Supplementary Material

An *ab initio* investigation of alkali-metal non-covalent bonds B□LiR and B□NaR (R = F, H or CH_3) formed with simple Lewis bases B: The relative inductive effects of F, H and CH_3

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Table S1. Electronic energy (hartree) and optimized geometry (Å) at CCSD(T)/aug-cc-pVTZ computational level.

LiF	CCSD(T)/AVTZ ENERGY=-107.27525748		
	Li 0.0000000000	0.0000000000	-1.1652414625
	F 0.0000000000	0.0000000000	0.4257168874
OC···LiF	CCSD(T)/AVTZ ENERGY=-220.44912618		
	Li 0.0000000000	0.0000000000	0.9692965310
	F 0.0000000000	0.0000000000	2.5701576294
	C 0.0000000000	0.0000000000	-1.3381140958
	O 0.0000000000	0.0000000000	-2.4678856228
H_3P···LiF	CCSD(T)/AVTZ ENERGY=-449.98672970		
	Li -0.0000000000	0.0000000000	1.0285715779
	F -0.0000000000	0.0000000000	2.6345376154
	P 0.0000000000	0.0000000000	-1.6185730671
	H 1.2169209394	0.0000000000	-2.3341432148
	H -0.6084604697	-1.0538844479	-2.3341432148
	H -0.6084604697	1.0538844479	-2.3341432148
HCN···LiF	CCSD(T)/AVTZ ENERGY=-200.58144784		
	Li 0.0000000000	0.0000000000	0.7804484768
	F 0.0000000000	0.0000000000	2.3935177111
	N 0.0000000000	0.0000000000	-1.2867237442
	C 0.0000000000	0.0000000000	-2.4417905219
	H 0.0000000000	0.0000000000	-3.5111291480
H_2O···LiF	CCSD(T)/AVTZ ENERGY=-183.64375175		
	Li 0.0000000000	0.0000000000	0.1319172489
	F 0.0000000000	0.0000000000	1.7450488548
	O 0.0000000000	0.0000000000	-1.8261153977
	H 0.7661889844	0.0000000000	-2.4069033520
	H -0.7661889844	0.0000000000	-2.4069033520
H_3N···LiF	CCSD(T)/AVTZ ENERGY=-163.78729891		
	Li -0.0000000000	0.0000000000	0.1352918380
	F -0.0000000000	0.0000000000	1.7521609068
	N 0.0000000000	0.0000000000	-1.9397954536
	H 0.9366797533	0.0000000000	-2.3338646797
	H -0.4683398766	-0.8111884616	-2.3338646797
	H -0.4683398766	0.8111884616	-2.3338646797
LiH	CCSD(T)/AVTZ ENERGY=-8.02317396		
	Li 0.0000000000	0.0000000000	-0.2042051717
	H 0.0000000000	0.0000000000	1.4062226885
OC···LiH	CCSD(T)/AVTZ ENERGY=-121.19676288		
	Li 0.0000000000	0.0000000000	2.2592144340
	H 0.0000000000	0.0000000000	3.8779795090
	C 0.0000000000	0.0000000000	-0.0540531070
	O 0.0000000000	0.0000000000	-1.1838410305
H_3P···LiH	CCSD(T)/AVTZ ENERGY=-350.73440617		
	Li -0.0000000000	0.0000000000	2.1593808975
	H -0.0000000000	0.0000000000	3.7856040794
	P 0.0000000000	0.0000000000	-0.4895183931
	H 1.2174636504	0.0000000000	-1.2043373492

