AFFCK: Adaptive Force Field-Assisted *ab initio* Coalescence Kick Method for Global Minimum Search

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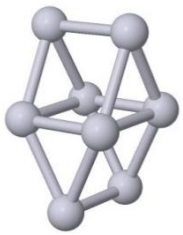
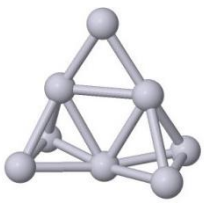
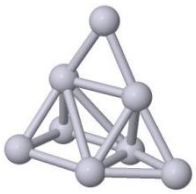
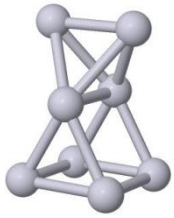
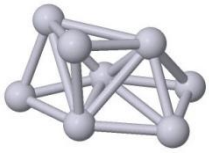
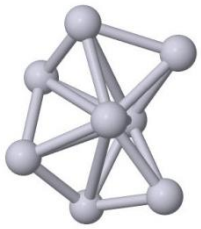
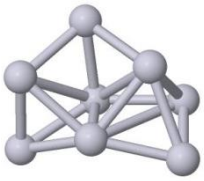
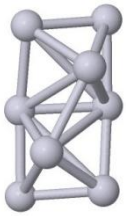
Supporting Information

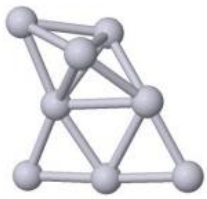
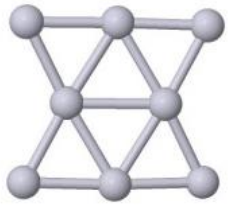
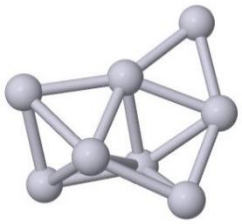
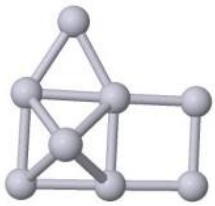
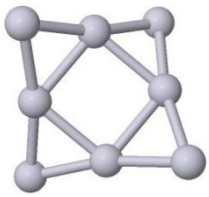
I. Pt_8 Minima with Different Functionals

Notes:

1. *N/A means that the structure was not found by the searching method.*
2. *For Turbomole-PBE/TPSS, a large number of optimizations did not converged. For AFFCK-VASP, we selected 44 of 200 initial structures that were converged in relatively small steps.*
3. *The frequency calculations were done for all listed optimized Turbomole-PBE0/PBE structures. (1i) means one imaginary frequency was found for the structure, otherwise all frequencies were found to be real.*
4. *The energies without units are in Hartree. The eV values are relative to the minimum of each column.*
5. *The energy in parentheses is the energy under the basis/functional of the structure (that was not found by the searching method), if it had been found.*
6. *The #xxxxx is the id of initial structures. The first digit denotes the spin multiplicity. For VASP-PBE the spin multiplicity was not distinguished, so the first digit is zero. Only the id (including spin multiplicity) with the lowest energy was listed for each geometry.*
7. *(mirror) means the found structure is the reflection of the picture.*
8. *(not a min) means the structure is not a minimum structure under the basis/functional. The energy that follows is the energy of the unstable structure. Frequency calculations were not done for unstable structures.*
9. *(quintet) means the structure was only calculated in quintet spin multiplicity.*

