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THE QUANTUM MECHANICAL STUDY OF CADMIUM SULFUR NANOPARTICLES IN BASIS OF STO's

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The electronic structure of the cadmium sulfur 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-, $5p_x$-, $5p_y$- and $5p_z$ - Slater type atomic orbitals(STO's) of cadmium atoms and 3s-, $3p_x$-, $3p_y$- and $3p_z$- orbitals of sulfur atoms. The exponential parameters of STO's 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 its own computer program. The orbital energies, potential ionization, the total electronic energy and effective charge of atoms of cadmium sulfur nanoparticles were calculated. The results indicate that the cadmium sulfur nanoparticle are soft, electrophile and semi-conductive stable material.

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1. Introduction

The cadmium sulfur nanoparticles have a wide range of applications due to their novel properties. Cadmium sulfur is broadly used as a p-type semiconductor in electronics. They are valuable materials in preparing photoelements, sun batteries, photo and light diods. For this reason, they have attracted the attention of great number of experimental and theoretical groups. [1, 2, 3].

The properties of nanoparticles depend on their size and number of atoms. In the presented work considered the determination of number of atoms in the dependence of size of differently structured nanoparticles. In order to define the number of atoms in nanoparticles, which is composed with the same type of atoms, in [4], is given the following formula.

$$N = \frac{\pi \rho D^3 N_A}{6M} \tag{1}$$

N - number of atoms, ρ - dencity of material, N_A -Avogadro number, M - molar mass, D - is diametr of sphere that nanoparticle is settled. There are some other equations for determination the number of atoms and size of nanoparticles. But these equations include more complicated parts and it is difficult to calculate them. The presented work is devoted to calculation of number of atoms in nanoparticles with given size, but composed by different atoms. It is supposed that nanoparticle has the spheroidal shape.

Let's consider the determination of "n" in $(CdS)_n$ nanoparticle. For spheroidal CdS compound the size of its radius is $r_h = r_{cd} + r_s$ (Pic.1.). Where r_{cd} and r_s - are covalent radius of Cd and S atoms. The number of atoms in nanoparticle with R radius (Pic. 2.) can be calculated (R - the given radius):

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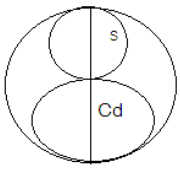
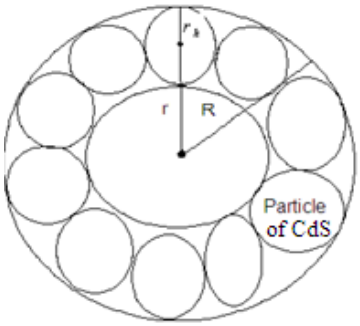
$$n = \frac{R^3 - r^3}{r_h^3} \tag{2}$$

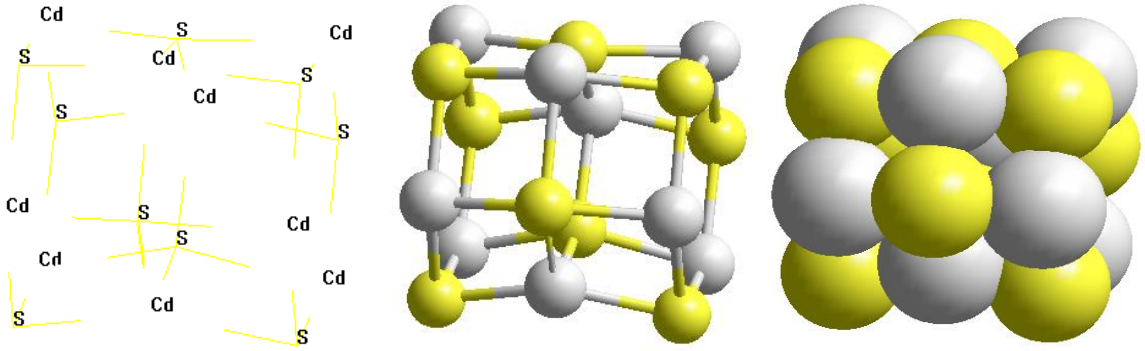
Where $r = R - 2r_h$, internal radius of nanoparticle (pic. 2.), r_h - radius of CdS (pic. 1.). When $R = 0{,}52\,nm$ then n=9 for $(CdS)_n$. The number of atoms is equal 18.



Pic 1.



