Digest Journal of Nanomaterials and Biostructures Vol. 5, No 1, March 2010, p. 153 – 159

MATHEMATICAL MODELING FOR THE SIMULATION OF HEAVY METAL IONS ADSORPTION BY SINGLE WALL CARBON NANOTUBES (SWCNTs) BASED ON COMPUTATIONAL CALCULATION

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We performed this work to calculate the carbon nanotube parameters for the M^{+2}@SWCNT model such as incapsulated Hg^{+2} and Pb^{+2} metal ions with nanotubes. With using this mathematic modeling for other M^{+2}@SWCNT models, based on total interaction energy between metal ions and carbon nanotube and this mathematical modeling, we can design a new approach for separation of mixture metal ions based on nanotechnology.

(Received January 25, 2010; February 24, 2010)

Keywords: Mathematical modeling, nanotechnology, nanotube, M^{+2}@SWCNT.

1. Introduction

After discovery of carbon nanotubes (CNTs) [1], numerous works have been devoted to study the properties and applications of this fascinating novel material [2]. The applications of CNTs are widely ranged from nano-biotechnology to nano-mathematic, e.g., [3,4]. However, based on nanotubes properties exhibiting absorption or storageing behavior depending upon the tubular diameter and chirality. Therefore, considerable efforts have been raised to synthesize CNTs with properties independent of tubular diameter and chirality [5].

Among them, the group of heavy metals and especially Hg^{+2} and Pb^{+2}, which always exhibit toxic behavior, are considered as proper alternates of other heavy metals [6].

The stable one-dimensional structure of CNT was either theoretically recognized or experimentally synthesized [1,7]. Previous studies indicated that CNTs are very important in the gas storage and electrochemical determination of the metal ions or molecules but the mathematical study for the preparation of the mathematical modeling has not been reported [8, 9]. This work studies the existence of mathematical modeling for separation of the metal ions based on the Gausian 98 software. Density functional theory (DFT) calculations on two considered structures of CNTs and CNTs@M^{+2} are performed employing BLYP methods and b3lyp/6-31+g* opt# standard basis set. The optimized geometry is exhibited in figure **1- 6**.

$$\mathbf{E_{tot} = [E_{M@CNT} - (E_M + E_{CNT})]_* 627.529} \quad \text{k cal/mol}$$

E.q. 1: Mathematic equation for total energy of heavy metal absorption.

Since optimal ground state energy is very useful elements to study the free structure and then comparison with optimized energy of M^{+2}@CNTs, calculation of RHF (Restricted Hartree-Fock) with then dot to 627.529 factor is used in this paper as a energy level based on k cal/mol Eq. **1**.

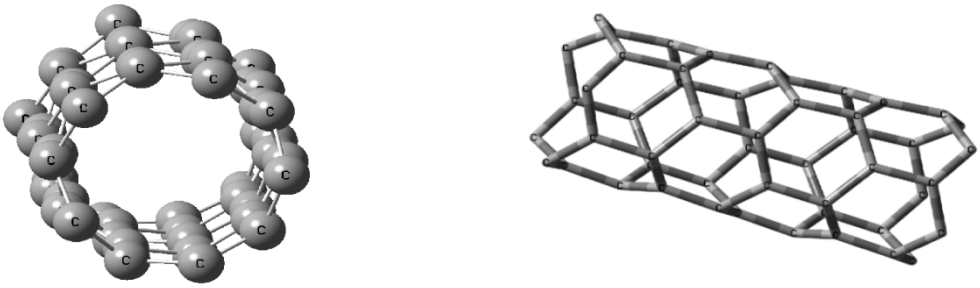

Fig. 1. The side and end view of geometry optimized (4,0) structure.

Fig. 2. The side and end view of geometry optimized (5,0) structure.

Fig. 3. The side and end view of geometry optimized (5,5) structure.

