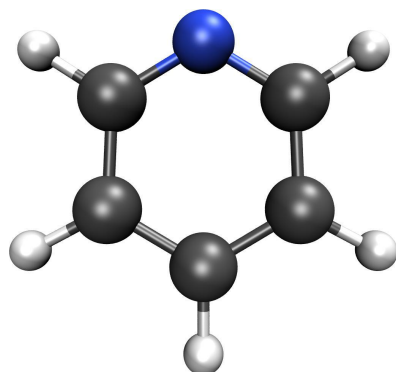




# A Report On The Calculation Of The Optimised Structure And Vibrational Frequencies Of Pyridine At The PBE0/6-31G\*\* Level

osl - 24<sup>th</sup> June 2022



## Abstract

The calculation of optimised structure and vibrational frequencies 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 9 steps. 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. The most intense vibrational frequencies were calculated to be at 722, 1028, 1494, 1668 and 3206 cm<sup>-1</sup>, and there were zero negative frequencies.

**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 <sup>[a]</sup>	Duration <sup>[b]</sup>	Success (Converged)	Computational package	Level of theory	Calculations	Wavefunction	Multiplicity	T <sup>[c]</sup> / K	p <sup>[d]</sup> / atm
24/06/2022 12:20:46	33 s	True (True)	Turbomole (7.5.0)	PBE0/6-31G**	Optimisation, Frequencies	restricted	1 (singlet)	N/A	N/A

## Summary Of Results

### Scf Energy

**Table 2:** Summary of SCF energy properties.

No. of steps	9
Final energy	-6748.4564 eV
Final energy	-651,127 kJ·mol <sup>-1</sup>

### Geometry

**Table 3:** Summary of geometry properties.

Formula	C <sub>5</sub> NH <sub>5</sub>
Molar mass	79.0999 g·mol <sup>-1</sup>
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 <sub>HOMO,LUMO</sub>	6.71 eV
E <sub>HOMO</sub>	-7.17 eV
E <sub>LUMO</sub>	-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 °

### Vibrations

**Table 6:** Summary of the properties of the calculated vibration frequencies.

No. frequencies	27
Simulated peaks	722, 1028, 1494, 1668 and 3206 ... cm <sup>-1</sup>
No. negative frequencies	0
Negative frequencies	N/A

## Methodology

### Metadata

The calculation of the optimised structure and vibrational frequencies 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 **24<sup>th</sup> June 2022** after a total duration of **33 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

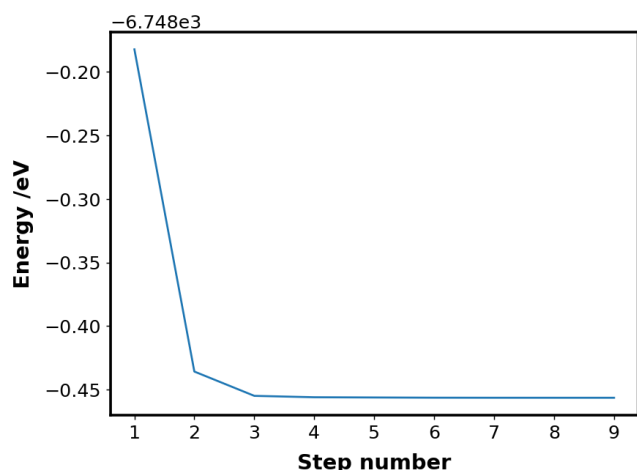
The report presented here was generated using the Silico software package. This toolset relies upon a number of third-party applications and libraries which should be cited appropriately in derivative works. In particular, the calculation results described within were parsed by the cclib library.<sup>1</sup> Scientific constants which were used, among other things, for the interconversion of scientific units were provided by SciPy.<sup>2</sup> Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using

Visual Molecular Dynamics (VMD)<sup>3</sup> and the Tachyon ray-tracer.<sup>4</sup> Finally, two-dimensional graphs were plotted using the Matplotlib library,<sup>5</sup> while this report itself was prepared using the Mako template library<sup>6</sup> and the Weasyprint library<sup>7</sup>, the latter of which was responsible for generation of the PDF file.

