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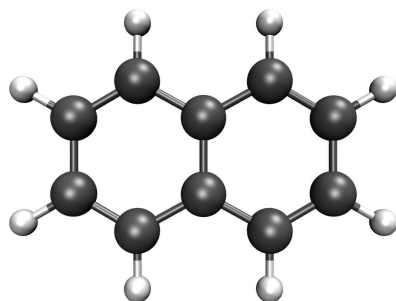
A Report On The Calculation Of The Optimised Structure And Vibrational Frequencies Of Naphthalene At The PBE1PBE/6-31G(d,p) Level

osl - 07th 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 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 -10488.99 eV after 5 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -6.13 and -0.92 eV respectively, corresponding to a HOMO-LUMO band gap of 5.21 eV. The permanent dipole moment (PDM) was calculated to be 0.00 D. The most intense vibrational frequencies were calculated to be at 487, 806, 1294, 1580 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
07/06/2022 16:39:10	4 m, 57 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	-10488.9903 eV
Final energy	-1,012,034 kJ·mol^{-1}

Geometry

Table 3: Summary of geometry properties.

Formula	$C_{10}H_8$
Exact mass	128.0626 g·mol^{-1}
Molar mass	128.1705 g·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.

$E_{HOMO,LUMO}$	5.21 eV
E_{HOMO}	-6.13 eV
E_{LUMO}	-0.92 eV

Permanent Dipole Moment

Table 5: Summary of the permanent dipole moment properties.

Total	0.00 D
X axis angle	0.00 °
XY plane angle	0.00 °

Vibrations

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

No. frequencies	48
Simulated peaks	487, 806, 1294, 1580 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 **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 **07th June 2022** after a total duration of **4 m, 57 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 five steps, the results of which are displayed in figure 1. The energy calculated by the final step was -10488.99 eV, corresponding to -1,012,034 KJmol⁻¹. A plot of the total SCF electron density is shown in figure 2.
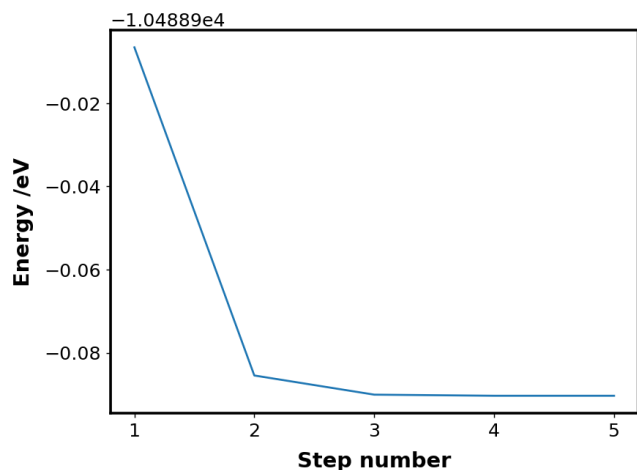
Figure 1: *Graph of calculated energies at the self-consistent field (SCF) level.*
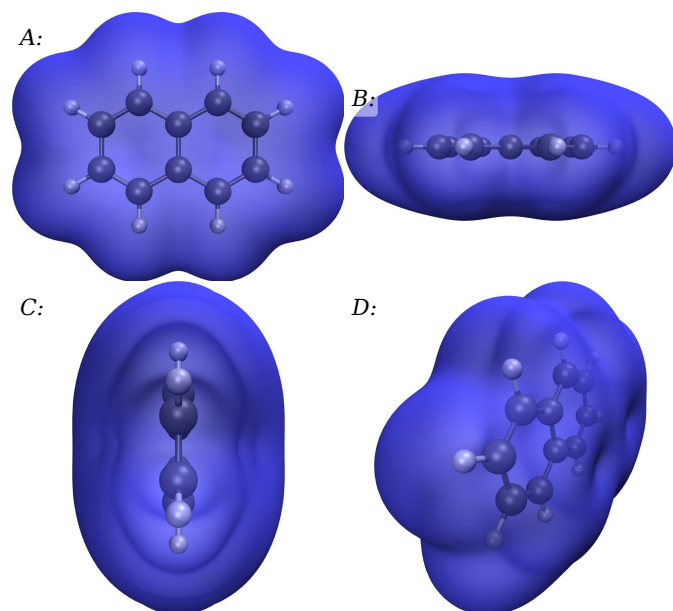
Figure 2: *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Geometry

The **empirical formula** of the studied system was $C_{10}H_8$, corresponding to a **molecular mass** of 128.17 gmol⁻¹ and an **exact mass**, considering only specific atomic isotopes, of 128.06 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 exactly 0 D.

