Density Functional Theory and its Uses in Computational Chemistry.

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An Introductory Text to the PHY3PRJ Project undertaken in 2025 by Jayson Baker as Supervised by David Hoxley, and with help from David Wilson.

**Don’t Panic.**

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Basics of Density Functional Theory (DFT).

**What is Density Functional Theory?**

Density Functional Theory (DFT), is a non-variational computation method of solving the time independent Schrodinger Equation. The method was first developed as additional lines of code to the Hartree-Fock method. DFT is used to solve many electron wave functions and finds the first principle’s adsorption energies, work functions, diffusion barriers and vibrational spectra. DFT is easily adaptable with various hybrid methods being developed for differing problems. A downside to this adaptability is that is it a delocalised and less exact method, much more so than the Hartree-Fock method. Chemists saw the advantages of DFT, and it became widely adopted as the most common computational chemistry method in the 1980s.

**What is Hartree-Fock?**

The Hartree Fock method (HF) is a computational algorithm designed to approximate a wave function and energy of a multi-electron system in a stationary state. It uses a variation of the Time-Independent Schrodinger Equation (1.a,b) to optimize the orbital function to find the minimum energy of a system in equation (2).

(1.a)

(1.b)

Where:

Eψ, is the net energy of the system,

Tψ, is the kinetic energy of the system,

Vψ is the potential energy of the system, and

Hψ, is the Hamiltonian Operator which is the sum of Tψ and Vψ.

(2)

Where:

Ia, is the one-electron integral,

Jab, is the one-electron Coulomb integral, and

Kab, is the one-electron exchange integral.

The method is named after Douglas Hartree and Vladimir Fock. As there are no known analytical solutions for multi electron systems, HF solves the wave function numerically. HF solves the equation using nonlinear methods such as iteration as there are nonlinearities introduced from the method itself.

The Hartree equation is an approximate solution of the Schrodinger equation with two main assumptions. Firstly, that the wave function can be approximated by a single Slater determinant. Secondly, that the final computed field is the same charge as the assumed initial field.

The Slater Determinate postulates that a multielectron wavefunction can be written as a n by n determinate, were n is the number of electrons present.

Where:

ψ is the wavefunction,

N ϵ ℕ is the number of electrons in the system,

χi is the *i*-th spin orbital, and

xj is the co-ordinates of the *j*-th electron.

The Slater Determinate can also be written in shorthand as:

There are five main approximations that the Hartree-Fock method assumes to solve the resulting problems. Firstly, the Born-Oppenheimer approximation is foundationally assumed. Which states that, the wave functions of electrons can be treated separately to the wave functions of atomic nuclei.

Secondly, relativistic effects are normally completely ignored. Thirdly, the solution is assumed to be a linear combination of basis sets, of which there is a finite number and are usually orthogonal. Fourthly, the energy eigenfunctions present are assumed to be an anti-symmetrical product of a one-electron wave function. Finally, the mean field theory is implied and all effects that arise are assumed to be part of electron correlation.

**Some Applications of DFT:**

DFT measures the energy in molecules by mapping the electron density this is used to; predict spectra of a molecule (including IR and NMR spectra), confirm the geometry of molecules, define the unicorn of chemical bonding, approximate excited molecular orbitals, etc.

Investigating Molecular Orbitals, Natural Bond Orbitals and Electron Density Using WebMO.

**Abstract**

*The program WebMO was used to calculate the Molecular Orbitals, Natural Bond Orders and Electron Density of; a lone carbon, carbon monoxide (CO), chloromethane (CH3Cl), ethylene (C2H4), benzene (C6H6), and three tautomers of n-heterocyclic Carbene (NHC). Using the ‘Molecular Orbital’ calculation the 1s and 2p orbitals of a lone carbon atom were calculated as a simple test of WebMO’s accuracy. The calculation was then run on our molecules to gauge the reactivity of each species by analysing both the separate molecule’s HOMOs and LUMOs. The ‘Natural Bond Orbitals’ calculation was run on Chloromethane to view the types of bond orbitals. The ‘Bond Order’ calculation was used to identify the kind of bonding present, and the electrostatic potential mapped the distribution of electrons.*

**Introduction**

The foundation of reactivity is built upon electronic structure. WebMO was used to visualise and analyse electronic structures, including electron density, molecular orbitals, and natural bond orbitals. This analysis was used to further chemical understanding of electronic structure.

**Background**

Molecular Orbitals (MOs) are mathematical functions which describe the behaviour of electrons in a molecule. The Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) gauge molecular properties and reactivity. HOMO is associated with nucleophilic characteristics[[1]](#endnote-1). Whereas the LUMO is associated with electrophilic characteristics[[2]](#endnote-2). The gap between the HOMO and LUMO is inversely proportional to the reactivity. Thus, stable molecules have large HOMO-LUMO gaps and highly reactive molecules have the inverse. The shape and location of the HOMO and LUMO can be used to predict how and where a reaction will occur.

Natural Bond Orbitals (NBOs) are transformations of MOs into a structure that represent Lewis structures. Lewis Structures are diagrams that show lone pairs, geometry, and formal charges of molecules. They are designed to be the single best structure of a molecule; however, this is not always possible. NBOs help to visualise the electronic structure and bonding in molecules.

Bond Orders are a simple mathematical indicator of bond strength and is defined by the following equation.

The calculated bond order is a representation of how many bonds are present. For example, H2 has a Bond Order of 1 and a single bond between the two H atoms. C2H4 has a Bond Order of 2 and double bonds between the two C atoms present.

**Materials and Method**

The investigation was conducted using the web program, ‘*WebMO*.’ It is a java scripted frontend over a gaussian based engine. The program was used to calculate and visualise the species in **Table 2.1**. Before starting each of the calculations the molecules were constructed and their geometries optimised using WebMO’s *‘Geometry Optimization’* calculation at the *‘B3LYP’* theory and the *‘Routine: 6-31G(d)’* basis set.

