Molecular Orbitals of Nitrogen molecule obtained through Gaussian using Jmol generated input file

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1. Introduction

The valence bond theory can't explain,

- Multiple bond formation
- Resonance
- Bond order
- Magnetic behaviour

To overcome the above mentioned shortfall the Molecular orbital theory was proposed

1.1 Molecular orbital theory

Molecular orbital theory is concerned with the combination of atomic orbitals to form new molecular orbitals. These new orbitals arise from the linear combination of atomic orbitals to form bonding and antibonding orbitals. The bonding orbitals are at a lower energy than the antibonding orbitals, so they are the first to fill up. By figuring out the molecular orbitals, it is easy to calculate bond order.

1.2 Basic principles of Molecular orbital theory

- When nuclei of two atoms come close to each other, their atomic orbitals interact leading to the formation of molecular orbitals
- The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of molecular orbitals
- Each molecular orbital is described by a wave function Ψ known as molecular orbital wave function
- The molecular orbital wave function Ψ is such that Ψ^2 represents the probability density or e^- charge density
- Each molecular orbital wave function Ψ is associated with a set of quantum numbers which determine the energy and shape of the molecular orbital
- Each Ψ is associated with a definite energy and the total energy of the molecule is the sum of the energies of occupied molecular orbitals

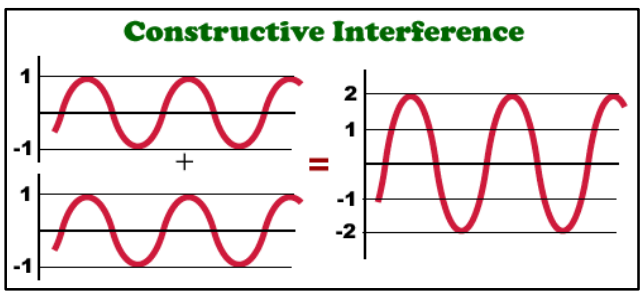
- Electrons fill the molecular orbitals in the same way as they fill the atomic orbitals following the Aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity
- Each electron in a MO belongs to all the nuclei present in the molecule
- Each e^- moving in a MO has a spin of + ½ or - ½

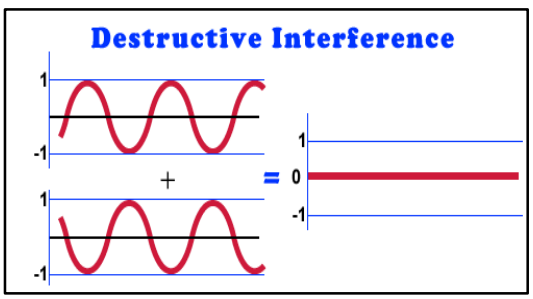
1.3 Salient features of Molecular orbital theory

- MOs are obtained through combination of atomic orbitals of comparable energies
- The number of MOs obtained is always same as that of the number of atomic orbitals from which they are formed
- Each molecular orbital has definite energy. Out of the two MOs formed through the combination of AOs, one MO has lower energy and the other has higher energy than the energy of either AOs. The MO lower energy (more stable) is called "Bonding Molecular Orbital". The molecular orbital with higher energy (less stable) is called "Antibonding Molecular Orbital"
- The shape of MOs depends upon the shape of combining AOs
- Each MO can accommodate a maximum of two electrons with opposite spins

1.4 Linear combination of atomic orbitals (LCAO)

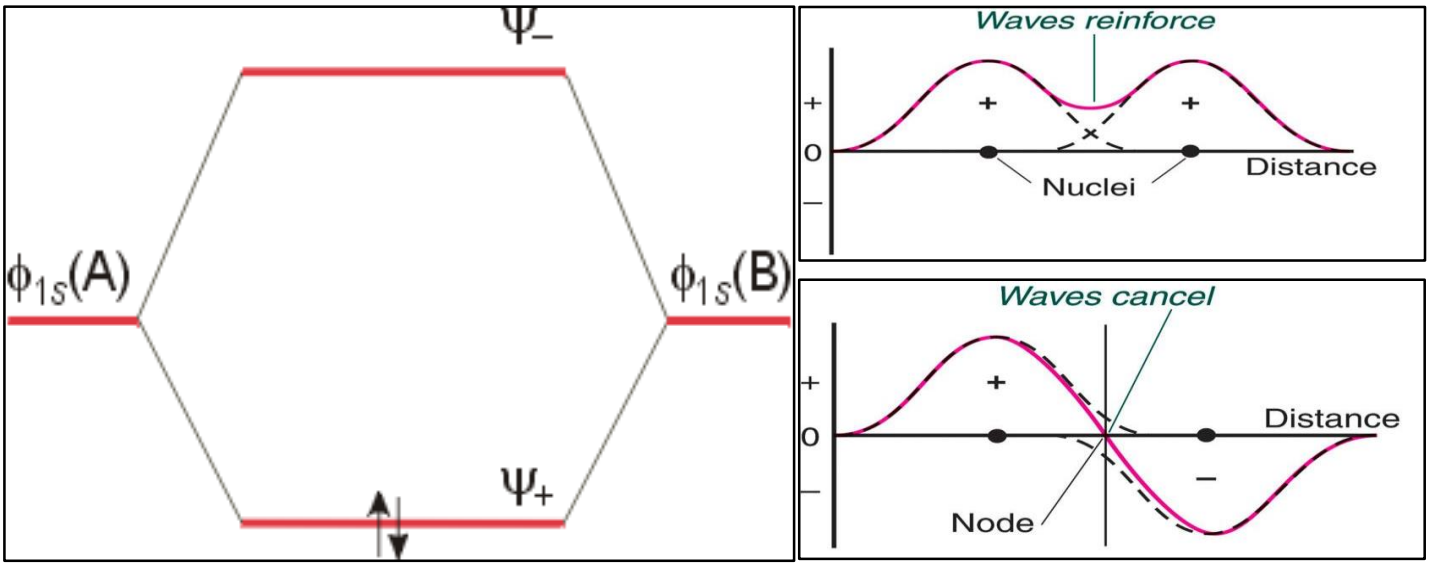
- Molecular orbitals result from the combination of atomic orbitals
- Orbitals are wave functions
    - Constructive overlap leads to bonding molecular orbital
    - Destructive overlap leads to an antibonding molecular orbital
- Molecular orbitals form by the overlap of atomic orbitals with similar energies and proper symmetry
- Atomic orbitals with differing energies or different spatial orientation (orthogonal) do not combine, and are called non-bonding orbitals





