

Modeling Dinitrogen Activation by Lithium: A Mechanistic Investigation of the Cleavage of N₂ by Stepwise Insertion into small Lithium Clusters

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Full Reference 12

- 1) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich,

S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

SI. Table 1. Atomization energies of N₂, Li₂, NLi₃, and N₂Li₂

	D_e						
	OLYP ^a	B3LYP ^a	MP2(full) ^b	CCSD(T,full) ^b	CCSD(T,fc) ^b	G3B3 ^c	Exp ^d
Li ₂	22.03	20.82	17.42	23.92	23.58	25.93	23.5
N ₂	225.08	224.81	231.27	218.61	217.03	222.12	221.7
NLi ₃	147.78	157.83	163.90	154.83	150.04	156.48	
N ₂ Li ₂	239.03	246.49	243.10	234.20	229.16	235.74	

a) /6-311+G* ultrafine grid. b) /6-311+G(2df) on OLYP/6-311+G* geometries. c) G3B3 De's were corrected by the B3LYP/6-31G* zero-point energies. d) From J. Chem. Phys. **1991**, 94, 7221.

SI. Table2. Reaction energies (ΔH_e in kcal/mol) of N₂+Li₂→N₂Li₂ and 1/2 N₂+3/2 Li₂ →NLi₃.

Reaction	OLYP	BLYP	PBEPBE	B3LYP	X3LYP	O3LYP	M052X	MP2 (full)	CCSD (T,full)	CCSD (T,fc)	G3B3
3/2Li ₂ +1/2N ₂ →NLi ₃	-2.20	-18.68	-14.75	-14.20	-14.19	-2.57	-13.9	-22.13	-9.64	-6.15	-6.51
N ₂ +Li ₂ →N ₂ Li ₂	8.08	-2.18	-1.83	-0.87	-1.20	7.03	1.31	5.59	8.33	11.45	12.31

SI. Table 3. The atomization energy/alkali metal (B3LYP/6-311+G*)

Li				Na			K		
	Bond length (Å)	AE kcal/mol	AE/atom kcal/mol	Bond length (Å)	AE kcal/mol	AE/atom kcal/mol	Bond length (Å)	AE kcal/mol	AE/atom kcal/mol
BM ₂	2.174 (D _{∞h})	62.3	31.2	2.477 (C _{2v})	32.7	16.4	2.750	8.7	4.4
BM ₄	2.122 (C ₁)	138.8	34.7	2.547 (C _s)	90.0	22.5	2.926 (C _s)	73.4	36.7
CM ₂	1.918	47.7	23.9	2.298	37.7	18.9	2.282	19.7	9.9
CM ₃	1.896	130.1	43.4	2.273	69.9	23.3	2.744	82.9	27.6
NM ₂	1.760	97.7	48.9	2.227	55.4	27.7	2.461	46.0	23
NM ₄	1.771	211.1	52.8	2.178	121.4	30.4	2.515	103.7	25.9
OM ₃	1.679	218.9	73.0	2.059	146.7	48.9	2.332	143.0	47.7
OM ₄	1.739	259.0	64.8	2.109	182.4	45.6	2.414	172.5	43.1

SI . Table 4. Bond length and Natural Charges for compounds of alkali metal- first row and second row elements (Charges computed with NBO 5.0 program@ B3LYP/6-311+G* level).

	Charge on first row elements	Charge on alkali metals
BLi ₃ (D _{3h})	B -2.361	Li + 0.787
BNa ₃ (D _{3h})	B -1.898	Na + 0.632
BK ₃ (D _{3h})	B -1.982	K + 0.660
CLi ₄ (T _d)	C -3.685	Li + 0.921
CNa ₄ (T _d)	C -3.293	Na 0.823
CK ₄ (T _d)	C -3.098	K +0.774
NLi ₃ (D _{3h})	N -2.816	Li +0.938
NNa ₃ (C _{2v})	N -2.328	Na+0.776

NK ₃ (D _{3h})	N -2.424	K +0.808
OLi ₂ (D _{∞h})	O -1.900	Li 0.950
ONa ₂ (D _{∞h})	O -1.858	Na 0.929
OK ₂ (D _{∞h})	O -1.803	K 0.901
PLi ₃ (C _{3v})	P -2.414	Li +0.804
PNa ₃ (C _{3v})	P -2.098	Na +0.699
PK ₃ (C _{3v})	P -2.321	K +0.773
SiLi ₄ (C _{2v})	Si -2.622	Li +0.763/+0.547
SiNa ₄ (C _{2v})	Si -2.198	Na+0.627/+0.472
SiK ₄ (C _{2v})	Si -2.990	K +0.748

XYZ co-ordinates for N₂:Li_n clusters

Stationary points N₂Li₈ (RB3LYP/6-311+G**, ultrafine grid)

8-I (SCF= -169.74225 a.u.)

10

Li -1.4014943 0.8100162 -2.2428085
 Li 0.0000022 -0.0028652 0.1994637
 Li 0.0001731 -1.6169809 -2.2463845
 Li 1.4013196 0.8103199 -2.2428118
 Li 2.4809935 -1.4331138 -0.6104489
 Li -0.0000043 0.0048184 -4.7786552
 Li -0.0003093 2.8629989 -0.6042571
 Li -2.4806841 -1.4336473 -0.6104433
 N 0.0000008 -0.0010656 2.2636128
 N 0.0000007 0.0004028 3.3662495

8-II (SCF= -169.73796 a.u.)