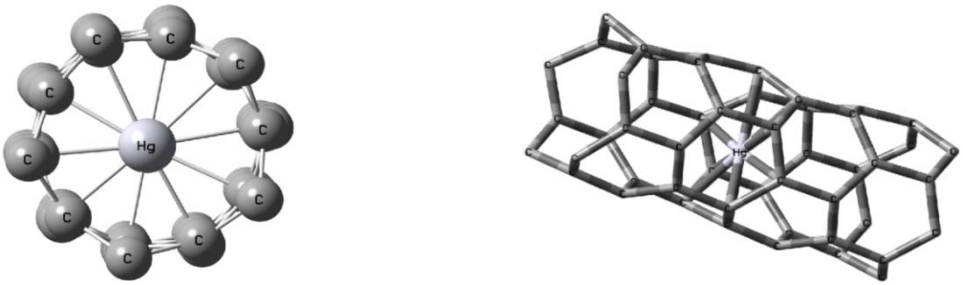

Fig. 4. The side and end view of geometry optimized Hg^{+2}@(4,0)CNT structure.

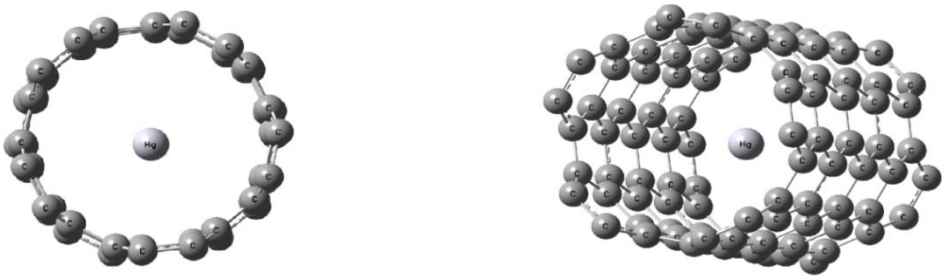

Fig. 5. The side and end view of geometry optimized Hg^{+2}@(5,0)CNT structure.

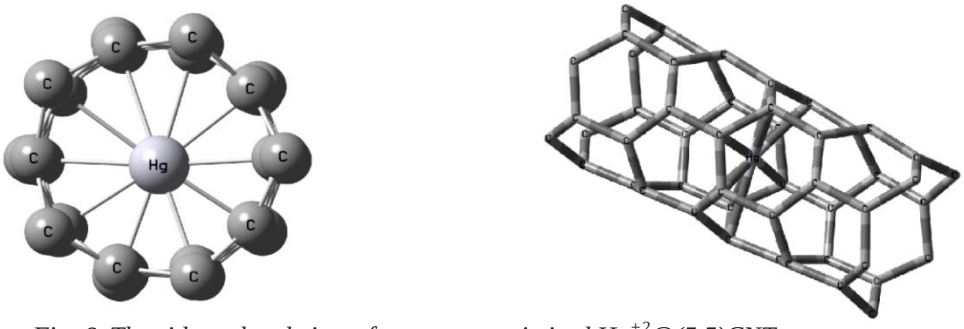

Fig. 6. The side and end view of geometry optimized Hg^{+2}@(5,5)CNT structure.

In the present study as a efficient mathematical modeling, a theoretical work has been carried out on a single-walled and endohedrally M^{+2}@SWCNT such as (4,0), (5,0) and (5,5), Hg^{+2}@C50H10, Hg^{+2}@C100H20 and Hg^{+2}@C50H10, for heavy metal separation, respectively, selected.

2. Computational procedure

In this study, two representative models of the SW zigzag and armchair CNTs are considered in the Gaussian calculations. The first model is the (4,0) SW-CNT consisting of 50 C and Hg^{+2} or Pb^{+2} atoms where the two ends of the tube are capped by 10 H atoms (see Fig. **1** and **4**). The second model is the (5,0) SW-CNT consisting of 100 C and Hg^{+2} or Pb^{+2} atoms where the two ends of the tube are capped by 20 H atoms (see Fig. **2** and **5**). The third model is the (5,5) SW-CNT consisting of 50 C and Hg^{+2} or Pb^{+2} atoms where the two ends of the tube are capped by 10 H atoms (see Fig. **3** and **6**). The quantum calculations were performed on the considered models using the Gaussian 98 [10] package of program. The quantumic calculations were performed on the geometrical optimized models by the B3LYP method and the # b3lyp/6-31+G*standard basis set to evaluate the Hartree -Fock energy and other parameters (see Tables **1** and **2**).