1.5 Characteristics of Bonding Molecular Orbitals (BMO):

- BMOs are denoted as σ_g, where the g stands for gerade, or symmetric with respect to a centre of inversion
- BMO energy is less than ABMO:
- The attraction of both the nuclei for both the electron (of the combining atom) is increased
- The signs on the molecular orbitals indicate the sign of the wave function, not ionic charge



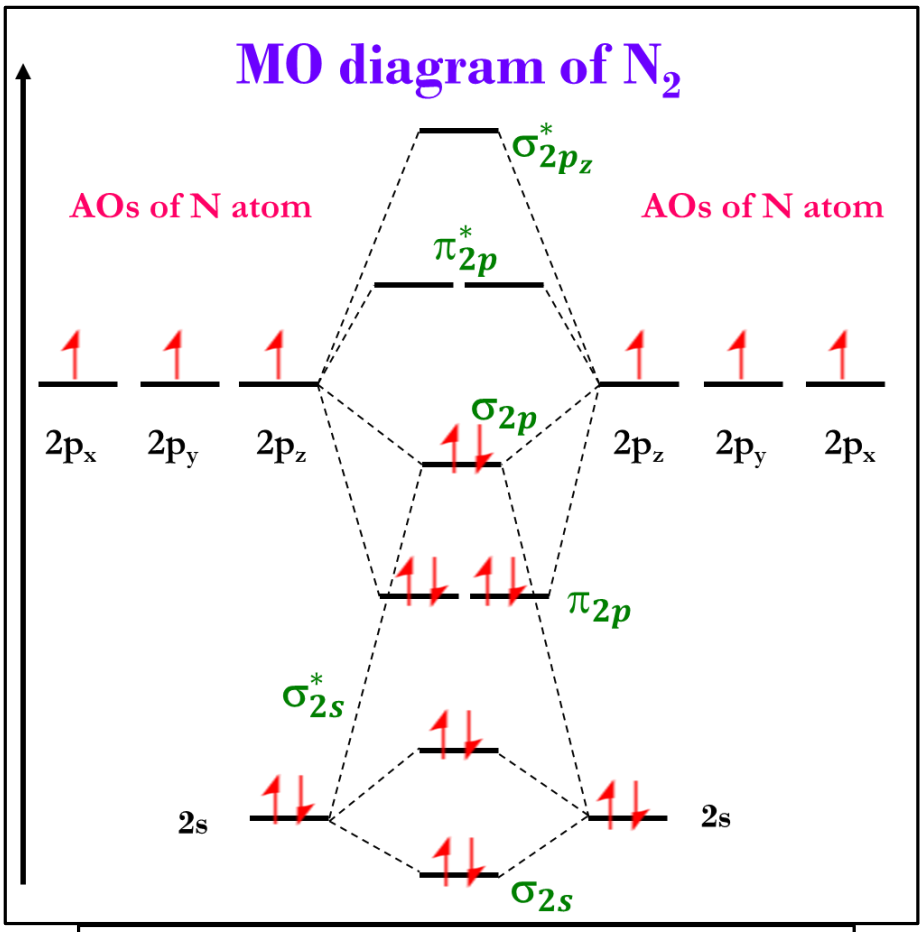
1.6 Characteristics of Antibonding Molecular Orbitals (ABMO):

- ABMOs are denoted as σ_u, where the u stands for ungerade, or asymmetric with respect to a centre of inversion
- BMO energy is less than ABMO
- The electron try to move away from the nuclei and are in repulsive state
- The signs on the molecular orbitals indicate the sign of the wave function, not ionic charge

2. Objectives

- To create 3D structure of nitrogen molecule in Jmol interface
- To optimize the 3D structure of nitrogen molecule and save as .mol file
- Importing the .mol file to the Gaussian engine in WebMO
- Generating the 3D molecular orbital diagram through Gaussian

3. Molecular orbital diagram of Nitrogen (theoretical)



Electronic configuration of N_2 molecule

$$[KK]\ \sigma_{2s}^{\ 2}\ \sigma^*_{2s}{}^{2} \left\{ \begin{matrix} \pi_{2px}^{\ 2} \\ \pi_{2py}^{\ 2}, \end{matrix} \right\} \sigma_{2pz2}$$

$$Bond\ Order = \frac{8-2}{2} = 3$$

No unpaired electrons: Diamagnetic

4. **Drawing the 3D structure of Nitrogen molecule in Jmol interface**

- Open Jmol interface select the model kit menu
- Select nitrogen atom and it appears as ammonia molecule
- Using delete atom option delete H atoms
- Drag from nitrogen atom to get another nitrogen
- Select the option to get a triple bond between two nitrogen atoms

5. **Energy optimization of nitrogen molecule in Jmol interface**

- Exit from the model kit menu
- Now right click on the molecule
- Select the option computation
- Then click optimize structure

6. **Save the 3D structure as .mol file**

- Click the model kit menu
- In the drop down list select the last option
- Click on the save file option
- Now the structure is saved in the .mol format