10

Li -0.5948627 -2.2669081 0.3764879
 Li 0.6604462 0.3884502 0.4456193
 Li 2.1767406 -1.9938543 0.0596561
 Li 0.3965840 -1.2549167 -1.9754475
 Li 2.8473572 0.4474787 -1.5011526
 Li 0.8822474 -4.2155352 -1.4419691
 Li -1.8971484 0.3094352 -0.6666208
 Li 1.0571120 -1.3800554 2.7458427
 N -0.7230876 1.8156480 0.4764220
 N -1.6462594 2.4554544 0.3625426

8-III (SCF= -169.73869 a.u.)

10

Li 1.0516024 -1.3746219 1.4811516
Li -0.9997445 -0.0022014 -0.0944422
Li -0.9933046 -0.0026523 2.7775142
Li 1.0449454 1.3795362 1.4813487
Li -1.7494643 2.4872105 1.3616751
Li 1.7046437 0.0038516 4.0938225
Li 1.6424565 0.0040022 -1.2636364
Li -1.7374222 -2.4957019 1.3608124
N -0.3355986 -0.0006758 -1.9435349
N 0.3511503 0.0009231 -2.8557133

8-IV (SCF= -169.73231 a.u.)

10

Li 1.3416550 -0.7255893 1.4732597
Li 0.0613519 -0.6068253 -1.1109016
Li -0.0008585 -3.0156195 0.5655475
Li -1.4692918 -0.7513767 1.3319130
Li -2.5538333 -2.4772700 -0.7779147
Li -0.1935668 -0.4620276 3.9324699
Li -0.0516460 1.6743163 0.7199047
Li 2.6637110 -2.4293982 -0.5155952
N 0.0535423 1.3150540 -1.3029820
N 0.0332342 2.4537132 -1.1050251

8-V (SCF= -169.73736 a.u.)

10

Li 1.5655610 -1.4571732 0.7458049
Li 0.2475615 1.1260474 0.5336444
Li 2.8292947 1.2928050 0.4189369
Li 1.3662198 -0.1848132 -1.8042572
Li 1.4600788 2.9323423 -1.5820624
Li 0.7189526 -3.3926960 -1.7480669
Li -0.9050494 -1.3515671 -0.6066374
Li 1.8158154 0.6073897 3.0776284
N -1.4637974 0.3837833 0.3104030
N -2.4355316 -0.2004982 0.1031724

8-VI (SCF= -169.72470 a.u.)

10

Li -1.6536801 -0.9743130 -1.0942157
Li 1.4455279 -0.6882677 -0.1344887
Li 0.3184064 -0.0023204 -2.7811779
Li -0.2452871 1.2565577 -0.2851641
Li 2.4302064 1.7336280 -1.7252622
Li -2.2395984 1.4674572 -2.5452800
Li -1.5914010 0.0105211 1.8549145
Li 0.4411843 -2.8346269 -2.1017251
N 0.2953522 0.0479823 1.2951302
N 0.1737800 -0.0345406 2.4816123

8-VII (SCF= -169.75697 a.u.)

10

Li 0.1721482 1.2385962 0.9785996
Li -0.0145764 0.7472938 -1.4012645
Li 2.3123654 -0.1480405 -0.1526155
Li 0.2218187 -1.7378794 0.3447475

Li 1.4748467 -2.1359804 -2.2093995
Li 1.8599382 -1.1264572 2.6262328
Li -2.6480632 -0.6621210 0.3435965
Li 2.1364717 2.7659992 -0.7391154
N -0.8339293 -0.2972873 0.1268092
N -1.5296204 0.7509685 -0.0371442

8-VIII (SCF= -169.75368 a.u.)

10

Li -0.1245664 0.7732344 -1.3478740
Li 0.1166208 1.4195525 1.0777778
Li -2.2314052 -0.0635272 0.3460239
Li -0.2432921 -1.8795386 -0.2692613
Li -0.7558514 -1.4170451 2.5889644
Li -2.4366851 -1.4248668 -2.2604693
Li 2.3379025 -0.7265642 0.8842061
Li -2.1308272 2.7874466 -0.3294641
N 0.8593337 -0.4282304 -0.1957236
N 1.4841395 0.6559340 -0.0999493

8-IX (SCF= -169.78870 a.u.)

10

Li 0.1764083 -1.2575197 1.3171109
Li -1.6670362 1.0263545 1.5870917
Li 0.5597431 0.9453311 -0.0412633
Li 0.7759966 -1.2186660 -1.6837082
Li 1.0297769 1.6490524 -2.8396147
Li 2.9322502 -0.3542751 0.4471504
Li -1.4022906 0.4930008 -1.4039724
Li 1.2948627 1.1206424 2.6879275
N -0.4411870 -0.8640899 -0.4329759
N -1.1444036 -0.1661616 0.4026665

8-X (SCF= -169.78576 a.u.)

