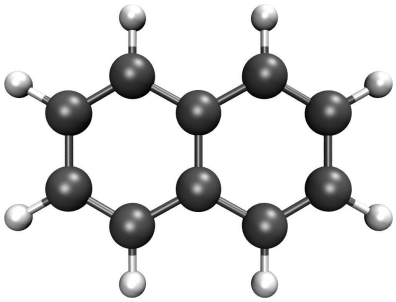
A Report On The Calculation Of The Optimised Structure And Vibrational Frequencies Of Naphthalene At The PBE0/6-31G** Level

osl - 24th June 2022



Abstract

The calculation of optimised structure and vibrational frequencies for the system 'Naphthalene' 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 -10488.80 eV after 4 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -6.07 and -0.87 eV respectively, corresponding to a HOMO-LUMO band gap of 5.20 eV. The permanent dipole moment (PDM) was calculated to be 0.00 D. The most intense vibrational frequencies were calculated to be at 488, 805, 1291, 1582 and 3224 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. [b]: 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 12:43:12	1 m, 43 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	4
Final energy	-10488.7997 eV
Final energy	-1,012,015 $kJ \cdot mol^{-1}$

Geometry

Table 3: *Summary of geometry properties.*

Formula	$C_{10}H_8$
Molar mass	128.1705 $g \cdot mol^{-1}$
Alignment method	Minimal
X extension	6.74 Å
Y extension	4.97 Å
Z extension	0.00 Å
Linearity ratio	0.26
Planarity ratio	1.00

Molecular Orbitals

Table 4: *Summary of HOMO & LUMO properties.*

$E_{HOMO,LUMO}$	5.20 eV
E_{HOMO}	-6.07 eV
E_{LUMO}	-0.87 eV

Permanent Dipole Moment

Table 5: *Summary of the permanent dipole moment properties.*

Total	< 0.01 D
X axis angle	90.00 °
XY plane angle	90.00 °

Vibrations

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

No. frequencies	48
Simulated peaks	488, 805, 1291, 1582 and 3224 ... 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 **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 **1 m, 43 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 library[6] and the Weasyprint library[7], 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 four steps, the results of which are displayed in figure 1. The energy calculated by the final step was -10488.80 eV, corresponding to -1,012,015 KJmol^{-1}. A plot of the total SCF electron density is shown in figure 2.

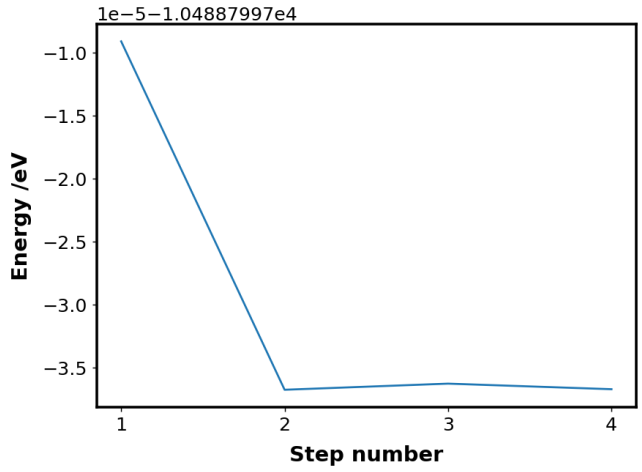


Figure 1: *Graph of calculated energies at the self-consistent field (SCF) level.*

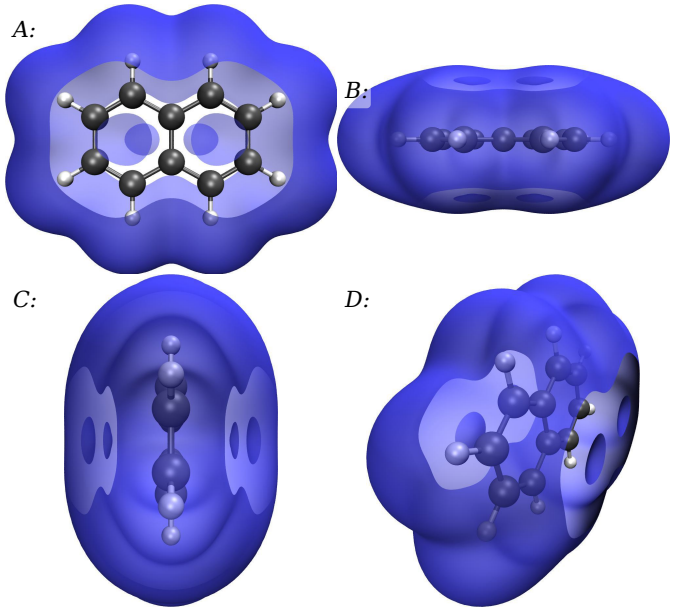


Figure 2: *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Geometry

The **empirical formula** of the studied system was $C_{10}H_8$, corresponding to a **molecular mass** of 128.17 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 6.74, 4.97 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 0.26 and 1.00 respectively.