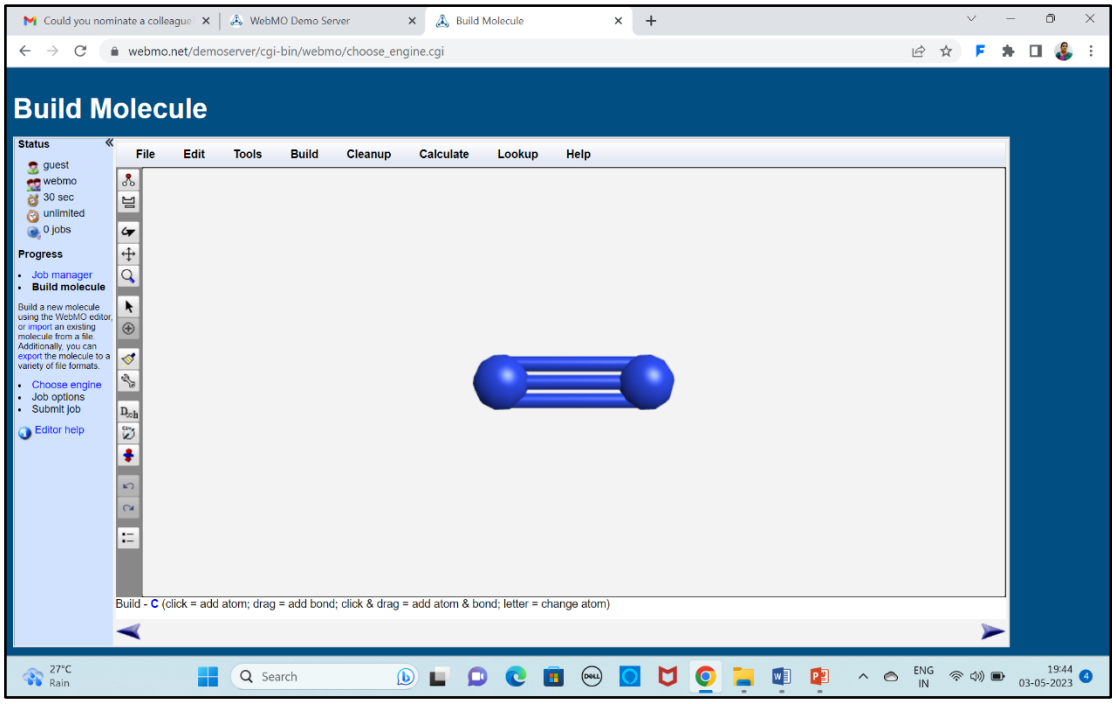
7. **Importing the .mol file to the Gaussian engine in WebMO**

- Open the WebMO web page https://www.webmo.net/
- Click on the DEMO icon
- Login into demo server https://www.webmo.net/demoserver/cgi-bin/webmo/login.cgi
- Click on the new job option- select – create new job
- Now Build molecule page opens
- Click on File menu-import molecule-select file type as mol
- Choose the .mol file saved already in the laptop/desktop
- Now the .mol file will be imported

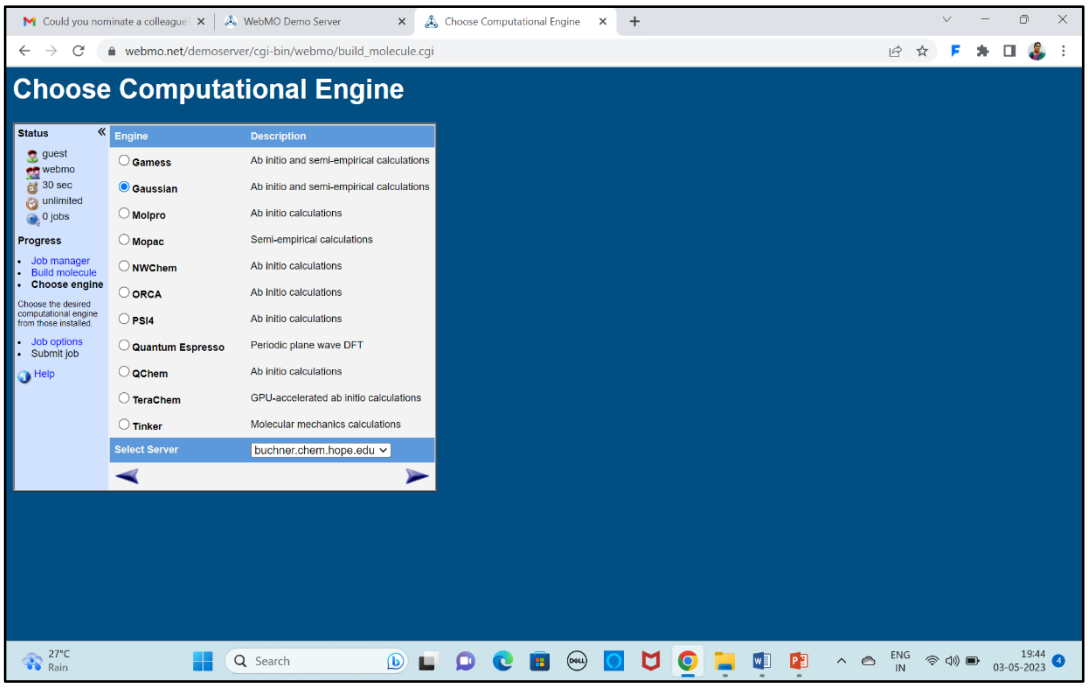
8. **Generating the Molecular Orbitals through Gaussian in WebMo interface**
    - Configure Gaussian Job option page opens
        - Give the Job name (here we have given as Nitrogen Molecule)
        - Calculation – select as Molecular Orbital
        - Theory – B3YLP
        - Basic set – cc-pVDZ
        - Charge – 0
        - Multiplicity – Singlet