10

Li 0.2416938 1.1819659 -1.4955121
Li -1.8306516 -0.7169133 -1.6146622
Li 0.2664547 -1.1871505 0.1066150
Li 0.9249307 1.0525386 1.7853167
Li 0.5159562 -1.5278208 3.1774152
Li 2.4980722 0.0826103 -0.3364014
Li -1.4857163 0.0296556 1.3877739
Li 1.2677843 -1.3008948 -2.7884221
N -0.0395959 0.7818863 0.3449752
N -0.9883429 0.2406890 -0.4401708

8-XI (SCF= -169.81922 a.u.)

10

Li -1.1527146 -0.3613184 -1.3079971
Li -1.8502097 1.5138572 0.4739271
Li 1.1526910 0.3613444 1.3079507
Li 1.8501852 -1.5139680 -0.4739209
Li 4.0552136 0.5828360 0.1206605
Li -1.1226701 -1.0248797 0.9269544
Li 1.1227512 1.0248238 -0.9269910
Li -4.0552874 -0.5826155 -0.1204068

N 0.4026945 -0.5911859 -0.1809238
N -0.4026770 0.5911517 0.1808480

8-XII (SCF= -169.80059 a.u.)

10

Li -1.1576071 0.4522326 -1.1561337
Li 1.5146457 0.0362177 -1.2193598
Li -0.8828255 -1.9431256 0.0000653
Li 2.1455010 -2.3017614 0.0000107
Li 1.5146957 0.0362760 1.2192958
Li -1.1575598 0.4522886 1.1561592
Li 0.8725221 2.5675649 -0.0000794
Li -3.8529029 -0.3861303 0.0000887
N 0.0997886 -0.4863527 0.0000096
N 0.3302961 0.9519688 -0.0000297

8-XIII (SCF= -169.80960 a.u.)

10

Li -0.8895299 -0.6367023 1.1947046
Li 1.6249552 0.2555102 1.2319339
Li -1.6419369 1.4414488 -0.0000747
Li 0.9157158 2.3732996 -0.0000702
Li 1.6249783 0.2554246 -1.2319185
Li -0.8895052 -0.6367942 -1.1946750
Li 1.5136885 -2.2095135 0.0000956
Li -3.8178110 -0.6367897 -0.0000205
N 0.0900210 0.6726432 -0.0000233
N 0.5783127 -0.7608790 0.0000339

8-XIV (SCF= -169.78783 a.u.)

10

Li 0.0235123 0.0583345 1.4118381
Li 0.3342468 1.9690706 -0.2939572
Li 1.3326575 -1.6210582 0.1314250
Li -1.7932373 -1.0859717 0.1613742
Li -0.0313987 -0.0843963 -1.7694342
Li 2.8376718 0.5405193 -0.3047154
Li -2.5015198 1.4544759 -0.2535476
Li -0.5091980 -3.0868286 2.0042657
N -0.8859515 0.5606100 -0.2238629
N 1.0176367 0.2347562 -0.2421008

8-XV (SCF= -169.85036 a.u.)

10

Li 0.0000133 0.2688224 -1.1190121
Li -0.0007506 -1.6591464 -0.0807984
Li 2.1699454 1.2471974 0.0607405
Li -2.1688607 1.2491404 0.0612512
Li 0.0001771 0.1591200 1.1393274
Li 2.8873080 -1.4601911 -0.0720210
Li -2.8886516 -1.4575492 -0.0715929
Li 0.0016930 3.5539578 0.1758398
N -1.4851067 -0.4067565 -0.0199309
N 1.4847322 -0.4081083 -0.0202411

8-XVI(SCF= -169.84452 a.u.)
 10
 Li -0.2895113 -1.5262971 -0.3315585
 Li -0.0647290 0.5024987 -1.0831033
 Li -3.0944984 -0.9549839 0.0134136
 Li 2.3742153 -1.6271166 0.8283399
 Li -0.0279592 0.0880523 1.1513293
 Li -2.0605142 1.6458851 0.1716826
 Li 1.0939739 2.7266335 0.3702418
 Li 2.5829353 0.4881284 -0.9000134
 N 1.3563753 -0.5035518 -0.0792985
 N -1.5766234 -0.0719341 -0.0151295

8-XVII (SCF= -169.88456 a.u.)
 10
 Li 0.1547650 -1.1947264 0.5657493
 Li 0.1431217 0.9920210 0.8760577
 Li 2.7597836 -1.3326167 -0.2453571
 Li -2.1807636 -1.2452631 -1.0652938
 Li 0.3056129 0.1757519 -1.2368976
 Li 2.7413493 1.3818757 0.1202623
 Li -2.1955693 1.4697389 -0.6785906
 Li -2.4090624 -0.2199110 1.4427346
 N -1.3468942 -0.0043073 -0.0223094
 N 1.6386497 -0.0072086 0.1171673

Stationary points N_2Li_6 [RB3LYP/6-311+G*, ultrafine grid]

8
 6-I (SCF= -154.69066 a.u)
 N 0.0000000 0.0000000 1.5823721
 N 0.0000000 0.0000000 2.6884550
 Li 1.4119555 -2.0274907 -1.6490622
 Li 2.0274907 1.4119555 -1.6490622
 Li -1.4119555 2.0274907 -1.6490622
 Li -2.0274907 -1.4119555 -1.6490622
 Li 0.0000000 0.0000000 -0.3913643
 Li 0.0000000 0.0000000 -2.9776500