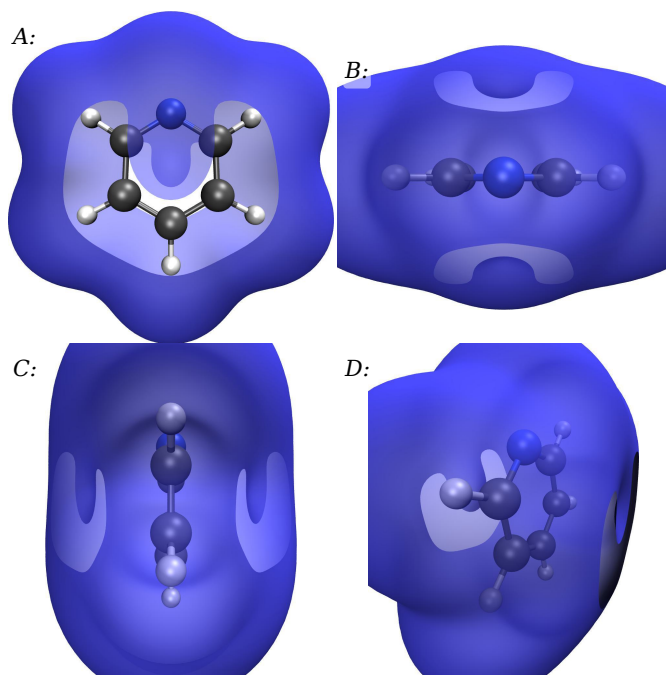
## Discussion

### 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, over a total of nine steps, the results of which are displayed in figure 1. The energy calculated by the final step was -6748.46 eV, corresponding to -651,127 KJmol<sup>-1</sup>. A plot of the total SCF electron density is shown in figure 2.



**Figure 1:** Graph of calculated energies at the self-consistent field (SCF) level.



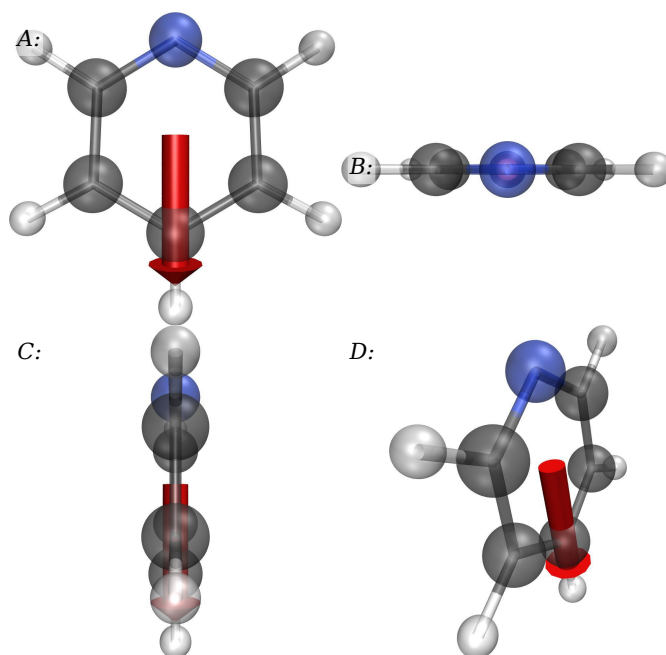
**Figure 2:** Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

### Geometry

The **empirical formula** of the studied system was C<sub>5</sub>NH<sub>5</sub>, corresponding to a **molecular mass** of 79.10 gmol<sup>-1</sup>. 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<sub>X</sub>, L<sub>Y</sub> and L<sub>Z</sub>, 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<sub>Y</sub>/L<sub>X</sub>)) and **planarity ratio** (1-(L<sub>X</sub>/L<sub>Y</sub>)) of 0.10 and 1.00 respectively.

