Chemistry in Computers; Understanding Orbital Interactions and Energies

AICTE Summer Internship Report

By

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Declaration by the Student

I, Syed Zainish Shah (Candidate ID: 5963), certify that this project is my own work, based on my personal study and work and that I have acknowledged all material and sources used in its preparation, whether they be books, articles, reports, lecture notes, and any other kind of document, electronic or personal communication. I also certify that this project has not previously been submitted for assessment in any academic capacity, and that I have not copied in part or whole or otherwise plagiarized the work of other persons. I confirm that I have identified and declared all possible conflicts that I may have.

Date: 18/07/2023

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Place: IISER Kolkata

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Certificate from the Supervisor / Project Investigator

Date: 18.07.2023

This is to certify that the report entitled "**Chemistry in Computers; Understanding Orbital Interactions and Energies**" submitted by Syed Zainish Shah, a student of Department of Chemical Sciences of the AICTE Summer Internship Program, is based upon his/her own research/study work under my supervision.

This is also to certify that neither the work/study nor any part of it has been submitted for any degree/diploma or any other academic award anywhere before.

Acknowledgements

I would want to convey my heartfelt gratitude to AICTE for providing me with this opportunity to work as an intern in India's top Institute. I would also like to extend my gratitude to the coordinator of this Internship**, Prof Alakesh Bisai** for making it easy for us to attend the internship. I would like to express my special thanks to **Prof Debasis Koley**, my mentor, for his invaluable advice and assistance in completing my project. He was there to assist me every step of the way, and his motivation is what enabled me to accomplish my task effectively. I would also like to thank all of the lab members who assisted me by supplying the equipment that was essential and vital, without which I would not have been able to perform efficiently on this project. I am highly thankful to my college faculty, especially, the HOD Biochemistry, Dr. Raies for being cooperative and providing constant support and encouragement as I worked on the project.

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Date: 18/07/2023

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Abstract

With Rapid development of computer hardware during the last few decades, there has been a significant increase in capability and reliability of computational quantum chemistry as a useful and accessible tool in the understanding of chemical structures, properties, and reactions. Initially, the focus was on force-field based methodologies for studying the structures, dynamics, and interactions of bio-molecules as such, and the development of accurate models for the main biological solvent, water. Our main motive in this project was somewhat like this study based on water. As we know water is an essential part of our biome as well as our body, we focused our work mainly on the structure and orbitals of water to know about its physio-chemical properties. We visualized the molecular orbitals of water using the fragment based orbital mixing. With the successful visualization of molecular orbitals of water, we broadened our study by working on the molecular models of simple molecules like CO, CN^-, homo-nuclear diatomic species like O_2. With the help of advanced software like Gaussview and Chemcraft, we were able to observe various parameters of these molecules like bond length, bond angle, dipole moment with its magnitude, orbital energies with the visualization of molecular orbitals. Later we went ahead with the computed structures of Lewis Acid-Base Adducts of various acid-base pairs where we calculated the binding energies of Adducts along with the hardness and softness of the individual acids and bases.