8
 6-II (SCF=-154.67479 a.u)
 N 1.4505508 0.0169650 0.0684443
 N 2.3625045 -0.4961215 -0.3260066
 Li 0.1149194 0.9960113 1.3341747
 Li -1.1485722 2.7923578 -0.7575826
 Li -1.4002932 -1.6432847 1.4953600
 Li -3.1158376 -1.6254831 -1.3303247
 Li -0.7278269 -0.1325068 -0.8532160
 Li -2.6195186 0.7309375 0.7125674

8

6-III (SCF= -154.67855 a.u)

N	-0.0009453	0.2379885	1.6366151
N	-0.0546662	-0.8826661	1.8146623
Li	0.1103553	1.9505882	0.6021740
Li	2.5090900	0.0336597	-1.5673092
Li	-2.4909192	0.2168896	-1.6521016
Li	-0.0265048	-1.5013074	-2.8932045
Li	-0.0363445	-0.5290279	-0.3640035
Li	0.0640835	1.3334457	-2.1785358

8

6-IV (SCF= -154.67478 a.u)

N	0.6929477	1.1762839	-0.2113545
N	1.6610584	0.6697402	-0.5533463
Li	-1.0644518	1.4850545	0.5687108
Li	-1.0384112	-0.2860032	3.1167077
Li	-0.4226072	-3.2010909	-1.0026367
Li	-0.9555241	-0.3704775	-1.8544980
Li	-2.3131126	-1.0699188	0.4605582
Li	0.3014260	-0.8649538	0.4954598

8

6-V (SCF= -154.68617 a.u)

N	0.8284852	-0.8454482	0.0815028
N	1.7618002	-0.2514886	-0.3332782
Li	-0.6893608	-1.6112841	0.8106105
Li	-3.1386622	-1.3478759	-0.7428579
Li	-0.5325671	3.2381199	-0.4607565
Li	0.9042363	1.0487259	0.8876741
Li	-1.9624084	0.9720011	1.1202626
Li	-0.6252369	0.2598324	-1.0274568

8

6-VI (SCF= -154.68123 a.u)

Li	-0.6160328	3.2386024	-0.1591055
Li	3.2549701	-0.3277669	-0.6524504
Li	1.1207163	-1.4155295	0.9162994
Li	-1.2048750	0.5814219	1.1021989
Li	1.4544103	1.4466260	1.0374355
Li	0.3029506	0.0859034	-1.4533280
N	-0.4661817	-1.0210995	0.1316863
N	-1.3818781	-0.5257251	-0.4707077

8

6-VII (SCF= -154.69484 a.u)

Li	-3.5405816	1.5158186	-0.2239143
Li	2.4738398	2.4878614	-0.5418150
Li	1.3247567	0.6933979	1.3311706
Li	-1.7122785	-0.6697724	0.5023346
Li	-0.5806790	1.3797128	-0.3794045
Li	1.6752481	-1.1364274	-0.7251559
N	0.3175721	-0.4934318	0.4018060
N	-0.1634173	-1.3368214	-0.3860414

8

6-VIII (SCF= -154.68991 a.u)
Li -1.2348590 -2.9051115 -0.7601870
Li 1.6024984 1.6708292 -2.6299916
Li 0.0468166 2.1404664 -0.2399729
Li -1.7649055 -0.5111367 0.8114799
Li -0.4244050 -0.2250386 -1.3223082
Li 1.7594106 0.0980553 0.5721496
N -0.0715059 0.5335326 0.5371698
N 0.0781247 -0.6484173 0.9923288

8
6-IX (SCF= -154.73398 a.u)
Li 0.4002211 -0.5696884 1.2994098
Li 0.4003795 -0.5699745 -1.2992368
Li 1.6373371 1.4290550 -0.0000570
Li -1.9786552 -1.6215317 0.0000585
Li -1.6206690 1.4308791 -0.0002544
Li 3.2549522 -1.1443989 0.0003277
N -0.9571159 -0.2856678 -0.0000280
N 0.0598734 0.7338076 -0.0000783

8
6-X (SCF= -154.72925 a.u)
Li -2.4541587 0.2250879 -0.6505371
Li 1.3023828 -2.4497940 0.1474705
Li 2.1983459 0.0417633 0.6033819
Li 0.0031630 1.9830011 0.1691479
Li 0.1798023 -0.4812403 -1.5251285
Li -0.5938052 -0.7218453 1.3100655
N 0.5605219 0.2182590 0.1714652
N -0.8329776 0.3830384 -0.1947796

8
6-XI (SCF= -154.75059 a.u)
Li 0.0000000 1.7785928 0.0000000
Li 0.0000000 -1.7785928 0.0000000
Li -1.7785928 0.0000000 0.0000000
Li 1.7785928 0.0000000 0.0000000
Li 0.0000000 0.0000000 2.4417322
Li 0.0000000 0.0000000 -2.4417322
N 0.0000000 0.0000000 -0.7431479
N 0.0000000 0.0000000 0.7431479