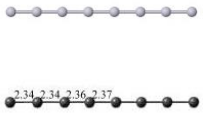
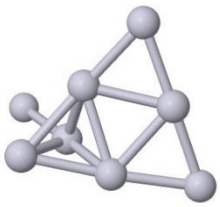
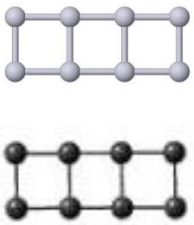
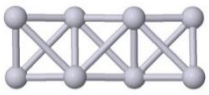
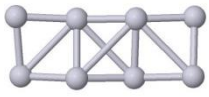
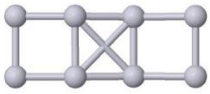
#	Structure	AFFCK Turbomole[1] PBE0[2] def2-TZVP[3]	CK Turbomole PBE0 def2-TZVP	CK Turbomole PBE def2-TZVP	CK Turbomole TPSS[4] def2-TZVP	AFFCK VASP[5] PBE PAW[6]
1 D2d		#58739 -954.8549 0.00 eV	#30260 -954.8527 0.06 eV	N/A (-955.3883) (0.059 eV)	N/A (0.14 eV)	#01691 0.19 eV
2 C2v		#58775 -954.8506 0.12 eV	#50978 -954.8506 0.12 eV	N/A (-955.3901) (0.010 eV)	#50071 0.09 eV	#07537 0.00 eV
3 Cs		#59331 -954.8503 0.13 eV	#50757 -954.8503 0.13 eV	#30371 -955.3904 0.003 eV	#30371 0.00 eV	#00609 0.18 eV

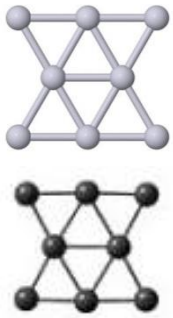
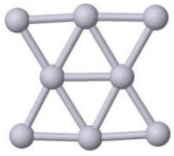
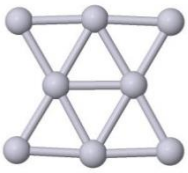
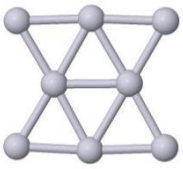
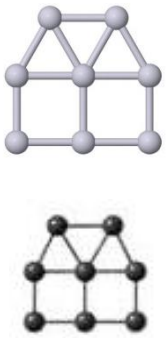
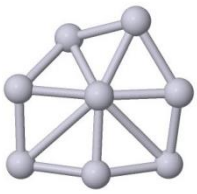
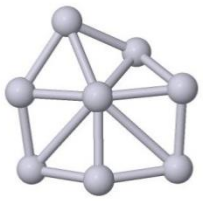
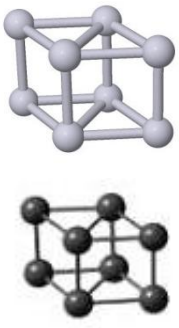
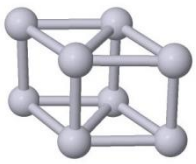
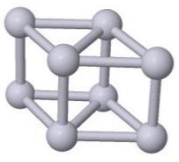
4 Cs		#52024 -954.8486 0.17 eV	#50064 -954.8486 0.17 eV	N/A (-955.3905) (0.000 eV)	N/A (0.01 eV)	#07232 0.05 eV
5 C2v		#59378 -954.8485 0.17 eV	#50601 -954.8485 0.17 eV	N/A (-955.3793) (0.30 eV)	#50219 0.31 eV	N/A
6 C1		#56775 -954.8464 0.23 eV	#50629 (mirror) -954.8465 0.23 eV	N/A (-955.3786) (0.32 eV)	#50003 (mirror) 0.28 eV	N/A
7 Cs		#50081 -954.8452 0.26 eV	#50610 -954.8430 0.32 eV	N/A (not a min) (quintet) (-955.3754) (0.41 eV)	N/A	N/A
8 C2		#51571 -954.8432 0.32 eV	#50997 -954.8432 0.32 eV	#50003 -955.3761 0.39 eV	#30003 (mirror) 0.45 eV	N/A
9 C1		#37285 -954.8431 0.32 eV	#30142 -954.8431 0.32 eV	N/A (-955.3753) (0.41 eV)	#50328 0.47 eV	#02492 (mirror) 0.49 eV
10 C2		#59798 -954.8425 0.34 eV	#30832 -954.8398 0.41 eV	N/A (-955.3735) (0.46 eV)	N/A	#02788 0.60 eV

