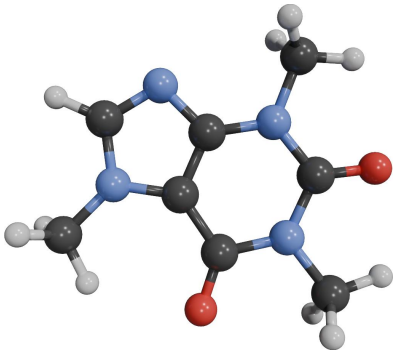
A Report On The Calculation Of The Optimised Structure Of Caffeine At The PBE1PBE/def2SVP Level

osl - 28th May 2025



Abstract

The calculation of optimised structure for the system 'Caffeine' is presented, accompanied by automated analysis and image generation provided by the Digichem software package. The calculation was performed using the Gaussian software package at the PBE1PBE/def2SVP level of theory. The total self-consistent field (SCF) energy of the system was found to be -18481.24 eV after 5 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -6.43 and -0.91 eV respectively, corresponding to a HOMO-LUMO band gap of 5.52 eV. The permanent dipole moment (PDM) was calculated to be 4.99 D.

Table 1: *Summary of overall calculation metadata.*

Date[a] (Duration[b])	CPUs (Memory)	Success (Converged)	Computational package	Level of theory	Solvent (model)	Calculations	Wavefunction	Multiplicity	T[c] / K	p[d] / atm
28/05/2025 07:47:47 (1 m, 10 s)	40 (20 GB)	True (True)	Gaussian (2016+C.01)	PBE1PBE/ def2SVP	Water (IEFPCM)	Optimisation	restricted	1 (singlet)	N/A	N/A

[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.

Summary Of Results

SCF Energy

Table 2: *Summary of SCF energy properties.*

No. of steps	5
Final energy	-18481.2379 eV
Final energy	-1,783,168 kJ·mol^{-1}

Geometry

Table 3: *Summary of geometry properties.*

Formula	$C_8N_4O_2H_{10}$
SMILES	Cn1c(=O)c2c(ncn2C)n(C)c1=O
Exact mass	194.0804 g·mol^{-1}
Molar mass	194.1906 g·mol^{-1}
Alignment method	Minimal
X extension	7.12 Å
Y extension	6.01 Å
Z extension	1.80 Å
Linearity ratio	0.16
Planarity ratio	0.70

Molecular Orbitals

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

$E_{HOMO,LUMO}$	5.52 eV
E_{HOMO}	-6.43 eV
E_{LUMO}	-0.91 eV

Permanent Dipole Moment

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

Total	4.99 D
X axis angle	10.53 °
XY plane angle	0.04 °

Methodology

Metadata

The calculation of the optimised structure was performed using the **Gaussian (2016+C.01)** program, the **DFT** method with the **PBE1PBE** functional and the **def2SVP** basis set. It was completed on the **28th May 2025** after a total duration of **1 m, 10 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 Digichem 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 -18481.24 eV, corresponding to -1,783,168 KJmol^{-1}. A plot of the total SCF electron density is shown in figure 2.

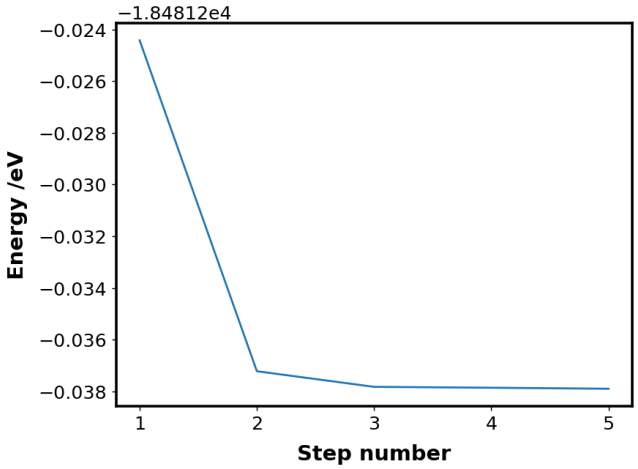


Figure 1: *Graph of calculated energies at the self-consistent field (SCF) level.*

