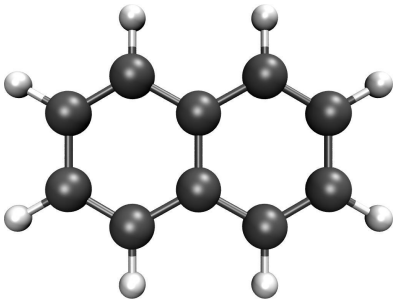
A Report On The Calculation Of The Excited States Of Naphthalene At The MP2/cc-pVDZ Level

osl - 07th June 2022



Abstract

The calculation of excited states 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 MP2/cc-pVDZ level of theory. The total self-consistent field (SCF) energy of the system was found to be -10432.31 eV after 1 step. The total Møller–Plesset (MP) energy of the system was found to be -10467.16 eV after 1 step. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -7.78 and 2.37 eV respectively, corresponding to a HOMO-LUMO band gap of 10.15 eV. The permanent dipole moment (PDM) was calculated to be 0.00 D. In total, 2 excited states were calculated with triplet multiplicity. The lowest energy triplet excited state (S_1) was calculated to be 3.27 eV (379 nm).

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 18:50:12	4 m, 5 s	**True** (N/A)	Turbomole (7.5.0)	MP2/cc-pVDZ	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	-10432.3114 eV
Final energy	-1,006,565 kJ·mol^{-1}

Mp Energy

Table 3: *Summary of MP energy properties.*

No. of steps	1
Final energy	-10467.1582 eV
Final energy	-1,009,927 kJ·mol^{-1}

Geometry

Table 4: *Summary of geometry properties.*

Formula	$C_{10}H_8$
Molar mass	128.1705 g·mol^{-1}
Alignment method	Minimal
X extension	6.80 Å
Y extension	5.02 Å
Z extension	0.00 Å
Linearity ratio	0.26
Planarity ratio	1.00

Molecular Orbitals

Table 5: *Summary of HOMO & LUMO properties.*

$\mathbf{E_{HOMO,LUMO}}$	10.15 eV
$\mathbf{E_{HOMO}}$	-7.78 eV
$\mathbf{E_{LUMO}}$	2.37 eV

Permanent Dipole Moment

Table 6: *Summary of the permanent dipole moment properties.*

Total	< 0.01 D
X axis angle	90.00 °
XY plane angle	75.96 °

Excited States

Table 7: *Summary of the calculated excited states. E_x: The energy of excited state x. λ_x: The wavelength of a photon of equivalent energy to excited state x. f_x: The oscillator strength of the excited state transition x. ΔE_{xy}: The difference in energy between the lowest excited states of multiplicity x and y.*

No. calculated triplets	2
$\mathbf{E_{T_1}}$	3.27 eV
$\mathbf{\lambda_{T_1}}$ **(colour, CIE)**	379 nm (Ultraviolet ■, (0.17, 0.00))
$\mathbf{f_{T_1}}$	0.00
Simulated Absorption Peaks	N/A

Methodology

Metadata

The calculation of the excited states was performed using the **Turbomole (7.5.0)** program, the **HF and MP2** methods and the **cc-pVDZ** basis set. It was completed on the **07th June 2022** after a total duration of **4 m, 5 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] Commission internationale de l'éclairage (CIE) coordinates, along with visual representations of the equivalent colour, were calculated using the Colour Science library.[3] Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using Visual Molecular Dynamics (VMD)[4] and the Tachyon ray-tracer.[5] Finally, two-dimensional graphs were plotted using the MatPlotlib library,[6] while this report itself was prepared using the Mako template library[7] and the Weasyprint library[8], 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 Hartree-Fock (HF) method, with a value of -10432.31 eV, corresponding to -1,006,565 KJmol^{-1}. A plot of the total SCF electron density is shown in figure 1.

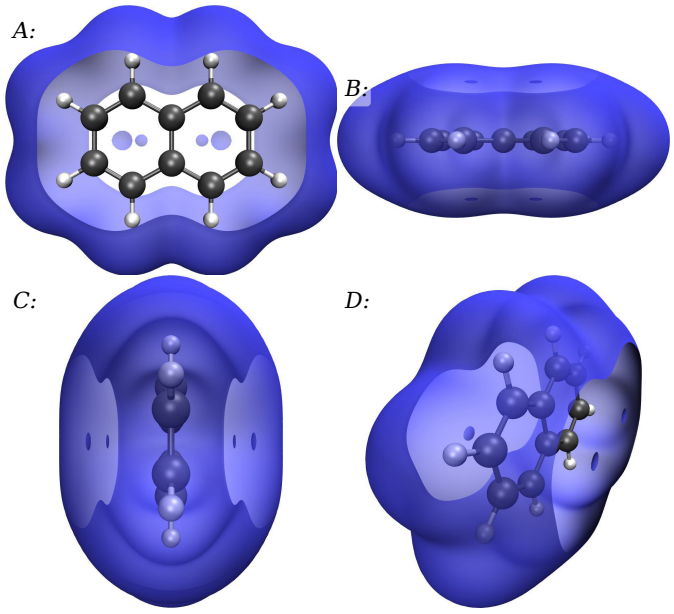


Figure 1: *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Total MP Energy

The total energy of the system was calculated at the **Møller–Plesset (MP)** level with a value of -10467.16 eV, corresponding to -1,009,927 KJmol^{-1}.

