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The Study of Gold Nanoparticles in basis of Slater Functions

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Abstract: The electronic structure of the gold 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 6s-, $6p_y$-, $6p_z$- and $6p_x$- Slater atomic orbitals of gold 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 own computer program. The orbital energies, potential ionization, the total electronic energy and effective charge of atoms of gold nanoparticles were calculated. The results indicate that the gold nanoparticles are soft, electrophile and conductive material.

Keywords: Quantum mechanical calculations, nanotechnology, computer modeling.

1. The used method

The gold nanoparticles have a wide range of applications due to their novel properties. These nanoparticles are using in the preparation of different transmitters, in electronics, in medicine the diagnostics of various diseases, in the chemical processes as a catalysts and its application fields is expanding . For this reason, the study of electronic structure of the gold nanoparticles (Fig.1) by quantum mechanics methods has a great importance (Ashkarran, 2012; Liu et al. 2007). It is obvious known 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 N atoms is given at the following formula (Liu et al. 2007).

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

Here, N - number of atoms, M- molar mass, ρ -material density and N_A –Avaqadro number . The calculated size of gold nanoparticles, consist of N = 16 atoms by the formula (1) is obtained D = 0.8 nm.

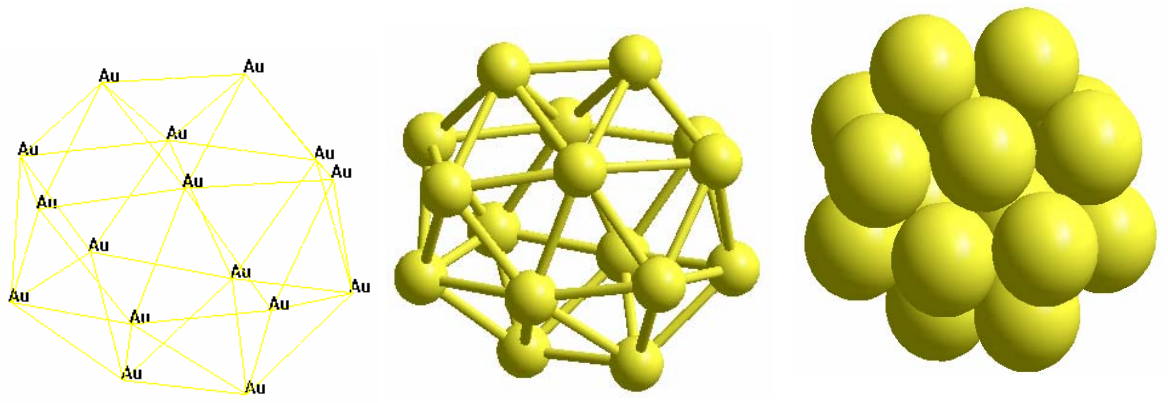

Fig 1. Gold nanoparticle

In this work the electronic structure of the Au_{16} gold 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 (Wolfsberg & Helmholz, 1952; Shembelov et al. 1980; Feodrov et al. 2006; Minkin et al. 2010; Streitwieser, 1961; Alieva et al. 2009). 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 variaus ways to construct molecular orbitals. One of them is MO LCAO approximation. In this approximation the molecular orbitals are written as a linear combinations of valence atomic orbitals of atoms:

$$U_i = \sum_{q=1}^{m} C_{qi}\chi_q \tag{2}$$

Where, C_{qi} - the unknown coefficients, χ_q - atom orbitals given as basis functions. In this work as basis functions were used the real Slater type atomic orbitals (STO's). It is well-known that the calculation of multicenter matrix elements over exponential type orbitals (ETO's) is the 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 calculation over the years have been carried out with STO's (Berlu & Safouhi, 2005; Safouhi, 2004; Berlu et al. 2004; Guseinov, 2004; Guseinov, 2005; Guseinov, 2009). The real STO's are determined as

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

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

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

Where $P_{\ell|m|}(\cos\theta)$ are the normalized associated Legendre functions (Gradshteyn & Ryzhik, 1980) and $n,\ \ell, m$ are the principial, orbital and magnetic quantum numbers, ξ is exponential parameter with determined by formulas (Besis & Besis, 1981).

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

$$\xi=\frac{Z-\gamma}{n} \tag{6}$$

there Z is atom number. 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 gold nanoparticles taken 4 valence atomic orbitals (6s, $6p_y$, $6p_z$, $6p_x$) from each gold atoms. Thus were used 64 Slater's atomic orbitals. The analytic expressions of atomic orbitals are considered as follow :

$$\chi_1=6s(Au)=\frac{1{,}027405}{\sqrt{\pi}}\cdot r^5e^{-2{,}599004r} \tag{7}$$

$$\chi_2=6p_y(Au)=\frac{1{,}316146}{\sqrt{\pi}}\cdot r^5e^{-2.481152r}\sin\theta\sin\varphi \tag{8}$$

$$\chi_3=6p_z(Au)=\frac{1{,}316146}{\sqrt{\pi}}\cdot r^5e^{-2.481152r}\cos\theta \tag{9}$$

$$\chi_4=6p_x(Au)=\frac{1{,}316146}{\sqrt{\pi}}\cdot r^5e^{-2.481152r}\sin\theta\cos\varphi \tag{10}$$

In the expressions of (7) – (10) r,θ,φ are spherical coordinates of electron. Based on the formula (2) had established 64 molecular orbital. The nanoparticle which was created from 16 gold atoms has $16*1=16$ valence electrons. They fill 8 low energetic levels. The basic functions of other gold atoms are determined in a similar manner. The unknown coefficients C_{qi} are found by solving the following system of equations[7]:

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

There the following definitions are introduced:

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

$$S_{pq}=\int\chi_p^*\chi_q dV \tag{13}$$

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:

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

The quantity Hpq are matrix elements of effective Hamiltonian (14), for one electron moving in a molecule in some effective field independent from other Thus, for solution of system of equations(11), 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 expressions for the operator is unknown. So need to estimate them by varios ways, one of which based quantium chemical semi-empirical method VH. Accoding method VH each diagonal matrix elements Hpq are guest equal to potential of ionization accoding valence state of the given atoms.The non-diagonal elements are defined by a ratio(Shembelov et al. 1980; Feodrov et al.2006).

