Test of Computational Approaches for Gold-Thiolate Clusters Calculation using Lomonosov Supercomputer

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High-level procedures (MP2, CCSD, CCSD(T)) and reliable experimental data have been used to assess the performance of a variety of exchange-correlation functionals for the calculation of structures and energies of small models of thiolate-protected gold clusters. Clusters represent rather complicated objects for examination, therefore the simple models including Au_2, AuS were considered to find an appropriate method to calculate Au-Au and Au-S interactions in protected clusters. The mean unsigned errors of the quantum chemical methods were evaluated via reliable experimental bond distances and dissociation energies of Au_2 and AuS. Based on the calculation, the SVWN5, TPSS+D3, PBE96+D3, and PBE0+D3 were found to give the most reliable results and can be recommended for calculation of the structure and properties of thiolate-protected gold clusters. The influence of the relativistic corrections calculated in Dirac-Coulomb-Breit framework and inclusion of dispersion corrections on the structure and energy of thiolate-protected gold clusters have been analyzed.

Keywords: density functional theory, parallel calculation, cluster, gold, dispersion correction, relativistic effects, computational chemistry.

Introduction

Supercomputer simulation based on quantum chemical methods is effectively applied to predict and examine the structure and properties of different compounds including nanoclusters, materials, metal-organic systems, and drugs [1, 2]. Thiolate-protected gold clusters, $Au_n(SR)_m$, are popular objects in theoretical and nano science. The quantum chemical study of clusters has a number of challenges: *(i)* To describe Au-Au and Au-S interactions correctly, the approach should take into account relativistic effects, dispersion interactions, and others features; *(ii)* High-level *ab initio* procedures are not feasible for $Au_n(SR)_m$, since they become very resource-intensive; *(iii)* Application of the $Au_n(SR)_m$ data in solid or liquid phases as a benchmark of theoretical methods is difficult due to that a majority of quantum chemical methods are related to a gas phase. The problem of an extensive global search of potential energy surface to locate global minima can be solved by the genetic algorithm with DFT calculation [3].

We propose new insights to choose the quantum chemical protocol of calculation of gold protected clusters and similar metal-organic systems performing benchmark study of the simple fragments of cluster. Clusters represent rather complicated objects for examination, therefore the simple models including Au_2, AuS were considered.

1. Calculation Details

Calculated interatomic distances (R_e) and bond energies (D_0) of the fragments were compared to available experimental spectroscopic data [4, 5] and values obtained by high-level *ab initio* methods (MP2, CCSD, CCSD(T)) to assess the performance of exchange-correlation functional (LSDA, GGA, meta-GGA, global-hybrid GGA, global-hybrid GGA, global-hybrid meta-

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GGA, range-separated hybrid GGA functionals). Effective core potential formalism using the cc-pVDZ/cc-pVDZ-PP [6, 7], 6-31G*/SBKJC [8], 6-31G*/LANL2DZ [9] (further referred to BS-1, BS-2, and BS-3) was applied.

The Dirac-Coulomb-Breit Hamiltonian (DCB) with separate spin-free and spin-dependent components [10] was employed. The energy-optimized extended Gaussian basis set of triple-polarized quality of the large component, and the corresponding kinetically balanced basis for the small component [11] was used (BS-4). The dispersion corrections with the Becke-Johnson damping (DFT+D3) [12] was also calculated.

For each protocol mean unsigned errors (MUEs) were established. The DFT MUEs were compared with the MP2, CCSD, and CCSD(T) MUEs and divided into three groups: *(i)* accurate procedure if MUE is less than CCSD(T)/BS-1 MUE; *(ii)* less accurate procedure if MUE is in the range between CCSD(T)/BS-1 and CCSD(T)/BS-2; and *(iii)* erroneous procedure if MUE is more than MUE of CCSD(T)/BS-2.

