Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary Material

Dependence of the Structures and Chemical Ordering of Pd-Pt Nanoalloys on Potential Parameters

Lauro Oliver Paz-Borbón[1], Abhishek Gupta[2] and Roy L. Johnston[1],*

[1]School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

[2]Department of Physics, Indian Institute of Technology, New Delhi, India

Parameters	***w* = 0.0**	***w* = 0.1**	***w* = 0.2**	***w* = 0.3**	***w* = 0.4**	***w* = 0.5**
***A* / eV**	0.2975	0.28521	0.27292	0.26063	0.24834	0.23605
ζ / eV	2.695	2.5973	2.4996	2.4019	2.3042	2.2065
p	10.612	10.6375	10.663	10.6885	10.714	10.7395
q	4.004	3.9778	3.9516	3.9254	3.8992	3.873
r_o/Å	2.7747	2.77208	2.76946	2.76684	2.76422	2.7616
	***w* = 0.6**	***w* = 0.7**	***w* = 0.8**	***w* = 0.9**	***w* = 1.0**	
***A* / eV**	0.22376	0.21147	0.19918	0.18689	0.1746	
ζ / eV	2.1088	2.0111	1.9134	1.8157	1.718	
p	10.765	10.7905	10.816	10.8415	10.867	
q	3.8468	3.8206	3.7944	3.7682	3.742	
r_o/Å	2.75898	2.75636	2.75374	2.75112	2.7485	

Table S1. Weighted Pd-Pt Gupta potential parameters.

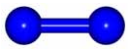
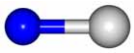
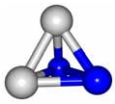
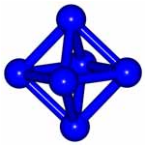
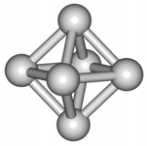
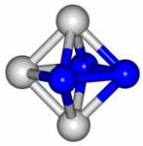
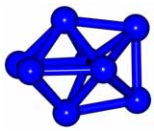
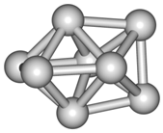
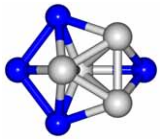
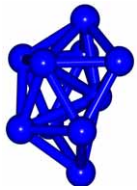
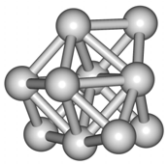
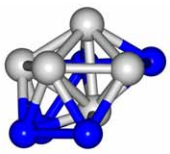
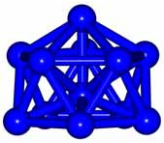
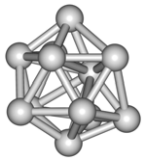
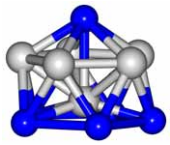
N	Pd	Pt	Pd-Pt
2	 E_{Gupta} = -4.2763 eV E_{DFT} = -255.8652 a.u	 E_{Gupta} = -7.0678 eV E_{DFT} = -238.8202 a.u	 E_{Gupta} = -5.6511 eV E_{DFT} = 247.3416 a.u
4	 E_{Gupta} = -11.1011 eV E_{DFT} = -511.8933 a.u	 E_{Gupta} = -17.5520 eV E_{DFT} = -477.7748 a.u	 E_{Gupta} = -14.6002 eV E_{DFT} = -494.8406 a.u
6	 E_{Gupta} = -17.9847 eV E_{DFT} = -767.9066 a.u	 E_{Gupta} = -28.0541 eV E_{DFT} = -716.7325 a.u	 E_{Gupta} = -23.6266 eV E_{DFT} = -742.3233 a.u
8	 E_{Gupta} = -24.7040 eV E_{DFT} = -1023.9064 a.u	 E_{Gupta} = -38.3200 eV E_{DFT} = -955.7024 a.u	 E_{Gupta} = -32.7172 eV E_{DFT} = -989.8047 a.u
10	 E_{Gupta} = -31.6402 eV E_{DFT} = -1279.9269 a.u	 E_{Gupta} = -48.8217 eV E_{DFT} = -1194.7150 a.u	 E_{Gupta} = -41.8096 eV E_{DFT} = -1237.3135 a.u
12	 E_{Gupta} = -38.5539 eV E_{DFT} = -1535.9486 a.u	 E_{Gupta} = -59.1719 eV E_{DFT} = -1433.6670 a.u	 E_{Gupta} = -50.9032 eV E_{DFT} = -1484.8324 a.u

Figure S1. GM structures found by optimized by DFT for Pd_N, Pt_N and $(Pd\text{-}Pt)_{N/2}$ clusters for N = 2-20 atoms. Parameter set **Ia** was used for the combined GA-Gupta global optimization calculations. Gupta potential and Density Functional Theory (DFT) cluster total energies are denoted by E_{Gupta} and E_{DFT} , respectively.