**Table 2.1.:** Species and WebMO Calculations.

|  |  |  |  |
| --- | --- | --- | --- |
| **Chemical Species:** | **Formula:** | **Structure:** | **WebMO Calculation** |
| **Carbon Atom.** | C |  | Molecular Orbital |
| **Carbon Monoxide.** | CO | Carbon monoxide - American Chemical Society | Molecular Orbital |
| **Chloromethane.** | CH3Cl | Chloromethane - American Chemical Society | Molecular Orbital |
| **Ethylene.** | C2H4 | Ethylene - American Chemical Society | Molecular Orbital, Natural Bond Orbital, and Bond Order. |
| **Benzene.** | C6H6 | Benzene - American Chemical Society | Molecular Orbital, Natural Bond Orbital, and Bond Order. |
| **nNHC.** | C3H4N2 |  | Molecular Orbital, Natural Bond Orbital, and Bond Order. |
| **aNHC.** | C3H4N2 |  | Molecular Orbital, Natural Bond Orbital, and Bond Order. |
| **IMID.** | C3H4N2 |  | Molecular Orbital, Natural Bond Orbital, and Bond Order. |

First the Molecular Orbitals of the lone Carbon atom were calculated using the *‘Molecular Orbital’* calculation at the *‘B3LYP/6-31G(d)’* level of theory. The calculation was used to show the expected *s* and *p* Atomic Orbitals of Carbon. Then the MOs of Carbon Monoxide (CO) were calculated using the same method as above. Using the calculation, the HOMO of CO was then found and investigated. Thirdly the same calculation was applied to Chloromethane (CH3Cl) to highlight the characteristics of the LUMO. Ethylene (C2H4) was then run under three separate calculations the *‘Molecular Orbital’* calculation, a *‘Natural Bond Orbital’* calculation, and the *‘Bond Orders’* calculation. All of the calculations were made at the *‘B3LYP/6-31G(d)’* level of theory. The MO calculation was made to gauge the reactivity, based on the HOMO, the NBO calculation showed the occupancy of the various orbitals, and the Bond Order calculation was made to confirm the bond orders of the bonds present in ethylene. The same three calculations were made with Benzene (C6H6) and the three tautomers[[3]](#endnote-3) of NHC. Finally, the electrostatic potential of the IMID tautomer was shown using a built in function of WebMO’s MO calculations.

**Results and Discussion**

In the following figures, the CPK conventional colours of atoms are followed: the colours of the atomic and molecular orbitals conform to the convention that, blue represents positive and red represents negative in the Bonding Orbitals, and green being positive with yellow being negative in the Anti-Bonding Orbitals[[4]](#endnote-4).

|  |  |
| --- | --- |
|  | the 1s orbital |
|  | ... |

**Fig 2.1:**Comparison of the calculated *s* and *p* Atomic Orbitals of Carbon with the values from the Orbitron.

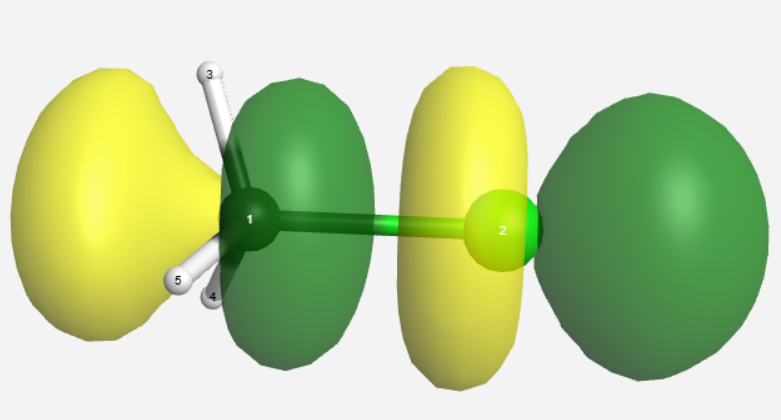
**Figure 2.1a** (top left) shows the calculated 1s atomic orbital of a lone carbon atom. The calculated orbital matches with the literature present of a 1s orbital. **Figure 2.1b** (top right) shows the literature 1s Atomic Orbital as taken from the University of Sheffield site *‘The OrbitronTM’* created, and updated by, Prof. Mark J. Winter, of the Department of Chemistry at the University of Sheffield. **Figure 2.1c** (bottom left) shows the calculated 2p Atomic Orbital of a lone carbon atom. The calculated orbital matches the literature sources of the 2p Atomic Orbital. **Figure 2.1d** (bottom right) shows the literature 2p Atomic Orbital as taken from the University of Sheffield site *‘The OrbitronTM’* created, and updated, by Prof. Mark J. Winter of the Department of Chemistry at the University of Sheffield. In this figure the yellow and white represent the positive and negative solutions to the wave function.

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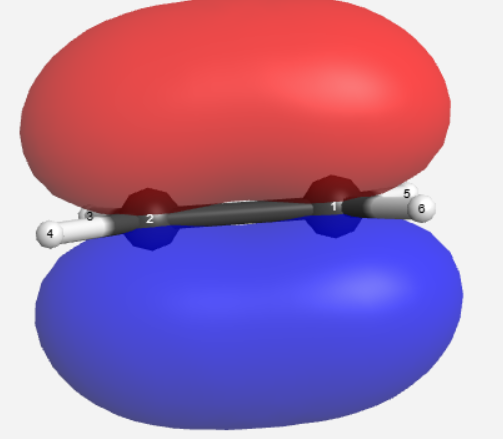
**Fig 2.2:** The Calculated HOMO and LUMO of Carbon Monoxide (CO).

**Figure 2.2a** (left) shows the calculated HOMO of the CO molecule. The orbital is a combination of the C atom’s bonding 1s atomic orbital and the O atom’s bonding 2p atomic orbital. The Molecular Orbital is also shown to be ‘in-line’ with the triple bond present in the CO molecule. **Figure 2.2b** (right) shows the calculated LUMO of the CO molecule. The orbital is a destructive combination of the antibonding p atomic orbitals, specifically the π\* antibonding present in both the C and O atoms. The Molecular Orbital is also shown to be perpendicular with the triple bond present in the CO molecule.

**Fig 2.3:** The LUMO of Chloromethane (CH3Cl).



**Figure 2.3** shows the calculated LUMO of the CH3Cl molecule. The orbital is a destructive combination of the antibonding p atomic orbitals, specifically the σ\* antibonding present in both the C and Cl atoms. The Molecular Orbital is also shown to be ‘in-line’ with the single bond present between the C and Cl atoms.



**Fig 2.4:** The HOMO of Ethylene (C2H4).

**Figure 2.4** shows the calculated HOMO of the C2H4 molecule. The orbital is a constructive combination of the bonding 2p orbitals present in the C atoms. The Molecular Orbital is also shown to be perpendicular with the double bond present in the C2H4 molecule.