	H	-0.6087318252	-1.0543544494	-1.2043373492
	H	-0.6087318252	1.0543544494	-1.2043373492
$H_2S\cdots LiH$	CCSD(T)/AVTZ ENERGY=-406.97951133			
	Li	0.0000000000	0.1251399606	2.0388704669
	H	0.0000000000	-0.5572722859	3.5139351001
	S	0.0000000000	0.0459567692	-0.5177832966
	H	0.9711190506	-0.8831247193	-0.5424445729
	H	-0.9711190506	-0.8831247193	-0.5424445729
HCN···LiH	CCSD(T)/AVTZ ENERGY=-101.32915362			
	Li	0.0000000000	0.0000000000	2.0069461429
	H	0.0000000000	0.0000000000	3.6406692255
	N	0.0000000000	0.0000000000	-0.0549310634
	C	0.0000000000	0.0000000000	-1.2099684571
	H	0.0000000000	0.0000000000	-2.2793571576
$H_2O\cdots LiH$	CCSD(T)/AVTZ ENERGY=-84.39195836			
	Li	0.0000000000	0.0000000000	1.3307976868
	H	0.0000000000	0.0000000000	2.9641555130
	O	0.0000000000	0.0000000000	-0.6136884726
	H	0.7669612640	0.0000000000	-1.1935781411
	H	-0.7669612640	0.0000000000	-1.1935781411
$H_3N\cdots LiH$	CCSD(T)/AVTZ ENERGY=-64.53550029			
	Li	-0.0000000000	0.0000000000	1.3880334850
	H	-0.0000000000	0.0000000000	3.0259757564
	N	0.0000000000	0.0000000000	-0.6749652792
	H	0.9371459150	0.0000000000	-1.0682865540
	H	-0.4685729575	-0.8115921695	-1.0682865540
	H	-0.4685729575	0.8115921695	-1.0682865540
$LiCH_3$	CCSD(T)/AVTZ ENERGY=-47.27208228			
	Li	-0.0000000000	0.0000000000	-1.4175657655
	C	-0.0000000000	0.0000000000	0.5687417248
	H	1.0145143700	0.0000000000	0.9948234755
	H	-0.5072571850	0.8785952169	0.9948234755
	H	-0.5072571850	-0.8785952169	0.9948234755
$OC\cdots LiCH_3$	CCSD(T)/AVTZ ENERGY=-160.44558108			
	Li	-0.0000000000	0.0000000000	1.0331338534
	C	-0.0000000000	0.0000000000	3.0260766583
	H	1.0135841568	0.0000000000	3.4566773981
	H	-0.5067920784	0.8777896287	3.4566773981
	H	-0.5067920784	-0.8777896287	3.4566773981
	C	0.0000000000	0.0000000000	-1.2813618895
	O	0.0000000000	0.0000000000	-2.4112855116
$H_3P\cdots LiCH_3$	CCSD(T)/AVTZ ENERGY=-389.98301098			
	Li	-0.0000000000	0.0000000000	1.0890103056
	C	-0.0000000000	0.0000000000	3.0886053502
	H	1.0137062244	0.0000000000	3.5196602321
	H	-0.5068531122	0.8778953423	3.5196602321
	H	-0.5068531122	-0.8778953423	3.5196602321
	P	0.0000000000	0.0000000000	-1.5628303113

	H	-1.2167538347	0.0000000000	-2.2792849483
	H	0.6083769173	-1.0537397310	-2.2792849483
	H	0.6083769173	1.0537397310	-2.2792849483
$H_2S\cdots LiCH_3$	CCSD(T)/AVTZ ENERGY=-446.22809094			
	Li	0.0000000000	0.4153089743	0.9946050256
	C	0.0000000000	-0.0867715928	2.9294577136
	H	0.0000000000	0.7860513191	3.6013915573
	H	-0.8778156965	-0.6856282951	3.2195011220
	H	0.8778156965	-0.6856282951	3.2195011220
	S	0.0000000000	0.0180769348	-1.5366521190
	H	0.9712916342	-0.9078619355	-1.4605619751
	H	-0.9712916342	-0.9078619355	-1.4605619751
$HCN\cdots LiCH_3$	CCSD(T)/AVTZ ENERGY=-140.57749123			
	Li	-0.0000000000	0.0000000000	0.8261881908
	C	-0.0000000000	0.0000000000	2.8338245296
	H	1.0137452568	0.0000000000	3.2656282412
	H	-0.5068726284	0.8779291453	3.2656282412
	H	-0.5068726284	-0.8779291453	3.2656282412
	N	0.0000000000	0.0000000000	-1.2406577349
	C	0.0000000000	0.0000000000	-2.3958019466
	H	0.0000000000	0.0000000000	-3.4652983011
$H_2O\cdots LiCH_3$	CCSD(T)/AVTZ ENERGY=-123.64024509			
	Li	0.0000000000	-0.0136451590	0.1193074966
	C	0.0000000000	0.0030310992	2.1276057558
	H	0.0000000000	1.0206056606	2.5495663061
	H	-0.8781807448	-0.5003955712	2.5621962077
	H	0.8781807448	-0.5003955712	2.5621962077
	O	0.0000000000	-0.0012970471	-1.8289955598
	H	0.7667866177	0.0293096048	-2.4083003257
	H	-0.7667866177	0.0293096048	-2.4083003257
$H_3N\cdots LiCH_3$	CCSD(T)/AVTZ ENERGY=-103.78362601			
	Li	0.0000000000	0.0000000000	0.1240565508
	C	0.0000000000	0.0000000000	2.1367198396
	H	-1.0139693058	0.0000000000	2.5678128753
	H	0.5069846529	-0.8781231774	2.5678128753
	H	0.5069846529	0.8781231774	2.5678128753
	N	-0.0000000000	0.0000000000	-1.9436505379
	H	0.9372317875	0.0000000000	-2.3366775970
	H	-0.4686158937	0.8116665372	-2.3366775970
	H	-0.4686158937	-0.8116665372	-2.3366775970