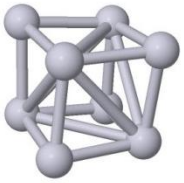
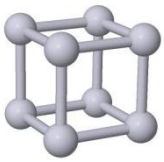
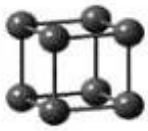
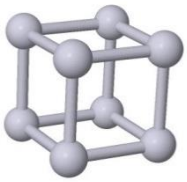
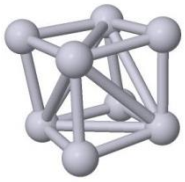
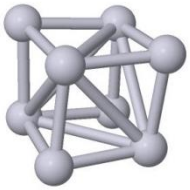
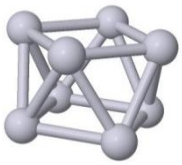
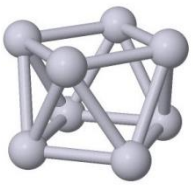
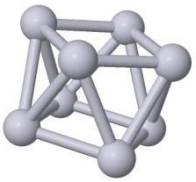
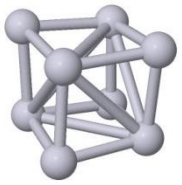
11 C1		#52399 -954.8270 0.76 eV	#50454 -954.8270 0.76 eV	#50161 -955.3779 0.34 eV	#50306 0.47 eV	#00441 0.28 eV
12 D2d		N/A (quintet) (-954.8120) (1.17 eV)	#50212 -954.8121 1.16 eV	#50923 (1i) -955.3745 0.43 eV	#50055 0.70 eV	#06904 0.19 eV
13 C1		#50972 -954.8339 0.57 eV	#50841 -954.8339 0.57 eV	#10142 -955.3714 0.52 eV	#30060 (mirror) 0.46 eV	N/A
14 C1		#50607 (mirror) -954.8211 0.92 eV	#50993 -954.8223 0.89 eV	#50783 -955.3713 0.52 eV	N/A	N/A
15 D2d		N/A (not a min) (quintet) (-835.4134) (3250 eV)	N/A (not a min) (quintet) (-835.4134) (3250 eV)	N/A (not a min) (quintet) (-835.9257) (3251 eV)	N/A	#00972 0.29 eV

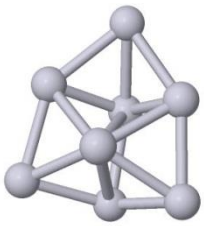
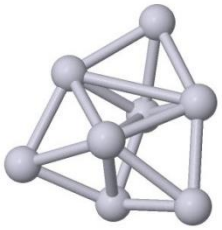
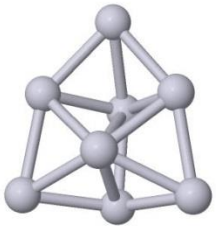
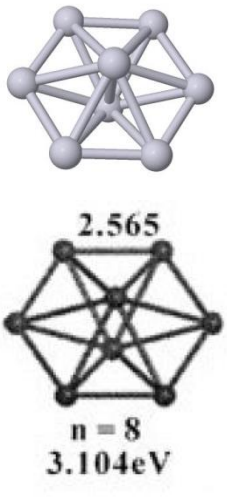
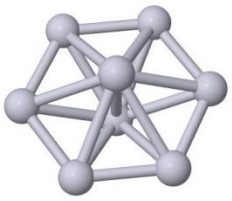
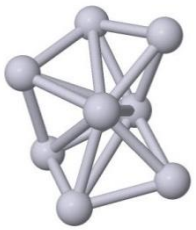
II. Pt_8 Structures Found in Previous Literatures

