THEORETICAL INVESTIGATION OF GOLD NANOCLUSTERS USING DIFFERENT DFT FUNCTIONALS

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Abstract:

This study investigates the structural and electronic properties of gold nanoclusters, specifically Au_8O_2 and its charged states ($Au_8O_2^+$ and $Au_8O_2^-$), using Density Functional Theory (DFT) with various functionals (BP, LDA, B3LYP, TPSS, PBEO). The primary focus is on understanding the stability, bonding characteristics, and potential catalytic behavior of these systems, particularly in relation to oxygen adsorption. Geometry optimization, bond lengths, vibrational frequencies, bond angles, dipole moments, and energies are calculated for both neutral and charged Au_8O_2 species in their different spin states (doublet and quartet). Our results show that the **$Au_8O_2^+$ doublet** state exhibits the highest bond length (1.285 Å) and lowest frequency (1213.05 cm^{-1}), suggesting significant activation of the O_2 molecule. This complex is identified as a promising nanocatalyst for oxidation reactions, such as CO oxidation. The theoretical bond length for $Au_8O_2^-$ (doublet) is found to be closest to the experimental O-O bond length of the O_2 molecule (1.21 Å), indicating its potential for similar catalytic applications. The study emphasizes the importance of choosing the appropriate DFT functional for accurate predictions of molecular properties and offers insights into the design of gold-based nanocatalysts for oxidation reactions.

INTRODUCTION:

Density-functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (or nuclear structure) (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined by using functional, i.e. functions of another function. In the case of DFT, these are functional of the spatially dependent electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry[15].

DFT has been extremely popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. Computational costs are relatively low when compared to traditional methods, such as exchange only Hartree–Fock theory and its descendants that include electron correlation. Since, DFT has become an important tool for methods of nuclear spectroscopy such as Mössbauer spectroscopy or perturbed angular correlation, in order to understand the origin of specific electric field gradients in crystals.

Despite recent improvements, there are still difficulties in using density functional theory to properly describe: intermolecular interactions (of critical importance to understanding chemical reactions), especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces, dopant interactions and some strongly correlated systems; and in calculations of the band gap and ferromagnetism in semiconductors[4]. The incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms)[5] or where dispersion competes significantly with other effects (e.g. in biomolecules)[6]. The development of new DFT methods designed to overcome this problem, by alterations to the functional[7] or by the inclusion of additive terms, is a current research topic. Classical density functional theory uses a similar formalism to calculate properties of non-uniform classical fluids.

Density-functional theory (DFT) is a successful theory to calculate the electronic structure of atoms, molecules, and solids[6-10]. Its goal is the quantitative understanding of material properties from the fundamental laws of quantum mechanics. DFT is helpful in calculating the energy, frequency, bond lengths, bond angle, dipole moment parameters to theoretically[11-17]. It is a computational method to study the structure and electronic properties of the molecules. So, that it does not lead to any environmental pollution in comparison to the traditional laboratory experimental methods of chemical studies.

COMPUTATIONAL DETAILS:

The geometry of the gold molecule was initially constructed using Avogadro[1]. Subsequently, the molecule underwent geometry optimization. An input file for the ORCA[2] software package was generated from Avogadro, specifying various Density Functional Theory (DFT) functionals. The ORCA input file was then executed through the command line to obtain the corresponding output file.

Theoretical calculations were carried out using the ORCA software package, employing the DFT method with the def2-SVP basis set[4]. Different exchange-correlation functionals were used, including BP, LDA, B3LYP, TPSS, and PBEO.

Finally, the ORCA output file was processed and visualized using software like Avogadro and Chemcraft[3], allowing for a clear representation of the resulting molecular geometry.

