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The Computer Program for the Study of Nanoparticles in Basis of Slater Atomic Orbitals

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Abstract. In this work we describe the possibility of using of the simple computer program developed in Delphi Studio working undo MS Windows OS for carrying out the quantum mechanical calculation of electronic structure of nanoparticles. Theoretical methodology is described for realization of this simple computer. The numerous quantum mechanical calculations show that this computer program works correctly and it is useful for use in basis of Slater Atomic Orbitals (SAOs).

Keywords: Nanotechnology, Quantum mechanical calculation, Computer modeling

1 Introduction and theoretical methodology

The computer program is developed by us, in Delphi Studio working under MS Windows for carrying out of quantum mechanical calculation of electronic structure of some nanoparticles (Au_{16}, Ag_{16} and $(CdS)_9$. The calculations carried out by by the Wolfsberg–Helmholz (WH) method [1–3] in basis of Slater Atomic Orbitals (SAOs). It is known, that WH method is one of the simple semi-empirical variants of the molecular orbital (MO) method [4, 5]. In method it is considered that each electron in a nanoparticle goes independently of another electrons in the certain effective field, which created by nucleus and other electrons [6]. The states of electrons in a nanoparticle are described by the one-electronic wave function called the molecular orbital. It is a multicenter function such includes distances from electron to various nuclears. There are various variants of searching for molecular orbital. One of them – search molecular orbitals U_i as a linear combination of atomic orbitals of the atoms which are included in a nanoparticle (method MO LCAO) [1–3]:

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

Where c_{qi} - unknown coefficients, χ_q - atomic orbitals, chosen as basic functions. In this work, real SAOs are used as basic functions [1–3]:

Usually in quantum mechanical calculations of electronic structure of nanoparticles limited to consideration of valence electrons of atoms and molecular orbitals are represented as linear combinations SAOs of these valence electrons. Coefficients c_{qi} in the formula (1) are found by the solution of the following system of equations:

$$\sum_q (H_{pq} - \varepsilon_i S_{pq}) c_{qi} = 0 \tag{2}$$

where the following designations are used:

$$H_{pq} = \int \chi_p^* \, \hat{H}ef \, \chi_q dV \tag{3}$$

$$S_{pq} = \int \chi_p^* \chi_q dV \tag{4}$$

S_{pq} - overlap integrals between atomic orbitals χ_p and χ_q. $\hat{H}ef$ effective Hamilton operator for one electron, moving in the certain effective field:

$$\hat{H}ef = -\frac{1}{2}\nabla^2 + U(r) \tag{5}$$

Expression of the effective Hamilton operator is not known, therefore the values of matrix elements H_{pq} can not be calculated analytically and it is estimated with various methods. The values of ionization potentials of atoms are used in WH method for the estimation of matrix elements H_{pq}. Diagonal elements H_{qq} of this matrix take to equal potentials of ionization of corresponding valence states of atoms. Non-diagonal elements calculated using the expression given in Ref. [1, 2]:

As can be seen from formula (2) for quantum mechanical calculation of nanoparticles by method WH it is necessary to know the values of overlap integrals. In this work for calculation of overlap integrals the formulas given in Ref. [7–9] are used. It is necessary to enter quantum numbers n, ℓ, m of corresponding atomic orbitals, values of exponential parameter ξ of STOs and Cartesian coordinates of atoms in molecular system of coordinates for carrying out computer calculations of overlap integrals under these formulas. Knowing values of matrix elements H_{pq} and S_{pq} , it is possible to solve the system of the equations (2) and to calculate orbital energy ε_i, total electronic energy $E = \sum\limits_i n_i \varepsilon_i$, values of ionization potential I_p of nanoparticle and values of coefficients c_{qi} in approach WH. Using values of coefficients c_{qi}, it is possible to calculate effective charges of atoms (q_A) and overlap populations (S_{op}) in a nanoparticle by the following formula given in Ref. [10]:

$$q_A = n_A^0 - \sum_i n_i \sum_{q \in A} \mid c_{qi} \mid^2 \tag{6}$$

$$s_{op} = \sum_i n_i \sum_{p \in A} \sum_{q \in B} c_{pi} \cdot c_{qi} \cdot S_{pq} \tag{7}$$

where n_A^0 - a positive charge of the atom (for atoms of gold and silver n_A^0 = 1, for atoms of Cd n_A^0 =2, for atoms of S n_A^0 =6), n_i - number of electrons on i-th molecular orbital. Summation over i is carried out on molecular orbital occupied by electrons. Using the described methodology developed computer program in Delphi Studio, working under MS Windows for carrying out of quantum mechanical calculation of electronic structure of the nanoparticles.

