Supplementary Material to: Electronic Properties of Zigzag Graphene Nanoribbons Studied by TAO-DFT

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TABLES

TABLE S1. Singlet-triplet energy gap [$E_T - E_S$] (in kcal/mol) of GNR[1,n] as a function of the ribbon length, calculated using spin-unrestricted KS-LDA [1, 2] and TAO-LDA [3]. The experimental data (uncorrected for zero-point vibrations, thermal vibrations, etc.) are taken from Refs. [4–7], the DMRG data are taken from Ref. [8], the CCSD(T)/CBS data are taken from Ref. [9], and the CAM-B3LYP data are taken from Ref. [10].

n	Experiment	DMRG/cc-pVDZ	DMRG/STO-3G	CCSD(T)/CBS	CAM-B3LYP	KS-LDA	TAO-LDA
2	61.0	61.0	61.5	65.83	64.57	65.19	64.77
3	43.1	44.0	45.9	48.21	43.12	43.40	43.22
4	29.3	31.9	34.7	33.49	28.59	29.06	29.01
5	19.8	23.4	26.7	25.27	18.45	19.20	19.60
6		17.5	21.0	17.71	13.38	12.16	13.55
7				13.40		6.98	9.91
8			14.2	9.20	11.07	3.07	7.85
9				7.00		0.99	6.66
10			11.6	4.64	13.38	0.53	5.91
11				3.65		0.86	5.32
12			10.7		17.99	1.59	4.82
13						2.52	4.38
14						3.50	3.98
15						4.34	3.65
16						4.43	3.37
17							3.14
18							2.94
19							2.77
20							2.62
21							2.49
22							2.37
23							2.25
24							2.15
25							2.06
26							1.98
27							1.90
28							1.83
29							1.76
30							1.70
31							1.64
32							1.59
33							1.54
34							1.49
35							1.45
36							1.40
37							1.36
38							1.33
39							1.29
40							1.26
41							1.23
42							1.20
43							1.17
44							1.14
45							1.11
46							1.09
47							1.07
48							1.04
49							1.02

50	1.00
51	0.98
52	0.96
53	0.94
54	0.92
55	0.91
56	0.89
57	0.87
58	0.86
59	0.84
60	0.83
61	0.82
62	0.80
63	0.79
64	0.78
65	0.76
66	0.75
67	0.74
68	0.73
69	0.72
70	0.71
71	0.70
72	0.69
73	0.68
74	0.67
75	0.66
76	0.65
77	0.64
78	0.64
79	0.63
80	0.62
81	0.61
82	0.60
83	0.60
84	0.59
85	0.58
86	0.58
87	0.57
88	0.56
89	0.56
90	0.55
91	0.54
92	0.54
93	0.53
94	0.53
95	0.52
96	0.51
97	0.51
98	0.50
99	0.50
100	0.49

TABLE S2. Singlet-triplet energy gap [$E_{\mathrm{T}} - E_{\mathrm{S}}$] (in kcal/mol) of GNR[2,n] as a function of the ribbon length, calculated using spin-unrestricted KS-LDA [1, 2] and TAO-LDA [3]. For comparison, the DMRG and CAM-B3LYP data are taken from Mizukami *et al.* [10].

n	DMRG/6-31G	CAM-B3LYP	KS-LDA	TAO-LDA

2	39.66	37.36	35.77	35.61
3	17.53	12.22	15.32	16.53
4	5.30	5.07	3.98	9.03
5	2.31	4.38	0.43	6.77
6	2.08	6.46	0.22	5.45
7	2.77	10.61	0.42	4.23
8		16.83	0.69	3.28
9			1.18	2.68
10		31.13	1.70	2.32
11			1.30	2.07
12		36.67		1.86
13				1.68
14				1.53
15				1.41
16				1.31
17				1.22
18				1.14
19				1.08
20				1.01
21				0.96
22				0.91
23				0.87
24				0.83
25				0.79
26				0.76
27				0.73
28				0.70
29				0.68
30				0.65
31				0.63
32				0.61
33				0.59
34				0.57
35				0.55
36				0.54
37				0.52
38				0.51
39				0.49
40				0.48
41				0.47
42				0.46
43				0.45
44				0.43
45				0.42
46				0.41
47				0.41
48				0.40
49				0.39
50				0.38