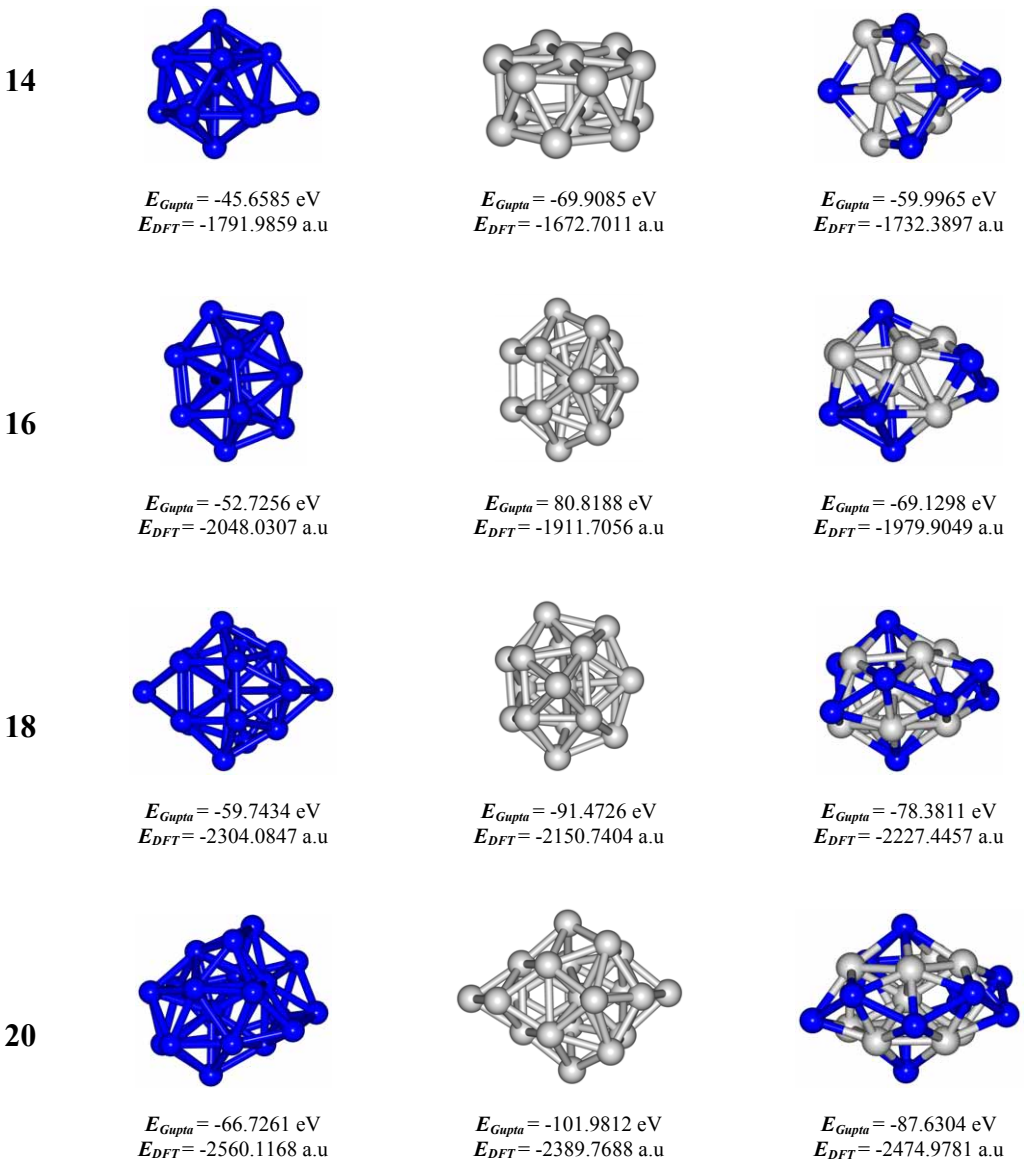


Figure S1. (continued) GM structures found by optimized by DFT for Pd_N, Pt_N and $(Pd\text{-}Pt)_{N/2}$ clusters for N = 2-20 atoms. Parameter set **Ia** was used for the combined GA-Gupta global optimization calculations. Gupta potential and Density Functional Theory (DFT) cluster total energies are denoted by E_{Gupta} and E_{DFT} , respectively.