**Table 2.:** The Calculated Natural Bond Orbitals of Ethylene (C2H4).

|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital:** | **Type:** | **Location/variant.** | **Occupancy:** |
| **1** | Bond. | C1-C2 π-bond. | 1.9999 |
| **2** | Bond. | C1-C2 σ-bond. | 1.9965 |
| **3** | Bond. | C1-H5 σ-bond. | 1.9872 |
| **4** | Bond. | C1-H6 σ-bond. | 1.9872 |
| **5** | Bond. | C2-H3 σ-bond. | 1.9872 |
| **6** | Bond. | C2-H4 σ-bond. | 1.9872 |
| **7** | Core. | C1 1s Orbital. | 1.9992 |
| **8** | Core. | C2 1s Orbital. | 1.9992 |

**Table 2.2** shows that the orbitals 1-6, arbitrary numbering provided by WebMO, are all bonding orbitals with orbital 1 being the π-bond between the C atoms, orbital 2 being the σ-bond between the C atoms, Orbitals 3-6 being the σ-bonds present between the C atoms and the H atoms, and orbitals 7-8 being the 1s atomic orbitals present in the separate C atoms. The occupancy of each orbital is also shown to be approximately 2 which is expected.

**Table 2.3.:** The Calculated Bond Orders of Ethylene (C2H4).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Atom:** | **C1:** | **C2:** | **H3:** | **H4:** | **H5:** | **H6** |
| **C1** | 0.00 |  |  |  |  |  |
| **C2** | 2.035 | 0.00 |  |  |  |  |
| **H3** | 0.01 | 0.93 | 0.00 |  |  |  |
| **H4** | 0.01 | 0.93 | 0.00 | 0.00 |  |  |
| **H5** | 0.93 | 0.01 | 0.00 | 0.02 | 0.00 |  |
| **H6** | 0.93 | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 |

In **Table 2.3** the bond order between the various atoms in the Ethylene molecule are shown. For example, C1 has a bond order of 0 with itself, 2 with C2, 0 with H3 and H4, and 1 with H5 and H6. The bond orders are computationally calculated as real numbers however they are often recorded as multiples of n½, because of the mathematical definition of bond orders.

|  |  |
| --- | --- |
|  |  |

**Fig 5:** The HOMO and HOMO-1 of a Benzene (C6H6) Ring.

**Figure 2.5a** (left) shows the calculated HOMO of the C6H6 molecule. The orbital is a constructive combination of the bonding 2p orbitals present in the C atoms. The Molecular Orbital is also shown to be perpendicular with the double bonds present in the C6H6 molecule. **Figure 2.5b** (right) shows the HOMO-1 of Benzene (C6H6), the penultimate occupied molecular orbital. The orbital is a constructive combination of the p orbitals present in all of the carbon atoms with a node ‘cutting’ across the symmetrical centre bonds. This shows the aromaticity of the benzene ring and combined with the HOMO (**Fig 2.5a**), shows the delocalised nature of the electrons present in C6H6.

**Table 2.4.:** CalculatedNatural Bond Orbitals of Benzene (C6H6).

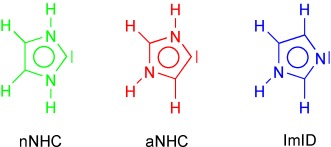
|  |  |  |  |
| --- | --- | --- | --- |
| **Orbital:** | **Type:** | **Location/variant.** | **Occupancy:** |
| **1** | Bond. | C1-C2 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **2** | Bond. | C2-C1 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **3** | Bond. | C1-C2 π(99.96%) Bond. | 0.99898 |
| **4** | Bond. | C2-C1 π(99.96%) Bond. | 0.99898 |
| **5** | Bond. | C1-C6 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **6** | Bond. | C6-C1 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **7** | Bond. | C1-H12 σ(29.55%) π(64.75%) Bond. | 1.23128 |
| **8** | Bond. | H12-C1 σ(100%) Bond. | 0.76406 |
| **9** | Bond. | C2-C3 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **10** | Bond. | C3-C2 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **11** | Bond. | C2-H11 σ(29.55%) π(70.4%) Bond. | 1.21279 |
| **12** | Bond. | H11-C2 σ(100%)Bond. | 0.76406 |
| **13** | Bond. | C3-C4 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **14** | Bond. | C4-C3 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **15** | Bond. | C3-C4 π(99.96%) Bond. | 0.99898 |
| **16** | Bond. | C4-C3 π(99.96%) Bond. | 0.99898 |
| **17** | Bond. | C3-H10 σ(29.55%) π(70.4%) Bond. | 1.23128 |
| **18** | Bond. | H10-C3 σ(100%) Bond. | 0.76406 |
| **19** | Bond. | C4-C5 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **20** | Bond. | C5-C4 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **21** | Bond. | C4-H9 σ(29.55%) π(70.40%) Bond. | 1.23128 |
| **22** | Bond. | H9-C4 σ(100%) Bond. | 0.76406 |
| **23** | Bond. | C5-C6 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **24** | Bond. | C6-C5 σ(35.21%) π(64.75%) Bond. | 0.99834 |
| **25** | Bond. | C5-C6 π(99.96%) Bond. | 0.99898 |
| **26** | Bond. | C6-C5 π(99.96%) Bond. | 0.99898 |
| **27** | Bond. | C5-H8 σ(29.55%) π(70.40%) Bond. | 1.23128 |
| **28** | Bond. | H8-C5 σ(100%) Bond. | 0.76406 |
| **29** | Bond. | C6-H7 σ(29.55%) π(70.40%) Bond. | 1.23128 |
| **30** | Bond. | H7-C6 σ(100%) Bond. | 0.76406 |
| **31** | Core. | C1 (s). | 1.99909 |
| **32** | Core. | C2 (s). | 1.99909 |
| **33** | Core. | C3 (s). | 1.99909 |
| **34** | Core. | C4 (s). | 1.99909 |
| **35** | Core. | C5 (s). | 1.99909 |
| **36** | Core. | C6 (s). | 1.99909 |

In **Table 2.4** the Natural Bond Orbitals of C6H6 are shown. The Natural Bond orbitals also help us to understand the aromatic/delocalised nature of Benzene. The Natural Bond Orbitals present in the C bonds are combinations of the C s and p atomic orbitals showing a *‘hybridised’* structure[[5]](#endnote-5).