3. Results and discussion

At the first step of this study, each of the considered zigzag and armchair representative models of SW-CNT was allowed to fully relax during the geometrical optimization at the level of the B3LYP DFT method and the # b3lyp/6-31+G* standard basis set. Tables **1** present the optimized geometries of the models Figs. **4**, **5** and **6**. And, table **2** present the optimized geometries of the models Pb^{+2} in the hole of Figs. **1**, **2** and **3**.

Table 1: The example mathematical calculation energy for SWCNT@Hg^{+2}

SWCNT	Etot kcal/mol
Armchair (4,0)	**-120.54**
Armchair (5,0)	-112.58
Chiral (5,5)	-110.96

Table 2: The example mathematical calculation energy for SWCNT@Pb^{+2}

SWCNT	Etot kcal/mol
Armchair (4,0)	**-115.47**
Armchair (5,0)	-110.89
Chiral (5,5)	-108.11

The results shown in table **1** and **2** indicates that interestingly the Hg^{+2} and Pb^{+2} can absorb inter hole of nanotubes, also the diameters of armchair (4,0) structures have better interaction with metal ions because those have less exothermic energy.

Based on the table **1** and comparison with **2**, total energy for Hg^{+2}@(4,0)SWCNT is more exothermicer than Pb^{+2}@SWCNT, however, armchair (4,0) SWCNT could apply for separation of the mixture ions of Hg^{+2} and Pb^{+2}. With using this mathematic modeling for other heavy metals, based on total interaction energy between metal ions and carbon nanotube and this mathematical modeling, we can design a new approach for separation of industrial waste mixture metal ions and others.

Table 4: The summarized example mathematical calculation parameters in the (4,0) SWCNT@Hg^{+2}

Mathematical simulation for Hg^{+2}@(4,0)SWCNT
(Summarized)

```
*********************************************
 Gaussian 03:  IA32W-G03RevD.01 13-Oct-2005
               26-Oct-2008
 *********************************************
 %chk=2
 %mem=500MB
 ----------------------
 # b3lyp/6-31+G*  opt extrabasis
 ----------------------
 1/38=1/1;
 2/17=6,18=5,40=1/2;
 3/6=3,10=1,11=2,16=1,25=1,30=1,74=-5/1,2,3;
 4//1;
 5/5=2,32=1,38=5/2;
 6/7=2,8=2,9=2,10=2,28=1/1;
 99/5=1,9=1/99;
 ------------------
 Title Card Required
 ------------------
 Symbolic Z-matrix:
 Charge =  0 Multiplicity = 1
 C                  0.       0.       0.
 H                  1.01627  0.       0.
 C                 -2.04819  1.42995  0.
                                          .
                                          .
                                          .
 C                 -9.15284 -0.27869 -1.96889
 Hg                -4.29226  1.36554 -2.28034

 Stoichiometry    C50H10Hg
 Framework group  C1[X(C50H10Hg)]
 Deg. of freedom   177
 Full point group                 C1
 Largest Abelian subgroup         C1      NOp   1
 Largest concise Abelian subgroup C1      NOp   1
                  Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
```

```
     1        6           0        4.613267   -0.183668   -2.160334
     2        1           0        5.622853   -0.172540   -2.044471
                                                    .
                                                    .
                                                    .
    60        6           0       -4.661799    1.052104   -1.742304
    61       80           0        0.045054   -0.080345   -0.013492
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      0.1918900      0.0696625      0.0696266
 Standard basis: 6-31+G* (5D, 7F)
 There are   278 symmetry adapted basis functions of A   symmetry.
 Integral buffers will be    262144 words long.
 Raffenetti 2 integral format.
 Two-electron integral symmetry is turned on.
   278 basis functions,   810 primitive gaussians,   280 cartesian basis functions
   195 alpha electrons      195 beta electrons
       nuclear repulsion energy     10285.8090264181 Hartrees.
                                                    .
                                                    .
                                                    .
NAtoms=   61 NActive=   61 NUniq=   61 SFac= 7.50D-01 NAtFMM=   80
NAOKFM=F Big=T
 One-electron integrals computed using PRISM.
 NBasis=   278 RedAO= T  NBF=   278
 NBsUse=   278 1.00D-06 NBFU=   278
 Defaulting to unpruned grid for atomic number  80.
 Harris functional with IExCor=  402 diagonalized for initial guess.
 ExpMin= 4.26D-02 ExpMax= 7.16D+01 ExpMxC= 7.16D+01 IAcc=2 IRadAn=
4 AccDes= 0.00D+00
 HarFok:  IExCor= 402 AccDes= 0.00D+00 IRadAn=         4 IDoV=1
 ScaDFX=  1.000000  1.000000  1.000000  1.000000
 Defaulting to unpruned grid for atomic number  80.
 Initial guess orbital symmetries:
      Occupied  (A) (A) (A) (A) (A) (A) (A) (A) (A) (A) (A) (A)
                                                    .
                                                    .
                                                    .
             (A) (A) (A) (A) (A) (A) (A) (A) (A) (A) (A)
Mulliken atomic charges:
           1
    1  C   -0.118403
    2  H    0.097701
                                                    .
                                                    .
                                                    .
   60  C   -0.036327
   61  Hg  47.817726
 Sum of Mulliken charges=   0.00000
Electronic spatial extent (au):  <R**2>= 17791.9414
 Charge=     0.0000 electrons
 Dipole moment (field-independent basis, Debye):
    X=    -8.2051    Y=    -5.6470    Z=    -1.0745  Tot=    10.0183
 Quadrupole moment (field-independent basis, Debye-Ang):
   XX=  -739.0291   YY=  -854.0948   ZZ=  -855.5219
   XY=    -0.4453   XZ=    -0.2133   YZ=    -0.1567
```