Molecular Orbitals

In total, 190 doubly occupied molecular orbitals were calculated, divided into 34 occupied orbitals and 156 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -6.13 and -0.92 eV respectively, corresponding to a **HOMO-LUMO band gap** of 5.21 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.
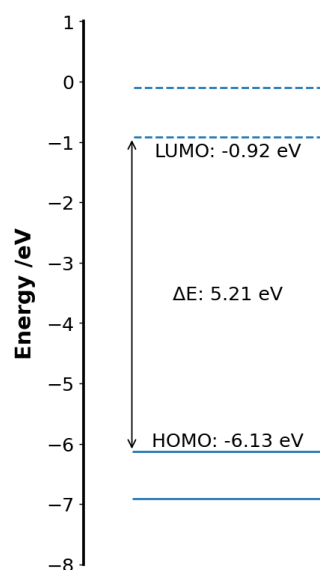
Figure 6: *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*
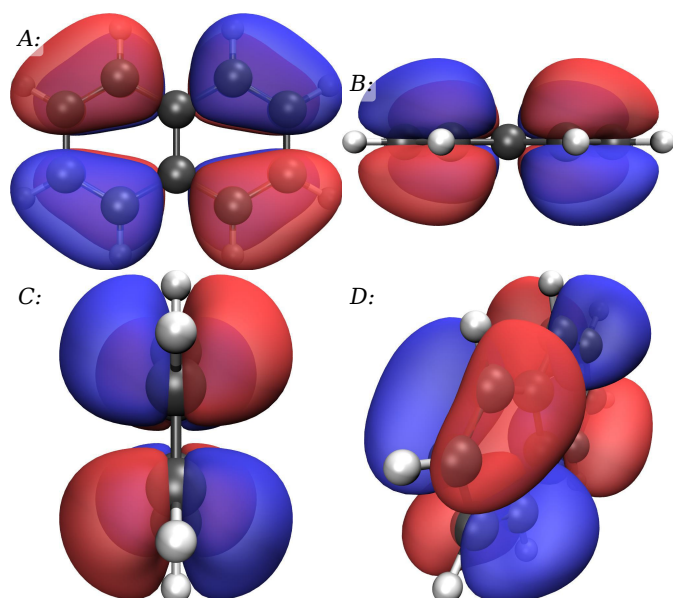
Figure 3: *Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*
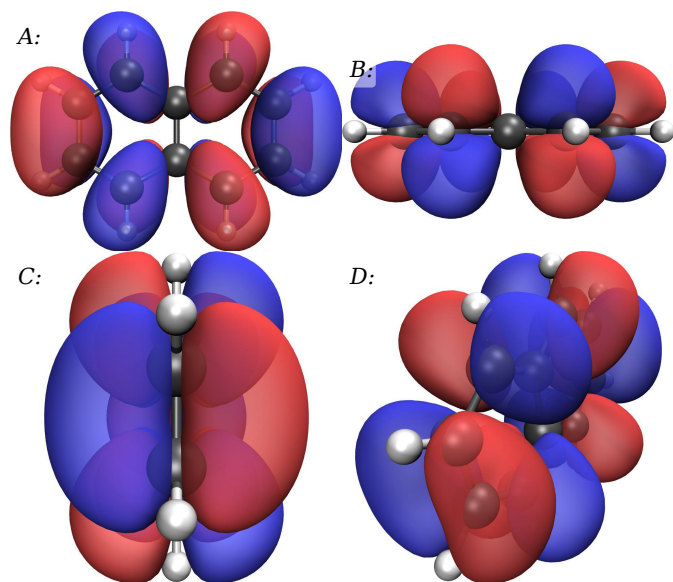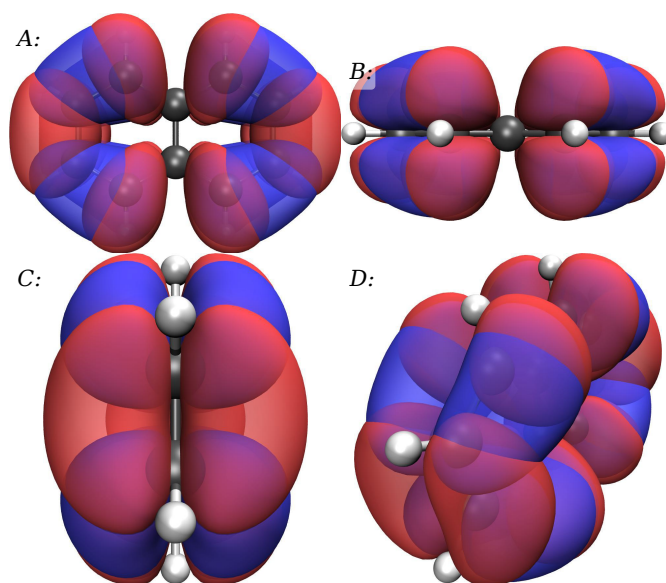