All calculations were performed with NWChem [13] and PRIRODA [14] codes. Server 1: HP DL160G6 server with 2 Intel Xeon E5504 (quad-core, 2.0 GHz) processors, 24 GiB DDR3 ECC RAM, 1.8 TiB HP P410/512MB based RAID 1+0 of 4 Seagate ST1000NM0033-9ZM disks. Servers 2 and 3: virtual machines with 8 processor cores (2.53 GHz), 24 GiB RAM and 300 GB VHDD, running on VMware vSphere 5.5 platform (M.V. Lomonosov Moscow State University Datacenter). All servers are running CentOS 6.7 Linux 64-bit, NWChem 6.6 64-bit built with Intel Compilers, MKL and Intel MPI from Intel Parallel Studio 2016 Cluster Edition). The calculation capacity offered by Supercomputing Center of M.V. Lomonosov Moscow State University has been also used [15].

2. Results and Discussion

The calculated R_e values of Au_2 molecule are compared to the experimental data 2.4719 [4]; the MUEs are shown on Fig. 1. Evidently, CCSD(T)/BS-1 and MP2/BS-1 protocols give the most accurate Au-Au distance among *ab initio* methods. For all *ab initio* methods, the MUEs increase in the order BS-1 <BS-2 <BS-3. Thus, the expanding of a basis set slightly improve the distance calculated at CCSD(T) level only. In contrast, the Re calculated by different functionals slightly varies from the basis sets. The first group of the high accurate functionals contains SVWN5/BS-1, SVWN5/BS-2, SVWN5/BS-3, and M11/BS-1. The homogeneous electron gas approximation to XC energy could be provided the advance of SVWN5. The second group is represented by PW91, PBE96, BP86, TPSS, PBE0, BHandH, MPW1K, B3P86, B3PW91, HSE06, TPSSh. Other functionals including BLYP, B3LYP, M06, M06L, M11L have high MUEs, more than 0.08 , and failed to describe the experimental Au-Au distance. It should be noted that the majority of protocols tend to overestimate R_e in Au_2, except MP2/BS-1 and SVWN5/BS-1. Dispersion corrections slightly effect the R_e. The Au-Au distance calculated by DCB framework is equal to 2.530 ; MUE=0.058 .

Among *ab initio* methods, CCSD(T)/BS-1 and MP2/BS-1 successfully predict the dissociation energy of Au_2 (Fig. 1). The errors of MP2/Def2-TZVPP and CCSD(T)/Def2-TZVPP are large and equal to 0.13 eV and 0.23 eV, respectively. Some of the functionals have less MUEs than *ab initio* methods. The PW91, PBE96, BP86, TPSS, M06L form the first group of accurate methods (MUE ¡ 0.1 eV). The SVWN5 and BHandH functionals, which have exactly predicted R_e, calculate $D_0(Au_2)$ with large MUE, as well as HCTH, B3PW91, B3LYP, HSE06, M11, M06.
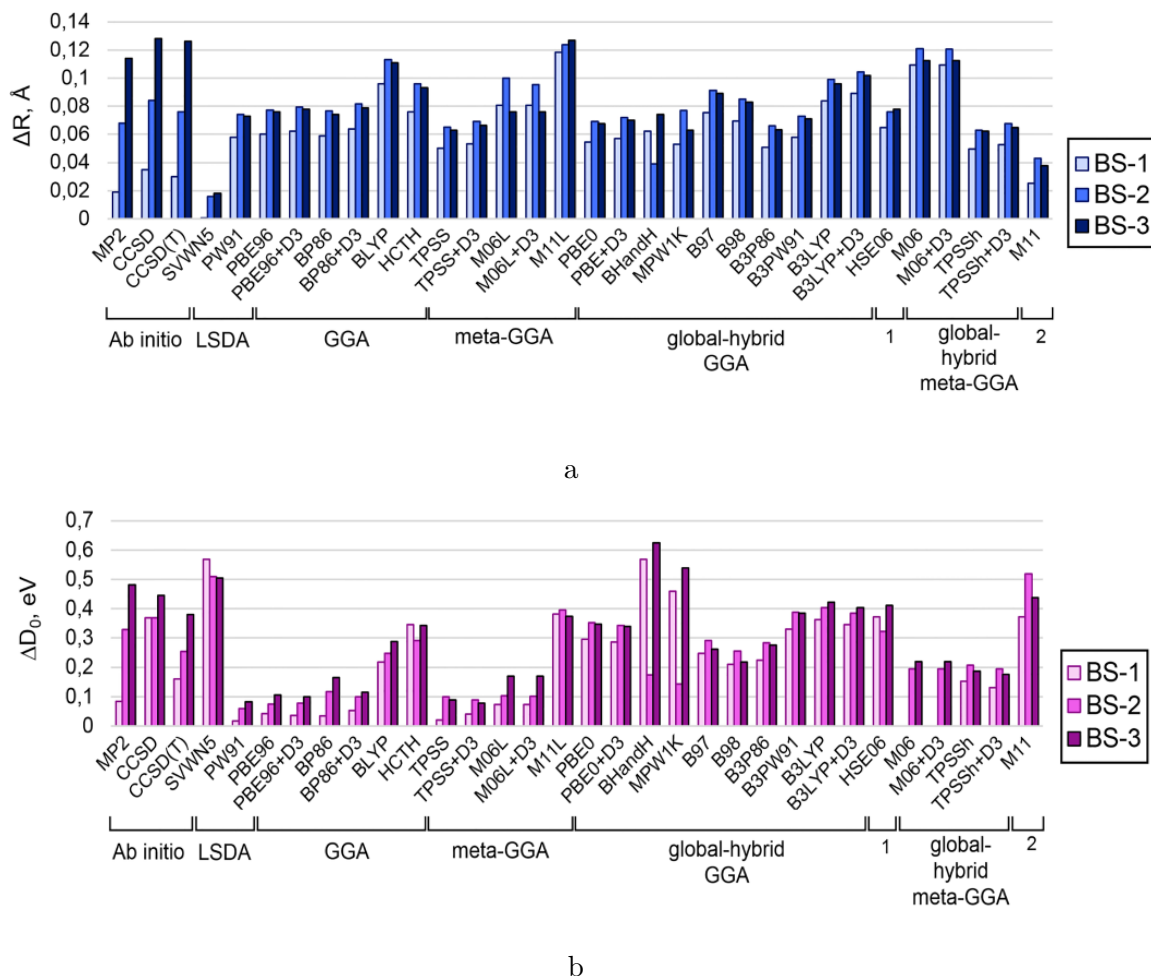
a