TABLE S3. Singlet-triplet energy gap [$E_{\mathrm{T}} - E_{\mathrm{S}}$] (in kcal/mol) of GNR[3,n] as a function of the ribbon length, calculated using spin-unrestricted TAO-LDA [3]. For comparison, the CAM-B3LYP data are taken from Mizukami *et al.* [10].

n	CAM-B3LYP	TAO-LDA
2	24.91	24.04
3	3.69	9.98

4	1.84	7.06
5	3.23	5.38
6	8.07	3.80
7		2.82
8	13.38	2.35
9		2.05
10	43.12	1.79
11		1.58
12	60.42	1.42
13		1.29
14		1.19
15		1.09
16		1.01
17		0.95
18		0.89
19		0.84
20		0.79
21		0.75
22		0.71
23		0.68
24		0.65
25		0.62
26		0.60
27		0.57
28		0.55
29		0.53
30		0.51

TABLE S4. Vertical ionization potential (in eV) for the lowest singlet state of GNR[1–3,n] as a function of the ribbon length, calculated using spin-unrestricted TAO-LDA [3]. For GNR[1,n], the experimental data are taken from the compilation in Ref. [11], and the CCSD(T)/CBS data are taken from Ref. [12].

	GNR[1,n]			GNR[2,n]	GNR[3,n]
n	Experiment	CCSD(T)/CBS	TAO-LDA	TAO-LDA	TAO-LDA
2	8.14	8.24	7.81	6.55	5.95
3	7.44	7.47	7.00	5.89	5.46
4	6.97	6.95	6.46	5.58	5.31
5	6.59	6.57	6.07	5.43	5.19
6		6.43	5.79	5.30	5.08
7			5.59	5.19	5.00
8			5.44	5.10	4.94
9			5.33	5.02	4.88
10			5.23	4.96	4.84
11			5.15	4.91	4.80
12			5.08	4.86	4.76
13			5.01	4.82	4.73
14			4.96	4.78	4.70
15			4.91	4.75	4.67
16			4.86	4.72	4.65
17			4.82	4.69	4.63
18			4.78	4.67	4.61
19			4.75	4.64	4.59
20			4.71	4.62	4.57
21			4.68	4.60	4.55

22	4.66	4.58	4.54
23	4.63	4.56	4.52
24	4.61	4.55	4.51
25	4.59	4.53	4.50
26	4.57	4.52	4.49
27	4.55	4.50	4.47
28	4.53	4.49	4.46
29	4.51	4.48	4.45
30	4.50	4.47	4.44
31	4.48	4.45	
32	4.47	4.44	
33	4.45	4.43	
34	4.44	4.42	
35	4.43	4.41	
36	4.42	4.41	
37	4.40	4.40	
38	4.39	4.39	
39	4.38	4.38	
40	4.37	4.37	
41	4.36	4.37	
42	4.35	4.36	
43	4.35	4.35	
44	4.34	4.35	
45	4.33	4.34	
46	4.32	4.34	
47	4.31	4.33	
48	4.31	4.32	
49	4.30	4.32	
50	4.29	4.31	
51	4.29		
52	4.28		
53	4.27		
54	4.27		
55	4.26		
56	4.26		
57	4.25		
58	4.24		
59	4.24		
60	4.23		
61	4.23		
62	4.23		
63	4.22		
64	4.22		
65	4.21		
66	4.21		
67	4.20		
68	4.20		
69	4.20		
70	4.19		
71	4.19		
72	4.18		
73	4.18		

74	4.18
75	4.17
76	4.17
77	4.17
78	4.16
79	4.16
80	4.16
81	4.15
82	4.15
83	4.15
84	4.15
85	4.14
86	4.14
87	4.14
88	4.14
89	4.13
90	4.13
91	4.13
92	4.13
93	4.12
94	4.12
95	4.12
96	4.12
97	4.11
98	4.11
99	4.11
100	4.11

TABLE S5. Vertical electron affinity (in eV) for the lowest singlet state of GNR[1–3,n] as a function of the ribbon length, calculated using spin-unrestricted TAO-LDA [3]. For GNR[1,n], the experimental data are taken from the compilation in Ref. [11], and the CCSD(T)/CBS data are taken from Ref. [13].

