Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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1 Cartesian coordinates of geometries

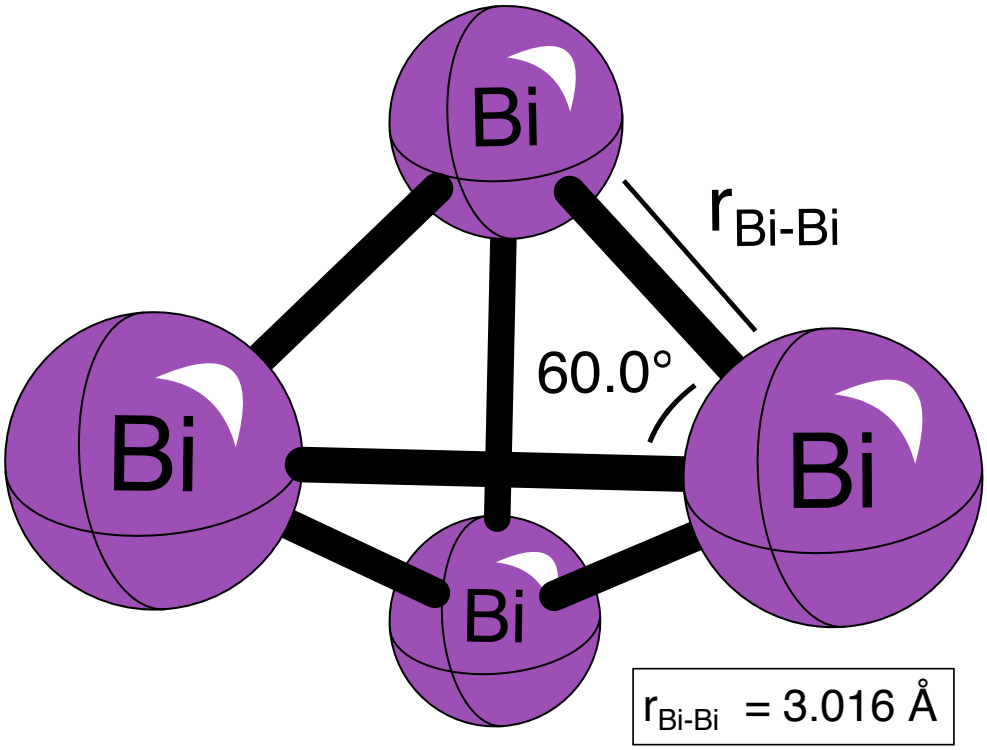

Figure 1: The equilibrium geometry of the T_d isomer of Bi_4 predicted at the CCSD(T)/cc-pVQZ-PP level of theory.

Table 1: Tetrahedral (T_d) Bi_4 cartesian coordinates of the CCSD(T)/cc-pVQZ-PP geometry in Å.

Atom	x	y	z
Bi	0.0000000000	-1.5302363927	1.0820405299
Bi	0.0000000000	1.5302363927	1.0820405299
Bi	1.5302363927	0.0000000000	-1.0820405299
Bi	-1.5302363927	0.0000000000	-1.0820405299