NaF	CCSD(T)/AVTZ ENERGY=-261.66313843			
	Na	0.0000000000	0.0000000000	-0.9033193067
	F	0.0000000000	0.0000000000	1.0931023914
OC···NaF	CCSD(T)/AVTZ ENERGY=-374.74700415			
	Na	0.0000000000	0.0000000000	0.8277404004
	F	0.0000000000	0.0000000000	2.7901444997
	C	0.0000000000	0.0000000000	-1.9290924670

	O 0.0000000000 0.0000000000 -3.0543401630
$H_3P\cdots NaF$ (I)	CCSD(T)/AVTZ ENERGY=-604.36997406 Na -0.0000000000 0.0000000000 0.9015934187 F -0.0000000000 0.0000000000 2.9146691495 P 0.0000000000 0.0000000000 -2.1737264899 H 1.2116074723 0.0000000000 -2.9013295471 H -0.6058037362 -1.0492828504 -2.9013295471 H -0.6058037362 1.0492828504 -2.9013295471
$H_3P\cdots NaF$ (II)	CCSD(T)/AVTZ ENERGY=-604.37400428 Na -0.8032241706 -1.5198022704 0.0000000000 F 1.1705758514 -1.0056260520 0.0000000000 P -0.1769877874 1.3418754856 0.0000000000 H 0.7478266111 1.4585173949 1.0550641415 H -0.5739771156 2.7093480471 0.0000000000 H 0.7478266111 1.4585173949 -1.0550641415
$H_2S\cdots NaF$	
HCN···NaF (I)	CCSD(T)/AVTZ ENERGY=-354.96316663 Na 0.0000000000 0.0000000000 0.6492267800 F 0.0000000000 0.0000000000 2.6703055601 N 0.0000000000 0.0000000000 -1.8323988708 C 0.0000000000 0.0000000000 -2.9889966318 H 0.0000000000 0.0000000000 -4.0582625690
HCN···NaF (II)	CCSD(T)/AVTZ ENERGY=-354.97103720 Na -0.8091143189 0.8898654447 0.0000000000 F 1.2924483940 1.0336017024 0.0000000000 N -0.4232204371 -2.0397734662 0.0000000000 C 0.5459058835 -1.3912220682 0.0000000000 H 1.2376098186 -0.4877751328 0.0000000000
$H_2O\cdots NaF$ (I)	CCSD(T)/AVTZ ENERGY=-338.02318343 Na 0.0000000000 0.0000000000 0.1277719809 F 0.0000000000 0.0000000000 2.1503380107 O 0.0000000000 0.0000000000 -2.3649309261 H 0.7654782807 0.0000000000 -2.9530400518 H -0.7654782807 0.0000000000 -2.9530400518
$H_2O\cdots NaF$ (II)	CCSD(T)/AVTZ ENERGY=-338.04080713 Na 1.4114384506 0.9838406068 -0.0952813994 F -0.5395163558 1.5489677771 0.4819927000 O -0.0858813570 -0.7483741585 -0.2501915541 H -0.5508891754 0.0983969852 0.0686058292 H -0.7410415624 -1.3022012106 -0.6751255756
$H_3N\cdots NaF$ (I)	CCSD(T)/AVTZ ENERGY=-318.16587806 Na -0.0000000000 0.0000000000 0.0902732978 F -0.0000000000 0.0000000000 2.1158292253 N 0.0000000000 0.0000000000 -2.4115069673 H 0.9351320001 0.0000000000 -2.8095236078 H -0.4675660001 -0.8098480680 -2.8095236078 H -0.4675660001 0.8098480680 -2.8095236078
$H_3N\cdots NaF$ (II)	CCSD(T)/AVTZ ENERGY=-318.17219053 Na 0.7479428299 1.6995237738 0.0000000000

