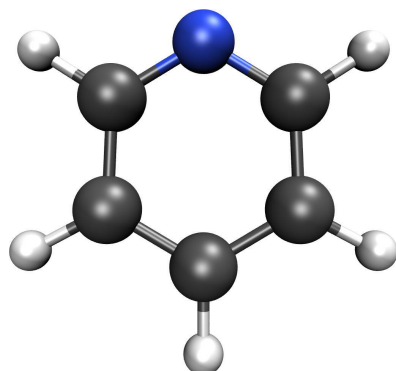




A Report On The Calculation Of The Excited States Of Pyridine At The PBE0/6-31G** Level

osl - 24th June 2022



Abstract

The calculation of excited states for the system 'Pyridine' is presented, accompanied by automated analysis and image generation provided by the Silico software package. The calculation was performed using the Turbomole software package at the PBE0/6-31G** level of theory. The total self-consistent field (SCF) energy of the system was found to be -6748.46 eV after 1 step. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -7.17 and -0.47 eV respectively, corresponding to a HOMO-LUMO band gap of 6.71 eV. The permanent dipole moment (PDM) was calculated to be 2.20 D.

Table 1: Summary of overall calculation metadata. [a]: The date and time at which the calculation was completed. [b]: Total combined duration in real-time (wall-time) for all components of the calculation. [c]: Temperature used for thermochemistry analysis. [d]: Pressure used for thermochemistry analysis.

Date ^[a]	Duration ^[b]	Success (Converged)	Computational package	Level of theory	Calculations	Wavefunction	Multiplicity	T ^[c] / K	p ^[d] / atm
24/06/2022 12:28:25	10 s	True (N/A)	Turbomole (7.5.0)	PBE0/6-31G**	Excited States	restricted	1 (singlet)	N/A	N/A

Summary Of Results

Scf Energy

Table 2: Summary of SCF energy properties.

No. of steps	1
Final energy	-6748.4564 eV
Final energy	-651,127 kJ·mol ⁻¹

Geometry

Table 3: Summary of geometry properties.

Formula	C ₅ NH ₅
Molar mass	79.0999 g·mol ⁻¹
Alignment method	Minimal
X extension	4.31 Å
Y extension	3.88 Å
Z extension	0.00 Å
Linearity ratio	0.10
Planarity ratio	1.00

Molecular Orbitals

Table 4: Summary of HOMO & LUMO properties.

E _{HOMO,LUMO}	6.71 eV
E _{HOMO}	-7.17 eV
E _{LUMO}	-0.47 eV

Permanent Dipole Moment

Table 5: Summary of the permanent dipole moment properties.

Total	2.20 D
X axis angle	89.98 °
XY plane angle	0.01 °

Methodology

Metadata

The calculation of the excited states was performed using the **Turbomole (7.5.0)** program, the **DFT** method with the **PBE0** functional and the **6-31G**** basis set. It was completed on the **24th June 2022** after a total duration of **10 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals. The full calculation metadata is tabulated in table 1.

Analysis

The report presented here was generated using the Silico software package. This toolset relies upon a number of third-party applications and libraries which should be cited appropriately in derivative works. In particular, the calculation results described within were parsed by the cclib library.¹ Scientific constants which were used, among other things, for the interconversion of scientific units were provided by SciPy.² Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using Visual Molecular Dynamics (VMD)³ and the Tachyon ray-tracer.⁴ Finally, two-dimensional graphs were plotted using the Matplotlib library,⁵ while this report itself was prepared using the Mako template library⁶ and the Weasyprint library⁷, the latter of which was responsible for generation of the PDF file.

Discussion

Total SCF Energy

The total energy of the system was calculated at the **self-consistent field (SCF)** level, corresponding to the energy calculated by the density-functional theory (DFT) method, with a value of -6748.46 eV, corresponding to -651,127 KJmol⁻¹. A plot of the total SCF electron density is shown in figure 1.

