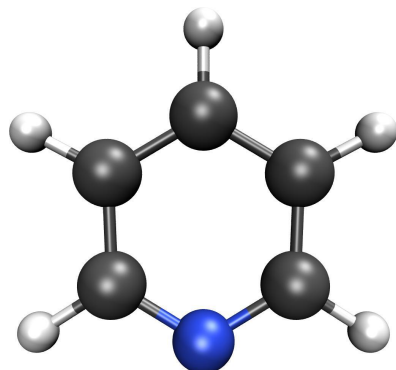




A Report On The Calculation Of The Optimised Structure And Vibrational Frequencies Of Pyridine At The PBE1PBE/6-31G(d,p) Level

osl - 15th 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 Gaussian software package at the PBE1PBE/6-31G(d,p) level of theory. The total self-consistent field (SCF) energy of the system was found to be -6748.61 eV after 5 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -7.28 and -0.51 eV respectively, corresponding to a HOMO-LUMO band gap of 6.77 eV. The permanent dipole moment (PDM) was calculated to be 2.51 D. The most intense vibrational frequencies were calculated to be at 724, 1028, 1493, 1667 and 3203 cm⁻¹, 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 ^[a]	Duration ^[b]	Success (Converged)	Computational package	Level of theory	Calculations	Wavefunction	Multiplicity	T ^[c] / K	p ^[d] / atm
15/06/2022 23:24:49	1 m, 23 s	True (True)	Gaussian (2016+C. 01)	PBE1PBE/ 6-31G(d,p)	Optimisation, Frequencies	restricted	1 (singlet)	298.15	1.0

Summary Of Results

Scf Energy

Table 2: Summary of SCF energy properties.

No. of steps	5
Final energy	-6748.6129 eV
Final energy	-651,142 kJ·mol ⁻¹

Geometry

Table 3: Summary of geometry properties.

Formula	C ₅ NH ₅
Exact mass	79.0422 g·mol ⁻¹
Molar mass	79.0999 g·mol ⁻¹
Alignment method	Minimal
X extension	4.31 Å
Y extension	3.89 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}	6.77 eV
E _{HOMO}	-7.28 eV
E _{LUMO}	-0.51 eV

Permanent Dipole Moment

Table 5: Summary of the permanent dipole moment properties.

Total	2.51 D
-------	--------

X axis angle 90.00 °

XY plane angle 0.00 °

Vibrations

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

No. frequencies	27
Simulated peaks	724, 1028, 1493, 1667 and 3203 ... cm ⁻¹
No. negative frequencies	0
Negative frequencies	N/A

Methodology

Metadata

The calculation of the optimised structure and vibrational frequencies was performed using the **Gaussian (2016+C.01)** program, the **DFT** method with the **PBE1PBE** functional and the **6-31G(d,p)** basis set. It was completed on the **15th June 2022** after a total duration of **1 m, 23 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, over a total of five steps, the results of which are displayed in figure 1. The energy calculated by the final step was -6748.61 eV, corresponding to -651,142 KJmol⁻¹. A plot of the total SCF electron density is shown in figure 2.

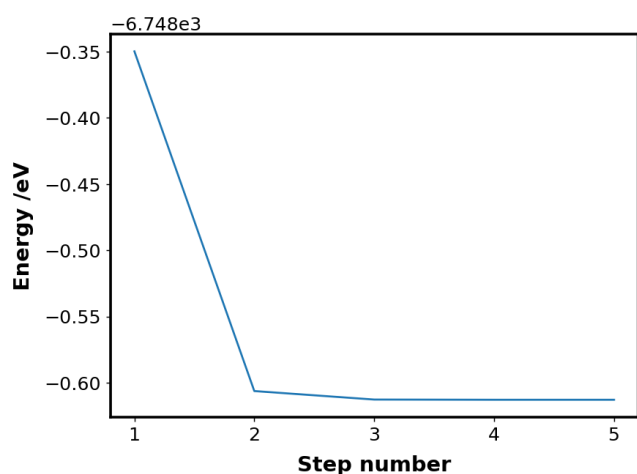


Figure 1: Graph of calculated energies at the self-consistent field (SCF) level.