RESULT AND DISCUSSION:

First of all, raw geometries of Au3 – Au8 molecules were prepared using Avagadro software and roughly optimized the geometry using Avogadro itself to get an appropriate raw geometry. Thereafter, we generated an orca input file using the coordinates of our raw molecule for actual geometry optimization[5] at DFT level using def2- SVP basis set and different DFT functionals. The results of the energies of these clusters have been presented in Table 1:

Energy Comparisons:

The different functionals (BP, LDA, B3LYP, TPSS, PBEO) produce slightly varying energy values for the clusters, but the trend of increasing stability with size is consistent across all functionals. The BP functional results in the most negative energies for all cluster sizes, suggesting it predicts the most stable configurations, followed by PBEO, which also gives relatively low energy values. LDA consistently provides the least negative energy values, indicating it predicts slightly less stable clusters compared to the other functionals.

Table 1: Energy of different gold nanoclusters calculated at DFT level (def2-SVP basis set) using various functionals: -

DFT Functional	Total Energy in Electron volt (eV)					
	Au_3	Au_4	Au_5	Au_6	Au_7	Au_8
BP	-11093.17	-14792.17	-18490.77	-22190.43	-25888.41	-29587.80
LDA	-11065.60	-14755.84	-18445.52	-22136.49	-25825.52	-29516.15

B3LYP	-11079.27	-14773.25	-18467.06	-22161.11	-25855.12	-29549.71
TPSS	-11078.42	-14772.56	-18466.24	-22159.21	-25854.28	-29548.73
PBEO	-11084.29	-14780.35	-18476.00	-22170.91	-25867.76	-29548.73

These Energies have been presented graphically in figure 1, depicting variation of energy with change in DFT functional for different gold clusters. Dipole moment values of each cluster system have been given in the Table 2.

Table 2: Dipole moment of Au molecules with different DFT Functional.