8
6-XII (SCF= -154.70709 a.u)
Li -0.2351526 -0.0489004 -1.4819421
Li -0.1830153 -0.4672575 1.4149210
Li -2.4309754 -1.1153898 -0.1173287
Li 1.4446008 -1.6823286 -0.2689591
Li 2.6020064 0.7606262 0.0630411
Li -0.1374849 1.6685588 0.2434394
N 0.8973890 0.0931709 -0.0026978
N -1.3516658 0.2859825 0.0656242

8
6-XIII (SCF= -154.74172 a.u)

Li	0.0000000	1.0498127	0.0000000
Li	0.0000000	-1.0498127	0.0000000
Li	-1.4613072	0.0000000	2.5320349
Li	1.4613072	0.0000000	2.5320349
Li	1.4613072	0.0000000	-2.5320349
Li	-1.4613072	0.0000000	-2.5320349
N	0.0000000	0.0000000	1.6004923
N	0.0000000	0.0000000	-1.6004923

Stationary points N₂Li₄ (RB3LYP/6-311+G*, ultrafine grid)

4

Li4 (SCF= a.u)

Li	1.2867075	0.0000000	0.0000000
Li	0.0008702	0.0000000	-2.7197603
Li	-1.2884480	0.0000000	0.0000000
Li	0.0008702	0.0000000	2.7197603

6

sigma complex 4-I (SCF= -139.63000 a.u)

Li	0.0000000	-2.6868590	-1.9289643
Li	0.0000000	2.6868590	-1.9289643
Li	0.0000000	0.0000000	-0.6212017
Li	0.0000000	0.0000000	-3.2523016
N	0.0000000	0.0000000	1.3841285
N	0.0000000	0.0000000	2.4895785

6

geom pi complex 4-II(SCF=-139.62143 a.u)

N	0.0000000	-0.5588220	-1.7182829
N	0.0000000	0.5588220	-1.7182829
Li	0.0000000	0.0000000	0.4363400
Li	0.0000000	2.6622823	1.6809516
Li	0.0000000	0.0000000	3.0607103
Li	0.0000000	-2.6622823	1.6809516

6

4-III (SCF= -139.62054a.u)

Li	-2.4882613	0.0000000	-0.0677176
N	-0.1322733	0.0000000	-1.6609884
N	0.9754443	0.0000000	-1.4512499
Li	0.2882614	0.0000000	0.5429183
Li	-1.2436988	0.0000000	2.6756348
Li	1.7608354	0.0000000	3.0608008

6

4-IV (SCF= -139.62521 a.u)

N	0.8965095	1.4508336	0.0869469
N	-0.2520721	1.3516800	0.0843993
Li	0.5402364	-0.5653537	-0.0366583

Li -2.0190712 0.6287209 0.0451948
Li -1.3613615 -2.3855115 -0.1433131
Li 1.5539800 -3.2713204 -0.2072090

6
4-V (SCF= -139.61664 a.u)
Li 2.2916974 0.0000000 -2.2927208
Li -0.8668055 0.0000000 1.9768382
Li 0.9647370 0.0000000 0.0424835
Li 2.0416288 0.0000000 2.6059592
N -1.0660307 0.0000000 0.0645291
N -0.8330798 0.0000000 -1.0641977

6
4-VI (SCF= -139.63302 a.u)
Li -0.2045922 -2.5067459 -1.0410879
Li 0.2455459 1.5817676 1.2494849
Li -0.2048287 0.3690551 -1.0422913
Li -0.2049915 3.3757251 -1.0431198
N 0.1560243 -0.2066863 0.7939455
N 0.0287902 -1.2061291 0.1465017

6
4-VII (SCF= -139.61596 a.u)
Li 0.0185605 0.0000000 -2.9505253
N -0.4138966 0.0000000 -1.0297616
N 0.5099592 0.0000000 -0.2255292
Li -1.1627418 0.0000000 0.7399015
Li 1.3525099 0.0000000 1.4086057
Li -0.4324748 0.0000000 3.7310298

6
4-VIII (SCF= -139.64694 a.u)
N 0.0011889 -0.4700284 -0.2780169
N 1.2278476 -0.3308419 -0.4487079
Li 0.7021814 -1.8857537 -1.2592149
Li 0.5714643 1.1550942 0.5647837
Li -1.7026927 -0.0658200 0.3122098
Li -2.0239545 2.3949158 1.8326724

Stationary points N_2Li_2 (RB3LYP/6-311+G* ultrafine grid)

2
Li2 (SCF= -15.01584 a.u)
LI 0.000000 0.000000 1.352537
LI 0.000000 0.000000 -1.352537

2
n2 (SCF= -109.55969 a.u)
N 0.000000 0.000000 0.547788
N 0.000000 0.000000 -0.547788

4
2-I (SCF= -124.57901 a.u)
N -0.752920 1.522048 0.000000

N 0.000000 0.720975 0.000000
 LI 0.949127 -1.259544 0.000000
 LI 0.807688 -3.974177 0.000000

4
 2-II (SCF= -124.56349 a.u)
 LI 2.371921 -0.240167 0.000000
 N 0.000000 0.626483 0.000000
 N -1.029276 0.121540 0.000000
 LI 0.029724 -1.505221 0.000000