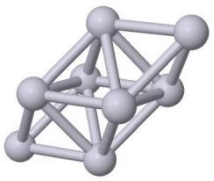
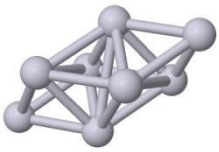
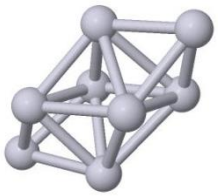
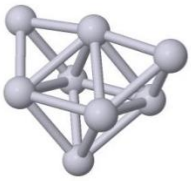
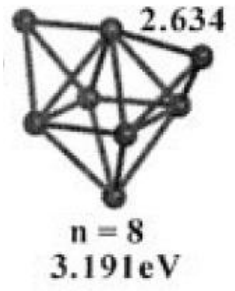
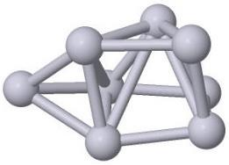
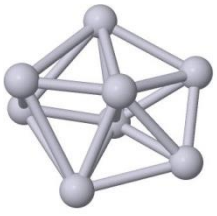
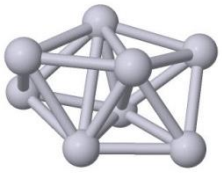
** The frequency calculation was not done for original structures. The energies without unit were in Hartree. The eV values are relative to 'AFFCK Reference'.*

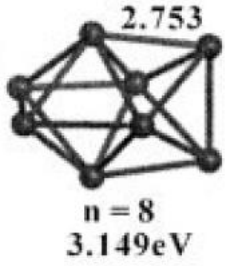
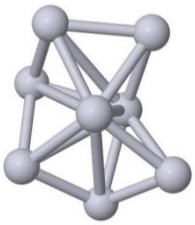
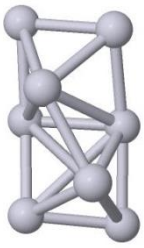
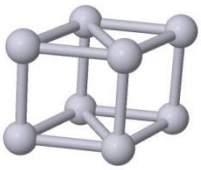
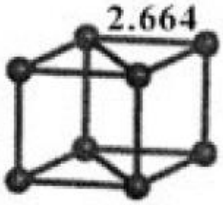
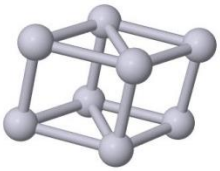
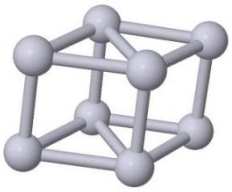
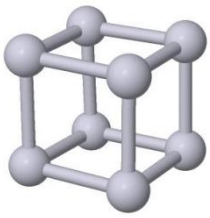
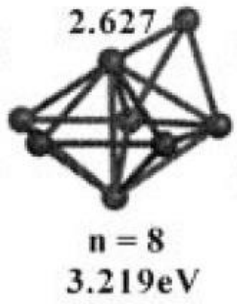
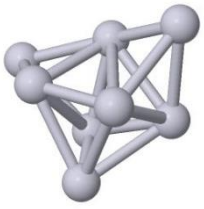
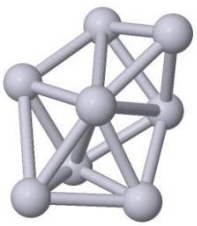
#	Original structure	Spin	Turbomole PBE0/def2-TZVP energy	Optimized structure	Optimized Turbomole PBE0/def2-TZVP energy
AFFCK Reference (AFFCK #58739) Quintet					-954.8548759911 0.00 **eV**
PART I: Structures from Xiao, L.; Wang, L. *J. Phys. Chem. A* **2004**, *108*, 8605-8614.					
L8		1	-954.4326719140 11.49 eV		-954.7245851684 3.55 eV
		3	-954.4864118316 10.03 eV		-954.5390904412 8.59 eV (8 imaginary freqs)
		5	-954.4986126653 9.69 eV		-954.7820281581 1.98 eV
P8-1		1	-954.7557125707 2.70 eV		-954.7833704692 1.95 eV
		3	-954.6923335106 4.42 eV		-954.7760728030 2.14 eV
		5	-954.6774769918 4.83 eV		-954.7740192163 2.20 eV (1 imaginary freq)