Introduction

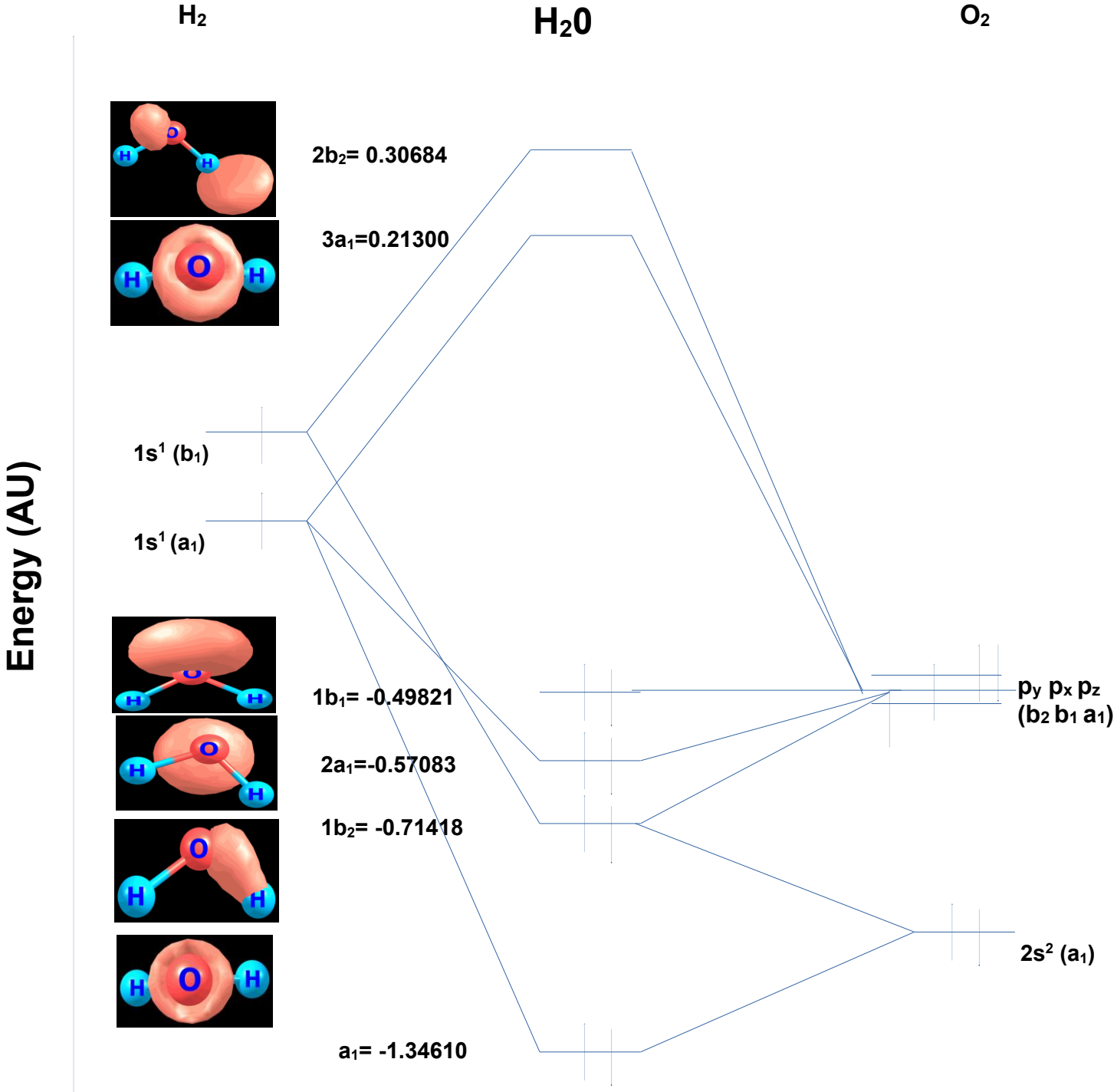
(Project 1st)

Computational chemistry provides valuable insights into the molecular structures and properties of diverse compounds. It complements experimental techniques and helps guide experimental design by providing detailed information that may not be easily accessible through direct observation. Researchers from different areas of chemistry routinely use electronic structure methods to understand and predict molecular structures, physio chemical properties and can even explain the outcome of chemical reaction. With the advent of powerful computers high level calculations can be achieved which shows excellent agreement with the experimental observations. The input for such calculations requires the use of a basis set, the molecular geometry, charge, and spin multiplicity. All calculations were performed using Gaussian 16 program package at HF/ 3-21G level and Chemcraft was used for calculating various parameters. In this experiment, we studied the molecular structures of various molecules like water, CO. CN, O_2 using the Gaussian software and Chemcraft software.

