The study of Silver Nanoparticles in basis of Slater functions

Tawfik Mahmood Mohammed Ali
Physics Department, AL-Dalaa Faculty of Education, University of Aden
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Abstract

The electronic structure of the silver nanoparticles were investigated by semi-empirical Wolfsberg – Helmholz method. It is avariant 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 $5p_x$- Slateratomic 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 thestructure and properties of nanoparticles is determined by the sizes and number of atoms in nanoparticles. The size of nanoparticles which consists ofN atoms is given in the following formula [2, 18, 19,24,25].

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

Here, N - number of atoms, M-molar mass, ρ -material density and

N_A–Avaqadro number . The calculated size of silver nanoparticles consist of N = 12 atoms by the formula (1) was D = 0.813 nm.

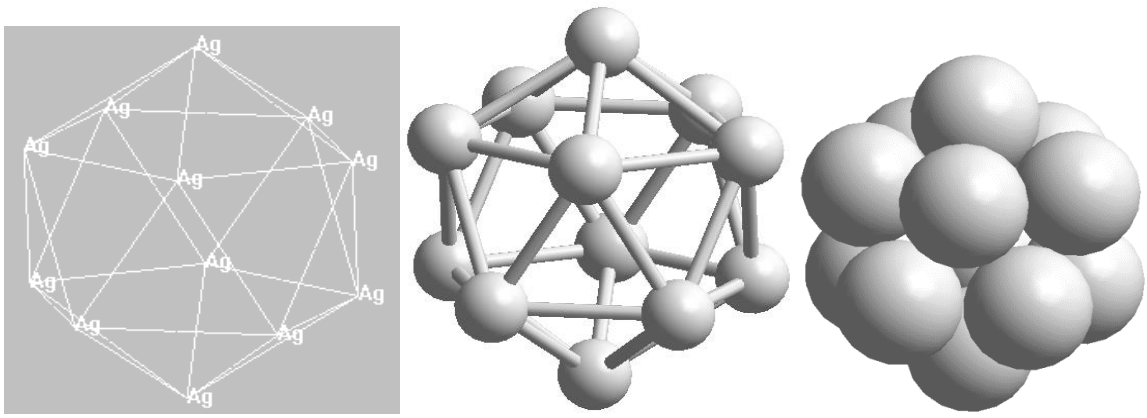

Fig 1. silver nanoparticles

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 ofthe molecularorbital (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 representedas as linear combinationof valence atomicorbital(MCLO) of the atomsof the nanoparticles. Molecular orbitals (U_i) are multicenter functions.Thus, the distances of electron from avariety nucleus of atoms was included into their expression.There are various ways to construct molecular orbitals. One of them isMolecular orbitals as aliner combination of atomic orbitals (MO LCAO) approximation, In this approximation, the molecular orbitals are written as a 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 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'scommonly 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

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

$S_{lm}(\theta,\varphi)$ - are real sphericalharmonics:

$$S_{\ell m}(\theta,\varphi) = \frac{1}{\sqrt{\pi(1+\delta_{m0})}} P_{\ell|m|}(\cos\theta)\begin{cases}\cos|m|\varphi, & m \geq 0\\ \sin|m|\varphi, & m < 0\end{cases} \qquad (4)$$

Where r,θ,φ are spherical coordinates of electron , δ_{m0} ;simbol of Kronekera, and $P_{\ell|m|}(\cos\theta)$ are the normalized associated Legendre functions[15] and $n,\ \ell,\ m$ are the principial, orbital and magnetic quantum numbers, ξ is exponential parameter which is determined by the following[16].