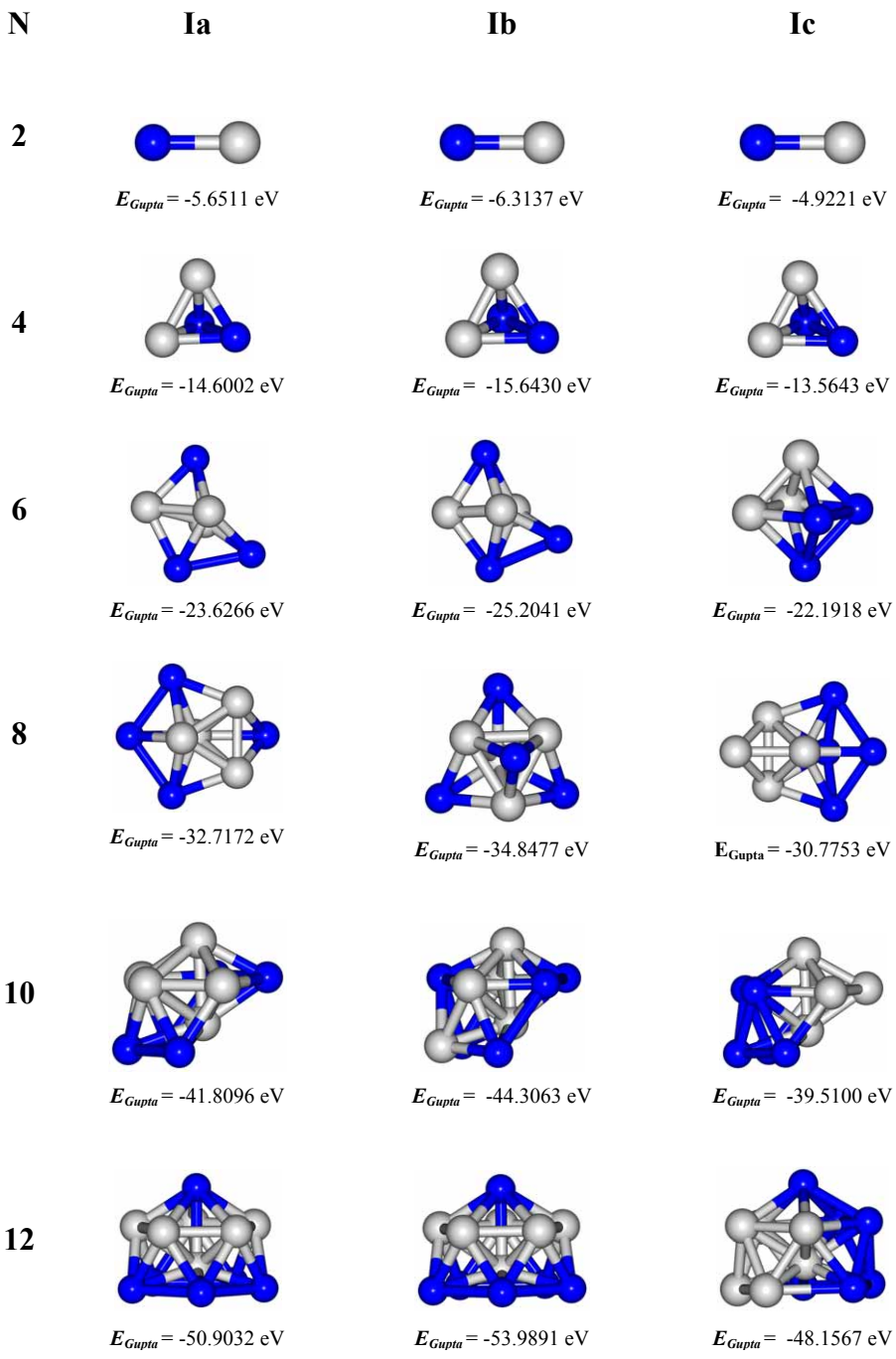


Figure S2. Comparison of structures and chemical ordering in $(Pd\text{-}Pt)_{N/2}$ clusters (for N = 2-20) using Gupta parameter sets **Ia** (w = 0.5), **Ib** (w = 0.25) and **Ic** (w = 0.75). Gupta potential cluster total energies are denoted by E_{Gupta}.