	F	-1.3241378419	1.7323740171	0.0000000000
	N	0.0433671879	-0.6265506398	0.0000000000
	H	-0.7734267064	0.0121464004	0.0000000000
	H	-0.0399727347	-1.2318667757	0.8100075974
	H	-0.0399727347	-1.2318667757	-0.8100075974
NaH	CCSD(T)/AVTZ ENERGY=-162.42854909			
	Na	0.0000000000	0.0000000000	-0.0809387306
	H	0.0000000000	0.0000000000	1.8461133219
OC···NaH	CCSD(T)/AVTZ ENERGY=-275.50970294			
	Na	0.0000000000	0.0000000000	1.8282870880
	H	0.0000000000	0.0000000000	3.7447979349
	C	0.0000000000	0.0000000000	-0.9922717079
	O	0.0000000000	0.0000000000	-2.1181076428
H_3P···NaH	CCSD(T)/AVTZ ENERGY=-505.13384720			
	Na	-0.0000000000	0.0000000000	1.8346336718
	H	-0.0000000000	0.0000000000	3.7785138290
	P	0.0000000000	0.0000000000	-1.2876324758
	H	1.2103452282	0.0000000000	-2.0185389373
	H	-0.6051726141	-1.0481897149	-2.0185389373
	H	-0.6051726141	1.0481897149	-2.0185389373
H_2S···NaH	CCSD(T)/AVTZ ENERGY=-561.37866103			
	Na	0.0000000000	0.0554897066	1.7533742867
	H	0.0000000000	-0.8415615408	3.4775807313
	S	0.0000000000	0.0421260336	-1.2802924501
	H	0.9705576493	-0.8820061835	-1.3735321336
	H	-0.9705576493	-0.8820061835	-1.3735321336
HCN···NaH	CCSD(T)/AVTZ ENERGY=-255.72627649			
	Na	0.0000000000	0.0000000000	1.6057441721
	H	0.0000000000	0.0000000000	3.5599617413
	N	0.0000000000	0.0000000000	-0.9015814073
	C	0.0000000000	0.0000000000	-2.0584047746
	H	0.0000000000	0.0000000000	-3.1275758493
H_2O···NaH (I)	CCSD(T)/AVTZ ENERGY=-238.78677928			
	Na	0.0000000000	0.0000000000	1.0557401596
	H	0.0000000000	0.0000000000	3.0140759017
	O	0.0000000000	0.0000000000	-1.4501299999
	H	0.7655389735	0.0000000000	-2.0378862621
	H	-0.7655389735	0.0000000000	-2.0378862621
H_2O···NaH (II)	CCSD(T)/AVTZ ENERGY=-238.79427059			
	Na	1.3852359632	1.0178461592	-0.0811924683
	H	-0.4870544721	1.5736037691	0.4827727733
	O	-0.0902971381	-0.7598453618	-0.2556779210
	H	-0.5667852343	0.0684025328	0.0630475693
	H	-0.7469891187	-1.3193770993	-0.6789499533
H_3N···NaH	CCSD(T)/AVTZ ENERGY=-218.92917091			
	Na	-0.0000000000	0.0000000000	1.0258168819
	H	-0.0000000000	0.0000000000	2.9835595738
	N	0.0000000000	0.0000000000	-1.4908969199