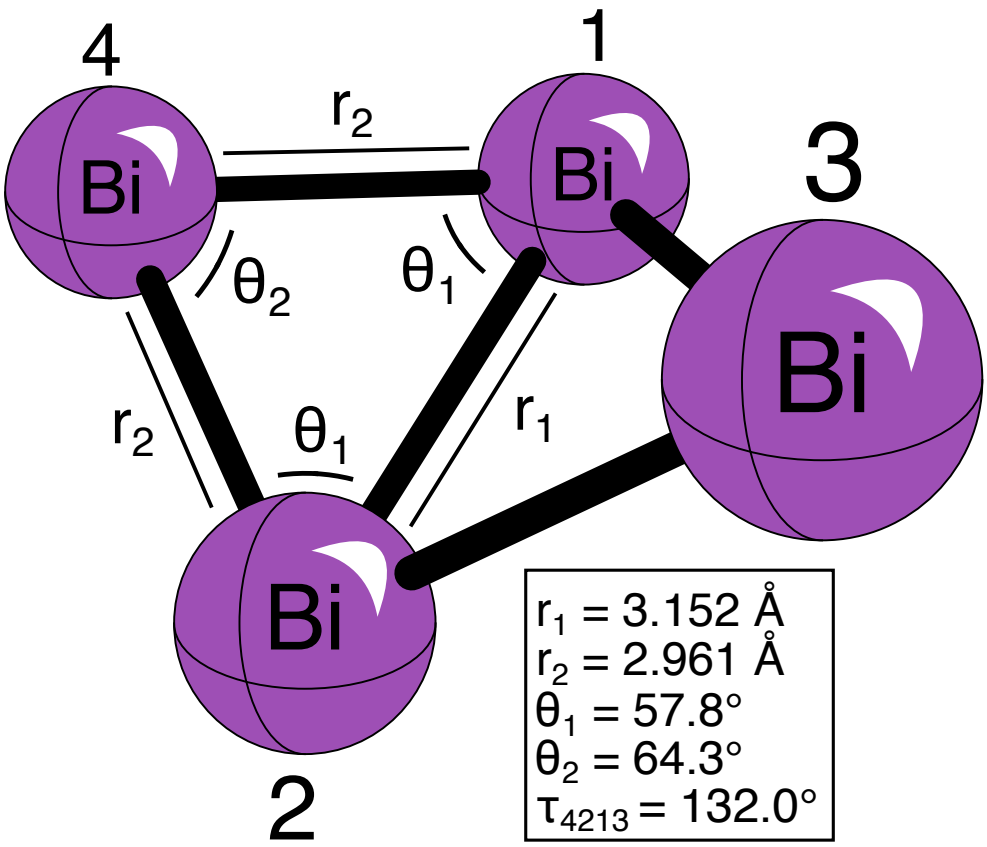

Figure 2: The equilibrium geometry of the C_{2v} isomer of Bi_4 predicted at the CCSD(T)/cc-pVQZ-PP level of theory.

Table 2: Tetrahedral (C_{2v}) Bi_4 cartesian coordinates of the CCSD(T)/cc-pVQZ-PP geometry in Å.

Atom	x	y	z
Bi	0.0000000000	-1.5758532126	-0.5093775319
Bi	0.0000000000	1.5758532126	-0.5093775319
Bi	2.2900687222	0.0000000000	0.5093775319
Bi	-2.2900687222	0.0000000000	0.5093775319

2 Absolute electronic energy focal point tables and corrections

Table 3: Valence focal point analysis of the absolute electronic energy of T_d Bi_4 in Hartrees. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory.

	HF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	+δQ
cc-pVDZ-PP	−854.2976737	−854.6516485	−854.6546264	−854.6834010	−854.6837169	−854.6898406	−854.6885150
cc-pVTZ-PP	−854.3244542	−854.7618166	−854.7618023	−854.8008450	−854.8003193	−854.8077054	[−854.8063798]
cc-pVQZ-PP	−854.3294516	−854.8071780	−854.7993980	−854.8429570	[−854.8424313]	[−854.8498174]	[−854.8484918]
cc-pV5Z-PP	−854.3302002	−854.8252684	−854.8116404	−854.8569174	[−854.8563917]	[−854.8637778]	[−854.8624522]
CBS	[−854.3303321]	[−854.8435949]	[−854.8238313]	[−854.8709109]	[−854.8703852]	[−854.8777713]	[−854.8764457]

$\Delta_{Bi_4\ (T_d),\mathrm{ZPVE,Harmonic}}$[CCSD(T)/cc-pVQZ-PP] = 1.0397 kcal mol^{-1}
$\Delta_{Bi_4\ (T_d),\mathrm{ZPVE,Anharmonic}}$[CCSD(T)/cc-pVQZ-PP] = 1.0377 kcal mol^{-1}
$\Delta_{Bi_4\ (T_d),\mathrm{DBOC}}$[HF/cc-pVTZ-PP] = 0.507344872 kcal mol^{-1}

$\Delta_{\mathrm{Bi_4}\ (T_d),\mathrm{rel}}$[CCSD(T)/cc-pVTZ-PP] = 35.764346293629 kcal mol^{-1}

Table 4: Valence focal point analysis of the absolute electronic energy of C_{2v} Bi_4 in Hartrees. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory.