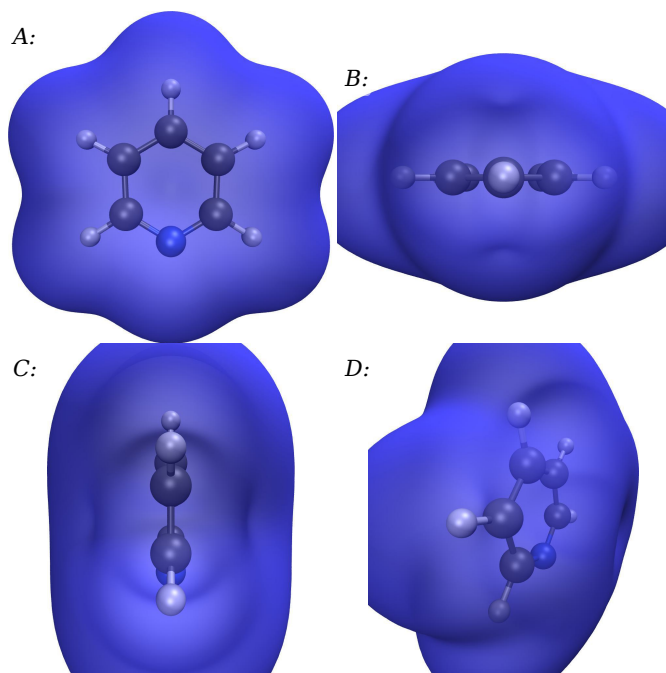


Figure 2: Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Geometry

The **empirical formula** of the studied system was C₅NH₅, corresponding to a **molecular mass** of 79.10 gmol⁻¹ and an **exact mass**, considering only specific atomic isotopes, of 79.04 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, 3.89 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 2.51 D, with a vector (x,y,z) of 0.00, 2.51, -0.00 D. The angle between the dipole moment vector and the x-axis was 90.00 °, while the angle between the dipole moment and the xy-plane was 0.00 °. A plot of the permanent dipole moment is shown in figure 3.

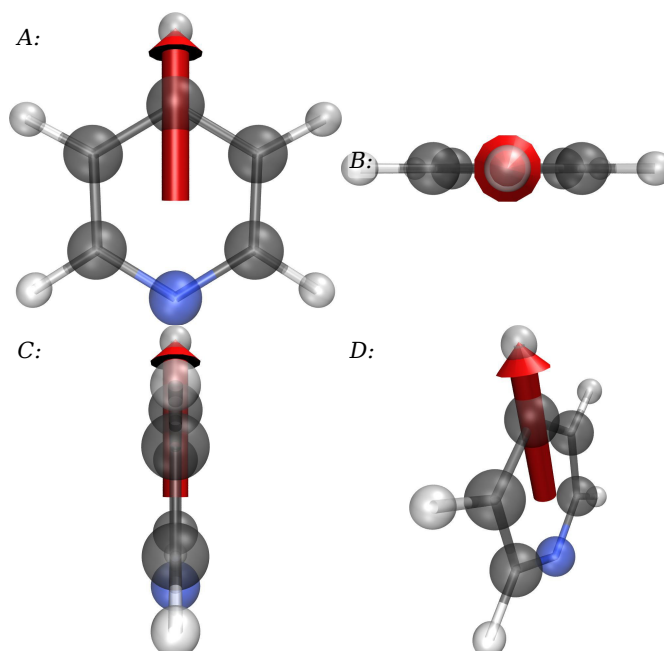


Figure 3: The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

Molecular Orbitals

In total, 115 doubly occupied molecular orbitals were calculated, divided into 21 occupied orbitals and 94 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -7.28 and -0.51 eV respectively, corresponding to a **HOMO-LUMO band gap** of 6.77 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.

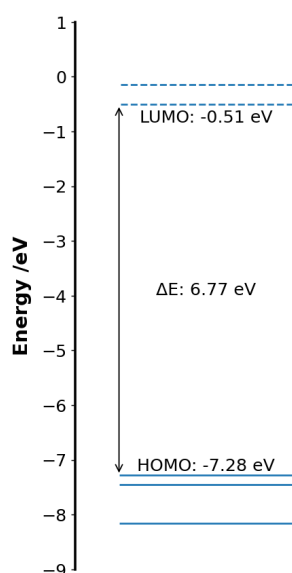


Figure 7: Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.