Pic. 2



Pic 3. Cadmium sulfur $(CdS)_9$ nanoparticle

In this work the electronic structure of the $(CdS)_9$ 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- 9]. In MO the state of the electron is described with one electron wave function so-called molecular orbital. Molecular orbitals U_i are multicenter functions. Thus, the distances from electron to various nucleus of atoms are include 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 represented as a linear combinations of valence atomic orbitals of atoms of the nanoparticles.

$$U_i = \sum_{q=1}^{m} C_{qi}\chi_q \tag{3}$$

where, C_{qi} - the unknown coefficients, χ_q - atom orbitals given as basis functions. In this work the real Slater type atomic orbitals (STO's) were used as basis functions. 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[10-16]. The real STO's are determined as

$$\chi_q \equiv \chi_{nlm}(\xi,\vec{r}) = \frac{(2\xi)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} r^{n-1} e^{-\xi r} S_{lm}(\theta,\varphi)\,. \tag{4}$$

$S_{lm}(\theta,\varphi)$- are real spherical harmonics and $n,\ \ell,\ m$ are the principial, orbital and magnetic quantum numbers, ξ is exponential parameter with determined by formulas given in [17].

Usually in quantum mechanics calculations of electronic structure molecules satisfied with only considering the atomic orbitals of valence electrons. For the creation of molecular orbitals of $(CdS)_9$ nanoparticles are used 5s-, $5p_x$-, $5p_y$-, $5p_z$- STO's from each Cd atoms and 3s-, $3p_x$-, $3p_y$-, $3p_z$- STO's from each S atoms. Thus, 72 STO's were used. The analytic expressions of atomic orbitals are considered as follow :

$$\chi_{3s}(Cd)=\chi_{500}(1{,}87625,\vec{r})=\frac{1{,}90753193}{\sqrt{\pi}}r^2e^{-1{,}87625r} \tag{5}$$

$$\chi_{3p_x}(Cd)=\chi_{311}(2{,}02889,\vec{r})=\frac{4{,}344171}{\sqrt{\pi}}r^2e^{-2{,}02889r}\sin\theta\cos\phi \tag{6}$$

$$\chi_{3p_y}(Cd)=\chi_{31-1}(2{,}02889,\vec{r})=\frac{4{,}344171}{\sqrt{\pi}}r^2e^{-2{,}02889r}\sin\theta\sin\phi \tag{7}$$

$$\chi_{3p_z}(Cd)=\chi_{310}(2{,}02889,\vec{r})=\frac{4{,}344171}{\sqrt{\pi}}r^2e^{-2{,}02889r}\cos\theta \tag{8}$$

$$\chi_{5s}(S)=\chi_{500}(2{,}3581535,\vec{r})=\frac{1{,}33014767}{\sqrt{\pi}}r^4e^{-2{,}3581535r} \tag{9}$$

$$\chi_{5p_x}(S)=\chi_{511}(2{,}19816183,\vec{r})=\frac{1{,}56541501}{\sqrt{\pi}}r^4e^{-2{,}19816183r}\sin\theta\cos\varphi \tag{10}$$

$$\chi_{5p_y}(S)=\chi_{51-1}(2{,}19816183,\vec{r})=\frac{1{,}56541501}{\sqrt{\pi}}r^4e^{-2{,}19816183r}\sin\theta\sin\varphi \tag{11}$$

$$\chi_{5p_z}(S)=\chi_{510}(2{,}19816183,\vec{r})=\frac{1{,}56541501}{\sqrt{\pi}}r^4e^{-2{,}19816183r}\cos\theta \tag{12}$$

In the expressions of (5) – (12) r,θ,φ are spherical coordinates of electron. Based on the formula (2) 72 molecular orbital had been established. The nanoparticle $(CdS)_9$ has $9*2+9*6=72$ valence electrons. They fill 36 low energetic levels. The unknown coefficients C_{qi} are found by solving the following system of equations[8]:

$$\sum_q (H_{pq}-\varepsilon_i S_{pq})C_{qi}=0 \tag{13}$$

There the following definitions are introduced:

$$H_{pq}=\int \chi_p^*\hat{H}_{ef}\,\chi_q dV \tag{14}$$

$$S_{pq}=\int \chi_p^*\chi_q dV \tag{15}$$

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.

$$\hat{H}_{ef}=-\frac{1}{2}\nabla^2+U(r) \tag{16}$$

The quantity Hpq are matrix elements of effective Hamiltonian (16), for one electron moving in a molecule in some effective field independent from other electrons. Thus, for solution of system of equations(13), i.e. for determination 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 various ways, one of which based quantium chemical semi-empirical method VH. Accoding method VH each diagonal matrix elements Hpq are guessed equal to potential of ionization according valence state of the given atoms. The non-diagonal elements are defined by a ratio[6, 7].

$$H_{pq} = 0.5 \cdot K \cdot S_{pq}(H_{pp} + H_{qq}) \tag{17}$$

where the meaning of coeficient K can be calculated theoretical due to the condition of minimum of energy or comparision with experimental data. As seen from (13) and (17) 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 the expressions from [18-21]. were used in order to calculate of overlap integrals in basis of STO's.