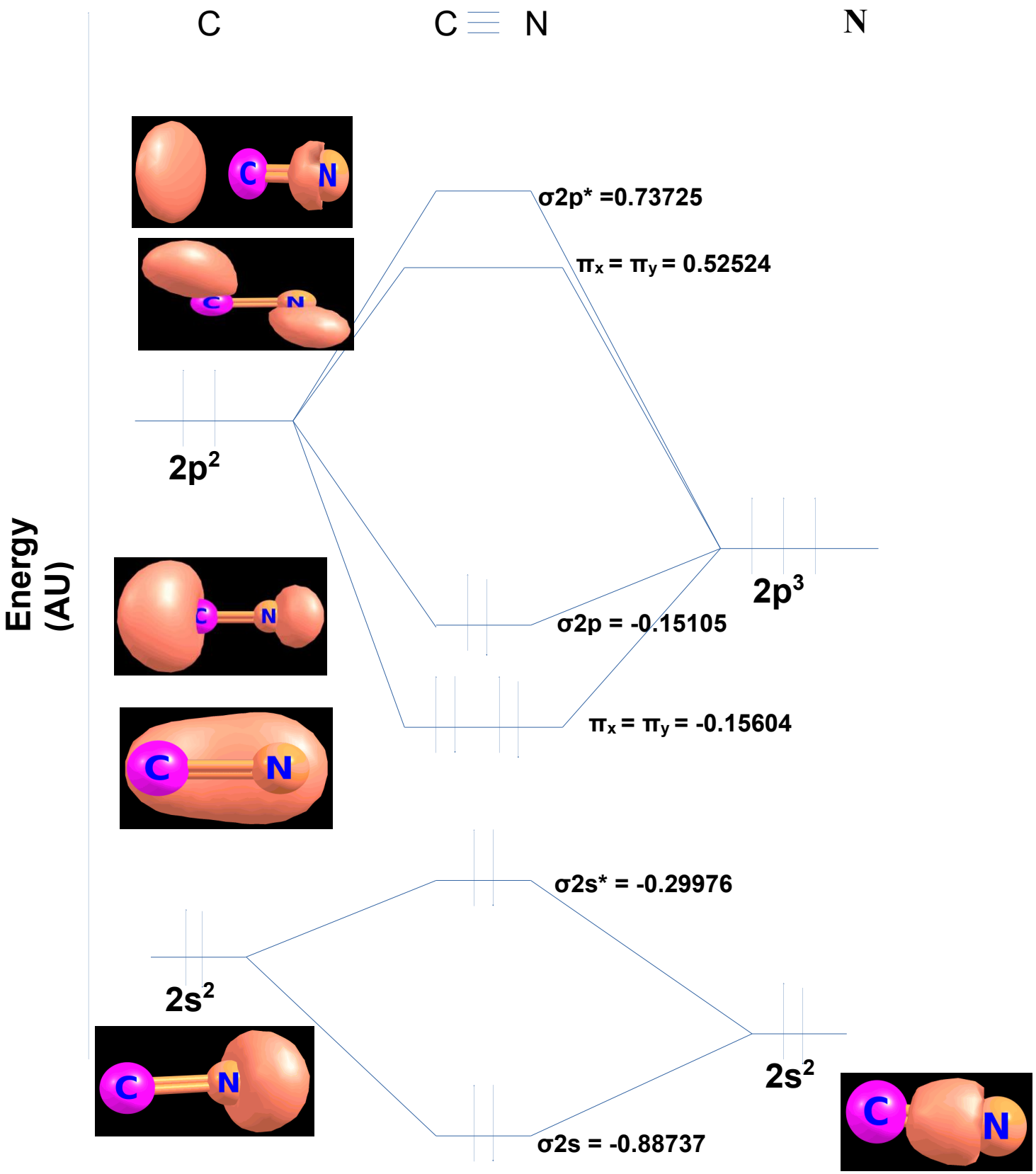
Results and Discussion

(Project 1st)

Molecular Orbital Diagram of Water

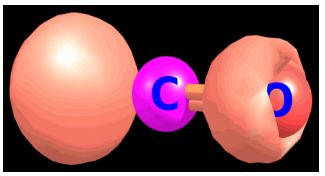


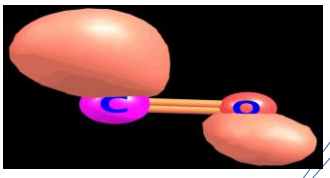
Molecular Orbital diagram of CN



Molecular Orbital diagram of CO

C C O



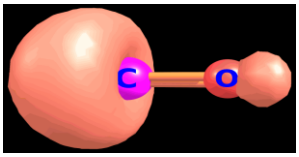


Energy (AU)