Traceless Quadrupole moment (field-independent basis, Debye-Ang):
XX= 77.1862 YY= -37.8795 ZZ= -39.3067
XY= -0.4453 XZ= -0.2133 YZ= -0.1567
Octapole moment (field-independent basis, Debye-Ang**2):
XXX= -370.2324 YYY= 52.8066 ZZZ= 10.0890 XYY= -69.9395
XXY= 2.8571 XXZ= -0.3846 XZZ= -74.1530 YZZ= 19.1769
YYZ= 0.8164 XYZ= 1.4202
Hexadecapole moment (field-independent basis, Debye-Ang**3):
XXXX=-15348.4471 YYYY= -5867.5167 ZZZZ= -5850.6177 XXXY= 28.0668
XXXZ= -2.4100 YYYX= 1.8558 YYYZ= -12.5603 ZZZX= -5.2509
ZZZY= 8.5331 XXYY= -4104.8612 XXZZ= -4085.4512 YYZZ= -1943.9803
XXYZ= -7.2043 YYXZ= 3.6073 ZZXY= -5.8527

.
.
.

evD.01|State=1-A|HF=-3463.6644426|RMSD=9.176e-005|Thermal=0.|Dipole=-3
.279406,1.7797181,1.2702808|PG=C01 [X(C50H10Hg1)]||@

4. Conclusion

We performed this work to calculate the carbon nanotube parameters in the representative zigzag and armchair models of SWCNT for the M^{+2}@SWCNT model such as incapsulated Hg^{+2} and Pb^{+2} metal ions with nanotube. To this end, the geometry optimization and ground state energy calculations were performed on three proper models of H-capped (4,0), (5,0) and (5,5) SWCNTs. From the results, some trends were obtained. First, the results shown in table **1** and **2** indicates that the Hg^{+2} and Pb^{+2} can absorb inter hole of nanotubes, also the diameters of armchair (4,0) structures have better interaction with metal ions. Second, based on the table **1** and comparison with **2**, total energy for Hg^{+2}@(4,0)SWCNT is more exothermicer than Pb^{+2}@SWCNT. Third, armchair (4,0) SWCNT could apply for separation of the mixture ions of Hg^{+2} and Pb^{+2}. Fourth, finally with using this mathematic modeling for other M^{+2}@SWCNT models, based on total interaction energy between metal ions and carbon nanotube and this mathematical modeling, we can design a new approach for separation of mixture metal ions.

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