Permanent Dipole Moment

The calculated **permanent dipole moment** was < 0.01 D, with a vector (x,y,z) of -0.00, -0.00, -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 90.00 °. A plot of the permanent dipole moment is shown in figure 3.

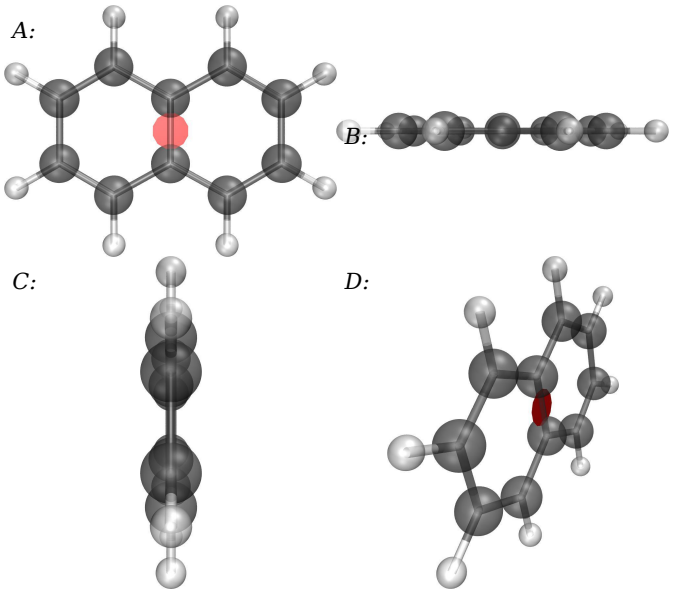


Figure 3: *The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Molecular Orbitals

In total, 180 doubly occupied molecular orbitals were calculated, divided into 34 occupied orbitals and 146 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -6.07 and -0.87 eV respectively, corresponding to a **HOMO-LUMO band gap** of 5.20 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.