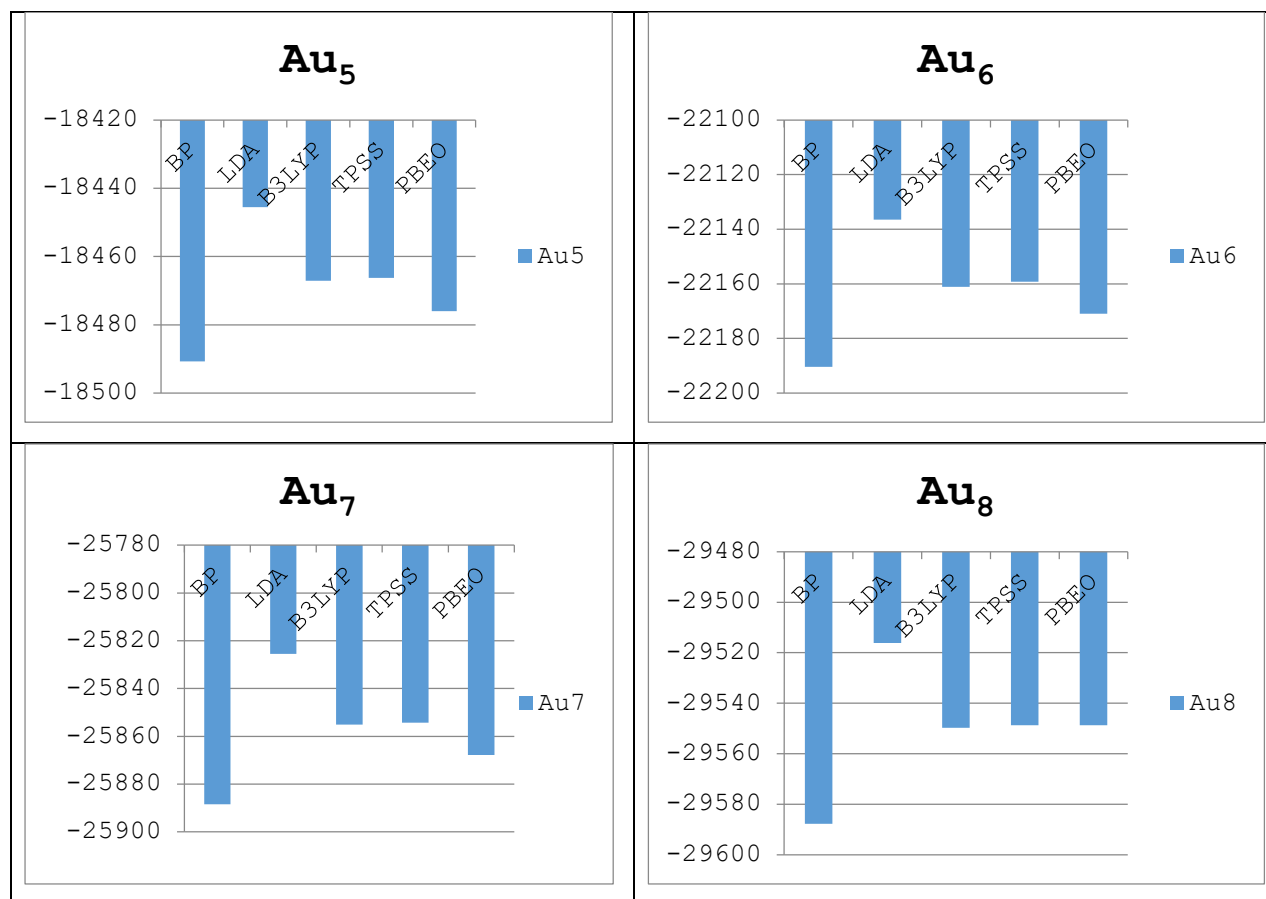| DFT Functional → Nanocluster ↓	BP	LDA	B3LYP	TPSS	PBEO
Au_3	0.87492	0.89921	0.33215	0.95229	0.88475
Au_4	0.0034	0.0002	0.00008	0.00015	0.00027
Au_5	0.03687	0.11311	0.12054	0.02274	0.03253
Au_6	0.00099	0.00113	0.00357	0.00212	0.90626
Au_7	0.65385	0.73559	0.65124	0.44602	0.65218
Au_8	0.00055	0.00241	0.00067	0.0014	0.00046
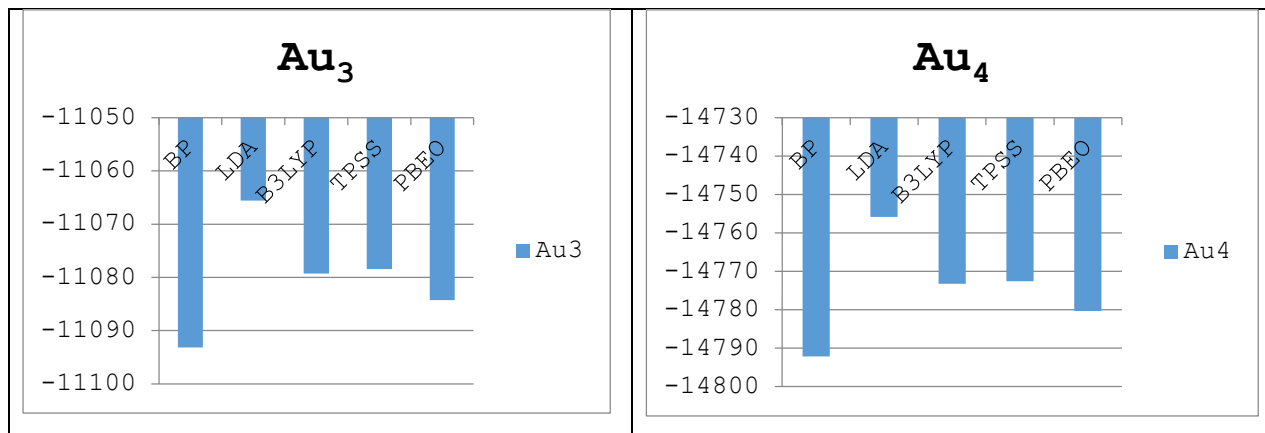
Fig 1 Variations of Energy of different gold nanoclusters with different DFT functionals

The energy differences between the functionals are small, suggesting that the overall trends and conclusions about the energy stability of gold nanoclusters remain similar regardless of the chosen functional. However, the BP and PBEO functionals give slightly more negative energies, which may suggest a more favorable description of electronic interactions for these functionals in this system.