	GNR[1,n]			GNR[2,n]	GNR[3,n]
n	Experiment	CCSD(T)/CBS	TAO-LDA	TAO-LDA	TAO-LDA
2	-0.20	-0.48	-0.62	0.74	1.40
3	0.53	0.28	0.28	1.49	1.98
4	1.07	0.82	0.90	1.89	2.21
5	1.39	1.21	1.34	2.10	2.38
6		1.47	1.66	2.27	2.54
7			1.89	2.41	2.65
8			2.06	2.53	2.74
9			2.19	2.62	2.82
10			2.30	2.70	2.89
11			2.39	2.77	2.94
12			2.48	2.83	3.00
13			2.55	2.89	3.04
14			2.61	2.93	3.08
15			2.67	2.98	3.12
16			2.72	3.01	3.15
17			2.77	3.05	3.18
18			2.81	3.08	3.21

19	2.85	3.11	3.24
20	2.89	3.14	3.26
21	2.92	3.16	3.28
22	2.95	3.19	3.30
23	2.98	3.21	3.32
24	3.00	3.23	3.34
25	3.03	3.25	3.36
26	3.05	3.27	3.37
27	3.07	3.29	3.39
28	3.09	3.30	3.40
29	3.11	3.32	3.42
30	3.13	3.33	3.43
31	3.15	3.34	
32	3.16	3.36	
33	3.18	3.37	
34	3.19	3.38	
35	3.21	3.39	
36	3.22	3.40	
37	3.23	3.41	
38	3.25	3.42	
39	3.26	3.43	
40	3.27	3.44	
41	3.28	3.45	
42	3.29	3.46	
43	3.30	3.47	
44	3.31	3.48	
45	3.32	3.48	
46	3.33	3.49	
47	3.33	3.50	
48	3.34	3.50	
49	3.35	3.51	
50	3.36	3.52	
51	3.36		
52	3.37		
53	3.38		
54	3.39		
55	3.39		
56	3.40		
57	3.40		
58	3.41		
59	3.42		
60	3.42		
61	3.43		
62	3.43		
63	3.44		
64	3.44		
65	3.45		
66	3.45		
67	3.46		
68	3.46		
69	3.46		
70	3.47		

71	3.47
72	3.48
73	3.48
74	3.48
75	3.49
76	3.49
77	3.50
78	3.50
79	3.50
80	3.51
81	3.51
82	3.51
83	3.52
84	3.52
85	3.52
86	3.52
87	3.53
88	3.53
89	3.53
90	3.54
91	3.54
92	3.54
93	3.54
94	3.55
95	3.55
96	3.55
97	3.55
98	3.56
99	3.56
100	3.56

TABLE S6. Fundamental gap (in eV) for the lowest singlet state of GNR[1–3,n] as a function of the ribbon length, calculated using spin-unrestricted TAO-LDA [3]. For GNR[1,n], the experimental data are taken from the compilation in Ref. [11], and the CCSD(T)/CBS data are taken from Refs. [12, 13].

	GNR[1,n]			GNR[2,n]	GNR[3,n]
n	Experiment	CCSD(T)/CBS	TAO-LDA	TAO-LDA	TAO-LDA
2	8.34	8.72	8.43	5.82	4.55
3	6.91	7.19	6.73	4.40	3.48
4	5.90	6.13	5.56	3.69	3.11
5	5.20	5.37	4.73	3.32	2.81
6		4.96	4.13	3.04	2.54
7			3.69	2.78	2.34
8			3.38	2.57	2.19
9			3.13	2.40	2.06
10			2.93	2.26	1.95
11			2.76	2.14	1.85
12			2.60	2.03	1.76
13			2.46	1.94	1.69
14			2.34	1.85	1.62
15			2.23	1.77	1.55