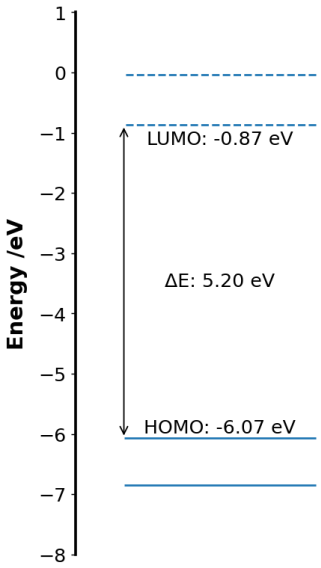


Figure 7: *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*

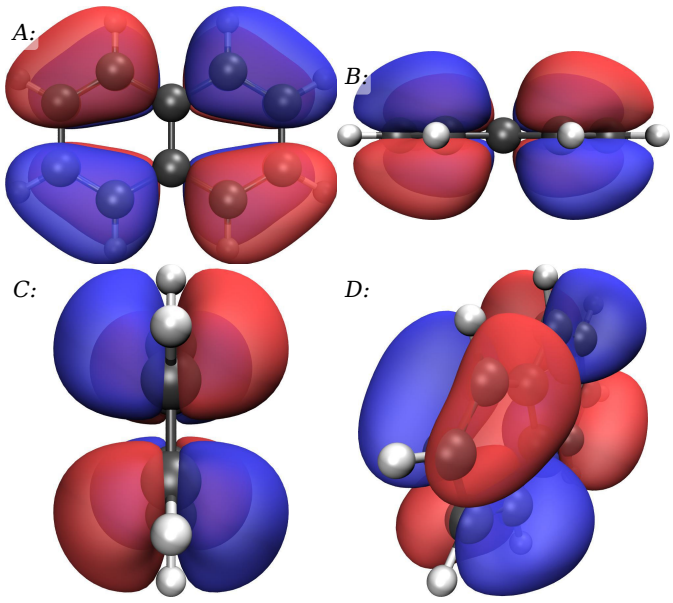


Figure 4: *Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

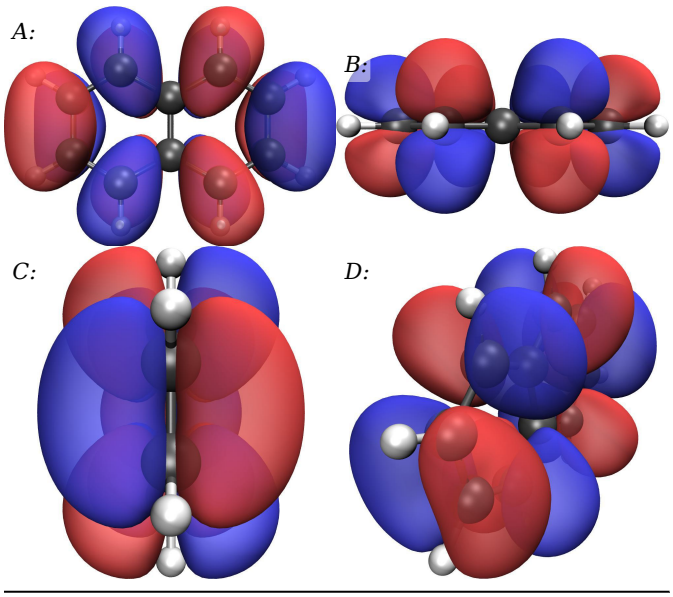


Figure 5: *Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

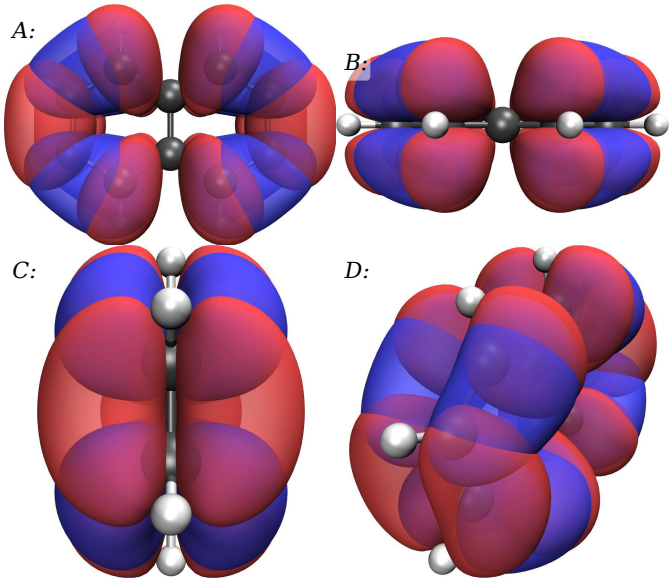


Figure 6: *Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Vibrational Frequencies

The energies of a total of 48 vibrational transitions were calculated and vibrational absorption peaks were simulated using a gaussian function with full-width at half maximum (FHWM) of 80 cm^{-1}. From this analysis the **five most intense vibrational peaks** were found at 488, 805, 1291, 1582 and 3224 cm^{-1}. The full simulated vibrational frequency spectrum is shown in figure 8. Finally there were zero **calculated negative frequencies**.