- After providing all the above options click the next arrow
- We will get into WebMO Job Manager page
- We can view the execution of the job in progress
- Once the status of the Job is complete click to view the job

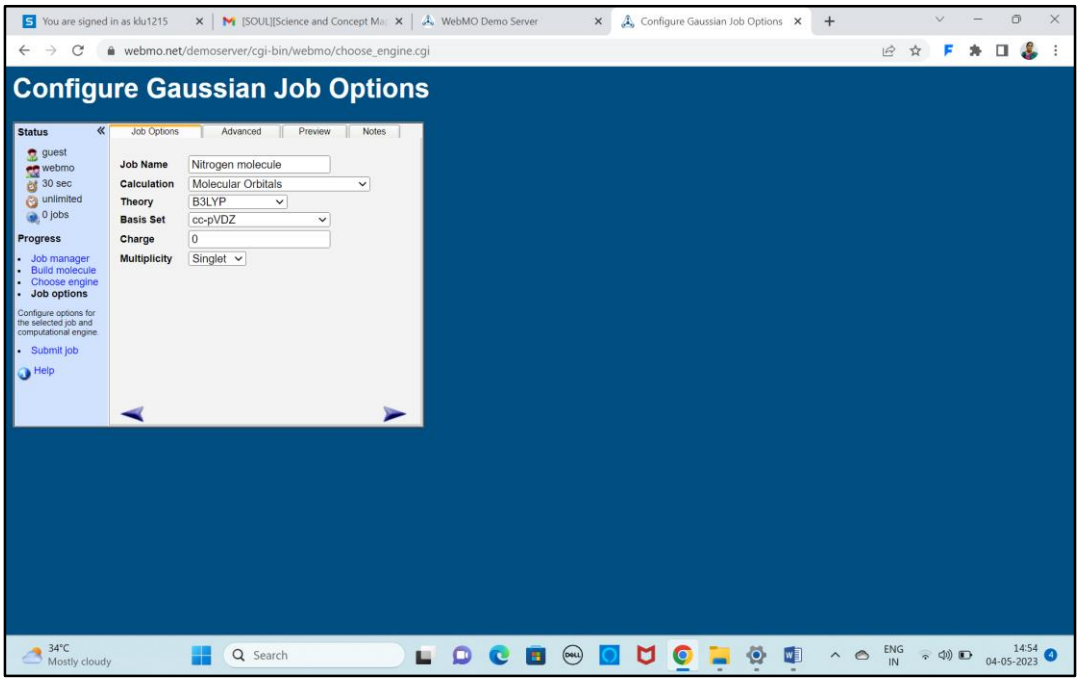
Step:1 The .mol file was imported to the WebMo interface



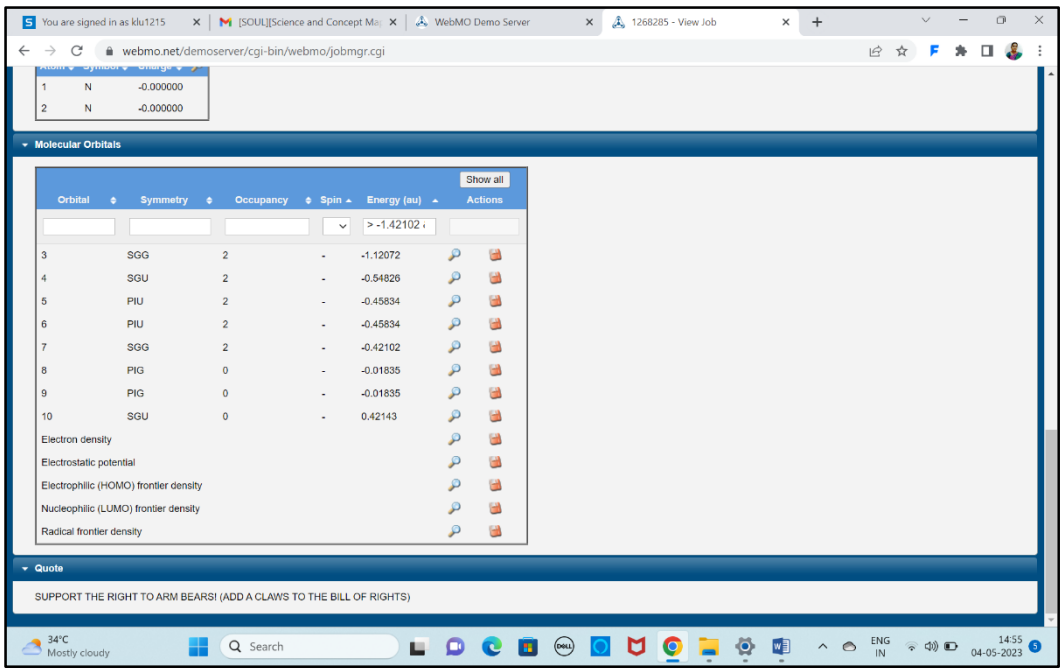
Step:2 The Gaussian computational engine was selected



