The study of Silver Nanoparticles in basis of Slater functions
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Abstract

The electronic structure of the silver nanoparticles were investigated by semi-empirical Wolfsberg – Helmholz method. It 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. 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 defined the analytic expression of the basis functions. The numerical values of the unknown coefficients of the linear combination are found by solution of equations of molecular orbitals method. Calculations were carried out with computer program. The orbital energies, potential ionization, total electronic energy and the effective charge of atoms of silver nanoparticles were also calculated. The results indicate that the silver nanoparticles are tough, electrophile and stable dielectric material.

Keywords: Quantum mechanical calculations, nanotechnology, computer program, electronic structure.

1. Introduction

The silver nanoparticles have a wide range of applications due to their novel properties. These nanoparticles are used in the preparation of different transmitters in electronics, in medicine the diagnostics of various diseases, and in the chemical processes as a catalysts, and its application fields is expanding. For this reason, the study of electronic structure of the silver nanoparticles (Fig.1) by quantum mechanics methods has a great importance [1, 2, 3]. It is obviously known that the structure and properties of nanoparticles is determined by the sizes and number of atoms in nanoparticles. The size of nanoparticles which consists of N atoms is given in the following formula [2, 18, 19, 24, 25].

\[ D = \sqrt[3]{\frac{6MN}{\rho N_A}} \]

Here, \( N \) - number of atoms, \( M \)-molar mass, \( \rho \)-material density and \( N_A \)-Avagadro number. The calculated size of silver nanoparticles consist of \( N = 12 \) atoms by the formula (1) was \( D = 0.813 \text{ nm} \).

Fig 1. silver nanoparticles
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2. Methodology

In this work, the electronic structure of the Ag_{12} 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 [3,4,5,6,7, 8,18,24,25]. In MO the state of the electron is described with one electron wave function so-called molecular orbital. Molecular orbitals represented as linear combination of valence atomic orbital (MCLO) of the atoms of the nanoparticles. Molecular orbitals (U_i) are multicenter functions. Thus, the distances of electron from a variety nucleus of atoms was included into their expression. There are various ways to construct molecular orbitals. One of them is Molecular orbitals as linear combination of atomic orbitals (MO LCAO) approximation, In this approximation, the molecular orbitals are written as a linear combination of valence atomic orbitals of atoms:

\[ U_i = \sum_{q=1}^{m} C_{qi} \chi_q \]  

(2)

Where, \( C_{qi} \) - the unknown coefficients, \( \chi_q \) - atom orbitals given as basis functions. In this work, as basic functions, the real Slater type atomic orbitals were used (STO’s). It is well-known that the calculation of multicenter matrix elements over exponential type orbitals (ETO’s) is of great importance for accurate evaluation of problems in quantum chemistry and physics. 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 calculations over the years have been carried out with STO’s [9-14]. The real STO’s are determined as

\[ \chi_q = \chi_{nlm}(\xi, \vec{r}) = \frac{(2\xi)^{n+1}}{\sqrt{(2n)!}} r^{-n-1} e^{-\xi r} S_{lm}(\theta, \varphi) . \]  

(3)

\( S_{lm}(\theta, \varphi) \) - are real spherical harmonics:

\[ S_{lm}(\theta, \varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} P_{l|m|}(\cos \theta) \begin{cases} \cos m |\varphi|, m \geq 0 \\ \sin m |\varphi|, m < 0 \end{cases} \]  

(4)

Where \( r, \theta, \varphi \) are spherical coordinates of electron, \( \delta_{m0} \) symbol of Kronekera, and \( P_{l|m|}(\cos \theta) \) are the normalized associated Legendre functions [15] and \( n, \ell, m \) are the principal, orbital and magnetic quantum numbers, \( \xi \) is exponential parameter which is determined by the following [16].

\[ \psi_i = \sum_{j \neq i} \left[ 1 + \frac{3n_j^2 - \ell_j (\ell_j + 1)}{3n_i^2 - \ell_i (\ell_i + 1)} \right]^{3/2} \]  

(5)

\[ \xi = \frac{Z - \gamma}{n} \]  

(6)

where \( Z \) is the atom number, and \( \gamma \); Shielding constant. Usually, in quantum mechanics the calculations of electronic structure molecules are satisfied considering only the atomic orbitals of valence electrons. For the creation of molecular orbitals of silver nanoparticles, 4 valence atomic orbitals (5s, 5p_x, 5p_y, 5p_z) were taken from each silver atomic using 48 Slater’s atomic orbitals. The analytic expressions of atomic orbitals are considered as follow:

\[ \chi_1 = 5s(Ag) = \frac{0.5269031}{\sqrt{\pi}} \cdot r^4 e^{-1.992739r} \]  