Cluster Size and Dipole Moment:

The dipole moment of gold nanoclusters shows considerable variation depending on the size of the cluster, as well as the chosen DFT functional. For smaller clusters (Au_3, Au_5, and Au_7), the dipole moments are higher compared to larger clusters (Au_4, Au_6, and Au_8). This suggests that smaller gold nanoclusters tend to exhibit stronger polarization effects. The dipole moment for the Au_4 and Au_8 clusters is consistently very small across all functionals, indicating that these clusters are more symmetric and less polarized.

The choice of DFT functional significantly influences the dipole moment values, especially for the smaller clusters. For instance, for Au_3, the dipole moment calculated with the TPSS functional (0.95229) is significantly larger than the values from the other functionals (e.g., BP: 0.87492, PBEO: 0.88475).

For some clusters (e.g., Au_4 and Au_8), the dipole moment is predicted to be essentially zero by most functionals, indicating that these clusters are more symmetric and have little or no net polarization.

Adsorption of O_2 on Au_8 clusters:

We have also studied the adsorption of oxygen molecule on Au_8 cluster in systems i.e. Au_8O_2, $Au_8O_2^-$, $Au_8O_2^+$. The energy value of the different cluster systems with varying spin state are presented in Table 3.

The total energy values for **Au_8O_2** and its charged states ($Au_8O_2^+$, $Au_8O_2^-$, and their respective spin states) show a consistent trend: the energies become more negative as the cluster is either oxidized or reduced, indicating that these charged states are more stable energetically compared to the neutral molecule, especially when considering the different functionals.

For all functionals (BP, LDA, B3LYP, TPSS, PBEO), the total energies of the Au_8O_2 and its charged states exhibit a similar pattern, with small variations in the energy values. These variations are likely due to the differences in how each functional describes electron exchange and correlation effects.

Table 3: Au cluster systems **Energy (eV)** calculated at DFT level (def2-SVP basis set) using various functional: -

System	BP	LDA	B3LYP	TPSS	PBEO
Au_8O_2	-33675.75104	-33575.34978	-33634.06577	-33636.91581	-33648.01374
$Au_8O_2^+$ (Doublet)	-33679.13519	-33578.87943	-33638.33889	-33640.07473	-33651.25046
$Au_8O_2^+$ (Quartet)	-33667.99594	-33567.41823	-33627.87891	-33629.47487	-33640.41881

$Au_8O_2^-$ (Doublet)	-33668.12338	-33567.63342	-33627.92687	-33629.59686	-33640.55244
$Au_8O_2^-$ (Quartet)	-33678.5339	-33578.22557	-33637.49041	-33639.42985	-33650.65066

Effect of Charge and Spin State on Energy:

Neutral Au_8O_2 has the least negative energy among all the states, indicating that the neutral molecule is the least stable configuration compared to its charged counterparts.

The **Au_8O_2+ (Doublet)** state has the most negative energy across all functionals, which suggests that the addition of a positive charge (Au_8O_2+) further stabilizes the system. This is true across all functionals, implying that a positively charged species is energetically favored.

The **Au_8O_2+ (Quartet)** and **Au_8O_2- (Doublet)** states exhibit energies that are slightly higher than the corresponding doublet or quartet states, indicating that these configurations are less stable than the doublet positive charge state.

Table 4: Bond length v/s Frequency of Au_8O_2, $Au_8O_2^+$, $Au_8O_2^-$ molecules with different DFT Functional.