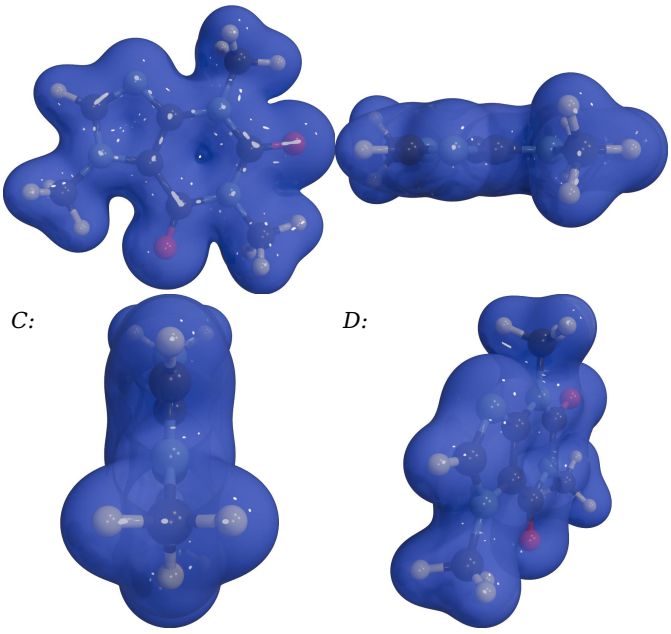


Figure 2: *Plot of the total SCF electron density, plotted with an isovalue of 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Geometry

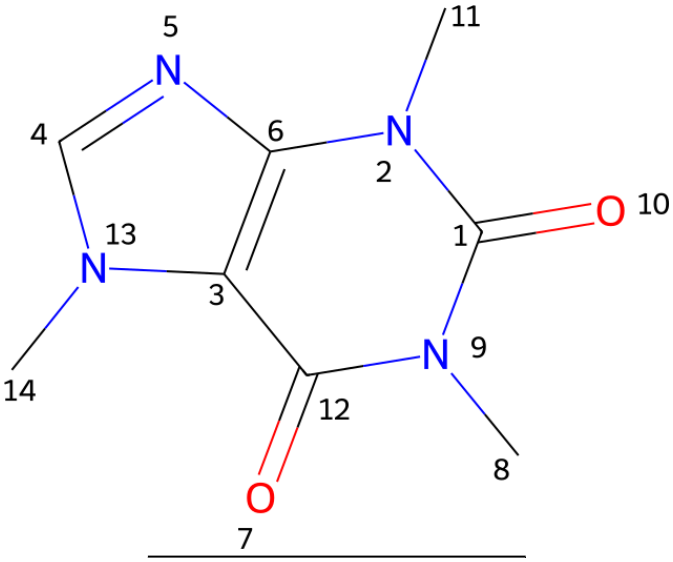


Figure 3: *Labelled structure of Caffeine.*

The **empirical formula** of the studied system was $C_8N_4O_2H_{10}$, corresponding to a **molecular mass** of 194.19 gmol^{-1} and an **exact mass**, considering only specific atomic isotopes, of 194.08 gmol^{-1}. The molecular structure, with atom labelling, is shown in figure 3. The molecular geometry was aligned to the cartesian (X, Y and Z) axes by the **Minimal (MIN)** method, and the resulting atomic position are displayed in figure 4. 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 7.12, 6.01 and 1.80 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 0.16 and 0.70 respectively.