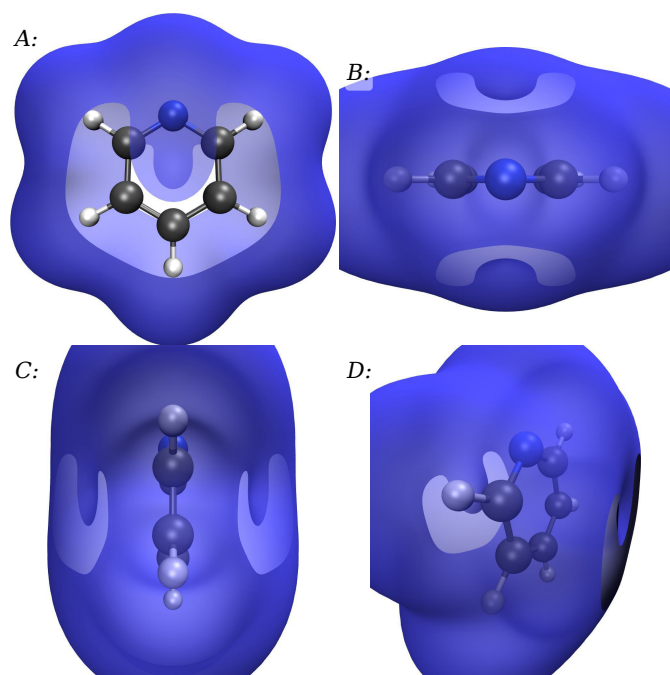


Figure 1: Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Geometry

The **empirical formula** of the studied system was C_5NH_5 , corresponding to a **molecular mass** of 79.10 gmol^{-1} . The molecular geometry was aligned to the cartesian (X, Y and Z) axes by the **Minimal (MIN)** method. Using this method, the **extent of the molecular system** in the X, Y and Z axes (L_X , L_Y and L_Z , corresponding to the molecular width, length and height respectively) was determined to be 4.31, 3.88 and 0.00 Å respectively. These extensions give rise to a **molecular linearity ratio** ($1-(L_Y/L_X)$) and **planarity ratio** ($1-(L_X/L_Y)$) of 0.10 and 1.00 respectively.

Permanent Dipole Moment

The calculated **permanent dipole moment** was 2.20 D, with a vector (x,y,z) of -0.00, -2.20, -0.00 D. The angle between the dipole moment vector and the x-axis was 89.98° , while the angle between the dipole moment and the xy-plane was 0.01° . A plot of the permanent dipole moment is shown in figure 2.

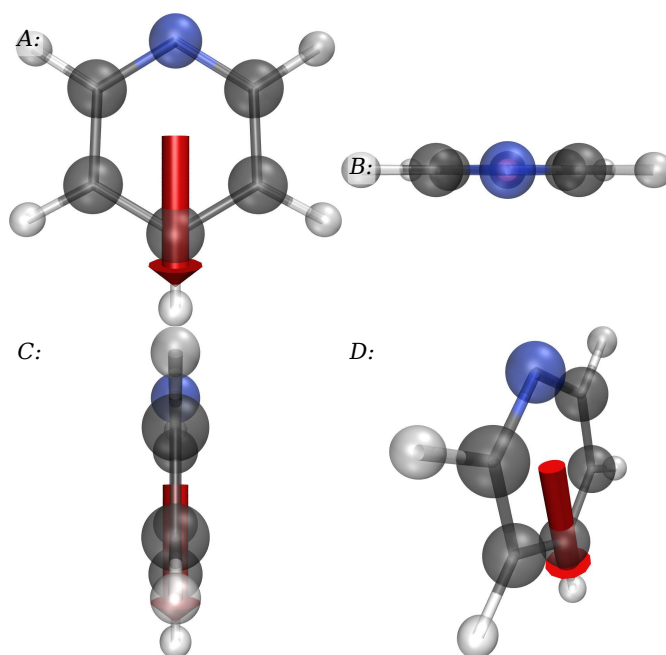


Figure 2: The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of $1 \text{ Å} = 1.0 \text{ D}$. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Molecular Orbitals

In total, 109 doubly occupied molecular orbitals were calculated, divided into 21 occupied orbitals and 88 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -7.17 and -0.47 eV respectively, corresponding to a **HOMO-LUMO band gap** of 6.71 eV (figure 6). Plots of the orbital density for the HOMO and LUMO are shown in figures 3-4 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 5.