Figure 4: *Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

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.*

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 487, 806, 1294, 1580 and 3224 cm^{-1}. The full simulated vibrational frequency spectrum is shown in figure 7. Finally there were zero **calculated negative frequencies**.
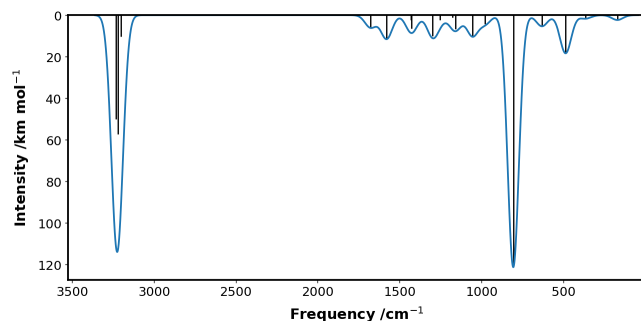
Figure 7: *Graph of simulated vibrational spectrum. Calculated vibrational frequencies are shown as vetical black bars while simulated peaks with a gaussian function with FHWM: 80 cm^{-1} are shown as a blue line. Peaks can be found at: 170, 368, 487, 631, 806, 1053, 1160, 1294, 1427, 1580, 1673 and 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	-1.2404550	-1.3991360	-0.0000000
C	-2.4260000	-0.7066350	-0.0000000
C	-2.4260000	0.7066350	0.0000010
C	-1.2404550	1.3991360	0.0000010
C	0.0000000	0.7142260	-0.0000010
C	0.0000000	-0.7142260	-0.0000010
C	1.2404550	-1.3991360	0.0000010
C	1.2404550	1.3991360	-0.0000000
C	2.4260000	0.7066350	-0.0000000
C	2.4260000	-0.7066350	0.0000010
H	-1.2366960	-2.4861970	-0.0000030
H	-3.3696970	-1.2439660	0.0000010
H	-3.3696970	1.2439660	-0.0000010
H	-1.2366960	2.4861970	0.0000000
H	1.2366960	-2.4861970	0.0000000
H	1.2366960	2.4861970	-0.0000030
H	3.3696970	1.2439660	0.0000010
H	3.3696970	-1.2439660	-0.0000010

Molecular Orbitals

Table 8: Energies of the calculated molecular orbitals.

Level	Label	Symmetry	Energy /eV
50	LUMO+15	A	8.6396
49	LUMO+14	A	7.9114
48	LUMO+13	A	6.9152
47	LUMO+12	A	6.0692
46	LUMO+11	A	5.7949
45	LUMO+10	A	5.3487
44	LUMO+9	A	5.1506
43	LUMO+8	A	5.0034
42	LUMO+7	A	4.9519
41	LUMO+6	A	3.6912
40	LUMO+5	A	3.4207
39	LUMO+4	A	2.9674
38	LUMO+3	A	2.9127
37	LUMO+2	A	1.0612
36	LUMO+1	A	-0.1010
35	**LUMO**	**A**	**-0.9244**
34	**HOMO**	**A**	**-6.1307**
33	HOMO-1	A	-6.9087
32	HOMO-2	A	-8.0747
31	HOMO-3	A	-9.1879
30	HOMO-4	A	-9.2562
29	HOMO-5	A	-9.4032
28	HOMO-6	A	-10.2679
27	HOMO-7	A	-11.0274
26	HOMO-8	A	-11.1363
25	HOMO-9	A	-11.5961
24	HOMO-10	A	-11.6187
23	HOMO-11	A	-12.3015
22	HOMO-12	A	-12.4753
21	HOMO-13	A	-13.7777
20	HOMO-14	A	-14.2411
19	HOMO-15	A	-14.3709

Vibrational Frequencies

Table 9: Energies of the calculated vibrational frequencies.

Number	Symmetry	Frequency /cm^{-1}	Intensity /km mol^{-1}
1	A	170.6603	2.3323
2	A	186.3677	0.0000
3	A	365.1609	1.6874
4	A	393.2304	0.0000
5	A	477.4391	0.0000
6	A	486.8646	18.3491
7	A	516.9575	0.0000
8	A	522.9547	0.0000
9	A	631.0734	5.3597
10	A	636.2303	0.0000
11	A	734.4453	0.0000
12	A	783.2293	0.0000
13	A	787.4275	0.0000
14	A	806.2853	121.0015
15	A	809.4087	0.2244
16	A	856.6594	0.0000
17	A	901.2132	0.0000
18	A	947.6833	0.0000
19	A	961.3577	0.0000
20	A	978.7553	4.2681
21	A	999.1135	0.0000
22	A	1006.5492	0.0000
23	A	1055.4957	10.0015
24	A	1066.4428	0.0000
25	A	1158.3757	6.7028
26	A	1178.7603	1.0658
27	A	1179.8776	0.0000
28	A	1188.4321	0.0000
29	A	1254.2980	2.4273
30	A	1274.8273	0.0000
31	A	1299.2065	10.0549
32	A	1426.1623	6.3760
33	A	1430.5870	2.2480
34	A	1451.2573	0.0000
35	A	1508.0715	0.0000
36	A	1510.3663	0.0000
37	A	1579.8388	11.4633
38	A	1655.4851	0.0000
39	A	1677.4730	5.9807
40	A	1714.4767	0.0000
41	A	3201.3483	0.0000
42	A	3202.4466	10.2646

43	A	3204.6890	0.2493	46	A	3220.5827	57.2959
44	A	3207.0173	0.0000	47	A	3232.8358	49.9545
45	A	3220.0583	0.0000	48	A	3233.8528	0.0000

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