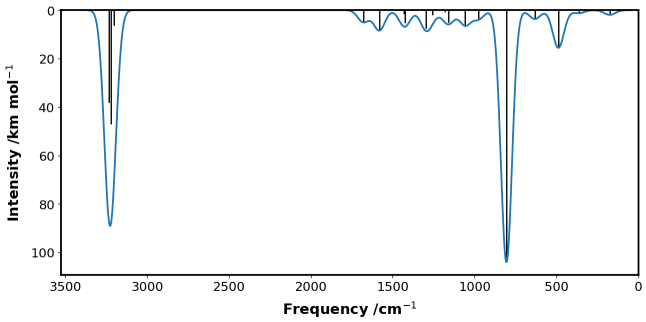


Figure 8: *Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vetical black bars while simulated peaks with a gaussian function with FHWM: 80 cm^{-1} are shown as a blue line. Peaks can be found at: 173, 365, 488, 631, 805, 1054, 1160, 1291, 1426, 1582, 1675 and 3224 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	-1.2401190	-1.3986652	0.0000236
C	-2.4257456	-0.7064589	-0.0000163
C	-2.4257455	0.7064589	-0.0000245
C	-1.2401189	1.3986651	0.0000155
C	0.0000000	0.7136890	0.0000487
C	0.0000000	-0.7136891	0.0000482
C	1.2401190	-1.3986652	0.0000162
C	1.2401189	1.3986651	0.0000249
C	2.4257455	0.7064589	-0.0000165
C	2.4257456	-0.7064589	-0.0000247
H	-1.2360956	-2.4857078	0.0000366
H	-3.3697021	-1.2435414	-0.0000442
H	-3.3697019	1.2435415	-0.0000637
H	-1.2360954	2.4857078	0.0000215
H	1.2360956	-2.4857078	0.0000257
H	1.2360954	2.4857078	0.0000403
H	3.3697019	1.2435415	-0.0000460
H	3.3697021	-1.2435414	-0.0000653

Molecular Orbitals

Table 8: *Energies of the calculated molecular orbitals.*

Level	Label	Symmetry	Energy /eV
50	LUMO+15	A	8.6772
49	LUMO+14	A	7.9408
48	LUMO+13	A	6.9385
47	LUMO+12	A	6.0199
46	LUMO+11	A	5.8556
45	LUMO+10	A	5.3160
44	LUMO+9	A	5.1150
43	LUMO+8	A	4.9563
42	LUMO+7	A	4.9002
41	LUMO+6	A	3.6416
40	LUMO+5	A	3.3840
39	LUMO+4	A	3.0181
38	LUMO+3	A	2.8726
37	LUMO+2	A	1.1210
36	LUMO+1	A	-0.0372
35	**LUMO**	**A**	**-0.8685**
34	**HOMO**	**A**	**-6.0723**
33	HOMO-1	A	-6.8459
32	HOMO-2	A	-8.0113
31	HOMO-3	A	-9.1658
30	HOMO-4	A	-9.1940
29	HOMO-5	A	-9.3747
28	HOMO-6	A	-10.2483
27	HOMO-7	A	-10.9559
26	HOMO-8	A	-11.1181
25	HOMO-9	A	-11.5629
24	HOMO-10	A	-11.5950
23	HOMO-11	A	-12.2691
22	HOMO-12	A	-12.4566
21	HOMO-13	A	-13.7514
20	HOMO-14	A	-14.2144
19	HOMO-15	A	-14.3454

Vibrational Frequencies

Table 9: *Energies of the calculated vibrational frequencies.*

Number	Symmetry	Frequency /cm^{-1}	Intensity /km mol^{-1}
1	A	173.8900	1.9600
2	A	188.7600	0.0000
3	A	363.1000	1.2600
4	A	395.4100	0.0000
5	A	478.4100	0.0000
6	A	488.2700	15.5600
7	A	517.1100	0.0000
8	A	523.4600	0.0000
9	A	632.0700	3.6700
10	A	636.9300	0.0000
11	A	733.3100	0.0000
12	A	783.2300	0.0000
13	A	789.1200	0.0000
14	A	805.2800	103.7700
15	A	809.9100	0.2400
16	A	854.7500	0.0000
17	A	900.3200	0.0000
18	A	948.3000	0.0000
19	A	958.2500	0.0000
20	A	975.8600	3.6500
21	A	995.7800	0.0000
22	A	1003.4600	0.0000
23	A	1057.1100	6.2700
24	A	1066.1500	0.0000
25	A	1157.9100	5.0900
26	A	1179.0900	0.8300
27	A	1179.9300	0.0000
28	A	1188.1900	0.0000
29	A	1256.2900	2.0900
30	A	1273.3900	0.0000
31	A	1296.9100	7.5700
32	A	1425.3000	5.2900
33	A	1432.3300	1.6100
34	A	1455.0500	0.0000
35	A	1507.0400	0.0000
36	A	1511.4100	0.0000
37	A	1581.5300	8.3900
38	A	1658.1900	0.0000
39	A	1678.9300	4.9400
40	A	1716.7200	0.0000
41	A	3201.6100	0.0000
42	A	3202.4800	6.2700

43	A	3205.4800	0.4000	46	A	3220.9700	47.0100
44	A	3207.6900	0.0000	47	A	3233.1600	38.0800
45	A	3220.3300	0.0000	48	A	3234.0200	0.0000

References

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