### Permanent Dipole Moment

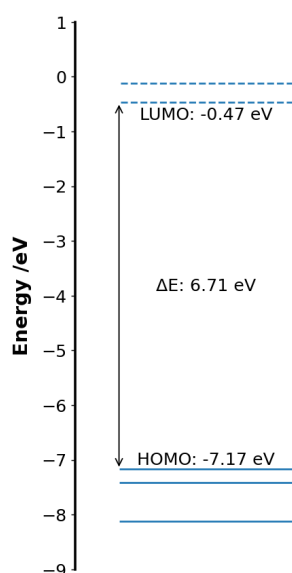
The calculated **permanent dipole moment** was 2.20 D, with a vector (x,y,z) of -0.00, -2.20, -0.00 D. The angle between the dipole moment vector and the x-axis was 89.98 °, while the angle between the dipole moment and the xy-plane was 0.01 °. A plot of the permanent dipole moment is shown in figure 3.



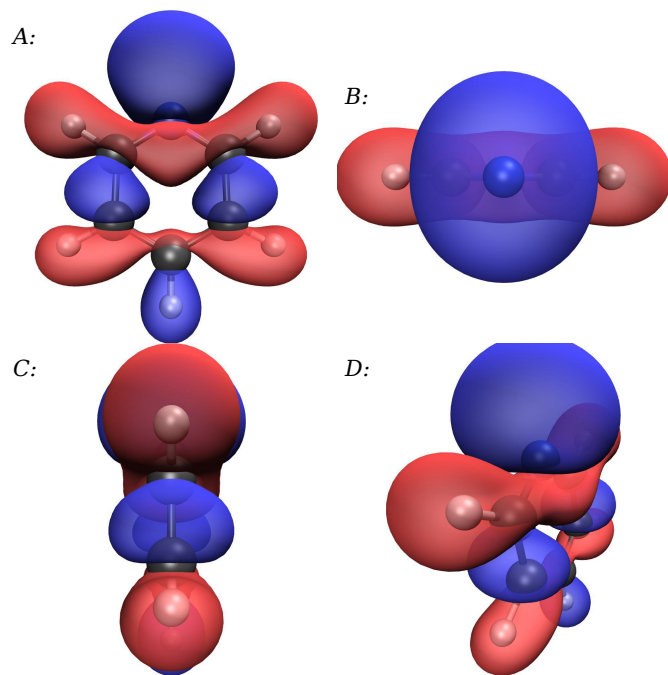
**Figure 3:** The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

### Molecular Orbitals

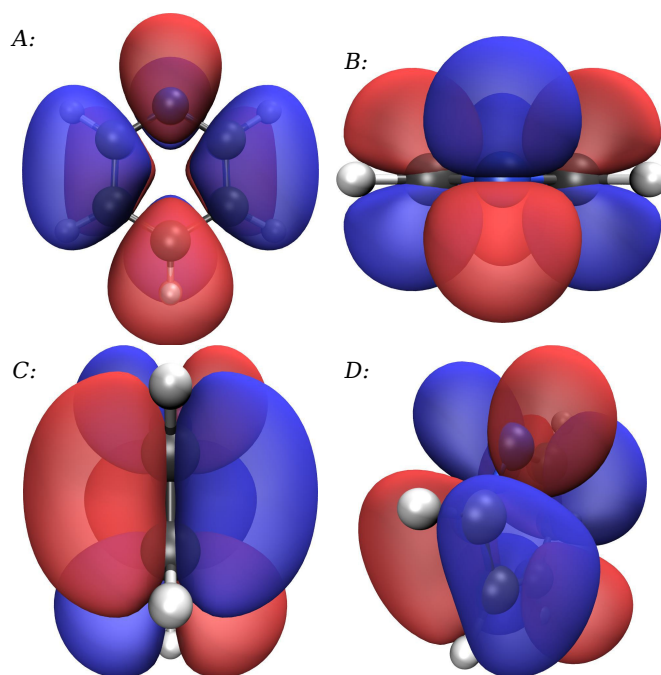
In total, 109 doubly occupied molecular orbitals were calculated, divided into 21 occupied orbitals and 88 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -7.17 and -0.47 eV respectively, corresponding to a **HOMO-LUMO band gap** of 6.71 eV (figure 7). Plots of the orbital density for the HOMO and LUMO are shown in figures 4-5 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 6.