**Table 2.5.:** Bond Orders of Benzene(C6H6).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Atom:** | **C1:** | **C2:** | **C3:** | **C4:** | **C5:** | **C6** | **H7** | **H8** | **H9** | **H10** | **H11** | **H12** |
| **C1** | 0.00 |  |  |  |  |  |  |  |  |  |  |  |
| **C2** | 1.44 | 0.00 |  |  |  |  |  |  |  |  |  |  |
| **C3** | 0.01 | 1.44 | 0.00 |  |  |  |  |  |  |  |  |  |
| **C4** | 0.11 | 0.01 | 1.44 | 0.00 |  |  |  |  |  |  |  |  |
| **C5** | 0.01 | 0.11 | 0.01 | 1.44 | 0.00 |  |  |  |  |  |  |  |
| **C6** | 1.44 | 0.01 | 0.11 | 0.01 | 1.44 | 0.00 |  |  |  |  |  |  |
| **H7** | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.92 | 0.00 |  |  |  |  |  |
| **H8** | 0.01 | 0.00 | 0.01 | 0.00 | 0.92 | 0.00 | 0.00 | 0.00 |  |  |  |  |
| **H9** | 0.00 | 0.01 | 0.00 | 0.92 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |  |  |  |
| **H10** | 0.01 | 0.00 | 0.92 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |  |  |
| **H11** | 0.00 | 0.92 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |  |
| **H12** | 0.92 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**Table 2.5** shows the bond orders between the various elements in Benzene. It is shown that the carbon ring has a more delocalised characteristic than that of a traditional double bond, where the bond order is exactly two. However here in the benzene the C atoms traditionally thought of as being double bonded only have a bond order of ~1.5. This is already known in literature and is a confirmation.

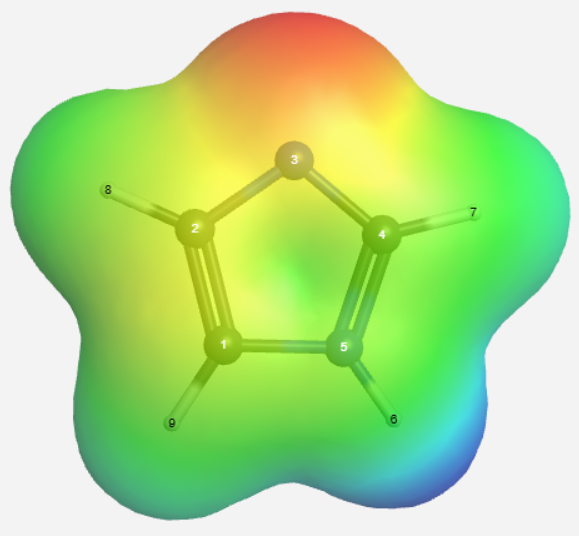


**Fig 6:** The three Tautomers of N-Heterocyclic Carbenes (NHC). (Arbitrary Colours.)

|  |  |
| --- | --- |
|  | A blue and red molecule  AI-generated content may be incorrect. |
|  | |

**Fig 2.7:** The HOMO of the nNHC, aNHC, and IMID Tautomers.

**Figure 2.7a** (top left) shows the HOMO of the aNHC Tautomer. The Nucleophilic character of the molecule is shown in the lone pair present in the *‘peak’* C atom in the ring similar to the nNHC Tautomer. The orbitals are the result of interference between the two N atoms’ p atomic orbital and the *‘peak’* C atom’s s atomic orbital. **Figure 2.7b** (top right) shows the HOMO of the aNHC Tautomer. The Nucleophilic character of the molecule is shown in the lone pair present in the *‘peak’* C atom in the ring similar to the nNHC Tautomer. The orbitals are the result of interference between the two N atoms’ p atomic orbital and the *‘peak’* C atom’s s atomic orbital. **Figure 2.7c** (bottom) shows the HOMO of the IMID Tautomer. The molecular orbital is shown to have a node between two, p molecular orbitals.



**Fig 2.8:** The Electrostatic Potential of the IMID Tautomer.

The Electrostatic Potential of the IMID Tautomer of nNHC shown in **Figure 2.8** visualises the theoretical spread of the electrons present in the molecule using a gradual shift from Red, being high density of electrons, to Blue, being the inverse.

Using the Molecular Orbital calculation on a lone Carbon atom the following orbitals were produced. (**Fig 2.1a.** & **Fig 2.1b.**) The calculated orbitals follow the expected shapes as seen in literature (**Fig 2.1c.** & **Fig 2.1d.**). The calculations on the lone carbon were carried out to ensure accuracy in the WebMO program and show that it functions for simple MOs.

The nucleophilic character of the HOMO is shown in the visualisation obtained by the MO calculation of CO (**Fig 2.2a.**) The nucleophilic characteristic of CO is shown through the large blue sphere, representing the lone pair present on the C atom. This shows that CO is a sigma donor[[6]](#endnote-6) on the Carbon atom, this is expected as CO is commonly used as a ligand in organometallic chemistry[[7]](#endnote-7) with the C atom forming a sigma bond[[8]](#endnote-8) with the metal centre. In the same CO molecule, the electrophilic nature of the LUMO is shown by the 3p shape of the LUMO itself (**Fig 2.2b.**). This electrophilic character explains how CO can also be used as a π donor[[9]](#endnote-9) in organometallic chemistry. As a π-donor the CO molecule donates electrons to bind to the metal perpendicular to its present triple bond.

The Electrophilic character of chloromethane and it’s receptibility to Sn2[[10]](#endnote-10) reactions is shown by the calculated LUMO (**Fig 2.3.**). The molecule has a large empty orbital on the carbon opposite the chlorine; this is where a potential nucleophile can attack. This attack results in a transition state where both the chlorine and the electrophile are bonded to the methyl group. The state is short lived however as the electrons in C-Cl bond are returned to their initial atoms. The formula for the general Sn2  reaction of CH3Cl is shown as:

The HOMO of ethylene shows that it has nucleophilic properties and is readily accessible to an electrophilic reaction (**Fig 2.4.**). Whereas both the HOMO (**Fig 2.4a.**) and HOMO-1 (**Fig 2.4b.**) of Benzene show that the aromaticity of the ring protects the molecule from a direct electrophilic reaction and is thus less reactive than the Ethylene.

The HOMO of both the nNHC (**Fig 2.7a.**) and aNHC (**Fig 2.7b.**) tautomer distinctly show the presence of the lone pair of the *‘peak’* Carbon atom. The lone pair is shown to be in an s atomic orbital of the referenced Carbon. However, in the IMID tautomer (**Fig 2.7c.**), the HOMO shows a distinct node separating the N-C=N side of the molecule from the C=C side. This is the result of constructive interference in the p atomic orbitals of the double bonded carbons, and the p atomic orbitals of the N-C=N atoms forming two separate, and distinct p molecular orbitals. The structure of the HOMO shows that the IMID tautomer has π-acceptor characteristics.