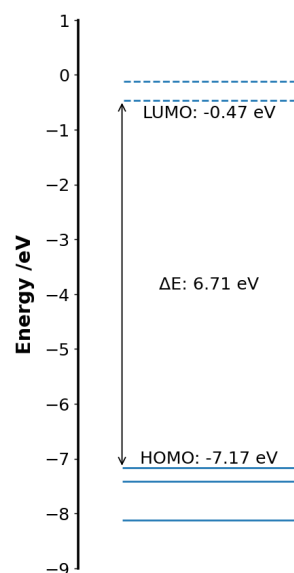


Figure 6: Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.

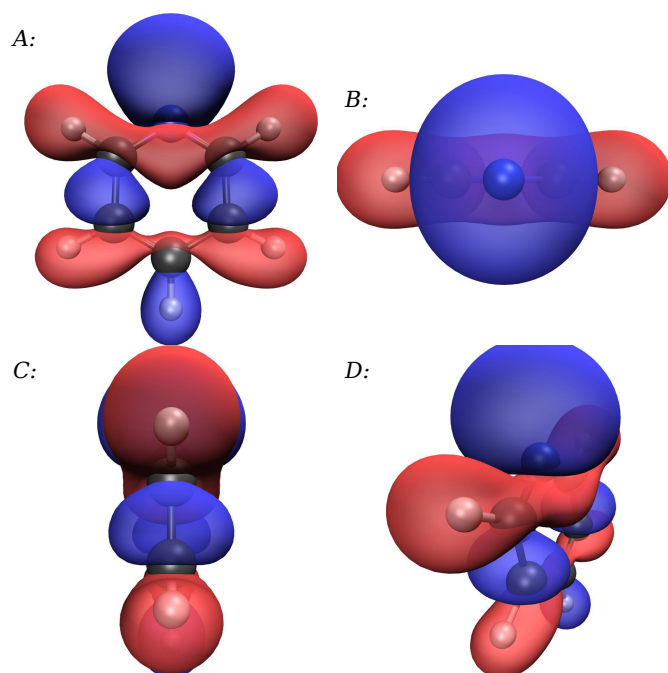


Figure 3: Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

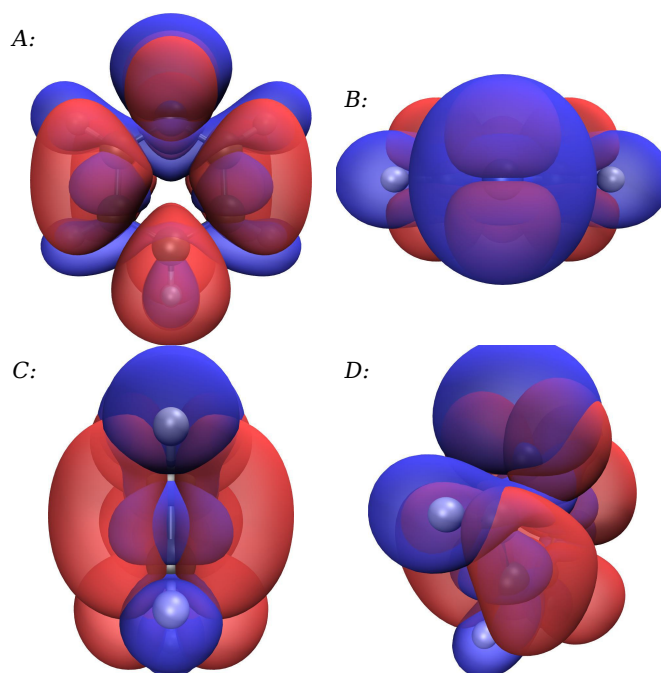


Figure 5: Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

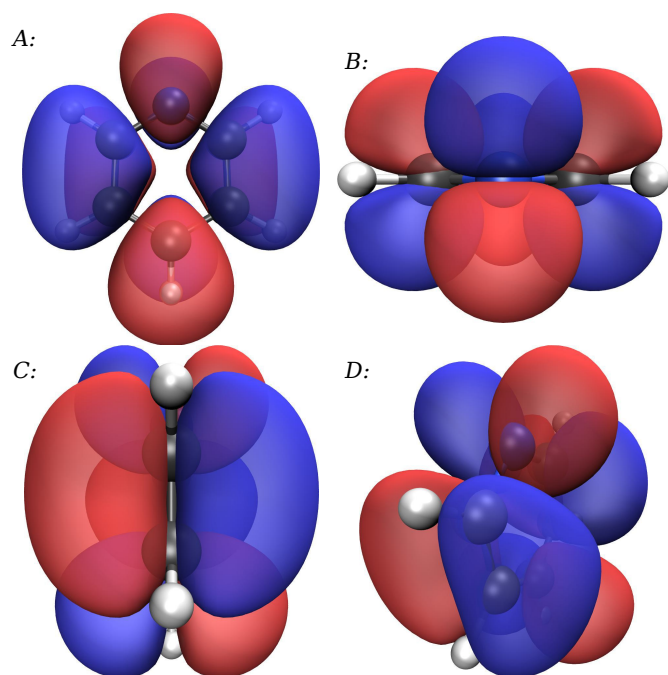


Figure 4: Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Tables Of Results

Atom Coordinates

Table 6: Coordinates of the atoms of the system under study, as aligned to the cartesian axes by the Minimal method.

Element	X Coord /Å	Y Coord /Å	Z Coord /Å
C	-1.1374900	0.6846500	-0.0000200
C	-1.1954400	-0.7066400	0.0000700
C	-0.0004700	-1.4179200	0.0000700
C	1.1949700	-0.7074400	-0.0001500
C	1.1379500	0.6838900	0.0000900
N	0.0004600	1.3802200	0.0002000
H	-2.0551200	1.2706900	-0.0006000
H	-2.1544700	-1.2150500	0.0001500