DFT functional	Cluster Systems	BOND LENGTH (A)	FREQUENCY (cm^{-1})
BP	Au_8O_2	1.235	1427.58
	$Au_8O_2^+$ (doublet)	1.278	1246.5
	$Au_8O_2^+$ (quartet)	1.222	1505.34
	$Au_8O_2^-$ (doublet)	1.229	1431.74
	$Au_8O_2^-$ (quartet)	1.244	1388.06
LDA	Au_8O_2	1.225	1466.17
	$Au_8O_2^+$ (doublet)	1.258	1330.27
	$Au_8O_2^+$ (quartet)	1.222	1505.48

	$Au_8O_2^-$ (doublet)	1.218	1477.48
	$Au_8O_2^-$ (quartet)	1.237	1408.81
B3LYP	Au_8O_2	1.203	1654.63
	$Au_8O_2^+$ (doublet)	1.27	1235.09
	$Au_8O_2^+$ (quartet)	1.201	1665.39
	$Au_8O_2^-$ (doublet)	1.202	1641.31
	Au_8O_2- (quartet)	1.225	1562.09
TPSS	Au_8O_2	1.234	1425.27
	$Au_8O_2^+$ (doublet)	1.285	1213.05
	$Au_8O_2^+$ (quartet)	1.222	1505.53
	$Au_8O_2^-$ (doublet)	1.227	1441.34
	$Au_8O_2^-$ (quartet)	1.247	1362.22
PBEO	Au_8O_2	1.232	1442.38
	$Au_8O_2^+$ (doublet)	1.274	1261.55
	$Au_8O_2^+$ (quartet)	1.219	1521.66
	$Au_8O_2^-$ (doublet)	1.227	1445.81
	$Au_8O_2^-$ (quartet)	1.241	1401.52

Oxygen-Oxygen bond length and frequency of Au_8O_2, $Au_8O_2^+$, $Au_8O_2^-$ molecules with different DFT Functional has been summarized in table 4. It is evident from the table 4 that as B3LYP generally predicts the shortest bond lengths and highest frequencies, suggesting stronger bonds, especially for the neutral and positive states. PBEO and TPSS provide results that are closer to B3LYP in terms of bond length and frequency for both neutral and charged states. LDA predicts longer bond lengths and lower frequencies, indicating weaker bonding in the Au_8O_2 system.

Overall, oxidation ($Au_8O_2 \rightarrow Au_8O_2+$) tends to increase bond lengths and lower vibrational frequencies, while reduction ($Au_8O_2 \rightarrow Au_8O_2-$) typically leads to slightly stronger bonds (shorter bond lengths and higher frequencies). In this study, our results have re-established the various structural parameters of gold molecule using DFT, which are found to be very close to the experimental values.

CONCLUSION:

Based on the results of this study, we conclude that the minimum energy for the Au_3 to Au_8 molecules was obtained using the BP DFT functional. The theoretical analysis of simple molecules such as Au_8 proves to be an effective and accurate approach to understanding their stability and investigating various structural properties. Additionally, this study also explored the adsorption of the O_2 molecule on gold nanoclusters. Using different DFT functionals, we performed geometry optimization and calculated several key properties, including energy, bond length, bond angle, frequency, and dipole moment, for the following molecules: Au_8O_2, $Au_8O_2^+$ (doublet), $Au_8O_2^+$ (quartet), $Au_8O_2^-$ (doublet), and $Au_8O_2^-$ (quartet).

From the Bond Length vs. Frequency graph, we conclude that the **Au_8O_2+ doublet** (cationic complex with a doublet spin state) exhibits the highest bond length and the lowest frequency among all the Au molecules studied (Au_8O_2, Au_8O_2+ doublet, Au_8O_2+ quartet, Au_8O_2- doublet, Au_8O_2- quartet). Specifically, the bond length is 1.285 Å, and the frequency is 1213.05 cm^{-1}, as predicted by the TPSS DFT functional. The increase in O-O bond length from the experimental value[18] of 1.21 Å to 1.285 Å indicates that the activation of the O_2 molecule is most pronounced in the **Au_8O_2+ doublet** complex. This suggests that, among the gold nanoclusters studied, **Au_8O_2+ doublet** is the most suitable candidate for use as a nanocatalyst in oxidation reactions, such as CO oxidation.

For the **Au_8O_2+ doublet** state, the bond angle (O-O-Au) is 117.27° and the dipole moment is 6.08894 Debye. The minimum energy of this species, calculated using the BP DFT functional, is **-33679.13519 eV**.