	H	0.9356650524	0.0000000000	-1.8877139139
	H	-0.4678325262	-0.8103097048	-1.8877139139
	H	-0.4678325262	0.8103097048	-1.8877139139
$NaCH_3$	CCSD(T)/AVTZ ENERGY=-201.67349521			
	Na	-0.0000000000	0.0000000000	-0.9597213301
	C	-0.0000000000	0.0000000000	1.3884720148
	H	1.0244149501	0.0000000000	1.7815008712
	H	-0.5122074750	0.8871693708	1.7815008712
	H	-0.5122074750	-0.8871693708	1.7815008712
$OC\cdots NaCH_3$	CCSD(T)/AVTZ ENERGY=-314.75423543			
	Na	-0.0000000000	0.0000000000	0.9274219125
	C	-0.0000000000	0.0000000000	3.2629201498
	H	1.0207875727	0.0000000000	3.6691618468
	H	-0.5103937864	0.8840279699	3.6691618468
	H	-0.5103937864	-0.8840279699	3.6691618468
	C	0.0000000000	0.0000000000	-1.9132725647
	O	0.0000000000	0.0000000000	-3.0392900868
$H_3P\cdots NaCH_3$	CCSD(T)/AVTZ ENERGY=-544.37830054			
	Na	-0.0000000000	0.0000000000	1.0015877140
	C	-0.0000000000	0.0000000000	3.3614407281
	H	1.0212521626	0.0000000000	3.7673210990
	H	-0.5106260813	0.8844303165	3.7673210990
	H	-0.5106260813	-0.8844303165	3.7673210990
	P	0.0000000000	0.0000000000	-2.1347917648
	H	-1.2097470478	0.0000000000	-2.8671733265
	H	0.6048735239	-1.0476716755	-2.8671733265
	H	0.6048735239	1.0476716755	-2.8671733265
$H_2S\cdots NaCH_3$	CCSD(T)/AVTZ ENERGY=-600.62312227			
	Na	0.0000000000	0.3896132785	0.9380424058
	C	0.0000000000	-0.3151072872	3.1901591805
	H	0.0000000000	0.5385204009	3.8821460843
	H	-0.8844944306	-0.9235599599	3.4246395684
	H	0.8844944306	-0.9235599599	3.4246395684
	S	0.0000000000	-0.0581690550	-2.0765832475
	H	0.9705196433	-0.9864267823	-2.0456848974
	H	-0.9705196433	-0.9864267823	-2.0456848974
$HCN\cdots NaCH_3$	CCSD(T)/AVTZ ENERGY=-294.97047050			
	Na	-0.0000000000	0.0000000000	0.7275014709
	C	-0.0000000000	0.0000000000	3.0958715289
	H	1.0201485234	0.0000000000	3.5066125428
	H	-0.5100742617	0.8834745369	3.5066125428
	H	-0.5100742617	-0.8834745369	3.5066125428
	N	0.0000000000	0.0000000000	-1.7899077251
	C	0.0000000000	0.0000000000	-2.9468378402
	H	0.0000000000	0.0000000000	-4.0159906079
$H_2O\cdots NaCH_3$	CCSD(T)/AVTZ ENERGY=-278.03072750			
	Na	0.0000000000	0.0000227999	0.1800354548
	C	0.0000000000	-0.0000457555	2.5568484800

	H	0.0000000000	1.0213405071	2.9634587656
	H	-0.8845566069	-0.5107564776	2.9634145747
	H	0.8845566069	-0.5107564776	2.9634145747
	O	0.0000000000	0.0002517540	-2.3660240174
	H	0.7664063787	-0.0018992669	-2.9541501431
	H	-0.7664063787	-0.0018992669	-2.9541501431
$H_3N\cdots NaCH_3$	CCSD(T)/AVTZ ENERGY=-258.17327043			
	Na	-0.0000000000	0.0000000000	0.1322879591
	C	-0.0000000000	0.0000000000	2.5048378543
	H	1.0203684724	0.0000000000	2.9148245064
	H	-0.5101842362	0.8836650183	2.9148245064
	H	-0.5101842362	-0.8836650183	2.9148245064
	N	0.0000000000	0.0000000000	-2.3922806542
	H	0.9357790943	0.0000000000	-2.7888030953
	H	-0.4678895472	-0.8104084680	-2.7888030953
	H	-0.4678895472	0.8104084680	-2.7888030953

Correlating the 2s2p on Na (aug-cc-pwCVTZ on Na, aug-cc-pVTZ elsewhere)