2 Declaration of some programs

DKCTVK - definition of the data. nv - number of basic functions SAOs, mo - number of molecular orbitals, me - number of atoms in a nanoparticle, eos - number of molecular orbitals, occupied by electrons. nq - principal, lq - orbital and mq - magnetic quantum numbers of basic SAOs, tc - type of the centers, ch - a serial number of atoms included nanoparticles. zci - values of exponential parameter corresponding basic SAOs, xc, yc, zc - Cartesian coordinates of atoms in molecular system of coordinates:

```
unit dkctvk;
interface
type
    ms2   =array[1..20] of real;
    ms3   =array[1..50] of real;
    ms5   =array[1..30] of integer;
    ms6   =array[1..100] of real;
    ms7   =array[1..51] of extended;
    ms8   =array[1..400] of longint;
    ms9   =array[1..2111] of real;
    ms10   =array[1..2000] of real;
    ms11   =array[1..1326] of real;
    ms12   =array[1..800] of real;
    dm1   =array[1..NV,1..NV] of extended;
    dm2   =array[1..nv] of extended;
    dm3   =array[1..nv] of integer;
const
     { NV, MO, me, eos;                                                    }
    NQ, LQ, MQ, TC, CH                          :dm3;
    XC, YC, ZC,ZCI                              :dm2;
var
    os                                                                  :ms2;
    ww,ww1,vv,vs,wth                                                    :ms3;
    le2,le3,le4,le5,le6,le7,le8,knf                                      :ms5;
    at,av,bt,bv                                                         :ms6;
    fa,dg                                                               :ms7;
    le1,lt1,id4,id5                                                     :ms8;
     f                                                                  :^ms11;
     ws,dla                                                             :^ms3;
    dlb                                                                 :ms3;
    og                                                                  :^ms9;
    ii,jj,iz,kp,kq,kr,ks,itr,jp                                         :integer;
    za,zc1,zb,zd,rac,rad,rab,alp,
    bet,yj,hj,dp,zpr,eps,fmax,kor,kof                                   :extended;
    TP,SO,HP,FH,V,XX,C                                                  :dm1;
    OE,OE0,OED,X99,SD,FN                                                :dm2;
    IQ99                                                                :dm3;
Implementation
end.
```

DKBANTK - set of functions and procedures for calculation of overlap integrals in basis of SAOs:

```
unit dkbantk;
{$n+}
interface
uses  dkctvk,  Math;
function  OVER( n1,n2,l1,l2,mi,mj:integer;
x,ra:extended):extended;
function  CLEBS(var j1,j2,m1,m2,j,m:integer):extended;
function  GB(var l,l1,la,la1,ia,ib,lb:integer):extended;
function  FS(var n,n1,m:integer):extended;
procedure  DIS(i,j:integer;var r:extended);
function  DLM(var l,m:integer):extended;
procedure  BS(var n:integer;var p,t:extended;var b:ms6);
procedure  ASN(var n:integer;var p:extended;var a:ms6);
function  AF(var n1,n2,nq:integer; a,b:ms6):extended;
function  RC(k1,k2:integer; p,t,sp:extended):extended;
implementation

{  Text of procedures and functions  }

end.
```

OVER - calculates overlap integrals;
CLEBS - calculates the coefficients

$$\begin{aligned}\left(j_1 j_2 m_1 m_2 \mid j_1 j_2 J M\right) = \delta_{M,m_1+m_2}\times\\ \left[\frac{(2J+1)^2 F_{j_1+j_2-J}(j_1 j_2+j-1,0)}{(2j_1+1)(2j_2+1)F_{j_1-j_2+J}(j_1 j_2+j+1,0)}\times\right.\\ \left.\times\frac{F_{J+M}(2J,0)}{F_{j_2-j_1+J}(j_1+j_2+j+1,0)F_{j_1+m_1}(2j_1,0)F_{j_2+m_2}(2j_2,0)}\right]^{1/2}\times\\ \times\sum_n (-1)^n F_n(j_1+j_2-J,0)\times\\ \times F_{j_2+m_2-n}(J+M,0)F_{j_1-m_1-n}(J-M,0)\end{aligned} \tag{8}$$

where $F_m(N,0)=\frac{N!}{m!(N-,)!}$

$$n=\left\{\begin{array}{c}0\\ j_2+m_2-(J+M)\\ j_2-m_2-(J-M)\end{array}\right\}_{max\ ,\dots\ ,}\quad\left\{\begin{array}{c}j_1+j_2-J\\ j_2+m_2\\ j_1-m_1\end{array}\right\}_{min}$$