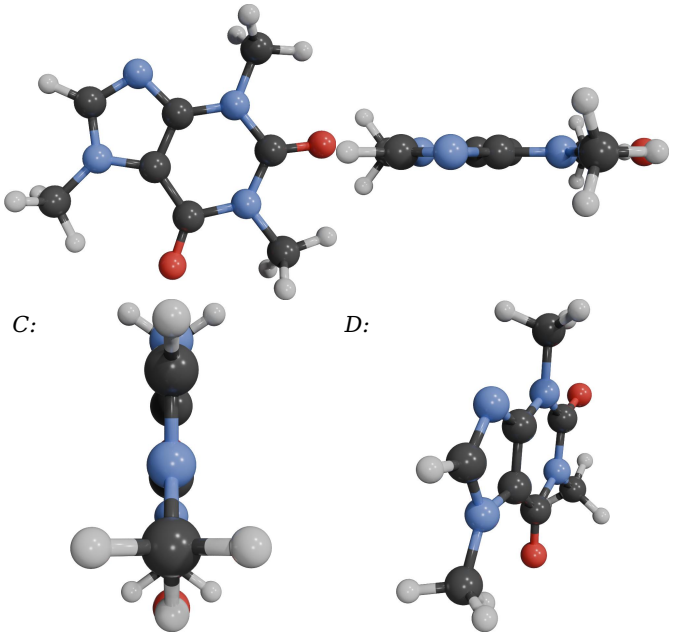


Figure 4: *The molecular structure, aligned using the Minimal (MIN) method. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Permanent Dipole Moment

The calculated **permanent dipole moment** was 4.99 D, with a vector (x,y,z) of -4.91, 0.91, -0.00 D. The angle between the

dipole moment vector and the x-axis was 10.53 °, while the angle between the dipole moment and the xy-plane was 0.04 °. A plot of the permanent dipole moment is shown in figure 5.

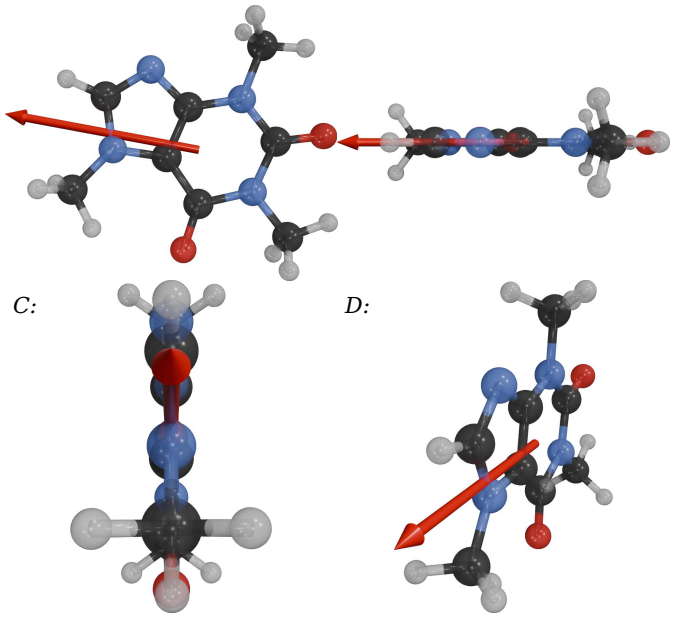


Figure 5: *The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Molecular Orbitals

In total, 246 doubly occupied molecular orbitals were calculated, divided into 51 occupied orbitals and 195 unoccupied (or virtual) orbitals. The calculated energies of the **HOMO and LUMO** were -6.43 and -0.91 eV respectively, corresponding to a **HOMO-LUMO band gap** of 5.52 eV (figure 9). Plots of the orbital density for the HOMO and LUMO are shown in figures 6-7 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 8.