4
 2-III (SCF= -124.56769 a.u)
 N -0.965591 -0.234691 0.000000
 N 0.000000 0.439978 0.000000
 LI 0.495007 -1.466388 0.000000
 LI 1.758038 0.987386 0.000000

4
 2-IV (SCF= -124.54387 a.u)
 N 0.240267 -0.224331 0.346979
 N -0.431602 0.689219 -0.080507
 LI 1.890349 -0.223858 -0.351915
 LI -1.443902 -0.860881 -0.269853

4
 2-V (SCF=-124.57691 a.u)
 N 0.000000 0.629954 0.000000
 N 0.000000 -0.629954 0.000000
 LI 0.000000 0.000000 1.708130
 LI 0.000000 0.000000 -1.708130

Geometries (Figure 1, B3LYP/6-311+G* , ultrafine grid)

6
 1, Figure 1 (SCF=-234.15466 a.u)
 Li 1.2549867 -0.0000000 -0.4500113
 Li -1.2549867 0.0000000 0.4500113
 N 0.2016122 0.0000000 -2.1638104
 N -0.2016122 -0.0000000 2.1638104
 N -0.5595822 -0.0000000 -1.2852684
 N 0.5595822 0.0000000 1.2852684

6
 2, Figure1 (SCF=-234.15422 a.u)
 Li 0.9854907 0.0000000 0.0000000
 N -0.4123461 0.0000000 -1.3958330
 N -0.4123461 0.0000000 1.3958330
 N 0.5808068 0.0000000 -1.9977255
 N 0.5808068 0.0000000 1.9977255
 Li -1.6579434 0.0000000 0.0000000

6
 3, Figure 1 (SCF=-234.15267 a.u)
 Li 0.0000000 0.0000000 -0.0136390
 N 0.0000000 0.0000000 3.0798838
 N 0.0000000 0.6186805 -1.7722805
 N 0.0000000 -0.6186805 -1.7722805
 N 0.0000000 0.0000000 1.9727180
 Li 0.0000000 0.0000000 -3.5051230

6
 4, Figure (SCF=-234.14593 a.u)
 Li 0.0000000 0.0000000 -0.1729205
 N 0.0000000 0.5587139 -2.2618390
 N 0.0000000 -0.5587139 -2.2618390
 N 0.0000000 0.6159063 1.5860953
 N 0.0000000 -0.6159063 1.5860953
 Li 0.0000000 0.0000000 3.3263912

6
 5, Figure 1 (SCF=-234.14003)
 Li 0.4651637 0.3284310 -0.3628208
 N 0.6932626 -1.1576536 2.3330649
 N 0.5902759 -0.6308874 1.3674637
 N -1.5815095 0.1120982 -0.9102438
 N -1.2167379 0.7074498 -1.7841339
 Li 2.5580050 1.6055576 -1.6453301

6
 6, Figure 1 (SCF= -234.13933 a.u)
 Li 1.7190568 1.4886602 0.0000000
 N 0.5460813 -2.1504040 0.0000000
 N 0.0048058 2.1365420 0.0000000
 N -0.5528767 -2.1507440 0.0000000
 N -0.0000000 0.8828490 0.0000000
 Li -1.7144132 1.5021058 0.0000000

3
 7, Figure 1(SCF= -117.05042)
 Li 0.0469710 2.0909127 -0.1166823
 N -0.0693160 0.0108235 0.1721901
 N 0.0457819 -1.0584409 -0.1137284

3
 8, Figure 1(SCF= -117.04850)
 Li -0.6078100 0.4877730 1.2674689
 N -0.1335685 -0.6226278 -0.1987565
 N 0.3940585 0.4135822 -0.3444445

KICK structures



8
K6-I (SCF= -154.67222 a.u)
Li -0.0004852 0.0000000 0.0849636
Li 1.4164485 0.0000000 2.8263696
Li -0.0033676 0.0000000 5.4411214
Li -1.4164010 0.0000000 2.8231654
Li -2.9837694 0.0000000 0.3131015
Li 2.9825913 0.0000000 0.3151920
N 0.0013224 0.0000000 -3.0818121
N 0.0008133 0.0000000 -1.9770080

8
K6-II (SCF= -154.6689 a.u)
Li -0.4584601 0.0000000 -0.0785489
Li -3.2139742 0.0000000 0.5656671
Li 0.8245322 0.0000000 5.0571042
Li -1.1622543 0.0000000 2.8136648
Li 2.2217742 0.0000000 -0.8728208
Li 1.5771165 0.0000000 2.1489801
N 0.5987383 0.0000000 -1.9193454
N -0.5081958 0.0000000 -2.2095317

8
K6-III (SCF= -154.6993 a.u)
Li 1.5325928 0.0000000 -0.5827234
Li 1.2057926 0.0000000 2.5310983
Li -1.4013079 0.0000000 0.0699298
Li -0.4402117 0.0000000 -2.7024405
Li 2.6179542 0.0000000 -3.2295528
Li -3.3626428 0.0000000 -2.1464920
N 0.3909378 0.0000000 0.8485047
N -0.4561566 0.0000000 1.7487156