$$\gamma_i = \sum_{j\neq i}^{N} \left\{1+\left[\frac{3n_j^2-\ell_j(\ell_j+1)}{3n_i^2-\ell_i(\ell_i+1)}\right]^2\right\}^{-\frac{3}{2}} \qquad (5)$$

$$\xi = \frac{Z-\gamma}{n} \qquad (6)$$

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

$$\chi_1 = 5s(Ag) = \frac{0{,}5269031}{\sqrt{\pi}} \cdot r^4 e^{-1.992739r} \qquad (7)$$

$$\chi_2 = 5p_y(Ag) = \frac{1,112997}{\sqrt{\pi}} \cdot r^4 e^{-2.065968r} \sin\theta \ \sin\varphi \quad (8)$$

$$\chi_3 = 5p_z(Ag) = \frac{1,112997}{\sqrt{\pi}} \cdot r^4 e^{-2.65968r} \cos\theta \quad (9)$$

$$\chi_4 = 5p_x(Ag) = \frac{1,112997}{\sqrt{\pi}} \cdot r^4 e^{-2.265968r} \sin\theta \ \sin\varphi \quad (10)$$

In the expressions of (7) – (10) r, θ, φ 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 $12*1=12$ valence electrons.They fill 6 low energetic levels. The basic functions of other silver atoms are determined in a similar manner.The unknowncoefficients C_{qi} are found by solving the following system of equations[4,20]:

$$\sum_q (H_{pq} - \varepsilon_i S_{pq}) C_{qi} = 0 \quad (11)$$

Here; ε_i orbital energies,

where the following definitions are introduced:

$$H_{pq} = \int \chi_p^* \hat{H}_{ef} \chi_q dV \quad (12)$$

$$S_{pq} = \int \chi_p^* \chi_q dV \quad (13)$$

S_{pq} - are the overlap integrals between atomic orbital's 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:

$$\hat{H}_{ef} = -\frac{1}{2}\nabla^2 + U(r) \quad (14)$$

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 ε_i 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). Accoding to the method (WH),each diagonal matrix elements $H_{pq}$is guest equal to potential of ionization accoding to the valence state of the given atoms.The non-diagonal elements are defined byaratio[4,5,9,10,11,19,24].

$$H_{pq} = 0.5 \cdot K \cdot S_{pq}(H_{pp} + H_{qq}) \quad (15)$$

where the coeficient(K=1.33)is establishedt heoretically from the condition of minimum of energy or from comparision with experimental data. As seen from (11) and (15)the expression for the implementation quantum mechanicalcal culating by VH method is important to know the value of overlapintegrals 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, ℓ, m quantum number, ξ - exponential parametersof atomic orbitalsand the cartesian coordinates of atomsshould be included.

In order to calculate H_{pq} matrix elements,we have used the following value of potential ionizationof 5s and 5p valence state of silver atoms:

(5s |*Ag* | 5s) = -0.789736 a.u
(5p|*Ag* | 5p) = -0.278332 a.u

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 ε_i with $E = \sum_i \varepsilon_i$ the total electronic energy, $I_p$potential ionizationand 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 [19 -26]:

$$q_A = n_A^o - \sum_i n_i \sum_{q \in A} |C_{qi}|^2 \qquad (16)$$

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 I_p and effective charge of atoms in VH approach,(table1,2).

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

Total electronic energy E = -61797.168985a.u.
Potential ionizationI_p= 2.464504eV

Table 1. The values of orbital energies of *Ag_{12}*

The values of orbital energies ε_i (a.u.)			
i= 1 ,….12*i* =13…..24*i* = 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	

Table 2. Effective charges and coordinates of atoms of Ag_{12}

N	Effective charge of atom	Coordinates (a.u.)		
		X	Y	Z
1	-1.167780	-0.334556	-0.267670	0.456720
2	-1.078900	-0.333450	-0.265454	0.398760
3	-1.056779	-0.332876	-0.240987	0.423467
4	-1.076543	-0.331878	-0.237890	0.545763
5	-0.987654	-0.328907	-0.123456	0.534569
6	-0.789006	-0.325678	-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	0.004898	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 bythe test calculations of the Ag_2 and Ag_{16} molecules, using the other methods, comparing the result of different methods for Ag_2 and Ag_{16} are given in (table 3).