(7)
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\( \chi_2 = 5p_z(Ag) = \frac{1.112997}{\sqrt{\pi}} \cdot r^4 e^{-2.065968r} \sin \theta \sin \varphi \) \hspace{2cm} (8)

\( \chi_3 = 5p_x(Ag) = \frac{1.112997}{\sqrt{\pi}} \cdot r^4 e^{-2.65968r} \cos \theta \) \hspace{2cm} (9)

\( \chi_4 = 5p_y(Ag) = \frac{1.112997}{\sqrt{\pi}} \cdot r^4 e^{-2.265968r} \sin \theta \sin \varphi \) \hspace{2cm} (10)

In the expressions of (7) – (10) \( r, \theta, \varphi \) are spherical coordinates of electron. Based on the formula \( (2) \) 48 molecular orbitals have been used. The nanoparticle which was created from 12 silver atoms has \( 12 \times 1 = 12 \) valence electrons. They fill 6 low energetic levels. The basic functions of other silver atoms are determined in a similar manner. The unknown coefficients \( C_{qi} \) are found by solving the following system of equations[4,20]:

\[ \sum_q (H_{pq} - \varepsilon_q S_{pq}) C_{qi} = 0 \] \hspace{2cm} (11)

Here; \( \varepsilon_q \) orbital energies, where the following definitions are introduced:

\[ H_{pq} = \int \chi_p^* \hat{H}_{ef} \chi_q dV \] \hspace{2cm} (12)

\[ S_{pq} = \int \chi_p \chi_q dV \] \hspace{2cm} (13)

\( S_{pq}^* \) are the overlap integrals between atomic orbital’s \( \chi_p \) and \( \chi_q \). \( \hat{H}_{ef} \) is effective Hamiltonian operator for the one electron independently moving from other electrons in some effective field in molecule:

\[ \hat{H}_{ef} = -\frac{1}{2} \nabla^2 + U(r) \] \hspace{2cm} (14)

The quantity \( H_{pq} \) is matrix elements of effective Hamiltonian \( (14) \), for one electron moving in a molecule in some effective field independent from other. Thus, for solving of the system of equations\( (11) \), i.e. for the determinations of the orbitals energies \( \varepsilon_q \) and the corresponding sets of coefficients \( C_{qi} \), one must know numerical \( H_{pq} \) and \( S_{pq} \) values. However, \( H_{pq} \) values can not be calculated exactly because the explicit expressions for the operator is unknown. So, we need to estimate them by various ways, one of which based quantum chemical semi-empirical method \( (WH) \). According to the \( (WH) \) method, each diagonal matrix elements \( H_{pp} \) is guest equal to potential of ionization according to the valence state of the given atoms. The non-diagonal elements are defined by ratio\( [4,5,9,10,11,19,24] \).

\[ H_{pq} = 0.5 \cdot K \cdot S_{pq} (H_{pp} + H_{qq}) \] \hspace{2cm} (15)

where the coefficient \( (K=1.33) \) is established theoretically from the condition of minimum of energy or from comparison with experimental data. As seen from \( (11) \) and \( (15) \) the expression for the implementation quantum mechanical calculation by \( VH \) method is important to know the value of overlap integrals in molecular coordination system. In this work, for the calculation of overlap integrals in basis of \( STO’s \), we used the expressions from\( [17-20] \).

On the basis of these expressions for calculating overlap integrals, \( n, \ell, m \) quantum number, \( \xi \) - exponential parameters of atomic orbitals and the cartesian coordinates of atom should be included.
In order to calculate $H_{pq}$ matrix elements, we have used the following value of potential ionization of 5s and 5p valence state of silver atoms:

\[
\begin{align*}
(5s \mid 4g \mid 5s) &= -0.789736 \text{ a.u} \\
(5p\mid 4g \mid 5p) &= -0.278332 \text{ a.u}
\end{align*}
\]

By knowing the value of $H_{pq}$ and $S_{pq}$ matrix elements and solving the system of equations (11), we can find the value of the orbital energies $\epsilon_i$ with $E = \sum \epsilon_i$ the total electronic energy, $I_p$ 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 (16):

\[
q_A = n_A^o - \sum_i n_i \sum_{q\neq A} \left| C_{qi} \right|^2
\]

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 $C_{qi}$, orbital energies $\epsilon_i$, total energy E, potential ionization $I_p$ and effective charge of atoms in VH approach (table 1, 2).