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 6.80, 5.02 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 75.96 °. A plot of the permanent dipole moment is shown in figure 2.

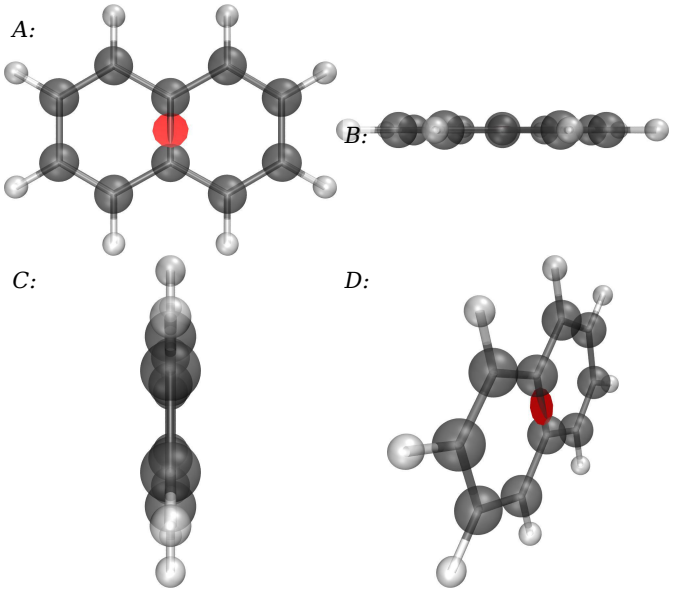


Figure 2: *The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

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 -7.78 and 2.37 eV respectively, corresponding to a **HOMO-LUMO band gap** of 10.15 eV (figure 8). Plots of the orbital density for the HOMO-1, HOMO, LUMO and LUMO+1 are shown in figures 3-5 and 7 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 6.

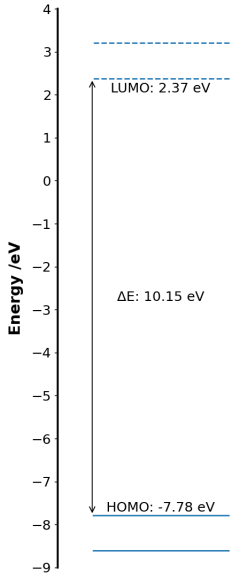


Figure 8: *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*

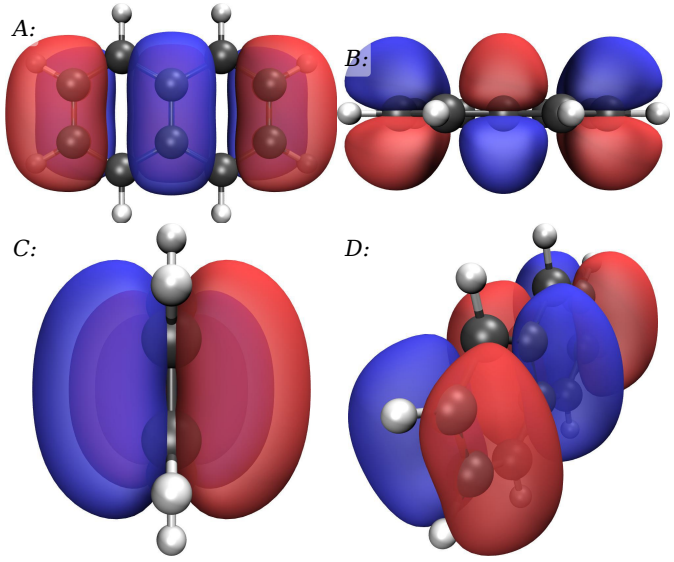


Figure 3: *Orbital density plots of the HOMO-1, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