**Conclusion**

WebMO was used to understand Electronic Structure and the *‘Molecular Orbital’*, *‘Natural Bond Orders’*, *‘Bond Orders’*, calculations including wait times and functions. Working through the program also furthered understanding of how WebMO is designed and how to extract the calculated data from the program. WebMO was found to follow expectations and provide results that adhere to chemical theory.

Variations in Computational Chemistry Methods and Basis Sets.

**Abstract**

*The Program WebMO was used to understand the various different methods and basis sets in computational chemistry. The ‘B3LYP’ theory was used to compare the bond size present in hydrogen fluoride (HF) using the Pople style basis set 6-31G and its variations to provided values calculated using the CCSD(T) theory and the same basis sets. The energies of cis-1,2-difluoroethene (C2H2F2), trans-1,2-difluoroethene and 1,1-difluoroethene were calculated and compared using the ‘Molecular Energy’ calculation, ‘B3LYP’ level of theory and three basis sets. These values were used to compare the differences between more exact basis sets.*

**Introduction**

Computational chemistry algorithms were created with adaptability in mind and engines like Gaussian can employ many different techniques to solve a problem. This means that many different methods, or theories, and basis sets have been created. They were created as new solutions to problems, or as a way to arrive at more exact answers. The Method describes electronic interactions within a molecule. Specifically, how the electrons interact to form molecular orbitals. The Basis Set describes the sets of atomic orbitals. The more exact the theory, and the more infinite the basis set become the more exact the calculated result. As exact theories and infinite basis sets are impossible, approximations are required.

The notation used through this document is that of the Nobel Laureate (1998, Chemistry) John Pople.

*method/basis set*

HF/6-31G Hartree-Fock wave function (method) with a 6-31G basis set.

B3LYP/6-31G B3LYP-DFT (method) with a 6-31G basis set.

CCSD(T)/TZVP CCSD(T) wave function (method) with a TZVP basis set.

**Background**

Methods are described by their mathematical approximations to the Schrödinger Equation. When a solution is calculated based solely on fundamental constants and theoretical understandings, they are may be called *ab initio* (Latin ‘from the beginning’). The three major classes of electronic structure methods are: *Semi-empirical methods*, *Ab initio methods*,and *Density Functional Theory*.

**Semi-empirical methods** are approximate methods that include some empirical parameters in place of integrals. Approximating some of the interactions between particles. These are fast but inaccurate as the particle interactions are not calculated.

**Ab initio methods** have no empirical parameters outside of conventional physical constants. They are systematic methods that can be improved to approach the exact result. The simplest method is *Hartree-Fock* which is limited as the electronic motion is, on average, only affected by other electrons. There are more sophisticated methods such as *Møller-Plesset* (MP2, MP3, MP4)[[11]](#endnote-11), *coupled-cluster* (CCSD,CCSD(T)), and *configuration-interaction* (CISD,CISD(T)). These methods overcome the electron correlation limitation present in *Hartree Fock*.

**Density Functional Theory**, is the most common method type used in contemporary computational chemistry. DFT has the same computational requirements as HF while including electron correlation. These methods are based on electron density rather than the wave function and are suited for modern cluster-computers. This makes DFT methods able to be processed over multiple cores in a process named parallelisation.

Basis sets are the mathematical description of atomic orbitals (AO) present in a system. In the bonding process these AOs are combined and undergo interference to form Molecular Orbitals (MO). Larger basis sets map more accurately to the AOs due to the reduction of electron distribution restrictions that arise. The computational cost and accuracy of a basis set is directly proportional to its size. The diameter and the direction of the MOs are described by the orbital wave function. Basis sets are series of functions designed to describe the atomic orbitals. Most of the quantum chemistry computer programs use Gaussian-type orbitals (GTO) of the form:

Where:

r is distance from the nuclei, and

ζ is a constant that describes the size of the function.

The size of ζ directly relates to how fast the function decays to zero. A small ζ will decay slowly and best describe the electrons away from the nucleus. These functions are called diffuse functions. However, a large will decay rapidly to zero and best describes the electrons close to the nucleus. These functions are called tight or core functions. A basis set that is more flexible describes the electron density in ***molecules*** in a more accurate way.

There are multiple families of basis sets. The most relevant for this text is the Pople-style family of basis sets. Basis sets are composed of various items. The most important being functions that describe each Atomic Orbital, basis sets require at least one function per AO to work. Increasing the number of functions per AO makes the basis set larger, more accurate, and more computationally expensive.

The group of basis sets that contain the minimum number of functions for each AO is known as a *minimal basis set*. An example of these types of basis sets is,

**H: 1s**

**C: 1s, 2s, 2px, 2py, 2pz**

The STO-3G basis set falls into this category.

*Double zeta basis sets*, have two functions for each AO. The two basic functions can differ in size. Due to the additional function, these basis sets are more accurate than *minimal basis sets*. An example of a *Double zeta basis set* is,

**H: 1s, 1s\***

**C: 1s, 2s, 2s\*, 2px, 2px\*,2py, 2py\*,2pz, 2pz\***

The 6-31G basis set falls into this category.

The addition of each function expands the basis set. These expansions are labelled: *single zeta (a minimal basis set)*, *double zeta*, *triple zeta*, *quadruple zeta*, etc. However, with each additional function the computational cost grows exponentially.

*Split valence basis sets*, were designed to increase efficiency and reduce computer power requirements. This is achieved by employing an approximation with core electrons modelled as a zeta, or minimal, basis set, and valence electrons modelled with higher zeta sets (double, triple, etc.). This is the most common form of basis set, as chemistry is dictated by valence electrons over core electrons.

The 6-311G, and cc-pVTZ basis sets fall into this category and employ triple zeta basis sets for the valence electrons.