FS - calculates coefficients of binomial product

$$F_m(N,N')=\sum_{\sigma=\frac{1}{2}\{(m-N)+|m-N|\}}^{min(m,N')}(-1)^\sigma F_{m-\sigma}(N,0)F_\sigma(N',0).;$$

GB - calculates coefficients

$$g^q_{\alpha\beta}(\ell\lambda,\ell'\lambda';\Lambda)=g^0_{\alpha\beta}(\ell\lambda,\ell'\lambda';\Lambda)F_q(\alpha+2\Lambda-\lambda,\beta-\lambda')$$

where $g^q_{\alpha\beta}(\ell\lambda,\ell'\lambda';\Lambda)=\sum_{i=1}^{\Lambda}(-1)^i F_j(\Lambda,0)K^{\ell\lambda}_{\alpha+2\Lambda-2i}K^{\ell'\lambda'}_\beta$,

$K^{\ell\lambda}_\beta=(-1)^{\frac{1}{2}(\ell-\beta)}\sqrt{\frac{2\ell+1(\ell-\lambda)!}{2\ \ (\ell+\lambda)!}}\ \frac{(\ell+\beta)!}{2^\ell\left[\frac{1}{2}(\ell-\lambda)\right]!\left[\frac{1}{2}(\ell+\lambda)\right]!(\beta-\lambda)!}$

DIS - calculates distance between nucleus of atoms;
DLM - calculates coefficients

$$d^0_{m0}(t) = \ell![(\ell+m)!(\ell-m)!]^{\frac{1}{2}} \sum_s \frac{(-1)^s \left[\frac{1}{2}(1-t)\right]^{s-\frac{m}{2}} \left[\frac{1}{2}(1+t)\right]^{\ell+\frac{m}{2}-s}}{s!(\ell-s)!(\ell-m)!(\ell+m-s)!};$$

BS - calculates values of function $B_n(\beta) = \int\limits_{-1}^{1} v^n e^{-\beta v}\, dv$ and also keeps in an one-dimensional massive;
ASN - calculates values of function $A_n(p) = \int\limits_{1}^{\infty} \mu^n e^{-p\mu}\, d\mu$ and also keeps in an one-dimensional massive;
AF - calculates values of function $Q^q_{NN'}(p,t) = \int\limits_{1}^{\infty}\int\limits_{-1}^{1} (\mu v)^q (\mu+v)^N (\mu-v)^{N'} e^{-p\mu - pt\,v}\, d\mu dv$
RC - calculates values of function $N_{nn'}(p,t) = \frac{(1+t)^{n+\frac{1}{2}}(1-t)^{n'+\frac{1}{2}}}{\sqrt{(2n)!(2n')!}} \cdot p^{n+n'+1}$
OVERRUN - calculates overlap integrals arising in research of properties of nanoparticles and preservation of results:

```
unit       overrun;
interface
uses DKBANTK,DKCTVK;
procedure OVERUN(var a,b:extended);

Implementation

procedure OVERUN(var a,b:extended);
label 1, 2,10;
var
  i,i1,i2,s,p,q,na,la,ma,nc,lc, mc,nb,lb,mb,nd,ld,
  md, j11:integer;
  sopq,a3,x,y,x1 :extended;
  sof :file of extended;
  nlms:TextFile;
  ch1,ch2,ch3,ch4,ch5,ch6,ch13,ch14,ch15,ch16,
  ch17,ch18,pch :string;
begin
  assign(sof,'sof.dta');  rewrite(sof); reset(sof);
  assign(nlms,'nlms.txt'); rewrite(nlms);
  zpr:=2; i:=1;
  for q:=1 to nv do
  begin
    for p:=1 to nv do q
    begin
      nc:=nq[q]; lc:=lq[q];mc:=mq[q];
      zc1:=zci[q]; i2:=tc[q];kq:=q;
      na:=nq[p]; la:=lq[p];ma:=mq[p];
      za:=zci[p]; i1:=tc[p];kp:=p;
      if i1=i2 then sopq:=OVER(na,nc,la,lc,ma,mc,0,0)
      else
       begin
        DIS(p,q,rac);  a3:=za+zc1;
        x:=rac*a3*0.5; y:=(za-zc1)/a3;
        j11:=na+nc+1; ASN(j11,x,av);
        BS(j11,x,y,bv); x1:=RC(na,nc,x,y,0.0);
        sopq:=OVER(na,nc,la,lc,ma,mc,x1,rac);
```

```
      end;
      Str(na,ch1); Str(la,ch2); Str(ma,ch3);
      Str(nc,ch4); Str(lc,ch5); Str(mc,ch6);
      Str(za:10:6,ch13); Str(zc1:10:6,ch14);
      if i1=i2 then
       begin ch15:=' ; ch16:=' ; end
      else
       begin
        Str(alp:10:6,ch15);Str(bet:10:6,ch16)
       end; Str(p:3,ch17); Str(q:3,ch18);
      pch:=ch1+ch2+ch3+ch4+ch5+ch6+ch13+
     ch14+ch15+ch16+ch17+ch18;
      write(nlms,pch); writeln(nlms,''); write(sof,sopq);
   end
  end; close(sof); close(nlms);
 end;

 end.
```