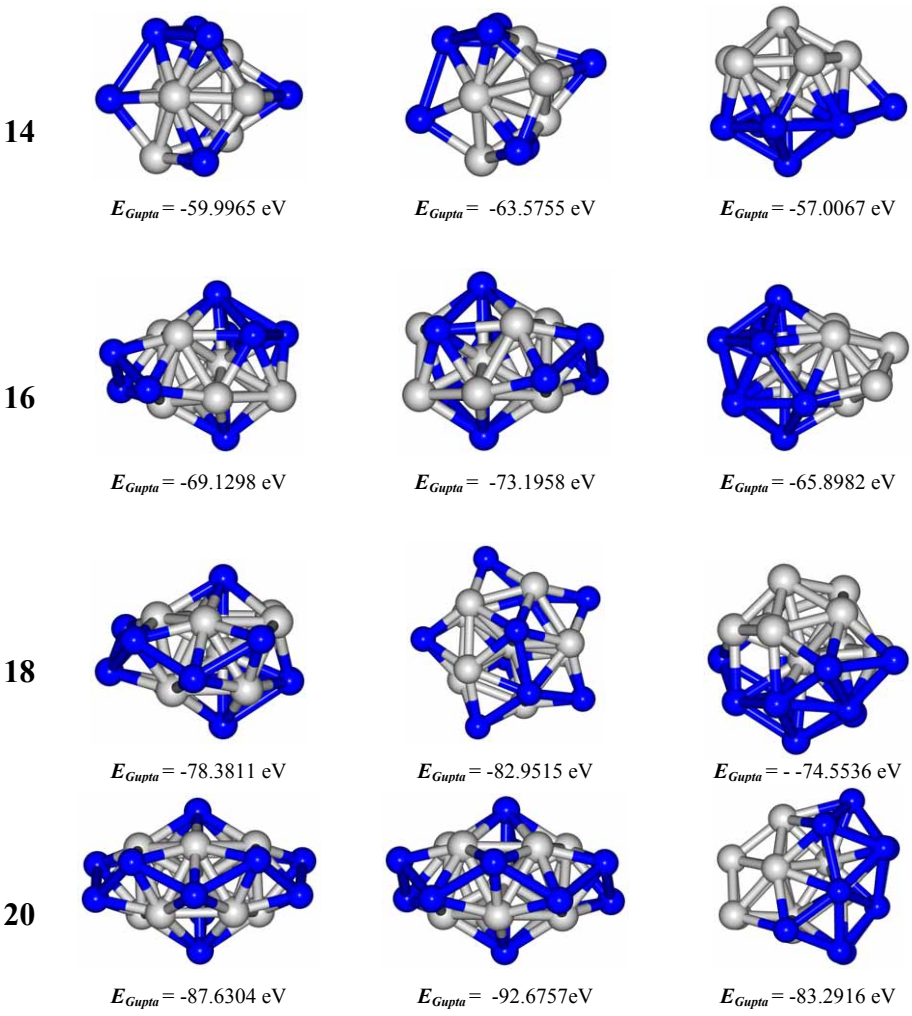


Figure S2. (continued) Comparison of structures and chemical ordering in $(Pd\text{-}Pt)_{N/2}$ clusters (for N = 2-20) using Gupta parameter sets **Ia** (w = 0.5), **Ib** (w = 0.25) and **Ic** (w = 0.75). Gupta potential cluster total energies are denoted by E_{Gupta}.