16	2.13	1.70	1.50
17	2.05	1.64	1.44
18	1.97	1.58	1.40
19	1.89	1.53	1.35
20	1.83	1.48	1.31
21	1.76	1.44	1.27
22	1.71	1.39	1.24
23	1.65	1.35	1.20
24	1.60	1.32	1.17
25	1.56	1.28	1.14
26	1.52	1.25	1.11
27	1.47	1.22	1.09
28	1.44	1.19	1.06
29	1.40	1.16	1.04
30	1.37	1.13	1.02
31	1.33	1.11	
32	1.30	1.09	
33	1.27	1.06	
34	1.25	1.04	
35	1.22	1.02	
36	1.20	1.00	
37	1.17	0.98	
38	1.15	0.97	
39	1.13	0.95	
40	1.11	0.93	
41	1.09	0.92	
42	1.07	0.90	
43	1.05	0.89	
44	1.03	0.87	
45	1.01	0.86	
46	1.00	0.84	
47	0.98	0.83	
48	0.96	0.82	
49	0.95	0.81	
50	0.94	0.80	
51	0.92		
52	0.91		
53	0.89		
54	0.88		
55	0.87		
56	0.86		
57	0.85		
58	0.84		
59	0.82		
60	0.81		
61	0.80		
62	0.79		
63	0.78		
64	0.77		
65	0.77		
66	0.76		
67	0.75		

68	0.74
69	0.73
70	0.72
71	0.72
72	0.71
73	0.70
74	0.69
75	0.69
76	0.68
77	0.67
78	0.67
79	0.66
80	0.65
81	0.65
82	0.64
83	0.63
84	0.63
85	0.62
86	0.62
87	0.61
88	0.61
89	0.60
90	0.59
91	0.59
92	0.58
93	0.58
94	0.58
95	0.57
96	0.57
97	0.56
98	0.56
99	0.55
100	0.55

TABLE S7. Symmetrized von Neumann entropy for the lowest singlet state of GNR[1–3,n] as a function of the ribbon length, calculated using spin-restricted TAO-LDA [3].

n	GNR[1,n]	GNR[2,n]	GNR[3,n]
2	0.00	0.08	0.29
3	0.03	0.59	1.18
4	0.15	1.21	1.44
5	0.40	1.45	1.68
6	0.75	1.65	2.15
7	1.08	1.98	2.63
8	1.34	2.38	3.00
9	1.52	2.74	3.38
10	1.67	3.07	3.79
11	1.82	3.40	4.21
12	1.98	3.74	4.61
13	2.16	4.08	5.01
14	2.36	4.42	5.41

15	2.55	4.76	5.82
16	2.75	5.09	6.22
17	2.94	5.43	6.62
18	3.13	5.77	7.03
19	3.31	6.11	7.43
20	3.50	6.45	7.84
21	3.69	6.79	8.24
22	3.88	7.12	8.64
23	4.07	7.46	9.05
24	4.26	7.80	9.45
25	4.44	8.14	9.86
26	4.63	8.48	10.26
27	4.82	8.82	10.66
28	5.01	9.15	11.07
29	5.20	9.49	11.47
30	5.39	9.83	11.88
31	5.58	10.17	
32	5.77	10.51	
33	5.95	10.85	
34	6.14	11.19	
35	6.33	11.52	
36	6.52	11.86	
37	6.71	12.20	
38	6.90	12.54	
39	7.09	12.88	
40	7.27	13.22	
41	7.46	13.55	
42	7.65	13.89	
43	7.84	14.23	
44	8.03	14.57	
45	8.22	14.91	
46	8.41	15.25	
47	8.59	15.58	
48	8.78	15.92	
49	8.97	16.26	
50	9.16	16.60	
51	9.35		
52	9.54		
53	9.73		
54	9.92		
55	10.10		
56	10.29		
57	10.48		
58	10.67		
59	10.86		
60	11.05		
61	11.23		
62	11.42		
63	11.61		
64	11.80		
65	11.99		
66	12.18		

67	12.37
68	12.56
69	12.74
70	12.93
71	13.12
72	13.31
73	13.50
74	13.69
75	13.88
76	14.06
77	14.25
78	14.44
79	14.63
80	14.82
81	15.01
82	15.20
83	15.38
84	15.57
85	15.76
86	15.95
87	16.14
88	16.33
89	16.52
90	16.70
91	16.89
92	17.08
93	17.27
94	17.46
95	17.65
96	17.84
97	18.02
98	18.21
99	18.40
100	18.59