3 Results and discussion

6s- 6px-, 6py- and 6pz- valence Au STOs of Au atoms, 5s- 5px-, 5py- and 5pz- valence orbitals of Ag atoms, 3s- 3px-, 3py- and 3pz- valence orbitals of S atoms, 5s- 5px-, 5py- and 5pz- valence orbitals of Cd atoms are used for the creation of molecular orbitals of nanoparticles. The analitical expressions of STOs given in Refs [1–3]. By solving the equations (2) we defined the values of orbital energies ε_i and the coefficient c_{qi} . The effective charges of atoms of nanoparticles and overlap populations can be calculated by using the values of coefficients c_{qi} [1–3].

By using the values of orbital energies, the stability can be determine, and the electrical, mechanical, optical, and magnetic properties of nanoparticles can be calculate. The valence electrons of nanoparticles are placed in the lowest energetic levels two by two. The value of band gap can be calculated as $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$. Here ε_{LUMO} is the energy of the lowest unoccupied molecular orbital and the ε_{HOMO} is the energy of the highest occupied by the valence electrons of molecular orbitals. If the value of E_g is in interval [0; 0,025] eV, the material is conductive; if E_g is in interval (0,025; 6) eV, the material is semiconductive; if $E_g > 6$ eV is dielectric. The ionization potential is equal to ε_{HOMO} with negative sign: Ip=$-\varepsilon_{HOMO}$. Strength of the material is calculated as $\eta = \frac{1}{2}E_g$. If $\eta > 1$ eV the material is strength, if $\eta < 1$ eV it is soft. When $\varepsilon_{LUMO} < 0$ the material is electrophile, when $\varepsilon_{LUMO} > 0$ it is nucleophile. The stability of nanoparticle can be calculated by formula $\Delta E = E_{np} - E_p$.

Here E_{np} is the total electronic energy of nanoparticle, and E_p is the sum of total electronic energy of atoms in the nanoparticle. When $\Delta E > 0$ the material is not stable, but when $\Delta E < 0$ material is stable. The wavelength of photon under emission of the material can be calculated by formula nm.

$$\lambda = \frac{c\cdot}{1,6 \cdot E_g} \times 10_{28} nm$$

Here $c = 3 \cdot 10^8$ m/s is the speed of the light in vacuum, $h = 6,63 \times 10^{-34}$ C·s

4 Conclusion

The semi-empirical WH method was used to investigate the properties of the nanoparticles. STO's are used as atomic orbitals. The computer calculations were carried out by authors own computer program Delphi studio system under the Windows operating system. The results of

the calculations indicate that STO's are useful in investigation of properties of multielectronical systems (molecules, nanoparticles). In valence, electronic approximation. The results of calculations are given in Table 1. As seen from the table the Au_{16} , Ag_{16}, $(CdS)_9$ nanoparticles are stable, soft, and semi-conductive materials.

Table 1: Results of calculations for some nanoparticles in basis SAOs

No	**Nano-particles**	**Total energy E (a.u.)**	**Parameter of stablity** ΔE **(a.u)**	**Potential of ionization** I_p**/(eV)**	**Band gap** $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ **(ev)**	**Strength 0f nanoparticles** μ	**Wave length** λ **(mkm)**
1	Au_{16}	-13.852070	-0.329446	16.648371	0.405018	0.202501	3.1
2	AG_{16}	-15.027638	-0.355782	19.771964	1.154508	0.577254	1.1
3	$(CdS)_9$	-39.103686	-0.650808	9.858220	0.099839	0.04991968	0.5

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