8
K6-IV (SCF=-154.71321 a.u)
Li -1.1158967 0.0000000 -1.4591730
Li 1.3599099 0.0000000 -2.0419323
Li 1.1159154 0.0000000 1.4591739
Li -1.3599236 0.0000000 2.0419187
Li 0.3544172 0.0000000 4.4225537
Li -0.3544509 0.0000000 -4.4225585
N -0.4914997 0.0000000 0.3789001
N 0.4915119 0.0000000 -0.3788926

8
K6-V (SCF=-154.69066 a.u)
Li 1.4119555 -2.0274907 -1.6490622
Li 2.0274907 1.4119555 -1.6490622
Li -1.4119555 2.0274907 -1.6490622
Li -2.0274907 -1.4119555 -1.6490622
Li 0.0000000 0.0000000 -0.3913643
Li 0.0000000 0.0000000 -2.9776500
N 0.0000000 0.0000000 1.5823721
N 0.0000000 0.0000000 2.6884550

8
 K6-VI (SCF=-154.67854 a.u)
 Li 0.1472039 -0.6162144 -0.1002788
 Li -0.8482533 -3.1299696 -0.3086630
 Li -1.0340813 1.7532950 0.2304173
 Li -2.4522932 -0.6870705 -0.1742839
 Li -1.1093061 -0.9174895 -2.6681724
 Li -1.2451354 -1.2871301 2.3230190
 N 1.8751950 0.7333749 0.1267032
 N 0.9284615 1.3600161 0.1724232

8
 K6-VII (SCF=-154.68616 a.u)
 Li -0.3546391 -1.0179654 0.5953111
 Li -1.2696162 1.1486642 1.7663058
 Li 0.8259294 -0.6901126 3.3280819
 Li -3.2844673 -0.4506425 0.0209319
 Li -0.8893518 0.8717395 -1.0720088
 Li 1.4836689 0.8163914 0.9250703
 N 0.9652296 0.0650580 -0.6848251
 N 0.5298316 -0.3556614 -1.6996144

8
 K6-VIII (SCF= -154.70157a.u)
 Li 0.7321295 1.5072519 -0.0016807
 Li -0.6981006 0.0001908 1.8042992
 Li 2.2047554 0.0001604 -2.3812335
 Li 2.2134101 0.0011328 2.3733530
 Li 0.7330169 -1.5070226 -0.0009492
 Li -0.7048321 -0.0005747 -1.8018533
 N -0.9597417 -0.6207826 0.0018580
 N -0.9604208 0.6202946 0.0015982

8
 K6-IX (SCF=-154.71588 a.u)
 Li 1.3514454 -1.0291859 -0.7621082
 Li -1.5711045 -0.6496611 -0.7587950
 Li -0.1932698 -1.4960830 1.5011735
 Li -1.1953503 0.9120406 1.5069783
 Li 1.3894551 0.5745054 1.5077232
 Li 0.2202561 1.6860649 -0.7554137
 N -0.0013311 0.0015934 -1.2668498
 N 0.0007174 -0.0005995 0.3070391

8
 K6-X (SCF= -154.73131 a.u)
 Li 1.2194744 0.0754769 -0.5337727
 Li -1.3554927 -1.2914220 -0.4469384
 Li -0.7313244 1.6392734 -1.1281388
 Li 0.8400868 -2.0712677 1.4569605
 Li -0.5085422 0.6029546 1.7565115
 Li 1.7929015 2.2537541 -2.6299827
 N 0.0284053 -0.8160315 0.6913281
 N -0.5671638 0.2979875 -0.0376021

8
 K6-XI (SCF= -154.74132a.u)
 Li 0.4934306 -1.1568297 0.2429524
 Li 0.6645157 1.0790623 0.2649732
 Li 0.0705441 -0.0295006 3.3411787
 Li 1.4384046 -0.0173507 -2.2940198
 Li -1.2608387 -0.0264694 -2.5520015
 Li -1.3079630 0.1151094 0.2978148
 N -0.0172522 0.0173819 -1.3112826
 N -0.0247878 -0.0019624 1.6108979

8
 K6-XII (SCF=-154.74177 a.u)
 Li 0.9082164 -0.5221948 0.0813049
 Li -0.9082275 0.5221650 -0.0813112
 Li 0.5000167 1.2718964 2.5841120
 Li 0.9460227 1.2623021 -2.4611609
 Li -0.9461319 -1.2621744 2.4612973
 Li -0.4998415 -1.2719314 -2.5842302
 N -0.1408414 0.0030175 1.5925842
 N 0.1408178 -0.0030444 -1.5925893

8
 K6-XIII (SCF= -154.7505a.u)
 Li -1.7785169 0.0000000 0.0000000
 Li 1.7785169 0.0000000 0.0000000
 Li 0.0000000 0.0000000 2.4421807
 Li 0.0000000 0.0000000 -2.4421807
 Li 0.0000000 1.7785247 0.0000000
 Li 0.0000000 -1.7785247 0.0000000
 N 0.0000000 0.0000000 0.7430035
 N 0.0000000 0.0000000 -0.7430035

N₂Li₈ (B3LYP/6-311+G*)

10
 K8-I (SCF=-169.78479 a.u)
 Li 0.0000000 1.6368150 0.0343773
 Li 0.0000000 0.0926926 -4.4705970
 Li 1.3692695 -0.0371642 1.7821493
 Li -1.3692695 -0.0371642 1.7821493
 Li 1.3692864 0.0375498 -1.7820857
 Li -1.3692864 0.0375498 -1.7820857
 Li 0.0000000 -1.6367048 -0.0345767
 Li 0.0000000 -0.0941255 4.4704684
 N 0.8741842 0.0001181 0.0000430
 N -0.8741842 0.0001181 0.0000430