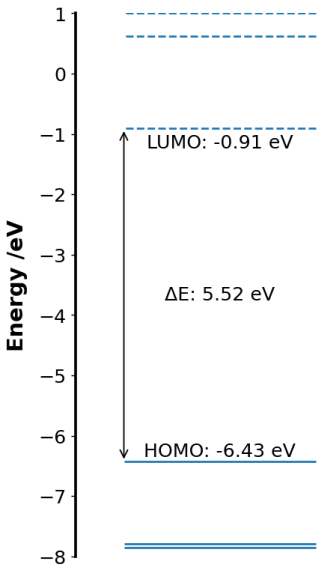


Figure 9: *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*

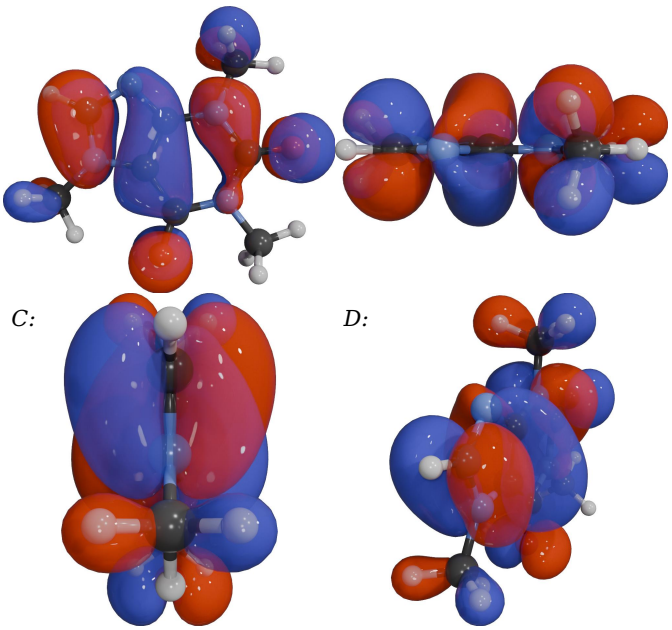


Figure 6: *Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

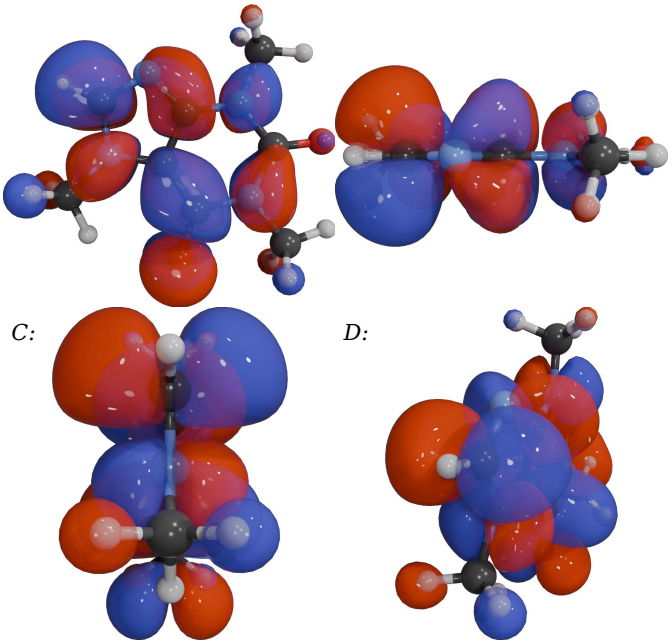


Figure 7: *Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

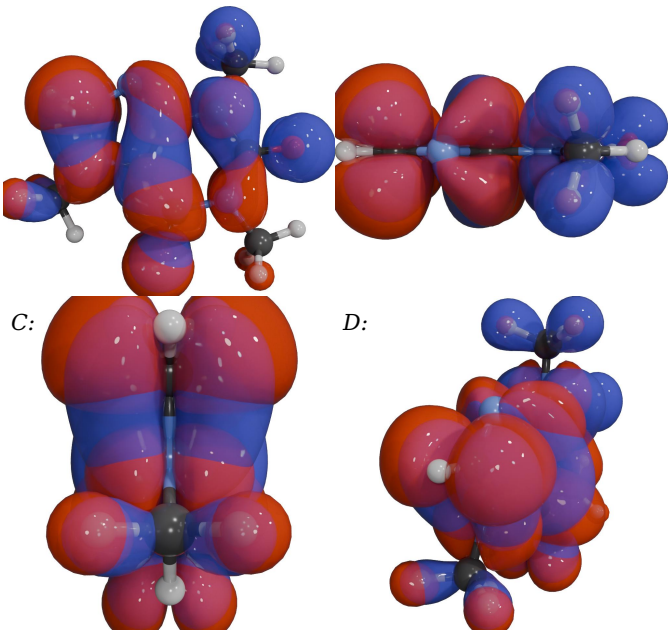


Figure 8: *Orbital density plots of the HOMO (red) and LUMO (blue), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