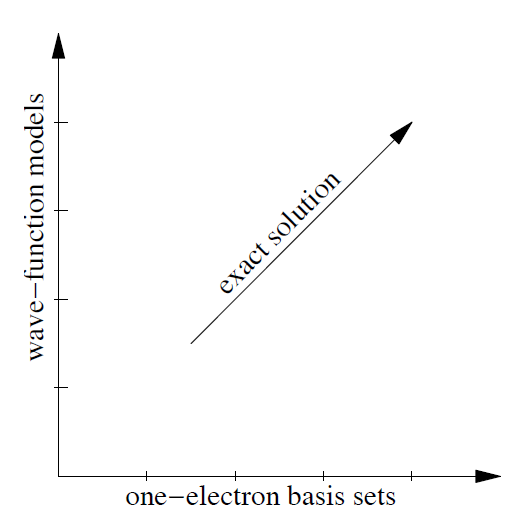
Basis functions that are of higher angular momentum than occupied AO are called *polarisation functions*. These are very important for calculations involving molecules and allow for changes in atomic and molecular orbital shapes. Unlike atoms, in molecules the electron density is distorted. Due to the distortions electron density polarisation has to occur and be considered. When only the valence occupied AOs are considered in a basis set, the radial extent of orbitals are able to change size while the shape remains the same. Polarised basic sets remove this limitation as the higher angular momentum of the functions account for the polarisation of the MOs. This can be done simply by adding functions of higher orbitals to a valence function (adding *p* functions to H).

The basis set 6-31G(d), also known as G-31G\*, is a common polarised basis set. The (d) denotes that *d* orbital functions are added to the heavy atoms only. The basis set 6-31G(d,p), also noted 6-31G\*\*, adds polarisation functions to both H and heavy atoms.

In *s, p, d* and higher orbitals with larger radial extent, *diffuse functions* are used to describe the electrons farther away from the nucleus. This kind of basis set is most useful in anions, molecules with lone pairs and molecules/systems in excited states with large negative charges.

The basis set 6-31+G(d) have *diffuse functions* added to any heavy atoms present. The ‘+’ denotes these functions. *Diffuse functions* can also be added to hydrogen, as denoted by ‘++’, however this generally has very little effect on accuracy.

In order to find which basis set is needed in a specific scenario, the *basis set convergence* is consulted. *Basis set convergence* occurs when the enlargement of the basis set on a repeated calculation has negligible impact on the results. This sweet spot is when we determine that the basis set is sufficient. As with every expansion of the basis set, the accuracy and precision of the result increases, the convergence of basis sets is vital.

**Fig 3.1:** The Relationship Between Wave Function Models and One-Electron Basis Sets.

**Materials and Method**

The program WebMO was used to understand the various methods and basis sets that are used in density functional theory. The program calculated and visualised the species in **Table 3.1**.

**Table 3.1.:** Species and Calculations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Chemical Species:** | **Formula:** | **Structure:** | **WebMO Calculation** | **Theory** | **Basis Set** |
| **Hydrogen Fluoride** | HF | Hydrogen Fluoride | History, Structure & Formula - Lesson | Study.com | Geometry Optimization | B3LYP | Various, See **Table 3.2.** |
| **Cis-1,2-difluoroethene** | C2H2F2 |  | Molecular Energy | B3LYP | def2svp, def2tzvp, & def2qzvp |
| **Trans-1,2-difluoroethene** | C2H2F2 |  | Molecular Energy | B3LYP | def2svp, def2tzvp, & def2qzvp |

The basis sets used in the repeated HF calculation, is shown in **Table 3.2**.

**Table 3.2.:** Table of Basis Sets Used for HF Calculations.

|  |
| --- |
| **Basis Sets** |
| 6-31G |
| 6-31+G |
| 6-31++G |
| 6-31G(d) |
| 6-31G(d, p) |
| 6-31+G(d,p) |
| 6-31++G(d,p) |

First the *‘Geometry Optimisation’* calculation was repeated on HF using the above basis sets. Then the same calculation was completed using the *‘def2svp’*, *‘def2tzvp’*, and the *‘def2qzvp’* basis sets on cis-1,2-difluoroethene, trans-1,2-difluoroethen and 1,1-difluoroethene and compared.

**Results and Discussion**

The experimental bond distance of hydrogen fluoride was found to be 0.917 Å. The *‘Geometry Optimisation’* calculation was repeated seven times using the ‘*B3LYP’* method and the basis sets shown in **Table 3.3**. The preview window was also amended to include **opt=tight** in order to narrow the threshold of the calculation.

**Table 3.3.:** Table of Calculated and Provided Bond Distances in Hydrogen Fluoride. Calculated Values shown in Bold.

|  |  |  |
| --- | --- | --- |
| **Basis Set:** | **Bond Distance (Å):** | |
| **B3LYP** | **CCSD(T):** |
| **6-31G** | **0.949** | 0.9487 |
| **6-31+G** | **0.952** | 0.9542 |
| **6-31++G** | **0.952** | 0.9543 |
| **6-31G(d)** | **0.934** | 0.9353 |
| **6-31G(d,p)** | **0.925** | 0.9211 |
| **6-31+G(d,p)** | **0.928** | 0.9253 |
| **6-31++G(d,p)** | **0.928** | 0.9253 |
| **6-311G(d,p)** | 0.9201 | 0.9129 |
| **6-311++G(d,p)** | 0.9222 | 0.9162 |
| **6-311G(3df,3pd)** | 0.9187 | 0.9127 |
| **6-311++G(3df,3pd)** | 0.9221 | 0.9159 |

The energies of cis-1,2-difluoroethene, and trans-1,2-difluoroethene were calculated using the *‘Molecular Energy’* calculation and the basis sets seen in **Table 3.4**. The energies were then compared by taking the difference of the energies of the same basis sets. Then the relative energies were calculated by taking the difference of the energies of the same molecule at the measured and the ‘*def2qzvp’* basis set[[12]](#endnote-12). The relative energies are given in kJ/mol. This was done by converting atomic units (Hartrees per particle) to kJ/mol by multiplying the value by the conversion factor, 2625.5.

**Table 3.4.:** Table of Calculated Energies of Difluoroethene Isomers.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Cis-1,2** | **Trans-1,2** | **1,1** |
| ETotal (Hartree) | | | |
| B3LYP/def2svp | -276.838 | -276.838 | 0.000011 |
| B3LYP/def2tzvp | -277.178 | -277.176 | -0.001063 |
| B3LYP/def2qzvp | -277.194 | -277.193 | -0.001425 |
| ERelative (kJ/mol) | | | |
| B3LYP/def2svp | 935.214 | 931.443 | 0.028889 |
| B3LYP/def2tzvp | 45.697 | 44.746 | -2.791 |
| B3LYP/def2qzvp | 0.000 | 0.000 | -3.741 |

The accuracy of a basis set was shown (**Table 3.3**) to increase with the addition of *polarisation*, and *diffuse functions*, as the difference between the calculated value of 6-31G and 6-31++(d,p) was found to be 0.021 Å. The calculated value using the 6-31++G(d,p) of 0.928 Å, was found to be the most accurate to the experimentally acquired value of 0.917 Å. This is off by a distance of 0.011 Å, which on the scale of an atom is not negligible but the narrowing effect is obvious. It was also observed that the addition of *diffuse functions* can have a broadening effect on the bond distance if there is no *polarisation functions* included alongside in the calculations.