10
 K8-II (SCF= -169.79788a.u)
 Li -1.6647007 -0.2954479 -1.3935936
 Li -1.6647007 -0.2954479 1.3935936
 Li 0.4443921 -1.6648706 0.0000000
 Li 2.7256668 0.1536054 0.0000000

Li	0.4043379	0.8524303	-1.5473195
Li	0.4043379	0.8524303	1.5473195
Li	-1.0327135	0.1048392	4.2076303
Li	-1.0327135	0.1048392	-4.2076303
N	1.0483552	0.0645898	0.0000000
N	-0.4414579	0.0158196	0.0000000

10

K8-III (SCF= -169.81496 a.u)

Li	1.5965653	1.2531379	1.2581322
Li	0.8354230	0.9685844	-1.2350107
Li	0.7019448	3.7977370	-0.1757115
Li	-0.4612768	-1.3246092	1.1027832
Li	1.5873496	-1.4646511	-0.5539053
Li	-0.9364926	0.8597503	0.3311353
Li	-3.4858503	-1.2003799	1.1486211
Li	-1.6015023	-1.2453430	-1.2609277
N	0.8267126	-0.0622083	0.3883618
N	-0.0707815	-0.6424602	-0.6519832

10

K8-IV (SCF= -169.81921 a.u)

Li	1.2040051	-1.5525714	1.4439632
Li	-0.5005180	-1.0280021	-1.3654104
Li	-1.2415436	-0.5097025	1.1705611
Li	-1.2055867	1.5525661	-1.4412147
Li	0.5008132	1.0287680	1.3628945
Li	1.2402318	0.5072666	-1.1709784
Li	0.0529038	0.4799633	-4.0741786
Li	-0.0481944	-0.4743541	4.0731074
N	-0.4442105	0.5339046	-0.2499435
N	0.4433057	-0.5355906	0.2504818

10

K8-V (SCF= -169.82330 a.u)

Li	1.3328206	0.0000000	1.5112688
Li	1.3328206	0.0000000	-1.5112688
Li	-0.9316237	-1.4825324	2.6193942
Li	-0.9316237	1.4825324	2.6193942
Li	-0.9316237	-1.4825324	-2.6193942
Li	-0.9316237	1.4825324	-2.6193942
Li	-0.8630783	0.0000000	0.0000000
Li	3.9932948	0.0000000	0.0000000
N	-0.4434348	0.0000000	-1.8484496
N	-0.4434348	0.0000000	1.8484496

10

K8-VI (SCF= -169.83797a.u)

Li	-0.5310552	1.1300888	-0.4266775
Li	-0.5310552	-1.1300888	-0.4266775
Li	-1.1562671	0.0000000	2.2820744
Li	1.2106097	0.0000000	2.4205015
Li	-1.5117608	0.0000000	-2.9151534
Li	1.3251684	0.0000000	-0.4865848
Li	1.1606300	0.0000000	-3.2983404

Li	-0.1830720	0.0000000	5.1889977
N	-0.0143378	0.0000000	-1.9794947
N	0.1072531	0.0000000	0.9774347

10

K8-VII (SCF=-169.85037 a.u)

Li	1.1267588	0.0912348	0.2193658
Li	-1.1267588	-0.0912348	0.2193658
Li	-0.1761151	2.1707015	1.2474388
Li	-0.2347213	2.8737024	-1.4648897
Li	0.2347213	-2.8737024	-1.4648897
Li	0.1761151	-2.1707015	1.2474388
Li	0.0000000	0.0000000	-1.6580874
Li	0.0000000	0.0000000	3.5499319
N	0.1198914	-1.4800966	-0.4062159
N	-0.1198914	1.4800966	-0.4062159

10

K8-VIII (SCF= -169.87342 a.u)

N	-0.1058159	-0.2155314	1.6208147
N	-0.1058159	0.2155314	-1.6208147
Li	-0.2927681	1.0393870	0.1588228
Li	1.6796918	-0.5314152	1.5971582
Li	1.6796918	0.5314152	-1.5971582
Li	-0.2927681	-1.0393870	-0.1588228
Li	-0.9580375	1.5230074	-2.4880986
Li	-0.9580375	-1.5230074	2.4880986
Li	-0.1819822	-1.0787741	-2.8639313
Li	-0.1819822	1.0787741	2.8639313

10

K8-IX (SCF= -169.88442 a.u)

Li	0.1484956	-1.3118931	0.1907993
Li	0.2178405	0.7243390	1.0757470
Li	2.8789949	-1.2972004	-0.0681596
Li	-2.3048751	-0.9209200	-1.2439379
Li	0.2371363	0.4381937	-1.2017025
Li	2.6364227	1.4347773	-0.0636444
Li	-2.1611416	1.6099290	-0.2000327
Li	-2.3308894	-0.5682175	1.4449793
N	-1.3492756	-0.0104935	0.0134653
N	1.6398539	-0.0362242	0.0147996