m	***w* = 0.5 (I=Ia)**	***w* = 0.25 (Ib)**	***w* = 0.75 (Ic)**
0	0	0	0
1	-0.39642	-1.01966	0.26429
2	-0.76776	-2.02695	0.37882
3	-1.15112	-3.03083	0.49056
4	-1.51217	-4.02219	0.61086
5	-1.86421	-5.0096	0.66161
6	-2.20773	-5.99083	0.77913
7	-2.5036	-6.97172	0.89549
8	-2.81745	-7.92706	0.95401
9	-3.28038	-8.79767	1.13155
10	-3.61876	-9.64389	1.13886
11	-3.94095	-10.48695	1.2143
12	-4.23176	-11.17044	1.3538
13	-4.49413	-11.7621	1.38263
14	-4.71513	-12.37177	1.39185
15	-4.88588	-12.77864	1.41484
16	-5.02678	-13.21403	1.37258
17	-5.13846	-13.53048	1.42971
18	-5.25458	-13.99968	1.48437
19	-5.34056	-14.15175	1.52644
20	-5.49545	-14.46693	1.62924
21	-5.66665	-14.89698	1.64461
22	-5.53617	-15.02801	1.68185
23	-5.4908	-14.4925	1.64364
24	-5.5527	-13.93693	1.50325
25	-5.22517	-13.29678	1.55289
26	-4.98501	-12.863	1.4951
27	-4.80734	-12.09242	1.44254
28	-4.58619	-11.34402	1.34171
29	-4.21343	-10.35142	1.07872
30	-3.83459	-9.34424	1.18415
31	-2.94599	-7.56053	1.1324
32	-1.91988	-5.11106	0.94808
33	-0.94286	-2.44698	0.60517
34	0	0	0

Table S2. Excess energy Δ_{34}^{Gupta} values for weighted **Ia**, **Ib** and **Ic** Pd-Pt Gupta potential parameters.

m	*w* = 0	*w* = 0.1	*w* = 0.2	*w* = 0.3	*w* = 0.4	*w* = 0.5
0	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1	-1.79142	-1.47095	-1.16642	-0.87657	-0.60028	-0.33651
2	-3.58284	-2.93717	-2.32308	-1.73807	-1.17985	-0.65607
3	-5.37425	-4.40238	-3.47733	-2.59502	-1.75300	-0.97144
4	-7.16565	-5.86088	-4.62047	-3.43860	-2.32130	-1.28434
5	-8.95609	-7.31733	-5.76038	-4.27747	-2.88414	-1.58136
6	-10.74479	-8.76966	-6.89511	-5.11229	-3.43714	-1.87457
7	-12.52764	-10.22125	-8.02942	-5.94000	-3.96017	-2.21678
8	-14.30708	-11.65340	-9.14032	-6.74330	-4.45701	-2.50066
9	-16.06414	-13.05941	-10.23037	-7.63559	-4.99134	-2.78404
10	-17.60753	-14.29236	-11.36188	-8.19134	-5.48853	-3.05553
11	-19.10822	-15.52921	-12.13633	-8.91368	-5.97764	-3.32681
12	-20.50207	-16.57235	-12.88340	-9.52917	-6.44978	-3.56974
13	-21.67322	-17.52306	-13.58245	-10.03839	-6.78903	-3.79644
14	-22.79106	-18.38291	-14.24218	-10.43920	-7.09939	-4.00066
15	-23.74606	-19.11625	-14.82350	-10.83268	-7.34474	-4.15183
16	-24.54731	-19.86792	-15.37552	-11.17346	-7.52510	-4.27221
17	-25.23610	-20.41653	-15.78646	-11.42202	-7.78994	-4.37586
18	-25.53841	-21.04733	-16.39914	-11.75333	-7.89050	-4.47331
19	-26.03168	-21.18634	-16.49859	-12.04466	-8.00555	-4.56907
20	-26.09738	-21.23602	-16.68455	-12.29376	-8.29140	-4.69758
21	-26.55824	-21.78451	-17.15663	-12.70022	-8.44009	-4.79261
22	-26.57585	-21.84368	-17.26219	-12.83837	-8.58048	-4.78921
23	-25.83920	-21.18414	-16.68397	-12.34688	-8.18274	-4.75719
24	-25.04467	-20.48530	-16.08051	-11.83905	-8.11093	-4.74070
25	-24.11176	-19.67140	-15.38312	-11.25753	-7.65555	-4.54639
26	-22.75698	-18.54469	-14.48636	-11.04478	-7.54132	-4.34291
27	-21.20212	-17.43587	-13.83396	-10.39491	-7.12754	-4.10255
28	-19.96086	-16.33121	-12.96750	-9.76349	-6.72599	-3.78906
29	-18.33189	-15.00139	-11.82823	-8.91413	-6.15234	-3.53801
30	-16.40381	-13.42515	-10.67173	-8.05266	-5.57114	-3.23240
31	-13.68559	-11.14764	-8.71933	-6.48679	-4.41256	-2.43763
32	-9.18050	-7.47271	-5.88056	-4.36109	-2.91420	-1.60890
33	-4.47310	-3.63488	-2.83389	-2.08323	-1.42440	-0.79599
34	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table S3. Excess energy Δ_{34}^{Gupta} values for weighted Pd-Pt Gupta potential parameters in the range $0 \le w \le 1$.