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

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 (11) and (15) expression for the implementation quantum mechanical calculating by VH method it 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 were used the expressions from (Guseinov et al. 1989 ; Guseinov, 2003 ; Guseinov et al. 1998 ; Pashaev, 2009).

On the basis of these expressions for the calculating overlap integrals should be included the n, ℓ, m quantum number, ξ - exponential parameters of atomic orbitals and the cartesian coordinates of atoms. In order t calculate of H_{pq} matrix elements we use the following value of potential ionization of 6s valence state of gold atoms.

$(6s \mid Au \mid 6s)$ = -0.3389363 *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 (Dmitriev, 1986).

$$q_A = n_A^o - \sum_i n_i \sum_{q \in A} |C_{qi}|^2 \tag{13}$$

where n_A^o is the positive charge of the nuclear core of atom *A* (for the gold 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 gold AU_{16} nanoparticles by the wolfsberg-helmholz method

Total electronic energy E = -6.339366 a.u.

Potential ionization I_p = 3.703389914eV

Orbital energies (a.u.)

-0.684817	-0.661433	-0.623058	-0.598719	-0.169649	-0.158814	-0.137098	-0.136096
-0.118915	-0.027240	-0.024011	-0.019275	-0.016488	-0.012503	-0.010608	-0.000524
-0.000000	-0.000000	-0.000000	-0.000000	-0.000000	-0.000000	-0.000000	-0.000000
-0.000000	-0.000000	-0.000000	-0.000000	-0.000000	-0.000000	-0.000000	-0.000000
-0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
0.016042	1.204702	1.229904	1.285250	1.303929	1.349486	1.407488	1.970694
2.249531	2.896924	3.378143	3.463406	3.665532	3.846329	3.914490	3.988562

Table 1: EFFECTIVE CHARGES OF ATOMS AND COORDINATES

N0	Z Atom	Charge	Coordinates(a.u.)		
			x	y	z
1	79	-0.477725	0.7273814	0.14770909	2.65187515
2	79	-0.556951	-1.87186795	0.56232986	2.58630971
3	79	-0.609782	0.3630383	-2.26437264	1.37450644
4	79	-0.477706	-2.20357127	-1.40494744	0.86809597
5	79	-0.489172	2.67199854	-0.86560465	1.07587674
6	79	-0.537255	2.24897258	1.75132253	1.07268487

7	79	-0.342177	-0.36228144	2.40525927	1.39682705
8	79	0.431552	0.00377388	0.05200688	-0.05143089
9	79	-0.590981	0.87839365	2.64291629	-0.99603353
10	79	-0.342212	-2.49680715	1.27442059	0.09783097
11	79	-0.498185	2.38512292	0.43716801	-1.35228525
12	79	-0.489191	-0.80251563	-2.70621679	-1.03866935
13	79	-0.537262	-2.39001153	-0.70620755	-1.75069312
14	79	-0.349636	1.78344705	-2.18175034	-1.03139997
15	79	-0.590996	-1.14737978	1.56980459	-2.22882881
16	79	-0.498192	0.21230642	-0.71383772	-2.67466599

3. Interpretation of results for gold AU_{16} nanoparicles

Starting from the lowest energy level the 16 valence electrons of Au_{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. $I_p = -\varepsilon_8 = 3.703389914$eV. The value of band gap can be calculated as the difference the energy lowest unoccupied molecular orbital $\varepsilon_{LUMO} = \varepsilon_9 = -3.235867414$eV and the energy of the highest occupied molecular orbitals $\varepsilon_{HUMO} = \varepsilon_8$. $\varepsilon_{LUMO} - \varepsilon_{HUMO} = 0.4675225$eV. It indicate that Au_{16} nanoparticles are conductors. Strength can be calculated as $\eta = \frac{1}{2}(\varepsilon_{LUMO} - \varepsilon_{HUMO})$ = 0.23376125a.u. Thus, $\eta < 1eV$ and Au_{16} nanoparticles are considered soft material. The energy of the lowest unoccupied molecular orbital is negative sign Au_{16} nanoparticles are electrophilic. The stability of Au_{16} nanoparticles can be expressed by the formula $\Delta E(Au_{16}) = E_{Au_8} - 8 \cdot E_{A_2}$. Here, $\Delta E(Au_{16})$ is the parameter which identified the stability of Au_{16} nanoparticles. If the $\Delta E(Au_{16}) > 0$ material is not stable, but if $\Delta E(Au_{16}) < 0$ material is considered stable. $E_{Au_{16}}$ - is total energy of Au_{16} nanoparticles, E_{Au_2} - is total energy of Au_2 molecules. Due to $E_{Au_{16}}$ =-6.339366a.u., E_{Au_2} =-0.759462a.u. and $\Delta E(Au_{16})$ = -0.26367a.u. $\Delta E(Au_{16}) < 0$ Au_{16} nanoparticles are stabile.

4. Result

The electronic structure of the gold nanoparticles was 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 gold nanoparticles were calculated. The results of calculations show that gold nanoparticles are soft, electrophile and conductive material and the using of Slater functions in study and application of nanosystems are appropriate.

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