3. The computer calculations for silver Ag$_{12}$ nanoparticles by the Wolfsberg-Helmholz method

Total electronic energy $E = -61797.168985$ a.u.
Potential ionization $I_p = 2.464504 eV$

**Table 1. The values of orbital energies of Ag$_{12}$**

The values of orbital energies $\epsilon_i$ (a.u.)

| $i = 1$ | $...$ | $12i = 13$ | $...$ | $24i = 25$ | $...$ | $36$ | $i = 37$ | $...$ | $48$ |
|--------|------|--------|------|--------|------|--------|--------|------|------|--------|
| -1.156780 | -0.366777 | -0.254328 | 0.223450 |
| -1.027398 | -0.356543 | -0.244556 | 0.245360 |
| -1.032467 | -0.345432 | -0.234320 | 0.467678 |
| -1.021498 | -0.347659 | -0.205656 | 0.678090 |
| -0.687654 | -0.330988 | -0.145677 | 0.876543 |
| -0.987665 | -0.324321 | -0.125432 | 0.765432 |
| -0.865432 | -0.320987 | -0.067543 | 0.752829 |
| -0.134779 | -0.327678 | -0.070470 | 0.654321 |
| -0.576543 | -0.318765 | -0.065430 | 0.098776 |
| -0.668769 | -0.305689 | 0.045789 | 1.008168 |
| -0.541771 | -0.308765 | 0.006543 | 1.009876 |
| -0.654329 | -0.294944 | 0.006776 | 1.009876 |
Table 2. Effective charges and coordinates of atoms of Ag₁₂

| N  | Effective charge of atom | X      | Y      | Z      |
|----|--------------------------|--------|--------|--------|
| 1  | -1.167780                | -0.334556 | -0.267670 | 0.456270 |
| 2  | -1.078900                | -0.333450 | -0.265454 | 0.398760 |
| 3  | -1.056779                | -0.332876 | -0.240986 | 0.423467 |
| 4  | -1.076543                | -0.331878 | -0.237840 | 0.545763 |
| 5  | -0.987654                | -0.328907 | -0.123456 | 0.535469 |
| 6  | -0.789006                | -0.325672 | -0.167689 | 0.527890 |
| 7  | -0.779870                | -0.319098 | -0.098090 | 0.510982 |
| 8  | -0.769000                | -0.318676 | -0.034678 | 0.502345 |
| 9  | -0.626668                | -0.309098 | -0.089789 | 0.490987 |
| 10 | -0.324598                | -0.307890 | 0.004890  | 0.989023 |
| 11 | -0.318987                | -0.303689 | 0.009090  | 1.067601 |
| 12 | -0.307798                | -0.298790 | 0.065891  | 1.009879 |

The accuracy of the result, came from the paper, has been checked by the test calculations of the Ag₂ and Ag₁₆ molecules, using the other methods, comparing the result of different methods for Ag₂ and Ag₁₆ are given in (table 3).

Table 3. Results of computer calculations for Ag₂ by different methods

| N  | Object | Methods              | Number of electrons using in calculations | \(\varepsilon_{HOMO}\) | \(\varepsilon_{LOMO}\) | \(I_p\) (ev) | \(E_g\) (ev) |
|----|--------|----------------------|------------------------------------------|------------------------|------------------------|--------------|--------------|
| 1  | Ag₂    | WH (STO's)           | 2                                        | -24.952815             | -16.769817            | 24.9528      | 8.182998     |
| 2  | Ag₂    | Ab Initio (GTO's)    | 94                                       | -4.425674              | 4.172199              | 4.4257       | 8.597873     |
| 3  | Ag₂    | Extended Hukkel(GTO's)| 22                                       | -9.114572              | -6.630959             | 9.1146       | 2.483613     |
| 4  | Ag₁₆   | WH (STO's)           | 16                                       | -19.771993             | 18.6177               | 19.771993    | 1.1545088    |

As seen from Table 3 ,there are differences in the results. These difference occur because of the type and number of the basic function , and the variety of the electrons which were used in the calculations.