The convergence of basis sets were also shown (**Table 3.4**) to expand with the addition of more basis functions[[13]](#endnote-13), from the double zeta (*def2svp*) to the quad zeta (*def2qzvp*) basis sets. When comparing the basis sets using the different molecules. The double zeta basis set was found to have an energy difference of 1.1 \* 10-5 whereas, the quad zeta set was found to have an energy difference of -1.425 \* 10-3. When comparing the relative energies of the same molecule using different basis sets. With the cis-1,2-difluoroethene the relative energy of the double zeta was found to be 935.214 kJ/mol and the relative energy of the triple zeta was found to be 45.697 kJ/mol. Whereas with the trans-1,2-difluoroethen the relative energy of the double zeta was found to be 931.443 kJ/mol and the relative energy of the triple zeta was calculated as 44.746 kJ/mol. All values are relative to the respective energy found of the quad zeta basis set.

**Conclusion**

With the addition of *polarisation functions* to a basis set, the accuracy increased as shown by the difference of the non-polarised*‘6-31G’* and double polarised *‘6-31G(d,p)’* basis sets. The addition of *diffuse functions* was found to broaden the bond distance of HF as shown by the difference of the *‘6-31G’* and *‘6-31+G’* basis sets. Increasing the size of the basis sets was shown to narrow the convergence of the basis set as shown by the relative energies between the calculated values of the difluoroethene isomers using double zeta, triple zeta, and quad zeta basis sets.

Using Computational Methods to Predict Spectroscopy.

**Abstract**

*The Program WebMO was used to calculate theoretical characteristic spectra of five chemical species being: methane (CH4), hydrogen fluoride (HF), benzene (C6H6), methanol (CH3OH), and ethene (C2H2). The three most common characteristic spectra (IR, NMR, and UV-Vis) are easily modelled using computation methods. The NMR and UV-Vis spectra were generated of the above species, under both theoretical, vacuum, and laboratory conditions. The generated spectra were used as a test of the capabilities of WebMO and were designed to further understanding of molecular properties.*

**Introduction**

Spectroscopy is a common basis for laboratory equipment designed to characterise the structure of an unknown product. The most common spectroscopy methods used in lab equipment are *vibrational IR*, *NMR*, and *UV-Vis* spectroscopy. The most important for this investigation are *NMR*, and *UV-Vis* spectroscopy.

**Background**

The nuclear spin of constituent atoms in molecules and the intramolecular interactions are the building blocks for the technique known as *nuclear magnetic resonance (NMR)*. *NMR* is a vital characteristic spectroscopy technique that is very sensitive to molecular geometry. This makes *NMR* a perfect tool when analysing molecular structure. The basis of *NMR* spectroscopy is the nuclear energy splitting that arises due to interactions between chemical species and external magnetic fields.

Central to *NMR* spectroscopy are the chemical shielding and spin-spin coupling constants. Spin-spin splitting arises from the coupling that occurs between two molecular nuclei. This effect is transferred between the nuclei by electrons. The effect is ‘felt’ greatest between neighbouring nuclei, however; the effect may still be observed up to five bonds away. In experiment, the reported shielding constants are relative values to a reference standard. In 1H NMR, also known as proton NMR, and 13C NMR the standard used is TMS (Si(CH3)4). This is the relative chemical shift.

*UV-Vis* spectra is directly related to the electronic transitions of molecules undergoing excitation. In *UV-Vis* spectroscopy the HOMO and LUMO molecular orbitals and the HOMO-LUMO gap are vital. Larger HOMO-LUMO gaps require smaller wavelengths of light with higher energy for excitations to take place. The absorbance (from 0 % - 100 %) is plotted against wavelength of light inputted into the system.

Computational Chemistry and its Uses in Chemical Kinetics.

**Abstract**

*The program WebMO was used to further understanding in the kinetics of chemical reactions. This was achieved by calculating the energies of the reactants, transition states, and products of a chemical reaction. The electron affinity of noble gases was calculated using the ‘Molecular Energy’ calculation and the element argon (Ar). Then the calculation was repeated to test if it is thermodynamically possible for a hydrogen to be bonded to argon (ArH) and expended to see if a fluorine could also be bonded to that argon (ArHF). The proton affinities of methanamine (CH2=NH), and 4-dimethylaminopyridine (DMAP) were found. Finally, the energetics of organic reactions were investigated. The reactions used were the decomposition of acetaldehyde (Eq 5.1), and the ozone cycle (Eq 5.2-3).*

**Introduction**

Thermochemistry is most useful to determine the feasibility of a reaction. The energetics of chemical reactions is the hurdle that stops a reaction from proceeding. Most reactions can be easily modelled using computational methods. This is most relevant for gas, and solvent phase reactions and reactions that take place on even surfaces. A simple use of these computational methods is gauging the stability of a proposed molecule by calculating its dissociation energy. This saves time for laboratories as the risk of trying to synthesise an unobtainable product is removed.

**Background**

Electron Affinity (EA) is the willingness for a chemical species to bind an electron. This is calculated by solving the energy change between the species before and after binding[[14]](#endnote-14). When the energy change is positive the binding is unfavourable and vice versa.

Proton Affinity (PA) is the willingness for a chemical species to bind a H+ atom. This is the main indicator of the basicity of a molecule. The PA is directly proportional to how basic the molecule is. Proton affinity is most important in biomolecules (amino acids) where is indicates the site of protonation and molecular structure at differing pHs. Proton affinity is always exothermic and, is mathematically described as the negative change in enthalpy.

The enthalpy of a reaction can be determined using the experimental enthalpies of formation ( by solving the equation (**Eq 5.1**). Thermochemical properties are calculated using standard lab conditions, 298.15 K , 1 atm. Using the equation, we can compare the calculated and experimental enthalpies of a reaction.

Where:

H, is the enthalpy of reaction,

Hproducts, is the enthalpy of the products, and

Hreactants, is the enthalpy of the reactants.

**Materials and Method**

WebMO was used to model and visualise the chemical species in **Table 5.1**. Each species was constructed and optimised using the *‘Geometry Optimization’* calculation[[15]](#endnote-15) before further calculations were conducted[[16]](#endnote-16).

