THE STUDY OF SILVER NANOPARTICLES IN BASIS OF SLATER FUNCTIONS

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Abstract. One of the variant of the molecular orbitals method - the semi-empirical Wolfsberg – Helmholz method was used in order to investigate the properties of the silver nanoparticles. For construction of molecular orbitals of Ag_{16} are used 5s-, $5p_y$-, $5p_z$-, and $5p_x$- valence Slater atomic orbitals of silver atoms.The analytic expression of the basis Slater functions were defined. The orbital energies, ionization potential, the total electronic energy and effective charge of atoms of silver nanoparticles were calculated by solution of equations of molecular orbitals method. The results indicate that the Ag_{16} nanoparticles are soft, electrophile and stabile semi-conductive material.
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1. Introduction

The silver nanoparticles have wide range of applications such as 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 size dependent structural and energetic properties of nanoparticles are determined by the number of atoms in the nanoparticles . The shape of Ag_{16} nanoparticles is considered as a sphere and the size of nanoparticles can be calculated by the following formula given in Ref.[4].

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

The calculated size of Ag_{16}, by the formula (1) is obtained $D \approx 0{,}8$ nm. The visual model of nanoparticles Ag_{16} was established and the cartesian coordinaties of atoms were calculated in molecular coordinate system(Fig. 1).

2. Methodology

The semi-empirical Wolfsberg – Helmholz(WH) method was used in order to investigate the properties of the silver nanoparticles. The WH method is a simple semi- empirical variant of the molecular orbital(MO) method [2, 5- 10]. In MO the state of the electron is described with one electron wave function so-called molecular orbital. Molecular orbitals can be represented as linear combinations of atomic orbitals of atoms of nanoparticles:

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

where, - C_{qi} the unknown coefficients, χ_q - valence atomic orbitals of silver atoms. We used the real Slater type atomic orbitals (STO's) as basis functions. In the quantum-mechanical investigation of the properties of molecules and nanoparticles the exponential type orbitals (ETO's) has great importance [11-12]. Gaussian type orbitals (GTO's) and STO's are the most commonly used ETO's. It is reasonable to use STO's in valence electronic approximation. The STO's have been used in many calculations over the years.[13-20]:

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

The quantity ξ was calculated by formula (10) given in Ref. [21]. $S_{lm}(\theta,\varphi)$ - are real spherical harmonical functions given in Ref. [22].

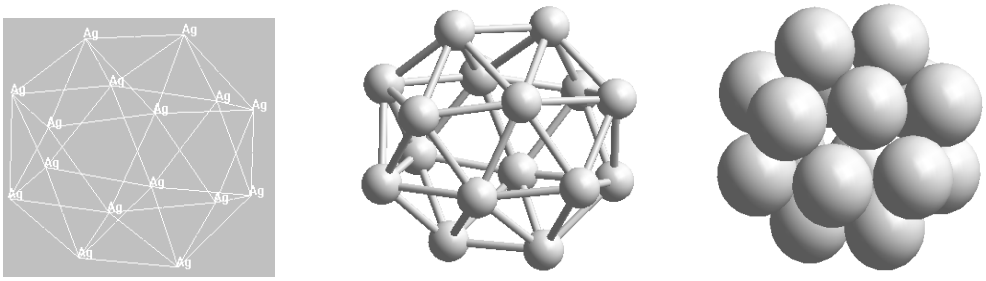

Fig 1. The theoretical visual model of silver nanoparticle

For the creation of molecular orbitals of Ag_{16} nanoparticles are taken 4 valence atomic orbitals 5s, $5p_y$, $5p_z$, $5p_x$ from each silver atoms. The analytic expressions of these atomic orbitals are considered as following:

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

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

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

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

Ag_{16} has 16*1=16 valence electrons. They are situated in eight low energetic levels. The quantities C_{qi} are found by solving the following system of equations given in Ref.[9]:

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

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

are the matrix elements of effective Hamiltonian

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

are the overlap integrals.

Thus, in order to solve the system of equations(8) one must know numerical H_{pq} and S_{pq} values[2, 3]. As the expression for the Hamiltonian is unknown, it is not possible to calculate the values H_{pq} precisely. So need to estimate them by several ways, one of which based quantum chemical semi-empirical WH method. According WH method each diagonal

matrix elements are guessed equal to ionization potential of valence state of the given atoms[2, 3]. The non-diagonal elements are calculated by the following formula given in Refs.[6, 7]:

$$H_{pq} = 0.5 \cdot K \cdot S_{pq}(H_{pp} + H_{qq}) \qquad (11)$$

As can be seen overlap integrals have great importance in the calculation by WH method. In order to calculate the overlap integrals, the analytical expressions given in Refs. [23- 28] can be used. To calculate the overlap integrals by these formulas the quantum numbers of atomic orbitals n, ℓ, m, ξ - exponential parameters and the cartesian coordinates of atoms should be included. The calculations indicate that analytical expressions and the created computer program for overlap integral are usable for any of quantum numbers n, ℓ, m. In order to calculate H_{pq} matrix elements we use the following values of ionization potential 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 solving the system equations (8) the values of orbital energies ε_i, total electronic energy $E = 2\sum_i \varepsilon_i$, ionization potential I_p and coefficients C_{qi} in the WH approach could be found. The effective charge (in a.u.) of an atom A in the nanoparticle can be calculated by the formula given in Refs. [2,3,28].