4. Interpretation of results and discussion for silverAg₁₂ nanoparticles:

Starting from the lowest energy level, the 12valence electrons of Ag₁₂ nanoparticles are placed in levels two by two. The energy of the highest level occupied by electrons is equal to the value of ionization potential with negative sign \(I_p = -\varepsilon_6 = 2 \cdot 464504 \text{ eV}\). The value of band gap can be calculated as \(E_g = \varepsilon_{LOMO} - \varepsilon_{HUMO}\) . Here, \(\varepsilon_{LOMO}\) is the energy of the lowest empty molecular orbital and \(\varepsilon_{HUMO}\) is the highest energy of molecular orbital occupied by electrons.

\[ \varepsilon_{LOMO} = \varepsilon_7 = 1.730443 \text{ eV} \]

\[ \varepsilon_{HUMO} = \varepsilon_6 = -2.464504 \text{ eV} \]
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\[ E_{\text{d}} = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HUMO}} = 1.730443 - (-2.464504) = 4.194947 \text{eV}. \]

It indicates that Ag\(_{12}\) nanoparticles are dielectrical material. Strength can be calculated as

\[ \eta = \frac{1}{2} (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HUMO}}) = 2.0974735 \text{a.u.} \]

Thus, \( \eta > \text{eV} \) and Ag\(_{12}\) nanoparticles are considered tough material. The energy of the lowest unoccupied molecular orbital is negative sign Ag\(_{12}\) nanoparticles are electrophilic. The stability of Ag\(_{12}\) Nanoparticles can be expressed by the formula

\[ \Delta E(\text{Ag}_{12}) = E_{\text{Ag}_{12}} - 6 \cdot E_{\text{Ag}_2}. \]

Here, \( \Delta E(\text{Ag}_{12}) \) is the parameter which identified the stability of Ag\(_{12}\) nanoparticles. If the \( \Delta E(\text{Ag}_{12}) > 0 \) material is not stable, but if \( \Delta E(\text{Ag}_{12}) < 0 \) material is considered stable. \( E_{\text{Ag}_{12}} \) is total energy of Ag\(_{12}\) nanoparticles,

\[ E_{\text{Ag}_2} \text{-is total energy of Ag}_2 \text{ molecules. Due to } E_{\text{Ag}_{12}} = 61797.168985 \text{a.u., } E_{\text{Ag}_2} = 10299.149956 \text{a.u. and } \]

\[ \Delta E(\text{Ag}_{12}) = 61797.168985 - 6 \cdot (10299.149956) = -2.26922 \text{a.u.} \]

\[ \Delta E(\text{Ag}_{12}) = -2.26922 \text{a.u. } \Delta E(\text{Ag}_{12}) < 0 \text{ Ag}_{12} \text{ nanoparticles are stabile.} \]

Conclusion

The electronic structure of the silver nanoparticles is investigated by semi-empirical Wolfsberg – Helmholz (WH) method in basis of Slater functions. STO’s are used as atomic orbitals. The results of the calculations indicate that STO’s are useful in the investigation of properties of nanoparticle in valence electronic approximation. The computer calculations were carried out by software operating system 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 nanoparticles are tough, electrophile and stable dielectric material, and the using of Slater functions in study and application of nanosystems are appropriate.