**Table 5.1.:** Table of WebMO Calculations and Chemical Species.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Chemical Species:** | **Formula:** | **Structure:** | **WebMO Calculation** | **Theory** | **Basis Set** |
| **Argon.** | Ar | Draw the Lewis dot diagram for argon. | Homework.Study.com | Molecular Energy | B3LYP | 6-311+G(2d,p) |
| **Argon Bonded with a Hydrogen and Fluorine.** | ArHF | n/a | CBS-QB3 |  |  |
| **Hydrogen Fluoride.** | HF | Hydrogen Fluoride | History, Structure & Formula - Lesson | Study.com | CBS-QB3 |  |  |
| **Methanamine.** | CH2NH | A black and white chemical structure  AI-generated content may be incorrect. | Optimization + frequency | B3LYP | 6-31G(d) |
| **Methylamine** | CH2NH2 | Organic Compound Hexamethylenetetramine Urotropine Structure Icon Stock  Illustration 1939897408 | Shutterstock | Optimization + frequency | B3LYP | 6-31G(d) |
| **Hydrogen Cation.** | H+ | Hydrogen Ion Nucleus Hydrogen Atom Separated Stock Illustration 2192948735  | Shutterstock | Frequency | B3LYP | 6-31G(d) |
| **4-Dimethylaminopyridine (DMAP).** | C6N2H12 | A black hexagon with black lines  AI-generated content may be incorrect. | Optimization + frequency | B3LYP | 6-31G(d) |
| **Acetaldehyde.** | C2H4O | Draw the line-angle structural formula for CH3CHO. | Homework.Study.com | Optimization + frequency | PM3 | *n/a* |
| **Carbon Monoxide.** | CO | Carbon monoxide - American Chemical Society | Optimization + frequency | PM3 | *n/a* |
| **Methane.** | CH4 | The Lewis structure for methane: a. shows that this is a binary compound.  b. shows that C has 4 single covalent bonds. c. shows that there are 4 H's  bonded to C | Optimization + frequency | PM3 | *n/a* |
| **Chlorine.** | Cl | Lewis Dot Structure for Chlorine Atom | Explained | Optimization + frequency | B3LYP / MP2 | 6-31G(d) |
| **Ozone.** | O3 | How the Ozone lewis structure is formed_Chemicalbook | Optimization + frequency | B3LYP / MP2 | 6-31G(d) |
| **Chlorine monoxide.** | ClO- | The substance chlorine monoxide, ClO(g), is important in atm | Quizlet | Optimization + frequency | B3LYP / MP2 | 6-31G(d) |
| **Oxygen.** | O2 | O2 Lewis Structure – Easy Hard Science | Optimization + frequency | B3LYP / MP2 | 6-31G(d) |

First the electron affinity of Ar was calculated by computing the enthalpy of reaction using the energies of a neutral Ar atom and a Ar – ion. Then the feasibility of a ArHF molecule was investigated by calculating the enthalpy of dissociation. These were done using obtained values from WebMO’s *‘Molecular Energy’* calculation and using **Eq 5.1**.

Then the proton affinity of methanamine and DMAP was calculated by using **Eq 5.1** to solve for the total enthalpy of the reaction. The negative was then taken to solve for the proton affinity.

The decomposition of acetaldehyde (**Eq 5.2**) was used as a model to calculate the feasibility of CH3CHO dissociating into carbon monoxide and methane. This was achieved by using the *‘Optimization + frequency’* calculation with the *PM3* semi-empirical method[[17]](#endnote-17). The calculation was edited to include *‘opt=tight’* in the preview pane. Then the same calculation was run on the carbon monoxide and methane products.

The cyclical reactions that stabilise the creation of ozone (**Eq 5.3-5.4**) were used as the guide to calculate the energetics of atmospheric ozone. First, the enthalpy change of **Eq 5.2** was manually computed, second the dissociation energy was also calculated. The values were obtained from WebMO.

References:

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[3] David Wilson. (2024). Bonding and Molecular Structure [PDF].

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[5] M. J. Winter. ‘1s atomic orbital’, *The Orbitron*. Accessed: Sep 02, 2025. [Online] Available: <https://winter.group.shef.ac.uk/orbitron/atomic_orbitals/1s/index.html>

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[7] D. Wilson, *Quantum Chemistry, Section 9: ’Methods and Basis Sets (How to Work With a Computational Chemistry Program)’*. La Trobe University.

[10] D. Wilson, *Quantum Chemistry, Section 10: ’Molecular Properties (Spectroscopy)’*. La Trobe University.

[11] D. Wilson, *Quantum Chemistry, Section 11: ’Energies of Reactions (Thermochemistry)’*. La Trobe University.

1. *That is the characteristic for the readiness for a chemical species donate an electron pair to form a bond.* [↑](#endnote-ref-1)
2. *That is the characteristic for the readiness of a chemical species to receive an electron pair to form a bond.* [↑](#endnote-ref-2)
3. S*tructural isomers that readily interconvert.* [↑](#endnote-ref-3)
4. *Electrons are of course always negative, the ‘positivity’ and ‘negativity’ of the orbitals is related to the algebraic solutions of the corresponding wave functions.* [↑](#endnote-ref-4)
5. *Hybridisation only exists as a model to help understand molecular geometry and bonding, not as a thing in the ‘real’ world.* [↑](#endnote-ref-5)
6. *A chemical species willing to donate a pair of electrons to the sigma orbital of a separate species. A metal in Organometallic Chemistry.* [↑](#endnote-ref-6)
7. *A chemical species willing to donate a pair of electrons to a metal centre.* [↑](#endnote-ref-7)
8. *The sharing of an electron pair between two sigma orbitals.* [↑](#endnote-ref-8)
9. *A chemical species willing to donate a pair of electrons to the pi orbital of a separate species.* [↑](#endnote-ref-9)
10. *A Substitution chemical reaction involving the nucleophilic attack of an electrophile.* [↑](#endnote-ref-10)
11. *Not the media file designation.* [↑](#endnote-ref-11)
12. *The Exception being the comparison, 1,1, as this value was just converted into kJ/mol as it is already a relative energy.* [↑](#endnote-ref-12)
13. *AKA increasing the size of a basis set.* [↑](#endnote-ref-13)
14. *Products – Reactants. In the case of Chlorine EEA = ECl- - ECl.* [↑](#endnote-ref-14)
15. *Unless otherwise stated in* ***Table 5.1****.* [↑](#endnote-ref-15)
16. *Not all species underwent further calculation.* [↑](#endnote-ref-16)
17. *Basis sets are not used with semi-empirical methods.* [↑](#endnote-ref-17)