Step :3 Configuration for Gaussian Job was provided as below

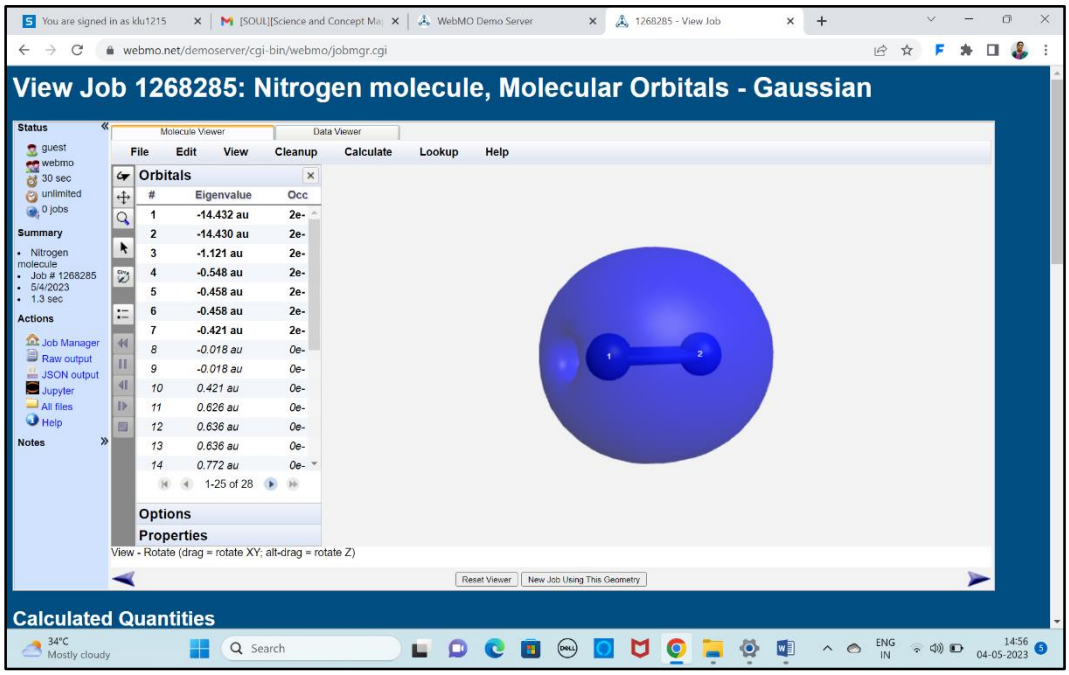


Step: 4 The Job was executed and Molecular orbitals were generated

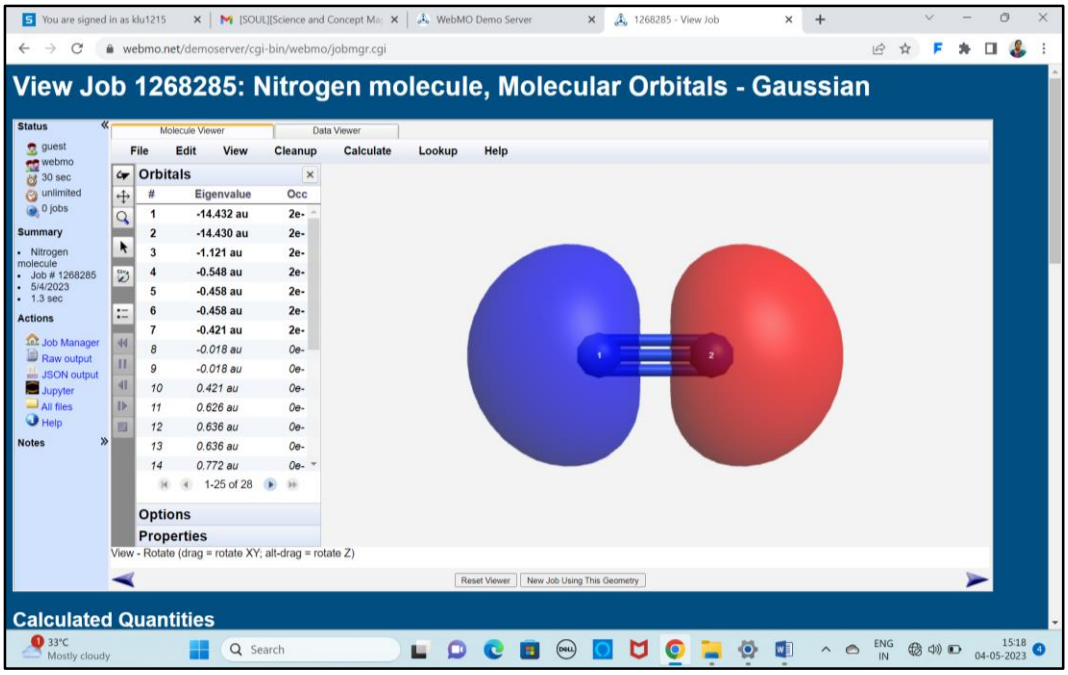


- Each molecular orbital with its energy, occupancy and symmetry was displayed
- By clicking on the view icon, we can view the 3D structure of each molecular orbital
- The energies of each molecular orbital was given in the table, in the WebMo interface
- The energy levels of the 3D molecular orbitals generated in the WebMo interface are in correlation with the MO diagram (Theoretical)