	HF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	+δQ
cc-pVDZ-PP	−854.3716361	−854.7145861	−854.7207238	−854.7428023	−854.7424185	−854.7455414	−854.7450601
cc-pVTZ-PP	−854.3983828	−854.8286873	−854.8301955	−854.8633170	−854.8622740	−854.8665538	[−854.8660724]
cc-pVQZ-PP	−854.4020911	−854.8746103	−854.8683428	−854.9063030	[−854.9052600]	[−854.9095398]	[−854.9090584]
cc-pV5Z-PP	−854.4026046	−854.8930851	−854.8810427	−854.9208364	[−854.9197934]	[−854.9240732]	[−854.9235918]
CBS	[−854.4026871]	[−854.9120124]	[−854.8939110]	[−854.9356284]	[−854.9345853]	[−854.9388651]	[−854.9383838]

$\Delta_{\mathrm{Bi_4}\ (C_{2v}),\mathrm{ZPVE,Harmonic}}$[CCSD(T)/cc-pVQZ-PP] = 0.8871 kcal mol^{-1}
$\Delta_{\mathrm{Bi_4}\ (C_{2v}),\mathrm{DBOC}}$[HF/cc-pVTZ-PP] = 0.517046279 kcal mol^{-1}
$\Delta_{\mathrm{Bi_4}\ (C_{2v}),\mathrm{rel}}$[CCSD(T)/cc-pVTZ-PP] = 35.762332985260 kcal mol^{-1}

Table 5: Valence focal point analysis of the absolute electronic energy of Bi_2 in Hartrees. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory.

	HF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	+δQ
cc-pVDZ-PP	−427.1375648	−427.3182280	−427.3219849	−427.3342986	−427.3346699	−427.3372520	−427.3368614
cc-pVTZ-PP	−427.1489818	−427.3650444	−427.3679834	−427.3848895	−427.3850675	−427.3881902	[−427.3877996]
cc-pVQZ-PP	−427.1510933	−427.3848200	−427.3841785	−427.4029479	[−427.4031259]	[−427.4062486]	[−427.4058580]
cc-pV5Z-PP	−427.1513961	−427.3929656	−427.3893783	−427.4088121	[−427.4089901]	[−427.4121128]	[−427.4117222]
CBS	[−427.1514468]	[−427.4012448]	[−427.3945668]	[−427.4146977]	[−427.4148757]	[−427.4179984]	[−427.4176078]

$\Delta_{\mathrm{Bi_2,ZPVE,Harmonic}}$[CCSD(T)/cc-pVQZ-PP] = 0.2641kcal mol^{-1}
$\Delta_{\mathrm{Bi_2,ZPVE,Anharmonic}}$[CCSD(T)/cc-pVQZ-PP] = 0.2636kcal mol^{-1}
$\Delta_{\mathrm{Bi_2,DBOC}}$[HF/cc-pVTZ-PP] = 0.147018442 kcal mol^{-1}
$\Delta_{\mathrm{Bi_2,rel}}$[CCSD(T)/cc-pVTZ-PP] = 17.88241774 kcal mol^{-1}

Table 6: Valence focal point analysis of the absolute electronic energy of 2Bi in Hartrees. Delta (δ) denotes the change in relative energy (ΔE_e) with respect to the preceding level of theory.

	HF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	+δQ
cc-pVDZ-PP	−427.1819483	−427.2575190	−427.2774270	−427.2781610	−427.2783520	−427.2784115	−427.2784304
cc-pVTZ-PP	−427.1885840	−427.2884351	−427.3089095	−427.3121565	−427.3129013	−427.3129604	[−427.3129793]
cc-pVQZ-PP	−427.1890378	−427.3002333	−427.3186177	−427.3227303	[−427.3234751]	[−427.3235342]	[−427.3235531]
cc-pV5Z-PP	−427.1891071	−427.3043778	−427.3211040	−427.3255074	[−427.3262522]	[−427.3263113]	[−427.3263302]
CBS	[−427.1891196]	[−427.3086659]	[−427.3236524]	[−427.3283609]	[−427.3291057]	[−427.3291648]	[−427.3291837]

$\Delta_{\mathrm{2Bi,rel}}$[CCSD(T)/cc-pVTZ-PP] = 17.87665078 kcal mol^{-1}

3 NBO analysis

NBO analysis transforms the computed wavefunction orbitals into natural bonding orbitals through the following process: input basis AOs → NAOs → NHOs → NBOs → NLMOs. For further information on these transformations, reference the the NBO 6.0 manual at http://nbo.chem.wisc.edu/nbo6ab_man.pdf.

SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

Threshold for printing: 0.50 kcal/mol
==========

within unit 1

Donor (L) NBO	Acceptor (NL) NBO	E(2) kcal/mol	E(NL)-E(L)a.u.	F(L,NL)a.u.
1. LP (1)Bi 1	16. BD*(1)Bi 3-Bi 4	2.30	0.35	0.026
2. LP (1)Bi 2	16. BD*(1)Bi 3-Bi 4	2.30	0.35	0.026
3. LP (1)Bi 3	13. BD*(1)Bi 1-Bi 4	0.85	0.50	0.018
3. LP (1)Bi 3	15. BD*(1)Bi 2-Bi 4	0.85	0.50	0.018
4. LP (1)Bi 4	12. BD*(1)Bi 1-Bi 3	0.85	0.50	0.018
4. LP (1)Bi 4	14. BD*(1)Bi 2-Bi 3	0.85	0.50	0.018
5. BD (1)Bi 1-Bi 2	12. BD*(1)Bi 1-Bi 3	6.85	0.28	0.039
5. BD (1)Bi 1-Bi 2	13. BD*(1)Bi 1-Bi 4	6.85	0.28	0.039
5. BD (1)Bi 1-Bi 2	14. BD*(1)Bi 2-Bi 3	6.85	0.28	0.039
5. BD (1)Bi 1-Bi 2	15. BD*(1)Bi 2-Bi 4	6.85	0.28	0.039
5. BD (1)Bi 1-Bi 2	16. BD*(1)Bi 3-Bi 4	33.37	0.13	0.058
5. BD (1)Bi 1-Bi 2	21. RY (5)Bi 1	2.89	4.60	0.103
5. BD (1)Bi 1-Bi 2	23. RY (7)Bi 1	2.67	6.22	0.115
5. BD (1)Bi 1-Bi 2	30. RY (5)Bi 2	2.89	4.60	0.103
5. BD (1)Bi 1-Bi 2	32. RY (7)Bi 2	2.71	6.28	0.116
5. BD (1)Bi 1-Bi 2	35. RY (1)Bi 3	1.08	1.44	0.035
5. BD (1)Bi 1-Bi 2	36. RY (2)Bi 3	2.08	1.00	0.041
5. BD (1)Bi 1-Bi 2	38. RY (4)Bi 3	2.92	5.26	0.111
5. BD (1)Bi 1-Bi 2	40. RY (6)Bi 3	1.87	1.32	0.044
5. BD (1)Bi 1-Bi 2	43. RY (9)Bi 3	2.77	3.30	0.085
5. BD (1)Bi 1-Bi 2	44. RY (1)Bi 4	1.08	1.44	0.035
5. BD (1)Bi 1-Bi 2	45. RY (2)Bi 4	2.08	1.00	0.041
5. BD (1)Bi 1-Bi 2	47. RY (4)Bi 4	2.92	5.26	0.111
5. BD (1)Bi 1-Bi 2	49. RY (6)Bi 4	1.87	1.32	0.044
5. BD (1)Bi 1-Bi 2	52. RY (9)Bi 4	2.73	3.10	0.082
6. BD (1)Bi 1-Bi 3	14. BD*(1)Bi 2-Bi 3	0.51	0.30	0.011