NaF	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-261.92565184			
	Na	0.0000000000	0.0000000000	-0.8757052475
	F	0.0000000000	0.0000000000	1.0596867499
OC⋯NaF	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-375.09608803			
	Na	0.0000000000	0.0000000000	0.8080213003
	F	0.0000000000	0.0000000000	2.7511063463
	C	0.0000000000	0.0000000000	-1.8968378512
	O	0.0000000000	0.0000000000	-3.0278375253
$H_3P\cdots NaF$ (I)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-604.63335864			
	Na	-0.0000000000	0.0000000000	0.8936727711
	F	-0.0000000000	0.0000000000	2.8416386961
	P	0.0000000000	0.0000000000	-2.1276344567
	H	1.2119515730	0.0000000000	-2.8543978093
	H	-0.6059757865	-1.0495808504	-2.8543978093
	H	-0.6059757865	1.0495808504	-2.8543978093
$H_3P\cdots NaF$ (II)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-604.63377724			
	Na	0.9211713273	1.3140248764	0.0000000000
	F	-1.0234891092	1.5487305927	0.0000000000
	P	0.0335620991	-1.4925457463	0.0000000000
	H	-1.3176860255	-1.0944534211	0.0000000000
	H	-0.0559176609	-2.4459372209	1.0431592755
	H	-0.0559176609	-2.4459372209	-1.0431592755
$H_2S\cdots NaF$				
HCN⋯NaF (I)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-355.22670513			
	Na	0.0000000000	0.0000000000	0.6309753237
	F	0.0000000000	0.0000000000	2.5852692299
	N	0.0000000000	0.0000000000	-1.7980288392
	C	0.0000000000	0.0000000000	-2.9544784427
	H	0.0000000000	0.0000000000	-4.0238630031
HCN⋯NaF	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-355.23276263			

(II)	Na 1.0138087574 0.8023316576 0.0000000000 F -0.9293148509 1.2431670916 0.0000000000 N 0.4096795531 -1.6776708683 0.0000000000 C -0.6739525851 -1.2562935156 0.0000000000 H -1.6121046945 -0.7327094152 0.0000000000
$H_2O\cdots NaF$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-338.28797965 Na 0.0000000000 0.0000000000 0.0378910258 F 0.0000000000 0.0000000000 1.9912530417 O 0.0000000000 0.0000000000 -2.2826254074 H 0.7620340642 0.0000000000 -2.8697098491 H -0.7620340642 0.0000000000 -2.8697098491
$H_2O\cdots NaF$ (II)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-338.30408428 Na 1.3524825900 0.9669046861 -0.0871610555 F -0.5057822353 1.5518067123 0.4812809968 O -0.0758591367 -0.7345855123 -0.2595742369 H -0.5516134454 0.1039437933 0.0634922974 H -0.7251177726 -1.3074396793 -0.6680380018
$H_3N\cdots NaF$ (I)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-318.42958739 Na -0.0000000000 0.0000000000 0.0982989129 F -0.0000000000 0.0000000000 2.0550936793 N 0.0000000000 0.0000000000 -2.3545921535 H 0.9351490084 0.0000000000 -2.7525818079 H -0.4675745042 -0.8098627976 -2.7525818079 H -0.4675745042 0.8098627976 -2.7525818079
$H_3N\cdots NaF$ (II)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-318.43565312 Na 0.6978945702 1.6676793672 0.0000000000 F -1.2969106325 1.7495836156 0.0000000000 N 0.0459613106 -0.6181426804 0.0000000000 H -0.7825847494 0.0037589276 0.0000000000 H -0.0252902494 -1.2245646150 0.8101281942 H -0.0252902494 -1.2245646150 -0.8101281942
NaH	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-162.68986318 Na 0.0000000000 0.0000000000 -0.0794754940 H 0.0000000000 0.0000000000 1.8127386872
$OC\cdots NaH$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-275.85858233 Na 0.0000000000 0.0000000000 1.8062117153 H 0.0000000000 0.0000000000 3.7094394444 C 0.0000000000 0.0000000000 -0.9695767125 O 0.0000000000 0.0000000000 -2.1011970243
$H_3P\cdots NaH$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-505.39557140 Na -0.0000000000 0.0000000000 1.8097272264 H -0.0000000000 0.0000000000 3.7199438508 P 0.0000000000 0.0000000000 -1.2690375450 H 1.2102594559 0.0000000000 -2.0001263943 H -0.6051297279 -1.0481154339 -2.0001263943 H -0.6051297279 1.0481154339 -2.0001263943
$H_2S\cdots NaH$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-561.64040744 Na 0.0000000000 0.0528783578 1.7284576390