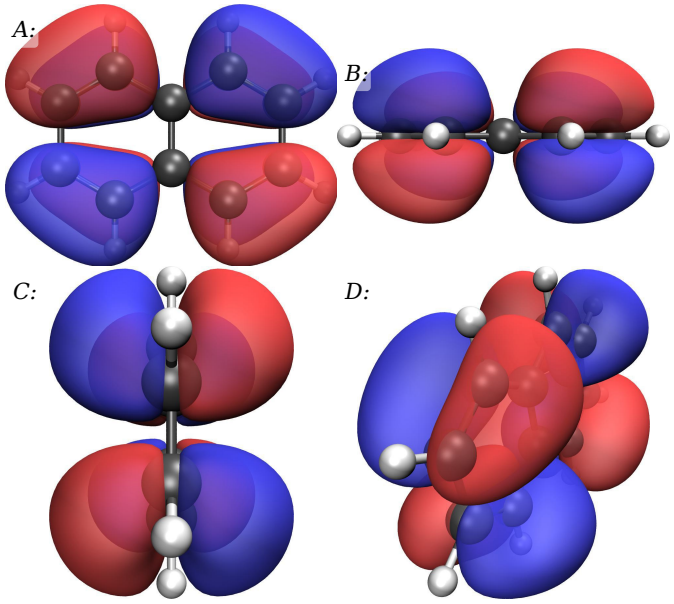


Figure 4: *Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

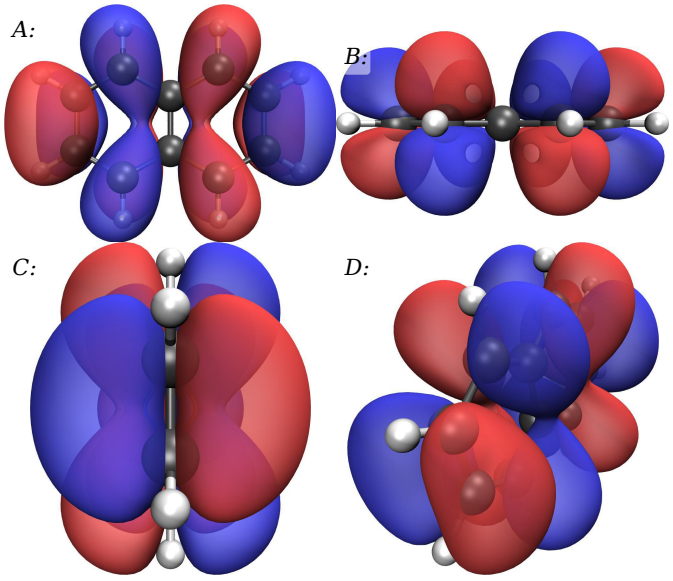


Figure 5: *Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

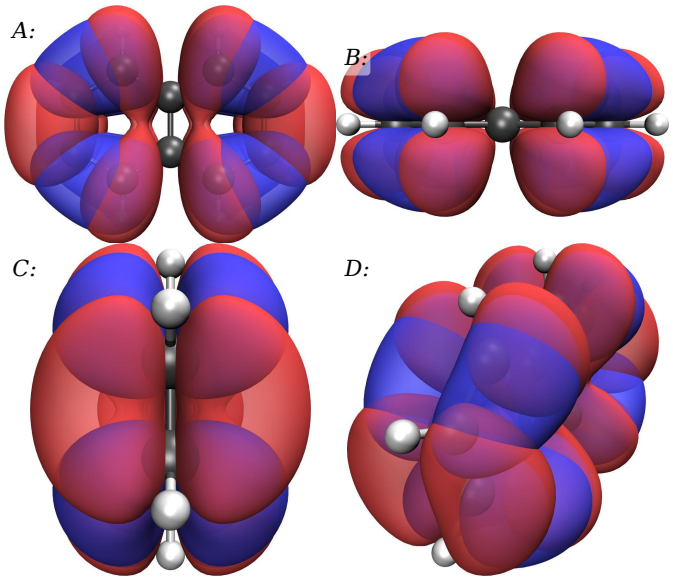


Figure 6: *Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

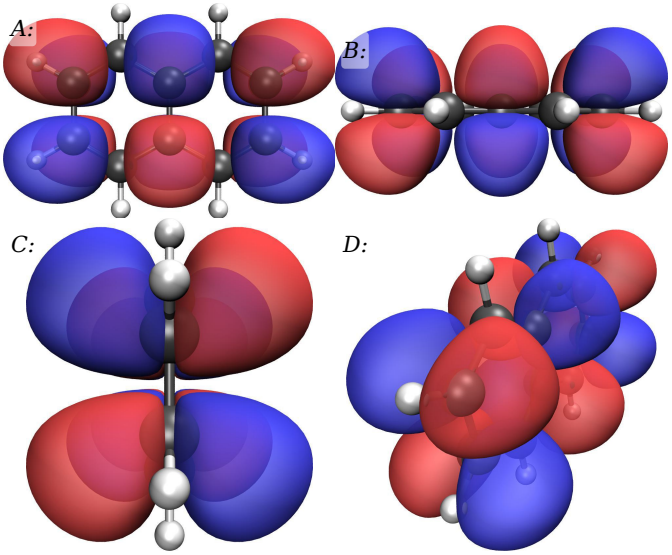


Figure 7: *Orbital density plots of the LUMO+1, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Excited States

In total, the energies of two triplet electronic excited states were calculated, which are shown in figure 9. The energy of the lowest **triplet excited state (T_1)** was 3.27 eV, corresponding to absorption by a photon with a wavelength of 379 nm, an ultraviolet 'color' ■ and CIE coordinates of (0.17, 0.00). A complete table of the calculated excited state properties is available in table 8.