Comparing these results with the experimental O-O bond length in the O_2 molecule (1.21 Å), we find that the **$Au_8O_2^-$ doublet** (using the LDA functional) provides the bond length closest to the experimental value: **1.218 Å** with a frequency of **1477.48 cm^{-1}**.

Therefore we conclude that the **Au_8O_2+ doublet** complex is identified as the most promising candidate for catalysis, with significant activation of the O_2 molecule, while the **Au_8O_2- doublet** closely resembles the experimental O-O bond length in O_2.

REFERENCES :

1. Marcus D Hanwell, Donald E Curtis, David C Lonie, Tim Vandermeersch, Eva Zurek and Geoffrey R Hutchison. Avogadro: An advanced semantic chemical editor, visualization, and analysis platform.

Journal of Cheminformatics **2012**, 4:17.

2.   Neese Frank. The ORCA program system,Wiley interdisciplinary Reviews - Computational Molecular Science **2012**, Vol 2, Issue 1, 73–78.

3.   Chemcraft - graphical software for visualization of quantum chemistry computations. https://www.chemcraftprog.com.

4.   *https://en.wikipedia.org/wiki/Basis_set_(chemistry).*

5.   *https://www.scm.com/doc/AMS/Tasks/Geometry_Optimization.html*

6.   Qian, H., Zhu, M., Wu, Z., & Jin, R. (**2012**). Quantum sized gold nanoclusters with atomic precision. *Accounts of Chemical Research*, *45*(9), 1470–1479.

7.   Pittaway, F., Paz-Borbón, L. O., & Johnston, R. L. (**2009**). Theoretical studies of palladium−gold nanoclusters: Pd−Au clusters with up to 50 atoms. *The Journal of Physical Chemistry C*, *113*(20), 9141–9147.

8.   Shahnazari, G. H., & Ganji, M. D. (**2021**). Understanding structural and molecular properties of complexes of nucleobases and Au_{13} golden nanocluster by DFT calculations and DFT-MD simulation. *Scientific Reports*, *11*, 12345.

9.   Tang, Q., Hu, G., Fung, V., & Jiang, D. (**2018**). Insights into interfaces, stability, electronic properties, and catalytic activities of atomically precise metal nanoclusters from first principles. *Accounts of Chemical Research*, *51*(11), 2793–2802.

10.   Gao, L., Zhai, J., & Gao, X. (**2016**). Atomic structure of a peptide coated gold nanocluster identified using theoretical and experimental studies. *Nanoscale*, *8*(2), 345–354.

11.   Fihey, A., Maurel, F., & Perrier, A. (**2014**). A DFT study of a new class of gold nanocluster-photochrome multi-functional switches. *Physical Chemistry Chemical Physics*, *16*(11), 5123–5133.

12.   Pundlik, S. S., & Kalyanaraman, K. (**2011**). First-principles investigation of the atomic and electronic structure and magnetic moments in gold nanoclusters. *The Journal of Physical Chemistry C*, *115*(11), 5135–5145.

13.   Jain, P. K. (**2005**). A DFT-based study of the low-energy electronic structures and properties of small gold clusters. *Structural Chemistry*, *16*(4), 325–334.

14.   Naveen, M. H., Khan, R., & Bang, J. H. (**2021**). Gold nanoclusters as electrocatalysts: Atomic-level understanding from fundamentals to applications. *Chemistry of Materials*, *33*(20), 8032–8048.

15.   Goel, S., Velizhanin, K. A., & Piryatinski, A. (**2010**). DFT study of ligand binding to small gold clusters. *The Journal of Physical Chemistry Letters*, *1*(2), 312–316.

16. Bagayoko, Diola. Understanding density functional theory (DFT) and completing it in practice. *AIP Advances* **2014**, (12), 127104.

17. C. Riplinger, B. Sandhöfer, F. Neese. Fast and Accurate Theoretical Chemistry, **2020.**

18. Huber, K. P., & Herzberg, G. (**2013**). *Molecular spectra and molecular structure: IV. Constants of diatomic molecules*. Springer. https://doi.org/10.1007/978-1-4757-0961-2