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

here n_A^o=1 for the Ag atoms.

3. Results and Discussions

Total electronic energy E = -15.027638 a.u.
Ionization potential I_p = 19.771994 eV

The values of orbital energies ε_i (a.u.)			
i = 1, 2, ..., 16	i = 17, 18, ..., 32	i = 33, 34, ... , 48	i = 49, 50, ... , 64
-1.170832	-0.361529	-0.255869	0.337688
-1.083916	-0.341670	-0.244131	0.381342
-1.066290	-0.338956	-0.214240	0.462554
-1.014616	-0.338876	-0.204089	0.536640
-0.837913	-0.327527	-0.137771	0.614872
-0.831932	-0.317396	-0.127481	0.627916
-0.781719	-0.316707	-0.073974	0.640551
-0.726601	-0.312671	-0.070470	0.752829
-0.684174	-0.312071	-0.064365	0.868786
-0.557607	-0.306468	0.002556	0.971381
-0.541771	-0.303170	0.005128	1.008168
-0.493868	-0.294944	0.058071	1.097059
-0.490898	-0.281399	0.060850	1.144841
-0.483505	-0.281077	0.067135	1.261422
-0.461802	-0.272556	0.185937	1.311763
-0.395196	-0.268143	0.190002	1.379747

Effective charges of atoms and coordinates

N	Effective charge of atom	Coordinates (a.u.)		
		X	Y	Z
1	0.257275	-5.03929687	-2.098277136	-2.31674846
2	0.257295	2.705200717	5.273547414	-0.180223252
3	0.257286	5.637206455	1.525236358	1.028937388
4	0.387377	2.580667716	1.011740873	-3.033484071
5	0.262163	4.730458807	-3.028967623	-0.790397164
6	0.280563	4.183666335	-2.054019733	4.15955342
7	0.387397	1.118094702	2.002600264	3.409842076
8	0.262116	-2.124922285	5.152529305	1.055620331
9	0.280535	-0.680717416	4.908508873	-3.803207622
10	0.387392	-3.602329655	0.378247732	1.940352661
11	0.262127	-0.723179579	-2.423045597	5.077885093
12	0.280534	1.53649913	-5.728612544	1.960251485
13	0.387382	-0.096300482	-3.392645561	-2.31674846
14	0.262172	-1.882432532	0.299653991	-5.343051569
15	0.280542	-5.03929687	2.873953328	-2.31674846
16	0.257269	-3.303337069	-4.700449944	1.468166606

The 16 valence electrons of Ag_{16} nanoparticles are placed in the first eight energetic levels two by two. The ionization potential is equal to ε_8 with negative sign. $I_p = -\varepsilon_8 = 19.7719938$ eV. The value of band gap can be calculated as $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$. Here, $\varepsilon_{LUMO} = \varepsilon_9 = -18.61748619$eV, is the energy of the lowest unoccupied molecular orbital and the $\varepsilon_{HOMO} = \varepsilon_8$ is the energy of the highest occupied molecular orbitals. So $E_g = 1.154508$ eV. Strength of the material is calculated as $\eta = \frac{1}{2}\left(\varepsilon_{LUMO} - \varepsilon_{HOMO}\right) = 0.577254$ eV. As can be seen, Ag_{16} nanoparticles are soft, semi-conductive material. ε_{LUMO} has negative sign, therefore, Ag_{16} are electrophilic. The stability of Ag_{16} nanoparticles can be expressed by the formula $\Delta E(Ag_{16}) = E_{Ag_{16}} - 8 \cdot E_{Ag_2}$. When the material is not stable $\Delta E(Ag_{16}) > 0$, but when material is stable $\Delta E(Ag_{16}) < 0$. $E_{Ag_{16}} = -15.027638$ a.u. is total energy of $E_{Ag_2} = -1.833982$ a.u is total energy of Ag_2 molecules. $\Delta E(Ag_{16}) < 0$ Ag_{16} nanoparticles are stable.

The accuracy of the results came from the paper has been checked by the test calculations of the Ag_2 molecule using the other methods. Comparison the results of different methods for Ag2 is given in the following table.

N	**Object**	Methods	Number of electrons using in calculations	ε_{HOMO}	ε_{LUMO}	I_p **(eV)**	E_g **(eV)**
1	Ag_2	WH (STO's)	2	-24.952815	-16.769817	24.9528	8.182998
2	Ag_2	Ab Initio (GTO's)	94	-4.425674	4.172199	4.4257	8.597873
3	Ag_2	Extended Hukkel (GTO's)	22	-9.114572	-6.630959	9.1146	2.483613

As seen from tha table there are differences in the calculations. These differences occur because of the type, and number of the basic functions, and the variety of the electrons which were used in the calculations.

4. Conclusion

The semi-empirical WH method was used in order to investigate the properties of the silver nanoparticles. STO's are used as atomic orbitals. The results of the calculations indicate that STO's are useful in investigation of properties of nanoparticles in valence electronic approximation. The computer calculations were carried out by authors' own computer program in Delphi Studio system under the operating system 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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