6. BD (1)Bi 1-Bi 3	16. BD*(1)Bi 3-Bi 4	1.64	0.15	0.014
6. BD (1)Bi 1-Bi 3	30. RY (5)Bi 2	0.55	4.62	0.045
6. BD (1)Bi 1-Bi 3	32. RY (7)Bi 2	0.52	6.30	0.051
7. BD (1)Bi 1-Bi 4	15. BD*(1)Bi 2-Bi 4	0.51	0.30	0.011
7. BD (1)Bi 1-Bi 4	16. BD*(1)Bi 3-Bi 4	1.64	0.15	0.014
7. BD (1)Bi 1-Bi 4	30. RY (5)Bi 2	0.55	4.62	0.045
7. BD (1)Bi 1-Bi 4	32. RY (7)Bi 2	0.52	6.30	0.051
8. BD (1)Bi 2-Bi 3	12. BD*(1)Bi 1-Bi 3	0.51	0.30	0.011
8. BD (1)Bi 2-Bi 3	16. BD*(1)Bi 3-Bi 4	1.64	0.15	0.014
8. BD (1)Bi 2-Bi 3	21. RY (5)Bi 1	0.55	4.62	0.045
8. BD (1)Bi 2-Bi 3	23. RY (7)Bi 1	0.52	6.23	0.051
9. BD (1)Bi 2-Bi 4	13. BD*(1)Bi 1-Bi 4	0.51	0.30	0.011
9. BD (1)Bi 2-Bi 4	16. BD*(1)Bi 3-Bi 4	1.64	0.15	0.014
9. BD (1)Bi 2-Bi 4	21. RY (5)Bi 1	0.55	4.62	0.045
9. BD (1)Bi 2-Bi 4	23. RY (7)Bi 1	0.52	6.23	0.051
10. BD (1)Bi 3-Bi 4	12. BD*(1)Bi 1-Bi 3	9.59	0.15	0.034
10. BD (1)Bi 3-Bi 4	13. BD*(1)Bi 1-Bi 4	9.59	0.15	0.034
10. BD (1)Bi 3-Bi 4	14. BD*(1)Bi 2-Bi 3	9.59	0.15	0.034
10. BD (1)Bi 3-Bi 4	15. BD*(1)Bi 2-Bi 4	9.59	0.15	0.034
10. BD (1)Bi 3-Bi 4	17. RY (1)Bi 1	0.68	0.65	0.019
10. BD (1)Bi 3-Bi 4	26. RY (1)Bi 2	0.68	0.65	0.019
10. BD (1)Bi 3-Bi 4	35. RY (1)Bi 3	5.31	1.32	0.075
10. BD (1)Bi 3-Bi 4	36. RY (2)Bi 3	3.53	0.88	0.050
10. BD (1)Bi 3-Bi 4	38. RY (4)Bi 3	6.09	5.14	0.158
10. BD (1)Bi 3-Bi 4	40. RY (6)Bi 3	2.21	1.20	0.046
10. BD (1)Bi 3-Bi 4	41. RY (7)Bi 3	1.67	0.75	0.032
10. BD (1)Bi 3-Bi 4	43. RY (9)Bi 3	4.89	3.17	0.111
10. BD (1)Bi 3-Bi 4	44. RY (1)Bi 4	5.31	1.32	0.075
10. BD (1)Bi 3-Bi 4	45. RY (2)Bi 4	3.53	0.88	0.050