H	-0.0008300	-2.5041600	0.0003500
H	2.1536600	-1.2164900	-0.0006400
H	2.0559700	1.2693200	0.0003000

Molecular Orbitals

Table 7: Energies of the calculated molecular orbitals.

Level	Label	Symmetry	Energy /eV
37	LUMO+15	A	15.0342
36	LUMO+14	A	14.5841
35	LUMO+13	A	12.7701
34	LUMO+12	A	12.6778
33	LUMO+11	A	9.0193

32	LUMO+10	A	8.9991
31	LUMO+9	A	8.2736
30	LUMO+8	A	6.8258
29	LUMO+7	A	5.1992
28	LUMO+6	A	5.1849
27	LUMO+5	A	4.5869
26	LUMO+4	A	4.2866
25	LUMO+3	A	4.1186
24	LUMO+2	A	2.8373
23	LUMO+1	A	-0.1197
22	LUMO	A	-0.4663
21	HOMO	A	-7.1728
20	HOMO-1	A	-7.4191
19	HOMO-2	A	-8.1231
18	HOMO-3	A	-10.1396
17	HOMO-4	A	-11.1929
16	HOMO-5	A	-11.2837
15	HOMO-6	A	-11.9543
14	HOMO-7	A	-13.1334
13	HOMO-8	A	-13.4086
12	HOMO-9	A	-14.7906
11	HOMO-10	A	-17.5660
10	HOMO-11	A	-17.6203
9	HOMO-12	A	-21.3179
8	HOMO-13	A	-22.5351
7	HOMO-14	A	-26.3511
6	HOMO-15	A	-278.7370

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