Tables Of Results

Atom Coordinates

Table 6: *Coordinates of the atoms of the system under study, as aligned to the cartesian axes by the Minimal method. Atoms that are chemically equivalent have been assigned the same group number.s*

Index	Element	Group	X Coord /Å	Y Coord /Å	Z Coord /Å
1	C	C_1	1.8589110	0.1981630	-0.0005060
2	N	N_2	0.9970070	1.2775970	-0.0005180
3	C	C_3	-0.9078570	-0.1949460	-0.0001430
4	C	C_4	-2.4487310	1.3436110	0.0006860
5	N	N_5	-1.3101620	2.0271030	0.0005140
6	C	C_6	-0.3570970	1.0726230	-0.0000840
7	O	O_7	-0.4851820	-2.5384240	0.0009580
8	C	C_8	2.1587690	-2.2217590	-0.0000010
9	N	N_9	1.2687520	-1.0727970	-0.0003220
10	O	O_{10}	3.0687540	0.3403020	-0.0001300
11	C	C_{11}	1.5201620	2.6288150	-0.0000320
12	C	C_{12}	-0.1023220	-1.3775940	0.0001390
13	N	N_{13}	-2.2715420	0.0071350	0.0004330
14	C	C_{14}	-3.2988960	-1.0162660	-0.0009170
15	H	H_4	-3.4444460	1.7874190	0.0011360
16	H	H_8	3.1880490	-1.8543890	-0.0015060
17	H	H_8	1.9779670	-2.8388410	0.8907480
18	H	H_8	1.9759190	-2.8407130	-0.8890110
19	H	H_{11}	2.6122710	2.5663830	-0.0075710
20	H	H_{11}	1.1699970	3.1717790	-0.8891440
21	H	H_{11}	1.1825180	3.1671310	0.8968300
22	H	H_{14}	-3.9330250	-0.9203360	0.8905200
23	H	H_{14}	-3.9214400	-0.9302010	-0.9015670
24	H	H_{14}	-2.8024120	-1.9924070	0.0073450

Molecular Orbitals

Table 7: *Energies of the calculated molecular orbitals.*

Level	Label	Symmetry	Energy /eV
67	LUMO+15	A	4.9487
66	LUMO+14	A	4.3021
65	LUMO+13	A	4.2610
64	LUMO+12	A	4.2180
63	LUMO+11	A	4.1576
62	LUMO+10	A	4.0784
61	LUMO+9	A	3.6967
60	LUMO+8	A	3.5228
59	LUMO+7	A	3.4177
58	LUMO+6	A	3.1508
57	LUMO+5	A	2.7805
56	LUMO+4	A	2.4909
55	LUMO+3	A	2.3266
54	LUMO+2	A	1.0087
53	LUMO+1	A	0.6256
52	**LUMO**	**A**	**-0.9089**
51	**HOMO**	**A**	**-6.4322**
50	HOMO-1	A	-7.7947
49	HOMO-2	A	-7.8562
48	HOMO-3	A	-8.1966
47	HOMO-4	A	-8.5193
46	HOMO-5	A	-8.7329
45	HOMO-6	A	-9.2102
44	HOMO-7	A	-11.0331
43	HOMO-8	A	-11.0424
42	HOMO-9	A	-11.2100
41	HOMO-10	A	-11.2693
40	HOMO-11	A	-11.5735
39	HOMO-12	A	-11.7118
38	HOMO-13	A	-12.1385
37	HOMO-14	A	-12.4827
36	HOMO-15	A	-12.7368

References

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