m	*w* = 0.6	*w* = 0.7	*w* = 0.8	*w* = 0.9	*w* = 1
0	0.00000	0.00000	0.00000	0.00000	0.00000
1	-0.08434	0.15398	0.37325	0.58344	0.78515
2	-0.22161	0.18600	0.56660	0.91968	1.24456
3	-0.28128	0.25316	0.71948	1.14317	1.52476
4	-0.36887	0.29817	0.91358	1.45430	1.88362
5	-0.48226	0.29953	1.00902	1.56315	1.99187
6	-0.59855	0.34125	1.14354	1.74824	2.27903
7	-0.71856	0.48990	1.26841	1.94913	2.46203
8	-0.76579	0.46549	1.31547	1.97461	2.55667
9	-0.88615	0.54264	1.55288	2.28341	2.74216
10	-0.96344	0.50796	1.64604	2.32902	2.80515
11	-1.03358	0.64497	1.74857	2.42602	2.86710
12	-1.10589	0.69530	1.85228	2.44645	2.87390
13	-1.21829	0.75185	1.90479	2.59586	3.11954
14	-1.24560	0.69202	1.82439	2.52110	3.12557
15	-1.30612	0.70055	1.89678	2.67120	3.23024
16	-1.38298	0.67897	1.91477	2.74178	3.21560
17	-1.48845	0.66891	1.98327	2.75584	3.27023
18	-1.48984	0.66115	2.05465	2.77958	3.28404
19	-1.55045	0.71312	2.16094	2.85924	3.41633
20	-1.62211	0.75605	2.14123	2.84390	3.34081
21	-1.74369	0.81561	2.14652	2.83701	3.36468
22	-1.81764	0.75379	2.12162	2.77726	3.30457
23	-1.82622	0.73806	2.05820	2.68990	3.21505
24	-1.83312	0.73342	1.94882	2.58491	3.13431
25	-1.76966	0.72260	1.93740	2.57952	3.08968
26	-1.73288	0.67697	1.97049	2.53331	3.02244
27	-1.70248	0.48103	1.82387	2.35329	2.79489
28	-1.55336	0.48669	1.68982	2.27892	2.79689
29	-1.49234	0.39379	1.77025	2.19165	2.56341
30	-1.12938	0.45664	1.61427	2.18298	2.54501
31	-0.78882	0.51992	1.62154	2.06762	2.43501
32	-0.45927	0.50220	1.38160	1.87084	2.23700
33	-0.19782	0.34956	0.85651	1.33698	1.79142
34	0.00000	0.00000	0.00000	0.00000	0.00000

Table S3. (continued) Excess energy Δ_{34}^{Gupta} values for weighted Pd-Pt Gupta potential parameters in the range $0 \le w \le 1$.

x	$\frac{A_{cap}}{\pi R^2} = \gamma(2-\gamma)$	$\frac{A_{core}}{\pi R^2} = x^{2/3}$	$\frac{A_{core}}{A_{cap}} = \frac{4x^{2/3}}{\gamma(2-\gamma)} = \eta$
0	0	0	0
0.007	0.19	0.148	0.779
0.028	0.36	0.368	1.022
0.061	0.51	0.620	1.216
0.104	0.64	0.884	1.381
0.156	0.75	1.160	1.547
0.216	0.84	1.440	1.714
0.282	0.91	1.720	1.89
0.352	0.96	1.996	2.079
0.425	0.99	2.260	2.283
0.500	1.00	2.520	2.52
0.575	0.99	2.764	2.792
0.648	0.96	2.996	3.121
0.718	0.91	3.208	3.525
0.784	0.84	3.400	4.048
0.844	0.75	3.572	4.763
0.896	0.64	3.716	5.806
0.939	0.51	3.836	7.522
0.972	0.36	3.924	10.90
0.993	0.19	3.980	20.947
1	0	4	∞

Table S4. Numerical values for x, A_{cap}, A_{core} and the ratio A_{core}/A_{cap} (see Section 2.5 and the Appendix).