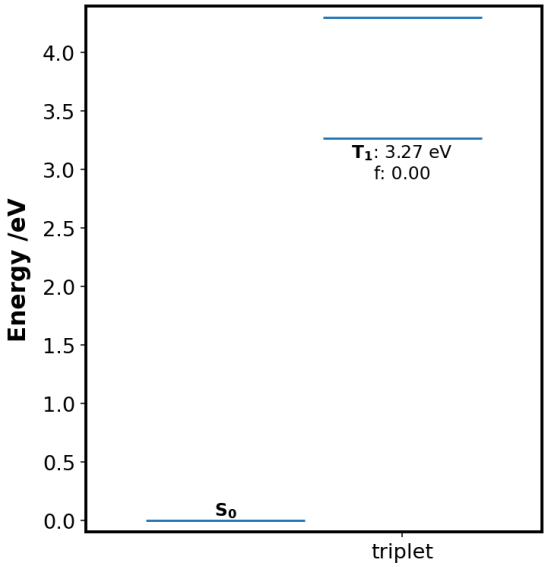


Figure 9: *Graph of the calculated excited states. f: oscillator strength of the relevant ground to excited state transition.*

Tables Of Results

Atom Coordinates

Table 9: *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	-1.2509100	-1.4118100	-0.0000100
C	-2.4487500	-0.7132700	0.0000100
C	-2.4487500	0.7132700	0.0000100
C	-1.2509100	1.4118100	-0.0000100
C	-0.0000000	0.7179300	-0.0000200
C	-0.0000000	-0.7179400	-0.0000200
C	1.2509100	-1.4118100	-0.0000100
C	1.2509100	1.4118100	-0.0000100
C	2.4487500	0.7132700	0.0000100
C	2.4487500	-0.7132700	0.0000100
H	-1.2480900	-2.5080700	-0.0000100
H	-3.4000100	-1.2561900	0.0000200
H	-3.4000100	1.2561900	0.0000300
H	-1.2480900	2.5080700	-0.0000100
H	1.2480900	-2.5080700	-0.0000100
H	1.2480900	2.5080700	-0.0000200
H	3.4000100	1.2561900	0.0000300
H	3.4000100	-1.2561900	0.0000200

Molecular Orbitals

Table 10: *Energies of the calculated molecular orbitals.*

Level	Label	Symmetry	Energy /eV
50	LUMO+15	A	11.9600
49	LUMO+14	A	11.7353
48	LUMO+13	A	10.6261
47	LUMO+12	A	10.4351
46	LUMO+11	A	7.9455
45	LUMO+10	A	7.4055
44	LUMO+9	A	7.3699
43	LUMO+8	A	6.8297
42	LUMO+7	A	6.4869
41	LUMO+6	A	6.3480
40	LUMO+5	A	5.4144
39	LUMO+4	A	5.4053
38	LUMO+3	A	4.9896
37	LUMO+2	A	4.7431
36	LUMO+1	A	3.2023
35	**LUMO**	**A**	**2.3705**
34	**HOMO**	**A**	**-7.7835**
33	HOMO-1	A	-8.6036
32	HOMO-2	A	-10.3698
31	HOMO-3	A	-12.0540
30	HOMO-4	A	-12.9253
29	HOMO-5	A	-13.1917
28	HOMO-6	A	-14.1706
27	HOMO-7	A	-14.3301
26	HOMO-8	A	-15.2492
25	HOMO-9	A	-15.7422
24	HOMO-10	A	-15.7464
23	HOMO-11	A	-16.4964
22	HOMO-12	A	-16.8787
21	HOMO-13	A	-18.2419
20	HOMO-14	A	-18.8268
19	HOMO-15	A	-19.1551

Excited States

Table 8: *Energies and other properties of the calculated excited states.*

Number	Symbol	Symmetry	Energy /eV	Wavelength /nm	Colour (CIE x,y)	Oscillator Strength	Transitions (Probability)
1	T_1	Triplet-A	3.2689	379.29	Ultraviolet (0.17, 0.00)	0.0000	HOMO → LUMO (0.85) HOMO-2 → LUMO+2 (0.06) HOMO-1 → LUMO+1 (0.05)
2	T_2	Triplet-A	4.2983	288.45	Ultraviolet (0.00, 0.00)	0.0000	HOMO-1 → LUMO (0.49) HOMO → LUMO+1 (0.46) HOMO-3 → LUMO+2 (0.02)

References

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