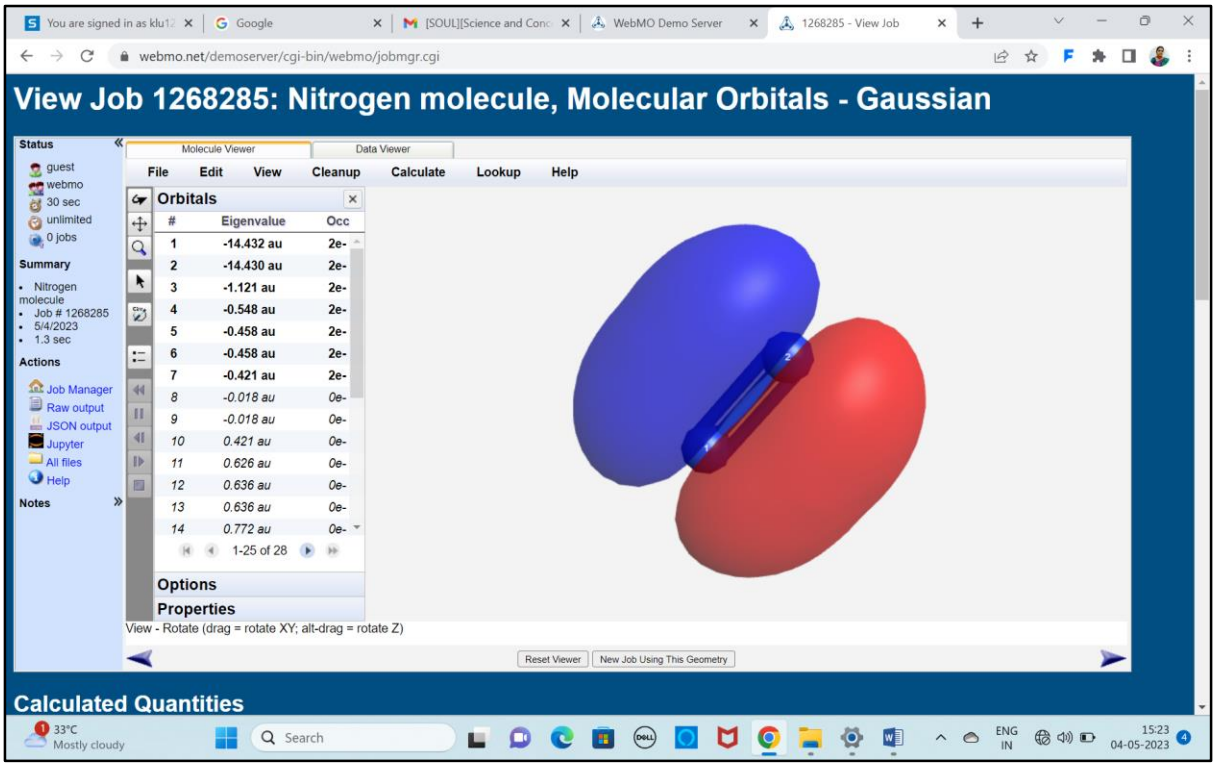
3D structure of σ 2s Bonding molecular orbital (Energy = -1.12072 au)



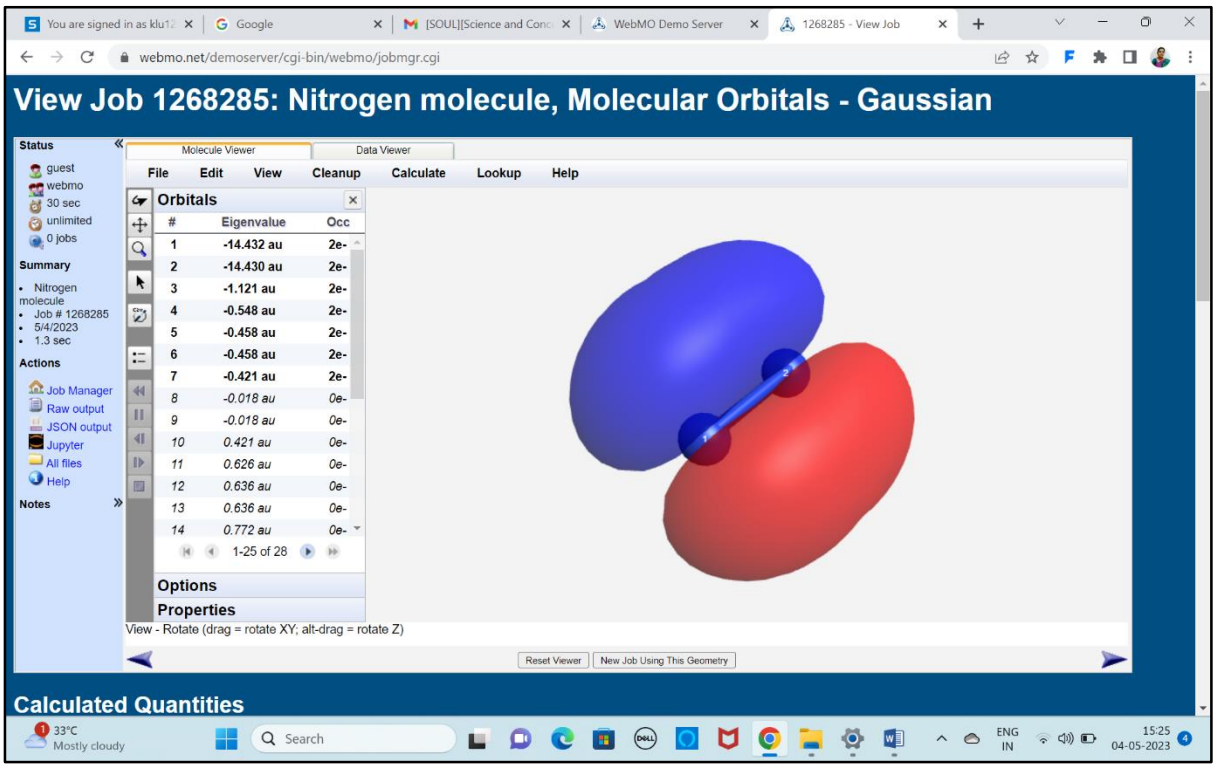
3D structure of σ* 2s Antibonding molecular orbital (Energy = -0.54826 au)



