16}}$ - is total energy of Ag_{16} nanoparticles, E_{Ag_2} - is total energy of Ag_2 molecules. Due to $E_{Ag_{16}} =$ -15.027638 a.u., $E_{Ag_2} =$ -1.833982 a.u. and $\Delta E(Ag_{16}) =$ -0.355782 a.u. $\Delta E(Ag_{16}) < 0$ Ag_{16} nanoparticles are stabile.

4. Conclusion

The electronic structure of the silver nanoparticles were investigated by semi-empirical Wolfsberg – Helmholz (VH) method in basis of Slater functions. The computer calculations were carried out by scientists of department of Chemical Physics of Nanomaterials of Baku State University through a software operating system Delphi Studio system in the Windows. The orbital energies, ionization potential, the total electronic energy and effective charge of atoms of silver nanoparticles were calculated. The results of calculations show that silver nanoparticle are soft, electrophile and stabile semi-conductive material.

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