b

Figure 1. Mean unsigned errors in calculation of ΔR (A) and ΔD_0 (B) of Au_2 (a – range-separated hybrid GGA functional; b – range-separated hybrid meta-GGA functional)

The dispersion corrections slightly influence the results. Relativistic DCB dissociation energy (2.30 eV) is completely in line with the experimental ones.

The equilibrium distance and dissociation energy of AuS are calculated using CCSD, CCSD(T), MP2, DFT, DCB. The experimental value of R_e, 2.156 [5] was used as a benchmark. MP2/BS-1 accurately predicts the Au-S distance among the considered *ab initio* methods. For MP2, CCSD, CCSD(T) the error increases in the order BS-1 <BS-2 <BS-3. The Au-S distance calculated using DFT also depends on the basis set and a functional type. The first group of accurate procedure (with MUEs less than 0.06) contains all considered functionals with BS-1 excluding BLYP, HCTH, M11L, BHandH, B97, B98, B3P86, B3LYP, M06. The dispersion and relativistic corrections slightly influence R_e value. For instance, the Au-S distance calculated in DCB approximation has the same error (0.07) as the first group of the DFT methods.

All *ab initio* methods accurately predict a dissociation energy of AuS excluding MP2/BS-2 procedure (MUE = 0.41 eV). The errors of MP2/Def2-TZVPP and CCSD(T)/Def2-TZVPP are larger than BS-1 and equal to 0.56 eV and 0.63 eV, respectively. Among DFT, MPW1K/BS-1 protocol calculates D0 more accurate than CCSD(T)/BS-1. For PBE96+D3, BP86+D3, HCTH, TPSS+D3, M06L, M06L+D3, M11L, PBE0, PBE0+D3, B97, B98, B3P86, B3PW91, B3LYP, B3LYP+D3, HSE06, M06, M06+D3, TPSSh, TPSSh+D3 with Lanl2DZ, MUEs are less then MUEs obtained by SBK and cc-pVDZ basis sets. It should be noted that PBE96/BS-

3, TPSS/BS-1, M11L/BS-3, PBE0/BS-3, MPW1K/BS-1, B98/BS-3, B3LYP/BS-3, M06/BS-3 could be recommended for AuS calculations. The dispersion corrections improve the calculated value in most cases excluding M06. Dissociation energy calculated by DCB approximation is 2.67 eV (MUS=0.08 eV) and in line with the experimental data.