Table 3. Results of computer calculations for Ag_2 by different methods

N	Object	Methods	Number of electrons using in calculations	ε_{HOMO}	ε_{LOMO}	$I_P(ev)$	$E_g(ev)$
1	Ag_2	WH (STO's)	2	-24.952815	-16.769817	24.9528	8.182998
2	Ag_2	Ab lnitio (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
4	Ag_{16}	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 silverAg_{12}nanoparticles:

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

$\varepsilon_{LUMO} = \varepsilon_7$ =1.730443eV, $\varepsilon_{HUMO} = \varepsilon_6$ =-2.464504eV

$E_{g=}\varepsilon_{LUMO} - \varepsilon_{HUMO} = 1.730443\text{-}(\text{-}2.464504)=4.194947eV.$

It indicates that Ag_{12} nanoparticles are dielectrical material.Strength can be calculated as $\eta = \frac{1}{2}(\varepsilon_{LUMO} - \varepsilon_{HUMO}) =$ 2.0974735a.u. Thus, $\eta > 1eV$ and Ag_{12} nanoparticles are considered tougt 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 $\Delta E(Ag_{12}) = E_{Ag_{12}} - 6 \cdot E_{Ag_2}$. Here, $\Delta E(Ag_{12})$ is the parameter which identified the stability of Ag_{12} nanoparticles. If the $\Delta E(Ag_{12}) > 0$ material is not stable, but if $\Delta E(Ag_{12}) < 0$ material is considered stable. $E_{Ag_{12}}$ - is total energy of Ag_{12}nanoparticles,

E_{Ag_2} -is total energy of Ag_2 molecules. Due to $E_{Ag_{12}}$=-61797.168985.a.u., E_{Ag_2}=-10299.149956a.u.and $\Delta E(Ag_{12}) = E_{Ag_{12}} - 6 \cdot E_{Ag_2}$;

$\Delta E(Ag_{12}) = -61797.168985 - 6(-10299.14995) = -2.26922$ a.u.

$\Delta E(Ag_{12})$= -2.26922a.u. $\Delta E(Ag_{12}) < 0$ Ag_{12} nanoparticles are stabile.

Conclusion

The electronic structure of thesilver nanoparticles is investigated bysemi-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 systemunder the operating system Windows. The orbital energies, ionization potential, the total electronic energyand effective charge of atoms ofsilver nanoparticles were calculated. The results of calculations show that silver nanoparticleis tough, electrophile and stable dielectric material, and the using of Slater functions in study and application of nanosystems are appropriate.

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دراسة جسيمات الفضة النانوية استناداً لدوال سلاتر

توفيق محمود محمد علي
قسم الفيزياء، كلية التربية، جامعة عدن
DOI: https://doi.org/10.47372/uajnas.2020.n1.a25

الملخص

تم فحص التركيب الإلكتروني لجسيمات الفضة النانوية بطريقة هلمولتز – فولفسيرج شبه التجريبية، وهي طريقة بديلة لطريقة المدارات الجزيئية، تم تمثيل المدارات الجزيئية على شكل مجموعة خطية من مدارات التكافؤ الذرية لذرات الجسيمات النانوية، واستخدمت كمدارات ذرية مدارات سلات الذرية لذرات الفضة 5s-, $5P_x$, $5P_y$, $5P_z$.

بعد ذلك حُسبِت العوامل الأُسية لدوال سلاتر وتعريف التعبير التحليلي من قاعدة هذه الدوال، وكذلك أوجدت القيمة العددية للمعاملات المجهوله لمجموعة التوافق الخطي بطريقة حل معادلات المدارات الجزيئية، وأجريت الحسابات بواسطة برامج الكمبيوتر، حيث حُسبِت قيمة الطاقات المدارية، وجهد التاين، والطاقة الالكترونية الكلية، والشحنة الفعالة (التاثيرية) لذرات جسيمات الفضة النانوية، وتشير النتائج إلى أن جسيمات الفضة النانوية تكون صلبة (متينة) جاذبة للالكترونات (الكتروفيل) وعازلة كهربائياً ومستقرة.

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

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