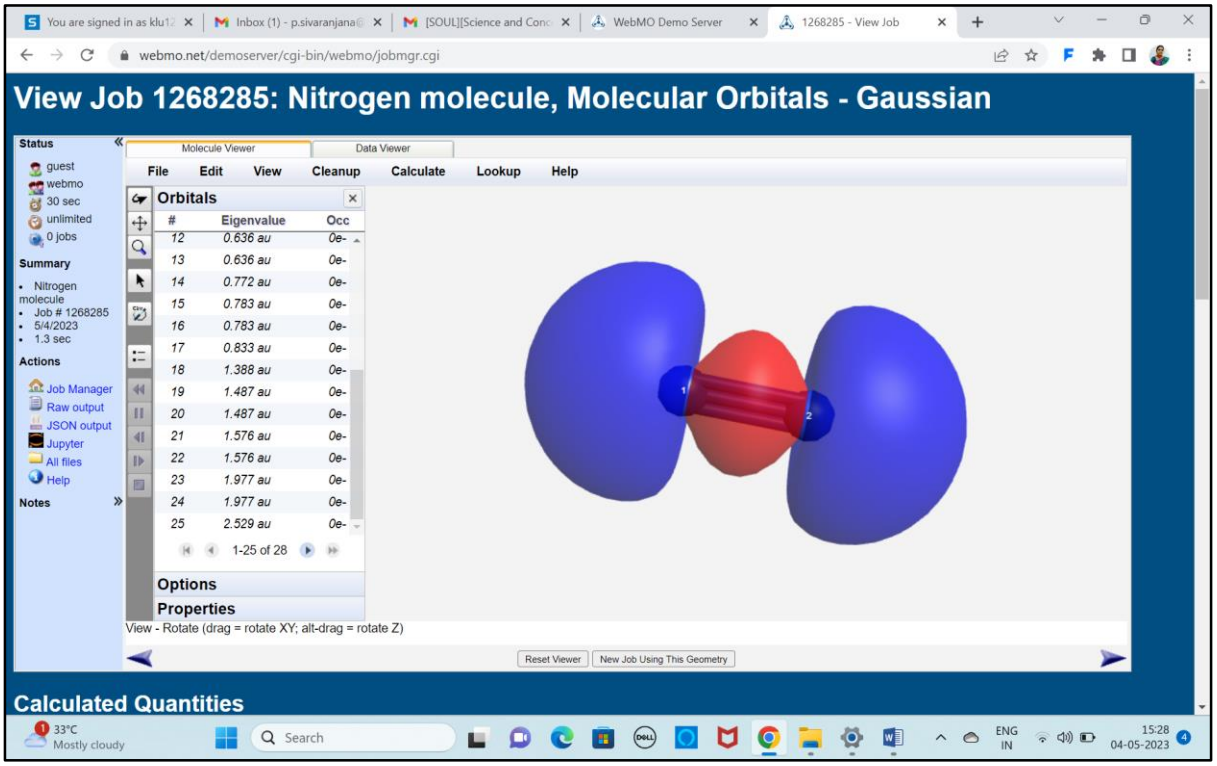
3D structure of π $2p_x$ Bonding molecular orbital (Energy = -0.45834 au)



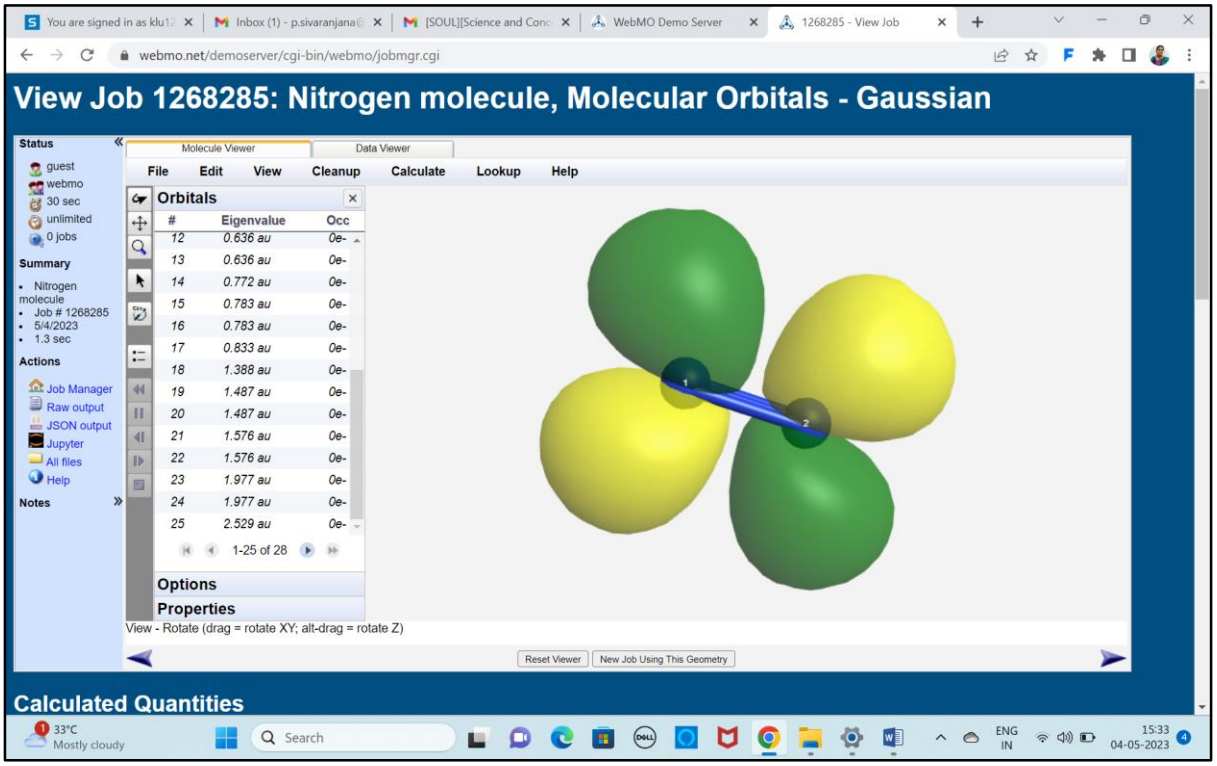
3D structure of π $2p_y$ Bonding molecular orbital (Energy = -0.45834 au)