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 to calculate of H_{pq} matrix elements, we use the following value of potential ionization of valence state of Cd and S atoms:

$$(5s \mid Cd \mid 5s) = \text{-0.621352092 a.u.}$$
$$(5p \mid Cd \mid 5p) = \text{-0.330410259 a.u.}$$
$$(3s \mid S \mid 3s) = \text{- 0.77871131 a.u.}$$
$$(3p \mid S \mid 3p) = \text{-0.35830275 a.u.}$$

By knowing the value of H_{pq} and S_{pq} matrix elements and solving the system equations (13) we can define 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 nanoparticles according to the MO LCAO method by the formula [22].

$$q_A = n_A^o - \sum_i n_i \sum_{q \in A} |C_{qi}|^2 \tag{18}$$

where n_A^o is the positive charge of the nuclear core of atom *A* (for the Cd atoms n_A^o=2, for the s atoms n_A^o=6), 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 $(CdS)_9$ nanoparticles by the Wolfsberg-Helmholz method

Total electronic energy E = -39.103686 a.u.
Potential ionization I_p = 9.858220 eV

Orbital energies (a.u.)

-0.921101	-0.879290	-0.868870	-0.849430	-0.813161	-0.812651	-0.797508
-0.766298	-0.752235	-0.630933	-0.608548	-0.607638	-0.585412	-0.575464
-0.534776	-0.519811	-0.500313	-0.442304	-0.430170	-0.426354	-0.424819
-0.411591	-0.410274	-0.408262	-0.405861	-0.398318	-0.393785	-0.390829
-0.385563	-0.377369	-0.376811	-0.375713	-0.374404	-0.370511	-0.363185
-0.362280	-0.358611	-0.354667	-0.351866	-0.343916	-0.341317	-0.333282
-0.322805	-0.284246	-0.267136	-0.262250	-0.251260	-0.242546	-0.242388
-0.226086	-0.216877	-0.204322	-0.203816	-0.175089	-0.169968	-0.162528
-0.155481	-0.152120	-0.151725	-0.138803	-0.131862	-0.115906	-0.110468
-0.093912	-0.082806	-0.040400	0.006568	0.013644	0.056849	0.071811
0.075005	0.135128					

EFFECTIVE CHARGES OF ATOMS AND COORDINATES

N0	Z Atom	Charge	Coordinates (a.u.)		
			x	y	z
1	48	-0.607926	-5.267462494	-2.494137122	-1.88973E-05
2	48	-0.366878	-0.757648197	-4.094849171	-1.88973E-05
3	48	-0.450846	3.654807371	-2.723946808	-1.88973E-05
4	48	-0.776372	2.739310287	1.851913443	-1.88973E-05
5	48	-0.978456	-1.090202333	4.585252194	-1.88973E-05
6	48	-0.596505	-5.267462494	2.338177963	-1.88973E-05
7	48	-0.596622	0.724974819	-4.555810249	4.541051482
8	48	-0.776375	4.810658815	-2.111202868	4.427554486
9	48	-0.978395	4.206758797	2.600472054	4.458546006
10	16	2.142611	0.168015617	5.082174773	4.460719192
11	16	1.718752	-3.533184549	2.135145707	4.417746803
12	16	2.020444	-3.501115884	-2.539717335	4.414156322
13	16	1.613004	-3.533260138	2.135183502	-4.417841289
14	16	1.642294	-3.5010025	-2.539755129	-4.414118527
15	16	2.550799	0.724993717	-4.555810249	-4.541013687
16	16	2.550808	4.810791096	-2.111146176	-4.427459999
17	16	1.613018	4.206815489	2.600434259	-4.45845152
18	16	1.642294	0.168015617	5.082174773	-4.460700295