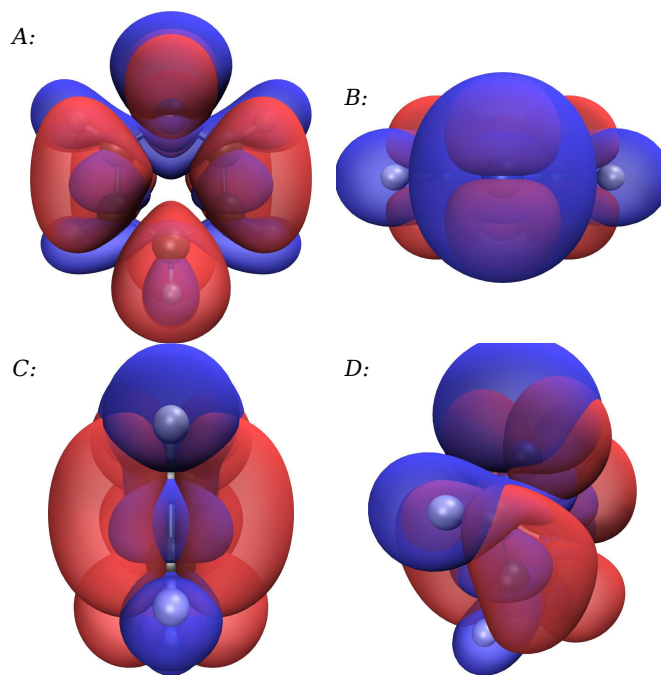
**Figure 7:** Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.



**Figure 4:** 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.



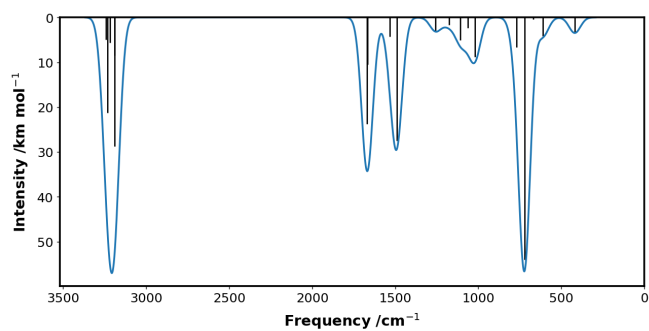
**Figure 5:** Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.



**Figure 6:** 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.

### Vibrational Frequencies

The energies of a total of 27 vibrational transitions were calculated and vibrational absorption peaks were simulated using a gaussian function with full-width at half maximum (FWHM) of 80  $\text{cm}^{-1}$ . From this analysis the **five most intense vibrational peaks** were found at 722, 1028, 1494, 1668 and 3206  $\text{cm}^{-1}$ . The full simulated vibrational frequency spectrum is shown in figure 8. Finally there were zero **calculated negative frequencies**.



**Figure 8:** Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vertical black bars while simulated peaks with a gaussian function with FWHM: 80  $\text{cm}^{-1}$  are shown as a blue line. Peaks can be found at: 418, 722, 1028, 1253, 1494, 1668 and 3206  $\text{cm}^{-1}$ .