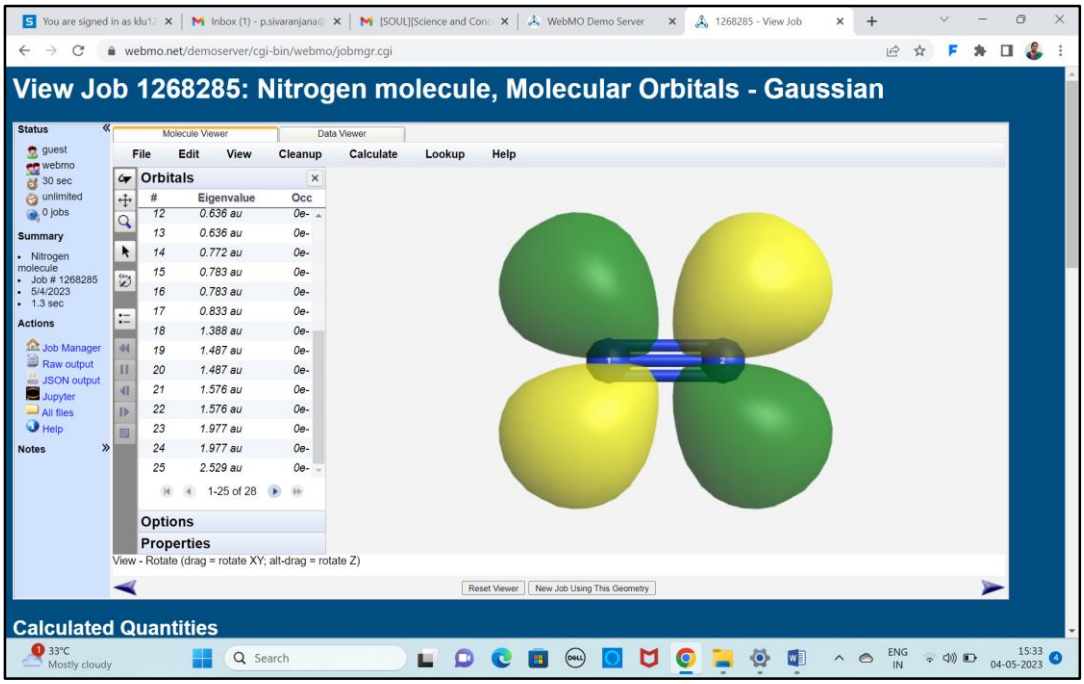
3D structure of σ $2p_z$ Bonding molecular orbital (Energy = -0.42102 au)



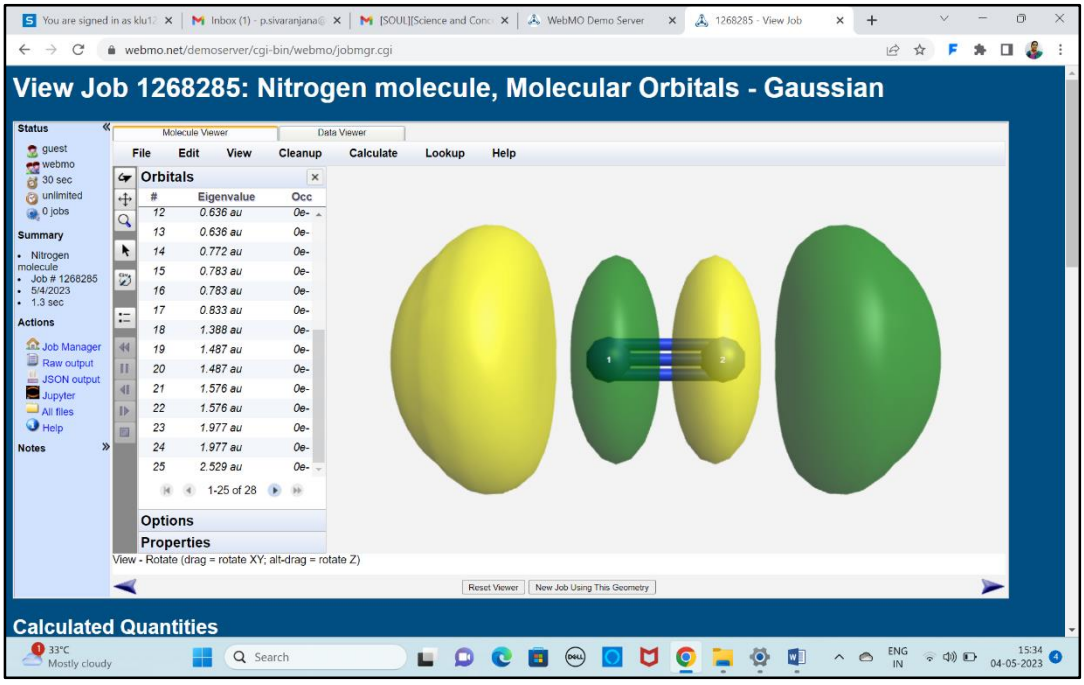
3D structure of π* $2p_x$ Bonding molecular orbital (Energy = -0.01835 au)



3D structure of π^* $2p_y$ Bonding molecular orbital (Energy = -0.01835 au)



3D structure of σ^* $2p_z$ Bonding molecular orbital (Energy = 0.42143 au)



Conclusion

- The 2s and $2p_z$ orbitals are forming sigma bonding
- The $2p_x$ and $2p_z$ are forming pi-bonding
- The energy of the molecular orbitals matches with the energy order represented in the theoretical MO diagram
- The energy of the $\pi 2p_x$ and $\pi 2p_y$ are equivalent

- The energy of the $\pi^{*}2p_x$ and $\pi^{*}2p_y$ are equivalent
- The energy of the $\sigma\ 2p_z$ is greater than $\pi 2p_x$ and $\pi 2p_y$
- The energy of the $\sigma^{*}2p_z$ is greater than $\pi^{*}2p_x$ and $\pi^{*}2p_y$
- The electron occupancy was also similar to that of the theoretical MO diagram

All the above observations are in coincidence with the theoretical MO diagram

Acknowledgement

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