The calculation of Au-Au and Au-S distances in Au_2 and AuS reveals the functionals which are close in accuracy to high-level *ab initio* procedures and experimental data. Due to SVWN5, B3PW91, PBE96, PBE0, B3LYP, TPSS, TPSSh, M06, M06L, M11, M11L, PW91, BP86 procedure have the least errors in the predicted properties of Au_2 and AuS, they are further applied to benchmark calculation of the cyclic gold-thiolate complexes.

Finally, the $Au_{20}(SR)_{16}$ structure is calculated by SVWN5, PBE96, TPSS, PBE96+D3, TPSS+D3, PBE0, PBE0+D3 methods using BS-2, BS-3 basis set and by DCB framework with BS-4 basis set to understand the accuracy and time of the DFT procedure to predict the interatomic distances in real thiol protected gold cluster. The main interatomic distances and average calculation time of one optimization step of calculation are collected in Tab. 1.

Table 1. The main interatomic distances () in $Au_{20}(SR)_{16}$ and average calculation time of one optimization step (t, min)

Method	Basis set	Au(1)-Au(2)	Au(2)-Au(3)	Au(3)-Au(4)	Au(2)-Au(5)	t
X-ray	-	2.717	2.870	2.982	3.120	-
SVWN5	BS-2	2.720	2.854	2.795	2.996	95
	BS-3	2.727	2.880	2.860	3.013	61
TPSS	BS-2	2.776	2.883	2.960	3.090	76
	BS-3	2.774	2.899	2.959	3.150	55
TPSS+D3	BS-2	2.750	2.849	2.836	2.965	83
	BS-3	2.740	2.872	2.845	3.013	67
PBE96	BS-2	2.810	2.967	3.123	3.232	79
	BS-3	2.801	2.944	3.034	3.256	60
PBE96+D3	BS-2	2.774	2.830	2.905	3.120	86
	BS-3	2.771	2.898	2.946	3.153	64
PBE0	BS-2	2.792	2.901	2.991	3.081	75
	BS-3	2.765	2.909	2.968	3.142	63
PBE0+D3	BS-2	2.772	2.894	2.951	3.098	78
	BS-3	2.749	2.882	2.934	3.156	69
PBE96+DCB	BS-4	2.810	2.952	3.063	3.204	142

The structure obtained at TPSS/BS-2 method proved to be more close to the experimental one than the structure predicted in PBE96/BS-2 and SVWN5/BS-2 approaches. It should be noted that dispersion corrections improve convergence of the calculated interatomic distances and the experimental ones using the PBE96 functional. The account of relativistic effects in DCB framework also improves the geometrical parameters, but the average calculation time of one optimization step is sufficiently longer than time of PBE96/BS-2 and PBE96/BS-3 protocols.

Conclusions

The structures and energies of small models of thiolate-protected gold clusters were calculated by ab initio methods (MP2, CCSD, CCSD(T)) and different exchange-correlation functionals including dispersion and relativistic corrections. To find the accurate method for the study of Au-Au and Au-S interactions, the diatomic Au_2 and AuS molecules were considered.

All calculated Au-Au bonds in the $Au_{20}(SR)_{16}$ are slightly larger than the corresponding values in crystal structure. The account of dispersion corrections and relativistic effects improves the geometrical parameterizes. So, SVWN5, TPSS+D3, PBE96+D3, PBE0+D3 using BS-2 and BS-3 could be recommended for $Au_n(SR)_m$ calculation, because they describe Au-Au and Au-S interactions more accurately.

The obtained results illustrated the complications of $Au_n(SR)_m$ for theoretical investigation and provide new information to theorists and chemists studying structure and properties of protected gold clusters or other complicated chemical systems including self-assembled monolayers, ligand-protected metal clusters, and organometallic complexes.

Acknowledgments

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