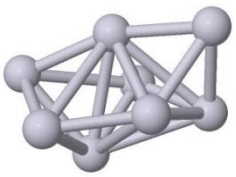
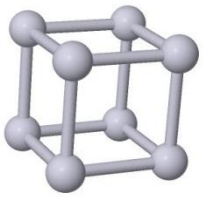
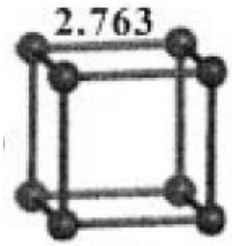
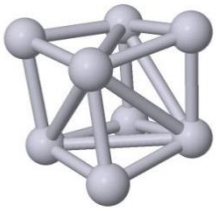
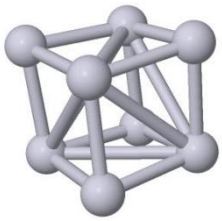
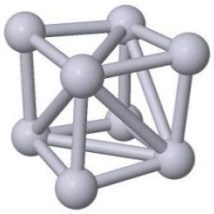
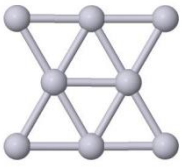
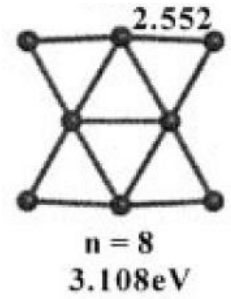
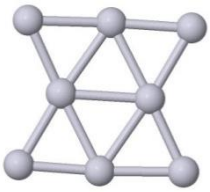
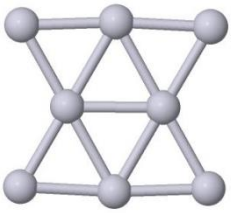
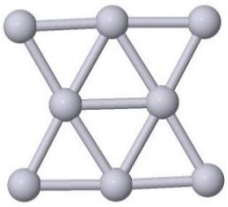
P8-2		1	-954.7718247505 2.26 eV		-954.7776279516 2.10 eV (2 imaginary freqs)
		3	-954.7694399533 2.32 eV		-954.7762554754 2.14 eV (2 imaginary freqs)
		5	-954.7679362820 2.37 eV		-954.7790363363 2.06 eV (2 imaginary freqs)
P8-3		1	-954.7203026735 3.66 eV		-954.8220248055 0.89 eV
		3	-954.7654761480 2.43 eV		-954.8095093328 1.23 eV (3 imaginary freqs)
		5	-954.7703351728 2.30 eV		-954.8283378093 0.72 eV
T8-1		1	-954.7582161157 2.63 eV		-954.8334469047 0.58 eV
		3	-954.8231162834 0.86 eV		-954.8309848664 0.65 eV

		5	-954.7903565356 1.76 eV		-954.8455060638 0.25 eV
T8-2	 	1	-954.7140576586 3.83 eV		-954.8318831692 0.63 eV (1 imaginary freq)
		3	-954.7264798743 3.49 eV		-954.8353974954 0.53 eV
		5	-954.8430984781 0.32 eV		-954.8455171469 0.25 eV
T8-3	 	1	-954.7507336552 2.83 eV		-954.8143754392 1.10 eV (1 imaginary freq)
		3	-954.7765973078 2.13 eV		-954.8150724887 1.08 eV (2 imaginary freqs)
		5	-954.7879618277 1.82 eV		-954.8455416515 0.25 eV

PART II: Structures from Nie, A.; Wu, J.; Zhou, C.; Yao,S.; Luo, C.; Forrey, R. C.; Cheng, H. *Int. J. Qunt. Chem.* **2007**, *107*, 219-224.					
1		1	-954.7276812800 3.46 eV		-954.8438482838 0.30 eV
		3	-954.7611228689 2.55 eV		-954.8417539134 0.36 eV
		5	-954.7720354250 2.25 eV		-954.8502664817 0.13 eV
2		1	-954.7163393957 3.77 eV		-954.7277002112 3.46 eV (3 imaginary freqs)
		3	-954.7550101358 2.72 eV		-954.8415556038 0.36 eV
		5	-954.7723744850 2.24 eV		-954.7825557634 1.97 eV (6 imaginary freqs)