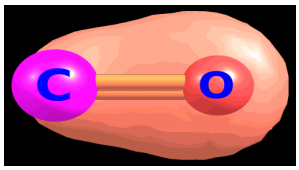
$2p^4$

σ2p* =0.40948

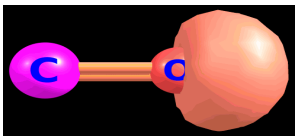
$\pi_x = \pi_y = -0.63923$



σ2p = -0.54592



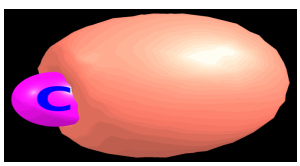
$\pi_x = \pi_y = 0.16793$



σ2s* = -0.79774

$2p^2$

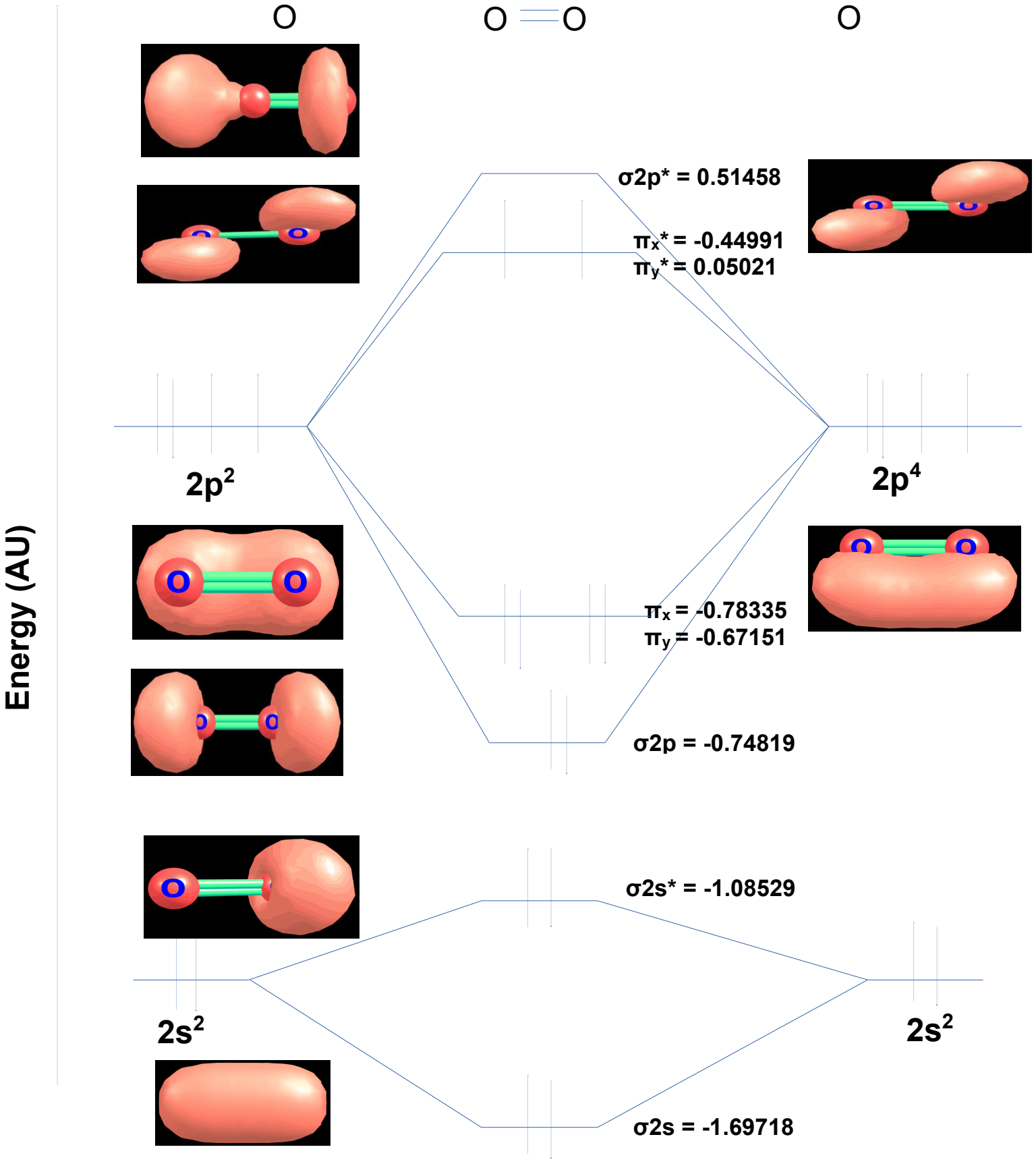
$2s^2$



$2s^2$ σ2s = -1.52923

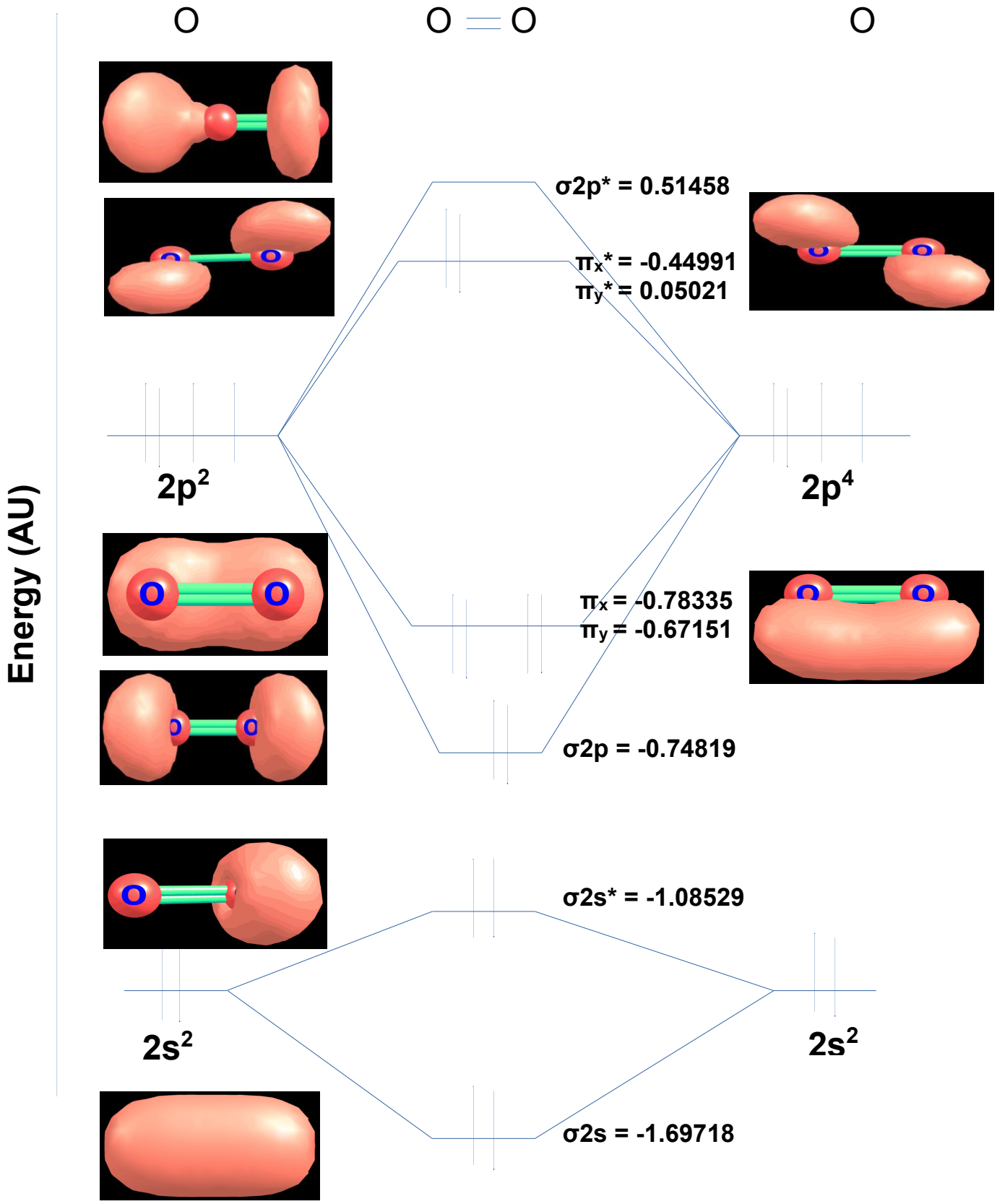
Molecular Orbital diagram of O_2

(Triplet state)



Molecular Orbital diagram of O_2

(Singlet state)



Conclusion

This experiment provides us with a short overview of employing computational chemistry and molecular modeling techniques to understand the structure and chemical bonding in water molecule. Calculated results help us to visualize most of the molecular orbitals with proper symmetry labels and absolute energies. This experiment also helped us in building the MO diagram using the fragment based orbital mixing.