10. BD (1)Bi 3-Bi 4 | 47. RY (4)Bi 4 | 6.09 | 5.14 | 0.158
10. BD (1)Bi 3-Bi 4 | 49. RY (6)Bi 4 | 2.21 | 1.20 | 0.046
10. BD (1)Bi 3-Bi 4 | 50. RY (7)Bi 4 | 2.05 | 0.88 | 0.038
10. BD (1)Bi 3-Bi 4 | 51. RY (8)Bi 4 | 1.43 | 0.96 | 0.033
10. BD (1)Bi 3-Bi 4 | 52. RY (9)Bi 4 | 4.63 | 2.97 | 0.105

NATURAL BOND ORBITALS (Summary):

Principal Delocalizations
NBO Occupancy Energy (geminal,vicinal,remote)
==========
Molecular unit 1 (Bi4)
—— Lewis ——————————
NBO | Occupancy | Energy | (geminal,vicinal,remote)
1. LP (1)Bi 1 | 1.98574 | -0.50270 | 16(v)
2. LP (1)Bi 2 | 1.98574 | -0.50270 | 16(v)
3. LP (1)Bi 3 | 1.98574 | -0.49342 | 13(v),15(v)
4. LP (1)Bi 4 | 1.98574 | -0.49342 | 12(v),14(v)
5. BD (1)Bi 1-Bi 2 | 1.60131 | -0.27584 | 16(v),12(g),13(g),14(g)
15(g),38(v),47(v),21(g)
30(g),43(v),52(v),32(g)
23(g),36(v),45(v),40(v)
49(v),35(v),44(v)
6. BD (1)Bi 1-Bi 3 | 1.92844 | -0.29491 | 16(g),30(v),32(v),14(g)
7. BD (1)Bi 1-Bi 4 | 1.92844 | -0.29491 | 16(g),30(v),32(v),15(g)
8. BD (1)Bi 2-Bi 3 | 1.92844 | -0.29491 | 16(g),21(v),23(v),12(g)
9. BD (1)Bi 2-Bi 4 | 1.92844 | -0.29491 | 16(g),21(v),23(v),13(g)
10. BD (1)Bi 3-Bi 4 | 1.80488 | -0.15072 | 12(g),13(g),14(g),15(g)
38(g),47(g),35(g),44(g)
43(g),52(g),36(g),45(g)
40(g),49(g),50(g),41(g)
51(g),17(v),26(v)
—— non-Lewis ——————————-
NBO | Occupancy | Energy
11. BD*(1)Bi 1-Bi 2 | 0.01125 | -0.04348
12. BD*(1)Bi 1-Bi 3 | 0.09138 | 0.00398
13. BD*(1)Bi 1-Bi 4 | 0.09138 | 0.00398
14. BD*(1)Bi 2-Bi 3 | 0.09138 | 0.00398
15. BD*(1)Bi 2-Bi 4 | 0.09138 | 0.00398
16. BD*(1)Bi 3-Bi 4 | 0.53998 | -0.14802
17. RY (1)Bi 1 | 0.00220 | 0.50324
18. RY (2)Bi 1 | 0.00153 | 0.52046
19. RY (3)Bi 1 | 0.00104 | 0.51990
20. RY (4)Bi 1 | 0.00025 | 0.66575
21. RY (5)Bi 1 | 0.00003 | 4.32517
22. RY (6)Bi 1 | 0.00000 | 0.62008
23. RY (7)Bi 1 | 0.00000 | 5.93928
24. RY (8)Bi 1 | 0.00000 | 0.77505
25. RY (9)Bi 1 | 0.00000 | 0.49016
26. RY (1)Bi 2 | 0.00220 | 0.50324
27. RY (2)Bi 2 | 0.00153 | 0.52046
28. RY (3)Bi 2 | 0.00104 | 0.51990
29. RY (4)Bi 2 | 0.00025 | 0.66575
30. RY (5)Bi 2 | 0.00003 | 4.32517
31. RY (6)Bi 2 | 0.00000 | 0.59523
32. RY (7)Bi 2 | 0.00000 | 6.00251

33. RY (8)Bi 2 | 0.00000 | 0.77505
34. RY (9)Bi 2 | 0.00000 | 0.45177
35. RY (1)Bi 3 | 0.00370 | 1.16869
36. RY (2)Bi 3 | 0.00072 | 0.72609
37. RY (3)Bi 3 | 0.00056 | 0.46244
38. RY (4)Bi 3 | 0.00012 | 4.98753
39. RY (5)Bi 3 | 0.00002 | 0.52181
40. RY (6)Bi 3 | 0.00000 | 1.04704
41. RY (7)Bi 3 | 0.00000 | 0.60360
42. RY (8)Bi 3 | 0.00000 | 0.73165
43. RY (9)Bi 3 | 0.00000 | 3.02157
44. RY (1)Bi 4 | 0.00370 | 1.16869
45. RY (2)Bi 4 | 0.00072 | 0.72609
46. RY (3)Bi 4 | 0.00056 | 0.46244
47. RY (4)Bi 4 | 0.00012 | 4.98753
48. RY (5)Bi 4 | 0.00002 | 0.52181
49. RY (6)Bi 4 | 0.00000 | 1.04704
50. RY (7)Bi 4 | 0.00000 | 0.72738
51. RY (8)Bi 4 | 0.00000 | 0.80916
52. RY (9)Bi 4 | 0.00000 | 2.82028