3. Interpretation of results for $(CdS)_9$ nanoparticles

Starting from the lowest energy level the 72 valence electrons of $(CdS)_9$ 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. $I_p = -\varepsilon_{36} = 9.858220$ eV. The value of band gap can be calculated as the difference the energy of the lowest unoccupied molecular orbital $\varepsilon_{LUMO} = \varepsilon_{37} =$ -9.758379 eV and the energy of the highest occupied molecular orbital $\varepsilon_{HUMO} = \varepsilon_{36}$. $\varepsilon_{LUMO} - \varepsilon_{HUMO} = 0.099839$eV. This indicates that $(CdS)_9$ nanoparticles are semi-conductors. Strength can be calculated as $\eta = \frac{1}{2}\left(\varepsilon_{LUMO} - \varepsilon_{HUMO}\right)$ = 0.04991968 eV. Thus, $\eta < 1eV$ and $(CdS)_9$ nanoparticles are considered soft material. The energy of the lowest unoccupied molecular orbital is negative sign $(CdS)_9$ and this indicates that nanoparticles are electrophilics. The stability of $(CdS)_9$ nanoparticles can be expressed by the formula. $\Delta E((CdS)_9) = E_{(CdS)_9} - 9E_{CdS}$. Here, $\Delta E((CdS)_9)$ is the parameter which identified the

stability of $(CdS)_9$ nanoparticles. If the $\Delta E((CdS)_9) > 0$ material is not stable, but if $\Delta E((CdS)_9) < 0$ material is considered stable. $E_{(CdS)_9}$ - is total energy of $(CdS)_9$ nanoparticles, E_{CdS} - is total energy of CdS molecules. Due to $E_{(CdS)_9}$ = -39.103686 a.u., E_{CdS} = --4.272542 a.u. and $\Delta E((CdS)_9)$ = -0.650808 a.u. $\Delta E((CdS)_9) < 0$ then $(CdS)_9$ nanoparticles are stable.

4. Results

The electronic structure of the cadmium sulfur nanoparticles were investigated by semi-empirical VH method in basis STO's. The computer calculations were carried out by scientists of Department of Chemical Physics of Nanomaterials of Baku State University with its own computer program through a Windows OS prepared Delphi Studio. The orbital energies, potential ionization, the total electronic energy and effective charge of atoms of cadmium sulfur nanoparticles were calculated. The results of calculations show that, cadmium sulfur nanoparticles are soft, electrophile and semi-conductive stable material.

Reference

[1] P.P. Favero, etc. Brazilian Journal of Physics. **36**(3B), 1032(2006).
[2] A.M. Magerramov M.A.Ramazanov, F.V. Gadjiyeva Optoelectron. Adv. Mater. – Rapid Commun **2**(11), 743(2008).
[3] Xuewu Ge, Yonghong Ni, Zhicheng Zhang, Radiation Physics and Chemistry, **64**, 223(2002)
[4] X. Liu, M. Atwater, J. Wang, Q. Huo Colloids and Surfaces B: Biointerfaces, **58**(1), 3 (2007).
[5] M. Wolfsberg, L.J. Helmholz, J.Chem.Phyc., **20**, 837, (1952).
[6] G.A. Shembelov, etc. Quantum chemical methods of calculation of molecules, M., Chemstry, 1980.
[7] A.S. Feodrov, P.B. Sorokin and etc. Modeling of the properties of the electronic structure of some carbon and non-carbon nanoclusters and their interaction with light elements. Novosibirsk, 2006.
[8] A. Streitwieser, Molecular orbital theory for organic chemist, New York, Wiley, 1961.
[9] R.A Alieva, F.G. Pashaev, A.G. Gasanov, K.T. Mahmudov Russion J. of Coor. Chemistry, **35**, 241, (2009).
[10] L. Berlu, H. Safouhi J. Theor. Comp. Chem., **4**, 787, (2005).
[11] H. Safouhi Int. J. Quantum Chem., **100**, 172, (2004).
[12] L. Berlu, H. Safouhi, P. Haggan Int. J. Quantum Chem., **99**, 121, (2004).
[13] J.F. Rico, etc. J. Comput. Chem. **25,** 1987(2004)
[14] I.I. Guseinov, J. Mol. Str., (Theochem) **757**, 165, (2005).
[15] I.I. Guseinov, J. Chem. Phys., **180**, 9454, (2004).
[16] I.I. Guseinov, J. Mol. Model., **9**, 190, (2009). .
[17] N Besis, G. Besis J. Chem, Phys., **47**(6), 3228, (1981).
[18] I.I. Guseinov, F.G. Pashaev and etc. J. Str. Chem., **30**, 183, (1989).
[19] I.I. Guseinov, Int. J. Quantum Chem., **91**, 62, (2003).
[20] I.I. Guseinov and etc., Int. J. Quantum Chem., **61**, 199, (1998).
[21] F.G. Pashaev, J. Math. Chem., **45**, 884 (2009).
[22] I.S. Dmitriev, Electron by eyes of chemists, L., Chem., 1986.