The structures of small molecules like H_2O. CO, CN, O_2 were made using the GaussView and were visualized using the chem craft software whereas the calculations were obtained from the Gaussian 16 Software.

Introduction

(Project 2nd)

The Lewis acids are the acceptors of the donated pair of electrons and have an empty orbital whereas the Lewis bases are the donors of the pair of electrons as they have a lone pair. The main motive of this exercise is to calculate the binding energy of the acid-base adducts along with their relative hardness and softness, steric interactions between acid and base. When the individual acid and base reorganize themselves to form Adducts, they require energy to optimize themselves in a way that favors the formation of Adducts, this energy known as Reorganisational energy is also calculated in this experiment. It can be observed in this experiments that the bond distance for M-X bond in an acid change after forming adduct with the base. All calculations were performed using Gaussian 16 program package at HF/3-21G level. BH_3, BF_3, BCl_3, AlH_3, and $AlCl_3$ are used as the Lewis acids whereas NH_3 and PH_3 are used as the Lewis bases

Results and Discussion

Adducts	ΔE^{a}/ Kcal mol^{-1}	r_{MN}^{b} / A	r_{MN}^{c} / A	$\angle XMX^{d}$ (°)	E_{reorg}^{e}/ kcal mol^{-1}	ΔQ_{BA}^{r}	ΔQ_{DA}^{g}	ΔQ_{AA}^{h}
H3N:AlCl3	-66.40	2.03	0.04	116.08	5.9 (0.54)	0.25	-1.01	1.40
H3N:BCl3	-49.13	1.62	0.16	113.48	25.1 (0.3)	0.35	-0.90	0.27
H3N:AlH3	-42.37	2.05	0.03	116.74	5.3 (0.31)	0.19	-0.96	0.73
H3N:BF3	-42.08	1.69	0.02	114.65	23.3 (0.28)	0.20	-0.96	1.19
H3N:BH3	-26.23	1.71	0.02	113.96	13.5 (0.31)	0.25	-0.85	0.001
H3P:AlCl3	-27.26	2.54	0.11	116.74	6.1 (2.5)	0.14	-0.03	1.42
H3P:AlH3	-12.69	2.71	0.02	118.66	2.2 (0.8)	0.54	0.004	0.79
H3P:BH3	-8.39	2.21	0.01	116.79	6.9 (1.05)	0.26	0.24	-0.16
H3P:BCl3	-7.72	2.06	0.15	113.85	23.7 (4.33)	0.65	0.48	1.20
H3P:BF3	-5.69	3.02	0.005	119.74	0.89 (0.16)	0.007	0.02	-0.17

[a]Binding energy

[b]Donor atom-acceptor atom bond distance in the adduct.

[c]Change in the M-X bond distance in the acid of the adduct.

[d]Value of the X-M-X bond angle in the acid of the adduct.

[e]Reorganisational energy of the acid (base) upon adduct formation as a result of a change in the structure

[f]Net Mulliken Charge transfer from the base to the acid upon adduct formation

[g]Charge on the donor atom of the base in the adduct.

[h]Charge on the acceptor atom of the acid in the adduct.

The results that were obtained from this experiment are:

1) The binding energies of the various adducts depending on the relative strengths of individual lewis acid and lewis base.

2) The charge capacities of the acid.

3) The reorganisational energy that is required to change the geometry of the acid and base into that present in the adduct.

4) The structural changes that occur upon adduct formation ;

a) Bond Lengths.

b) Bond angles.

Conclusion

Trends in binding energies and several of the factors that accompany adduct formation can be demonstrated by the calculations. Calculated trends using 3-21G *ab initio* basis set are in good agreement with those obtained from high level *ab initio* calculations. The factors that could affect the binding energy of the Lewis acid-base were calculated using these calculations.

References

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