Total Lewis 331.06290 (99.7177%)
Valence non-Lewis 0.91677 (0.2761%)
Rydberg non-Lewis 0.02034 (0.0061%)

Total unit 1 332.00000 (100.0000%)
Charge unit 1 0.00000

3.1 NBO input file

Below is the input file used to run the NBO computations for the C2v structure utilizing Qchem 5.0.

```
$comment
 Bi4 C2V NBO Analysis
$end

$molecule
0 1
BI 0.0000000000 -1.5758532126 -0.5093775319
BI 0.0000000000 1.5758532126 -0.5093775319
BI 2.2900687222 0.0000000000 0.5093775319
BI -2.2900687222 0.0000000000 0.5093775319
$end

$rem
 jobtype sp
 exchange b3lyp
 basis srlc
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 ecp srlc
 NBO 1
 RUN_NBO6 1
 MEM_TOTAL 2000
$end

$nbo
 nrt
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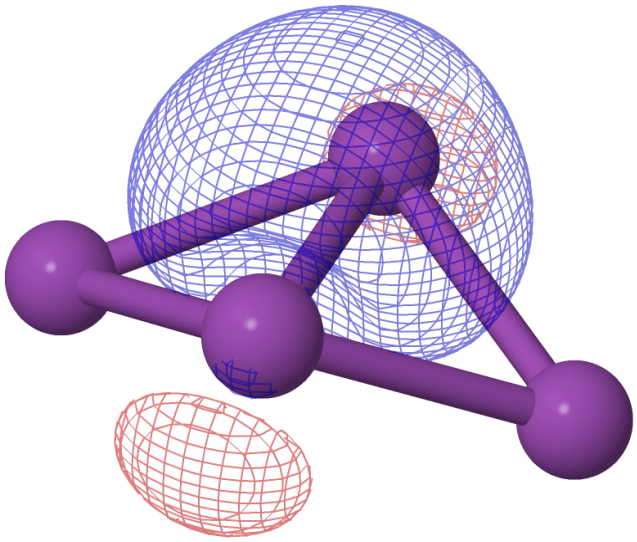
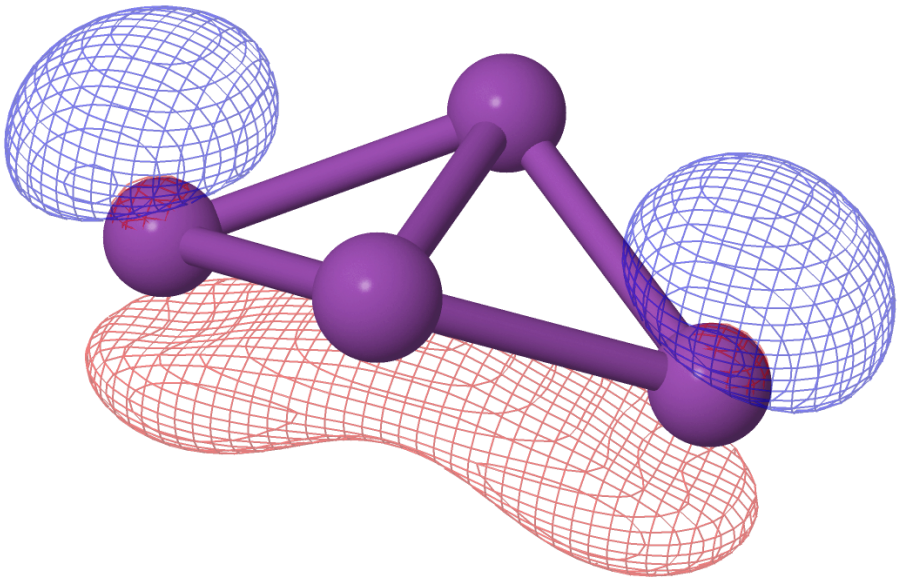
$end



(a) The Lewis NBO of the C_{2v} isomer.



(b) The non-Lewis, long-bonding NBO of the C_{2v} isomer.