3	 	1	-954.7954581347 1.62 eV		-954.8226175940 0.88 eV
		3	-954.7925950877 1.69 eV		-954.8130606172 1.14 eV
		5	-954.7770853239 2.12 eV		-954.8200290060 0.95 eV
4	 	1	-954.7448289464 2.99 eV		-954.8402434247 0.40 eV
		3	-954.7879193252 1.82 eV		-954.8457692470 0.25 eV
		5	-954.7966375620 1.58 eV		-954.8335455193 0.58 eV
5		1	-954.6933037637 4.40 eV		-954.8158396566 1.06 eV

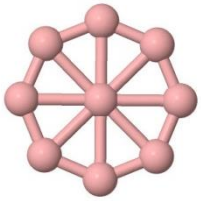
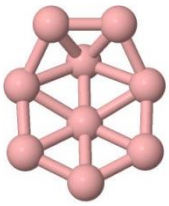
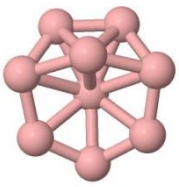
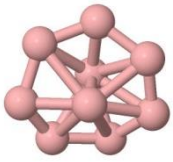
		3	-954.7392762623 3.15 eV		-954.8410945798 0.38 eV
		5	-954.7205513943 3.66 eV		-954.8356704132 0.52 eV
6	 	1	-954.7522116375 2.79 eV		-954.8334421459 0.58 eV
		3	-954.8134713263 1.13 eV		-954.8338329645 0.57 eV
		5	-954.8042684392 1.38 eV		-954.8366412238 0.50 eV
7	 	1	-954.5830744559 7.40 eV		-954.8276208895 0.74 eV
		3	-954.6147490962 6.53 eV		-954.8279522069 0.73 eV (1 imaginary freq)

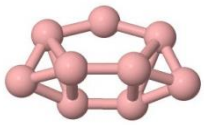
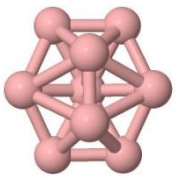
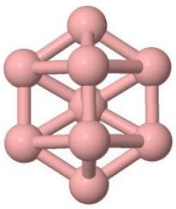
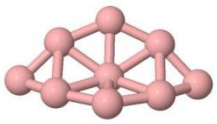
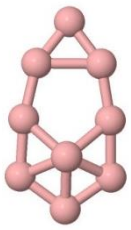
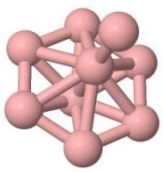
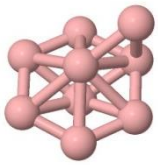
		5	-954.6185864004 6.43 eV		-954.8259423144 0.79 eV
8	 	1	-954.6530457433 5.49 eV		-954.8392485390 0.43 eV
		3	-954.6664674282 5.13 eV		-954.8353233547 0.53 eV
		5	-954.7528641392 2.78 eV		-954.8455399223 0.25 eV
9	 	1	-954.7192653826 3.69 eV		-954.8082015594 1.27 eV (1 imaginary freq)
		3	-954.7680172197 2.36 eV		-954.7727366929 2.24 eV
		5	-954.7699223292 2.31 eV		-954.7774126792 2.11 eV (1 imaginary freq)

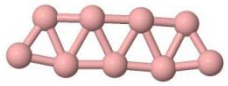
III. B_9^- Minima

Notes:

1. *The first four lowest structures confirm earlier reports (though the basis/functional used is different)* Zhai, H.-J.; Alexandrova, A. N.; Wang, L.-S.; Boldyrev, A. I. *Angew. Chem. Int. Ed.* **2003**, *42*, 6004-6008.
2. *The frequencies of all listed structures are calculated in both pbe and pbe0 functionals. The calculated frequencies are all real.*
3. *The percentage in parentheses is the proportion of each structure in all converged structures. 807 out of 1000 (CK) and 437 out of 500 (AFFCK) initial structures were converged, respectively.*
4. *The eV values are relative to the minimum of each column.*
5. *The minima searching was done using PBE functional. The found 12 minima were then re-optimized using PBE0 functional and the last column shows these results.*

#	Structure	CK Turbomole def2-TZVP PBE	AFFCK Turbomole def2-TZVP PBE	Turbomole def2-TZVP PBE0
1		#00041 0.0000 eV (15.2%)	#04061 0.0000 eV (11.4%)	-223.2357814349 E_h 0.0000 eV
2		#00296 0.0093 eV (9.4%)	#01991 0.0093 eV (5.7%)	-223.2246638661 E_h 0.3025 eV
3		#00852 0.0098 eV (5.5%)	#01844 0.0098 eV (3.2%)	-223.2283651226 E_h 0.2018 eV
4		#00677 0.0106 eV (8.1%)	#00379 (m) 0.0106 eV (6.8%)	-223.2304322258 E_h 0.1456 eV

5		#00444 0.0365 eV (11.9%)	#00449 0.0365 eV (8.0%)	-223.1974191608 E_h 1.0439 eV
6		#00664 0.0415 eV (1.7%)	#00041 0.0416 eV (1.6%)	-223.1944164686 E_h 1.1256 eV
7		#00701 0.0419 eV (1.9%)	#01906 0.0419 eV (3.5%)	-223.1954291358 E_h 1.098 eV
8		#00011 0.0569 eV (0.9%)	#00321 0.0569 eV (1.8%)	-223.1729033486 E_h 1.711 eV
9		#00394 0.0571 eV (5.1%)	#02090 0.0571 eV (5.0%)	-223.1770728206 E_h 1.5975 eV
10		#00764 0.0571 eV (0.9%)	#04445 0.0574 eV (0.2%)	-223.1869692006 E_h 1.3282 eV
11		#00267 0.0575 eV (5.6%)	#02203 0.0575 eV (2.5%)	(optimized to #10) -223.1869636515 E_h 1.3284 eV

12		#00413 0.0579 eV (4.8%)	#04418 0.0579 eV (9.6%)	-223.1686537877 E_h 1.8266 eV

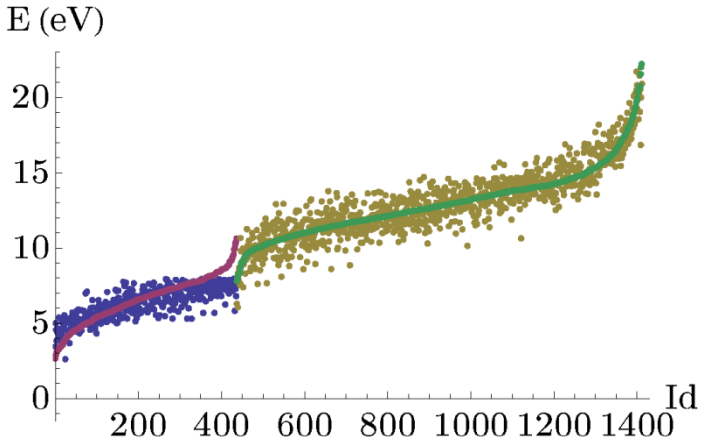
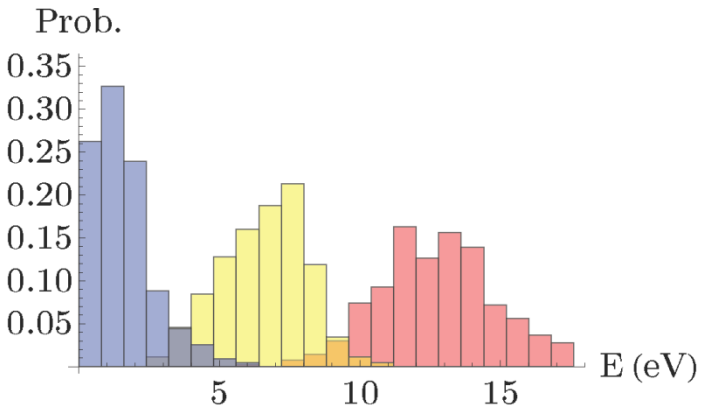