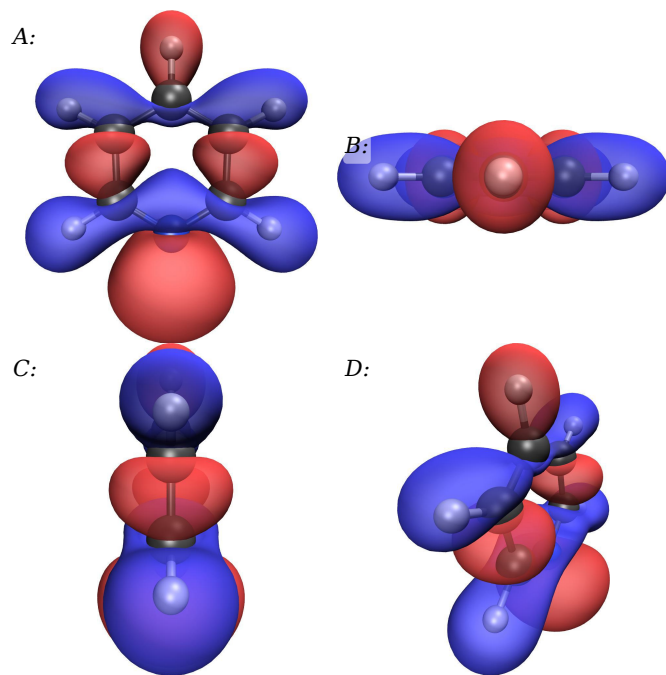


Figure 4: Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

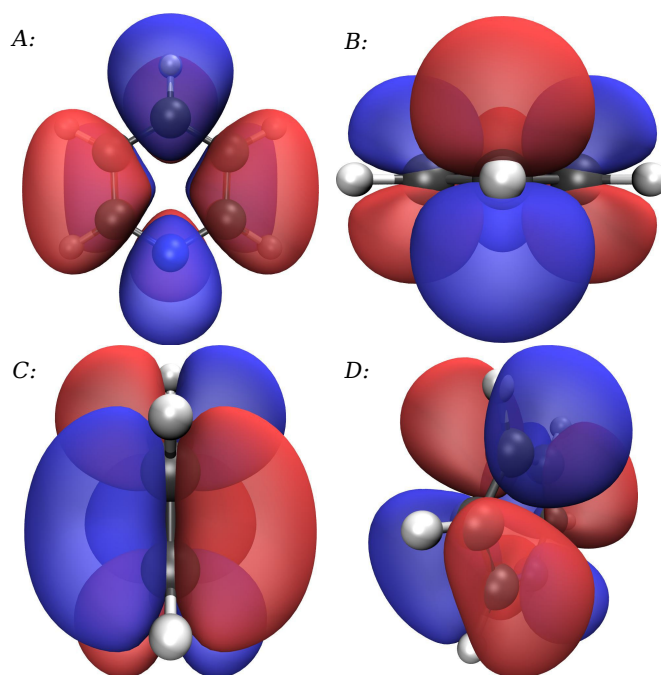


Figure 5: Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

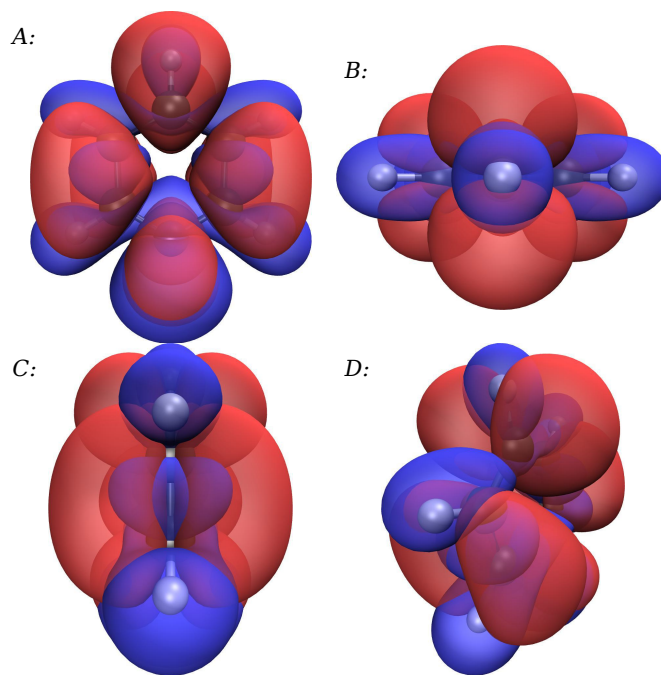


Figure 6: Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.