Tables Of Results

Atom Coordinates

Table 7: 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	-1.1374880	0.6846500	-0.0000203
C	-1.1954410	-0.7066373	0.0000749
C	-0.0004716	-1.4179164	0.0000717
C	1.1949723	-0.7074353	-0.0001501
C	1.1379485	0.6838900	0.0000885
N	0.0004626	1.3802168	0.0001982
H	-2.0551243	1.2706886	-0.0005978
H	-2.1544681	-1.2150527	0.0001467
H	-0.0008321	-2.5041577	0.0003545
H	2.1536570	-1.2164949	-0.0006432
H	2.0559747	1.2693189	0.0002970

Molecular Orbitals

Table 8: 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	5.1991
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	-0.1198
22	LUMO	A	-0.4664
21	HOMO	A	-7.1729
20	HOMO-1	A	-7.4192
19	HOMO-2	A	-8.1232
18	HOMO-3	A	-10.1396
17	HOMO-4	A	-11.1930

References

1. N. M. O'boyle, A. L. Tenderholt and K. M. Langner, *Journal of Computational Chemistry*, 2008, **29**, 839--845

16	HOMO-5	A	-11.2837
15	HOMO-6	A	-11.9543
14	HOMO-7	A	-13.1334
13	HOMO-8	A	-13.4087
12	HOMO-9	A	-14.7906
11	HOMO-10	A	-17.5660
10	HOMO-11	A	-17.6204
9	HOMO-12	A	-21.3179
8	HOMO-13	A	-22.5352
7	HOMO-14	A	-26.3512
6	HOMO-15	A	-278.7372

Vibrational Frequencies

Table 9: Energies of the calculated vibrational frequencies.

Number	Symmetry	Frequency /cm <sup>-1</sup>	Intensity /km mol <sup>-1</sup>
1	A	383.7300	0.0000
2	A	418.8300	3.4700
3	A	610.8100	4.1300
4	A	669.5500	0.4300
5	A	720.8700	53.9400
6	A	769.0500	6.6100
7	A	903.1900	0.0000
8	A	964.8600	0.0000
9	A	1006.5300	0.0000
10	A	1019.4400	8.7800
11	A	1019.6600	0.0100
12	A	1063.0900	2.3400
13	A	1094.9400	0.0300
14	A	1107.3800	5.0600
15	A	1176.8300	1.7100
16	A	1256.6600	3.0700
17	A	1347.6300	0.0200
18	A	1387.9500	0.0000
19	A	1491.3400	27.4400
20	A	1533.3700	4.3300
21	A	1666.2100	10.5600
22	A	1669.7000	23.7500
23	A	3189.0900	28.7200
24	A	3191.5700	8.4800
25	A	3216.3200	5.6200
26	A	3232.9100	21.2400
27	A	3240.5600	4.9800

2. P. Virtanen, R. Gommers, T. E. Oliphant, M. Haberland, T. Reddy, D. Cournapeau, E. Burovski, P. Peterson, W. Weckesser, J. Bright, S. J. van der Walt, M. Brett, J. Wilson, K. Jarrod Millman, N. Mayorov, A. R. J. Nelson, E. Jones, R. Kern, E. Larson, C. Carey, i. Polat, Y. Feng, E. W. Moore, J. Vand erPlas, D. Laxalde, J. Perktold, R. Cimrman, I. Henriksen, E. A. Quintero, C. R. Harris, A. M. Archibald, A. H. Ribeiro, F. Pedregosa, P. van Mulbregt and S. 1. O. Contributors, *Nature Methods*, 2020, **17**, 261--272

3. W. Humphrey, A. Dalke and K. Schulten, *Journal of Molecular Graphics*, 1996, **14**, 33--38

- 
4. J. Stone, Masters Thesis, Computer Science Department, University of Missouri-Rolla, 1998
  5. J. D. Hunter, *Computing in Science & Engineering*, 2007, **9**, 90--95
  6. M. Bayer, <https://www.makotemplates.org>, (accessed May 2020)
  7. K. Community, <https://weasyprint.org>, (accessed May 2020)