Figure B1. FF and DFT (PBE functional) energies of B_9^- clusters. *x* axes show the serial number of the structures. Green and yellow dots are FF (fitted) and DFT energies of initial structures, respectively; Red and blue dots are FF (predicted) and DFT energies of pre-relaxed structures, respectively. The structures are sorted by their FF energies. Some initial structures with very high energies are excluded in order to show more details of the main part of the plot. Energies relative to -223.2087831063 Hartree, which is the energy of the global minimum that we find, were used.



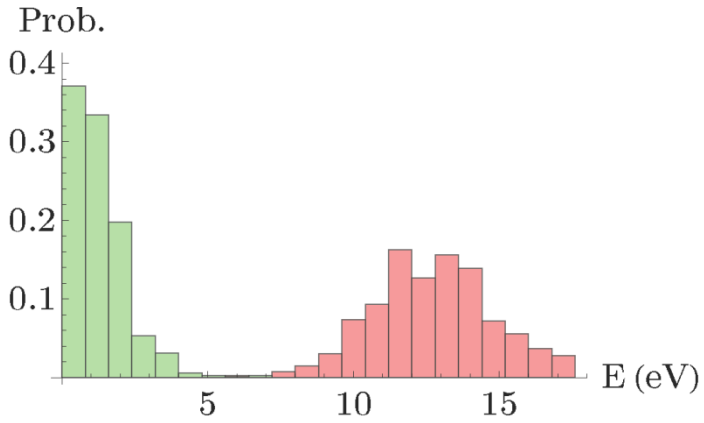


Figure B2. Frequency histograms for energy distributions of B_9^- clusters at different calculation stages. Energy shift by AFFCK and pure CK method are showed in upper and lower three plots, respectively. All energies are calculated using DFT with PBE functional. Red, yellow, blue, and green parts represent initial, pre-relaxed, DFT relaxed (from pre-relaxed ones), and DFT relaxed (from initial ones) structures, respectively. Energies relative to -223.2087831063 Hartree, which is the energy of the global minimum that we find, were used.

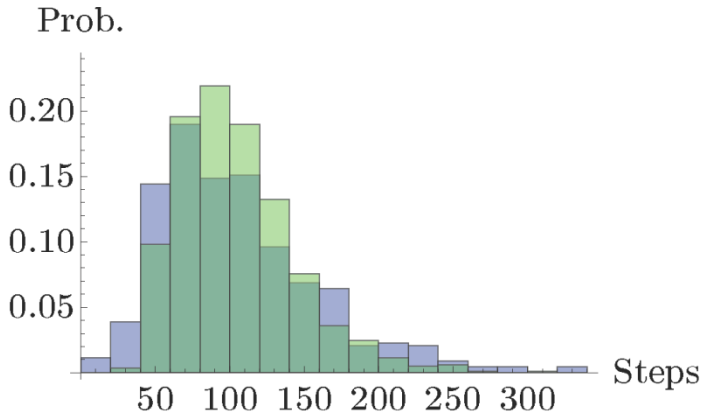


Figure B3. Frequency histograms for the distribution of the number of optimization (DFT with PBE functional) steps of converged B_9^- clusters. Blue and green bars stand for AFFCK method (optimizing from pre-relaxed structures) and pure CK method (optimizing from initial structures), respectively.

The mean numbers of optimization steps were 103.98 (pure CK) and 104.68 (AFFCK), which means that AFFCK is not efficient for B_9^- clusters.

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