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 cm^{-1} . From this analysis the **five most intense vibrational peaks** were found at 724, 1028, 1493, 1667 and 3203 cm^{-1} . The full simulated vibrational frequency spectrum is shown in figure 8. Finally there were zero **calculated negative frequencies**.

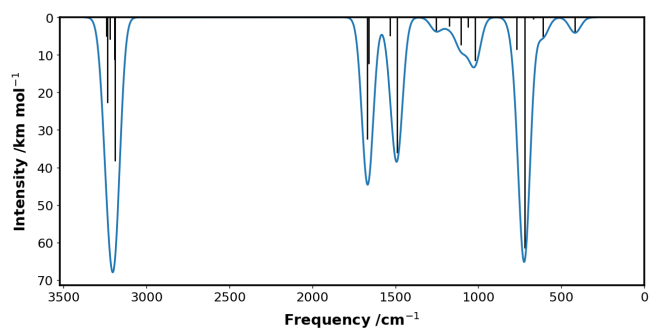


Figure 8: Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vertical black bars while simulated peaks with a gaussian function with FWHM: 80 cm^{-1} are shown as a blue line. Peaks can be found at: 417, 724, 1028, 1249, 1493, 1667 and 3203 cm^{-1} .

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	-1.1386600	-0.7199540	0.0000200
C	-1.1953980	0.6709320	-0.0000220
C	-0.0000260	1.3817850	-0.0000190
C	1.1953740	0.6709710	-0.0000200
C	1.1386890	-0.7199120	-0.0000270
N	0.0000240	-1.4172140	0.0000620
H	-2.0570650	-1.3046280	0.0000360
H	-2.1540460	1.1794230	-0.0000390
H	-0.0000390	2.4678210	-0.0000450
H	2.1539990	1.1795060	-0.0000200
H	2.0571100	-1.3045590	0.0000440

Molecular Orbitals

Table 8: Energies of the calculated molecular orbitals.

Level	Label	Symmetry	Energy /eV
37	LUMO+15	A	14.9940
36	LUMO+14	A	14.5273
35	LUMO+13	A	12.7428
34	LUMO+12	A	12.6081
33	LUMO+11	A	9.0029
32	LUMO+10	A	8.9866
31	LUMO+9	A	8.3038
30	LUMO+8	A	6.7868
29	LUMO+7	A	5.2853
28	LUMO+6	A	5.2515
27	LUMO+5	A	4.6436
26	LUMO+4	A	4.2561
25	LUMO+3	A	4.2020
24	LUMO+2	A	2.9309
23	LUMO+1	A	-0.1420
22	LUMO	A	-0.5097
21	HOMO	A	-7.2829
20	HOMO-1	A	-7.4475
19	HOMO-2	A	-8.1539
18	HOMO-3	A	-10.1324
17	HOMO-4	A	-11.2402

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	-11.2778
15	HOMO-6	A	-11.9507
14	HOMO-7	A	-13.1140
13	HOMO-8	A	-13.4217
12	HOMO-9	A	-14.7872
11	HOMO-10	A	-17.5723
10	HOMO-11	A	-17.6352
9	HOMO-12	A	-21.3397
8	HOMO-13	A	-22.5449
7	HOMO-14	A	-26.3953
6	HOMO-15	A	-278.8609

Vibrational Frequencies

Table 9: Energies of the calculated vibrational frequencies.

Number	Symmetry	Frequency /cm ⁻¹	Intensity /km mol ⁻¹
1	A	384.2445	0.0000
2	A	417.5700	4.1187
3	A	611.7278	5.2079
4	A	668.2642	0.4647
5	A	721.5500	61.5866
6	A	768.8726	8.6373
7	A	904.9758	0.0000
8	A	966.8891	0.0014
9	A	1007.7254	0.0000
10	A	1019.4319	11.5446
11	A	1023.1818	0.0001
12	A	1061.1575	2.6424
13	A	1094.9181	0.0005
14	A	1106.3118	7.3922
15	A	1176.6064	2.3938
16	A	1254.2108	3.6314
17	A	1342.5154	0.0027
18	A	1388.6405	0.0269
19	A	1490.0899	36.1488
20	A	1532.7236	4.9241
21	A	1661.7273	12.3410
22	A	1669.3960	32.4724
23	A	3188.5029	38.3142
24	A	3191.5774	11.3414
25	A	3219.0592	5.9386
26	A	3235.6160	22.7306
27	A	3242.8238	5.1354

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)