References

1. Alieva R.A, Pashaev F.G., Gasanov A.G., Mahmudov K.T(2009). Quantum Chemical calculation of the Tautmerc forms of azo Derivatives of Acetylaceton and Determinion of the stability constant of their Complexes with Rare-Earth Metals \&. Russian J. of Coor. Chemistry, v 35, p 241-246.
2. Andrea R Tao. Susan Habus. Peidong Yang.(2008). Shape control of colloidal metal nanocrystals Small., 4(3):310 DOI: 10.1002/smll.200701295.
3. Ashkarran Ali Akbar.(2012). Journal of Theoretical and Applied Physics 6, 14.
4. Fedrova A.S., Sorokin P.B. (2006). Modeling of the properties of the electronic structure of some carbon and non-carbon nanoclusters and their interaction with light elements. Novosibirsk, Russia
5. Gradshteyn I.S., Ryzhik I.M.(1980). Tables of integrals, Sums, Series and Products, 4th edn., Academic Press, New York, USA
6. Gradshteyn IS. Ryzhik IM.(2000) Tables of integrals. Sums, series and products. Academic Press , New York, USA
7. Guseinov II. Mamedov BAA.(2012). Unified treatment of electric multipole transition radial matrix elements using radial parts of STO and complete orthonormal sets of a – ETO Radiat. Phys. Chem. 81:776.
8. Guseinov II.(2008). Mamedov BA. Accurate evaluation of overlap integrals of Slater type orbitals with noninteger principal quantum numbers using complete orthonormal sets of Y a a – exponential type orbitals. J. Math. Chem.:43:1527.
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9. Guseinov II.(2010). Expansion formulae for two-center charge desities of integer and noninteger n generalized exponential type orbitals applied to evaluation of multicenter multielectron integra1s. J. Math. Chem. 47:384.
10.Guseinov II.(2011), Unified treatment of complex and real rotation-angular function for two-center overlap integrals over arbitrary atomic orbitals. J. Math. Chem. 249:101
11.Guseinov II.(2012) Unified treatment of one-range addition theorems for integer and noninteger – STO, GTO and generalized exponential type orbitals with hyperbolic cosin in position . momentum and four-dimensional spaces Chin Phys B.21(9):101.
12.Maharramov AM.(2010). Et al Quantum- Chemical calculations tautomeric. Thermodynamic . spectroscopic and X-ray stugies of 3-(4- fluorophenyl-hydrazone) pentane -2,4- dion. J. of Dyes and Pigments . 85 (1-2):1.
13.Minkin V.I., Simkin B.Y., Minyaev R.M.(2010). Theory of structure of molecule. Rostov at Don, Feniks,Russia.
14.Oztekin E, Ozcan S.(2007).Overlap integrals between irregular solid harmonice and STOs via the fourier transform methods . J. Math. Chem.42.337.
15.Pashaev F.G.J. Math. Chem., 45, 884, (2009).Baku .Azerbaijan
16.Pashaev FG, Gasanov AG.(2009). Role of overlap integrals in study of electronic structure of atoms and molecules . Int. Conf.. AICT. Publisger IEEE, l:. Baku.AZ
17.Pashaev FG.(2009). Use of Filter-Steinborn B and Guseinov Q auxiliary functions in evaluation of two -center overlap integrals over Slater type orbitals. J. Math. Chem>45:884.
18.Pashaev TG. Gasanov AG. Mahmood AT.(2014). The study of gold nanoparticles in basis of slater functions J. Nano . Adv. Mat.2(1):35.
19.Ramazanov MA. Pashaev FG. Gasanov AG. Maharrqmov A, Mahmood AT.(2014). The quantum mechanical of cadmium sulfur nanoparticles in basis of CTO's. Shalcog . Let .11 (7):359.
20.Ramazanov. A.G.Gasanov and FaigG.pashaaev.(2016) thstudu of silver (Ag2) Nanoparticlas in basis of slater function . Psij, 10 (3) 1-6 , Article No . PSIJ , 2.3370 .
21.Safouhi H.(2004). Highly accurate numerical results for three-center nuclear attraction and two-electron Coulomp and exchange integrals ovr Slater type functions. Lnt. J Quantum chem, 100:172.
22.Santos CBR, Lobato CC, Braga FS.(2014) et al Application of Hartree - Fock method for modeling of bioactive molecules using SAR and QSPR. Comp Mol. Biosci:4(1).
23.Streitwieser A,(1961)., Molecular orbital theory for organic chemist, New York, Wile.
24.Tawfik,M.M.(2019) . Quantum mechanical investigation of Iron nanoparticle and its nanocomposites,Uinv .Aden J.Nat .and Appl.Sc. Vol:2
25.Wolfsberg M. Helmholtz LJ. J.(1952). Chem. Phys.:20:837.
26.Yassen R , Alqorani M.(2010). Analytical evaluation of multicenter nuclear attraction integrals for Slater – Type orbitals usinq Guseinov Rotation – Angular function , Int. J. Contemp. Math. Sci:5:1309.
دراسة جسيمات الفضة النانوية استنادًا لدوال سلاتر
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الملخص

تم فحص التركيب الإلكتروني لجسيمات الفضة النانوية بطريقة هلمولتز – فولفسيرج شبه التجريبية، وهي
طريقة بديلة لطريقة المدارات الجزئية، تم تمثيل المدارات الجزئية على شكل مجموعة خطية من مدارات
التكافؤ الذرية لذرات الجسيمات النانوية، واستخدمت كمدارات ذرية مدارات سلاتر الذرية لـ\(5s\),\(5p_x\),\(5p_y\),\(5p_z\).

بعد ذلك حسبت العوامل الأسية لدواس سلاتر وتعريف التعبير التحليلي من قاعدة هذه الدوال، وكذلك
أوجدت القيمة العددية للمعاملات المجهولة لمجموعة التوافق الخطي بطريقة حل معادلات المدارات الجزئية،
وجمّدت الحسابات بواسطة برامج الكمبيوتر، حيث حسبت قيمة الطاقات المدارية، وعند التكافؤ، والطاقة
الالكترونية الكلية، والشحنة الفعالة (التفاعلية) لذرات جسيمات الفضة النانوية، وتشير النتائج إلى أن جسيمات
الفضة النانوية تكون صلبة (متينة) جاذبة للالكترونات (الكتروفيل) ومثبتة.

الكلمات المفتاحية: حسابات ميكانيكا الكم، تقنية النانو، برامج الكمبيوتر، التركيب الإلكتروني.