	H 0.0000000000 -0.8015276105 3.4367055737
	S 0.0000000000 0.0427283589 -1.2624488384
	H 0.9704686382 -0.8818215315 -1.3527153294
	H -0.9704686382 -0.8818215315 -1.3527153294
HCN···NaH	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-255.98804493
	Na 0.0000000000 0.0000000000 1.5816516009
	H 0.0000000000 0.0000000000 3.5020136726
	N 0.0000000000 0.0000000000 -0.8789631806
	C 0.0000000000 0.0000000000 -2.0357022145
	H 0.0000000000 0.0000000000 -3.1049492449
H_2O···NaH (I)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-239.04976045
	Na 0.0000000000 0.0000000000 0.9851445500
	H 0.0000000000 0.0000000000 2.9042813272
	O 0.0000000000 0.0000000000 -1.3540069605
	H 0.7623944449 0.0000000000 -1.9407873425
	H -0.7623944449 0.0000000000 -1.9407873425
H_2O···NaH (II)	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-239.05595329
	Na 1.3445856908 0.9860335098 -0.0800730240
	H -0.4647746112 1.5945900279 0.4931957225
	O -0.0811792818 -0.7378748448 -0.2738229394
	H -0.5780028195 0.0709894205 0.0542715977
	H -0.7265189784 -1.3331081134 -0.6635713569
H_3N···NaH	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-219.19103970
	Na -0.0000000000 0.0000000000 1.0089950272
	H -0.0000000000 0.0000000000 2.9333817479
	N 0.0000000000 0.0000000000 -1.4652518370
	H 0.9357330485 0.0000000000 -1.8618837970
	H -0.4678665242 -0.8103685911 -1.8618837970
	H -0.4678665242 0.8103685911 -1.8618837970
$NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-201.93580686
	Na -0.0000000000 0.0000000000 -0.9438146583
	C -0.0000000000 0.0000000000 1.3647729630
	H 1.0249824474 0.0000000000 1.7546993026
	H -0.5124912237 0.8876608379 1.7546993026
	H -0.5124912237 -0.8876608379 1.7546993026
OC···$NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-315.10410955
	Na -0.0000000000 0.0000000000 0.9140018888
	C -0.0000000000 0.0000000000 3.2295670098
	H 1.0216314430 0.0000000000 3.6324283775
	H -0.5108157215 0.8847587830 3.6324283775
	H -0.5108157215 -0.8847587830 3.6324283775
	C 0.0000000000 0.0000000000 -1.8806751560
	O 0.0000000000 0.0000000000 -3.0124967582
H_3P···$NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-544.64098583
	Na -0.0000000000 0.0000000000 0.9894825645
	C -0.0000000000 0.0000000000 3.3110239486
	H 1.0215044223 0.0000000000 3.7150573914
	H -0.5107522112 0.8846487798 3.7150573914

	H	-0.5107522112	-0.8846487798	3.7150573914
	P	0.0000000000	0.0000000000	-2.1041092077
	H	-1.2095586030	0.0000000000	-2.8369024373
	H	0.6047793015	-1.0475084776	-2.8369024373
	H	0.6047793015	1.0475084776	-2.8369024373
$H_2S\cdots NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-600.88583376			
	Na	0.0000000000	0.3281849899	0.9250553179
	C	0.0000000000	-0.2650899898	3.1690293823
	H	0.0000000000	0.6193546659	3.8204114784
	H	-0.8846972655	-0.8620842326	3.4287400031
	H	0.8846972655	-0.8620842326	3.4287400031
	S	0.0000000000	-0.0403573019	-2.0568040304
	H	0.9705733929	-0.9690534968	-2.0594760681
	H	-0.9705733929	-0.9690534968	-2.0594760681
$HCN\cdots NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-295.23321250			
	Na	-0.0000000000	0.0000000000	0.7169002387
	C	-0.0000000000	0.0000000000	3.0469815954
	H	1.0203076778	0.0000000000	3.4562495992
	H	-0.5101538389	0.8836123687	3.4562495992
	H	-0.5101538389	-0.8836123687	3.4562495992
	N	0.0000000000	0.0000000000	-1.7535654276
	C	0.0000000000	0.0000000000	-2.9104094318
	H	0.0000000000	0.0000000000	-3.9796300934
$H_2O\cdots NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-278.29493128			
	Na	0.0000000000	0.0014776952	0.1286568492
	C	0.0000000000	-0.0010992640	2.4587279473
	H	0.0000000000	1.0195168515	2.8660949007
	H	-0.8842691136	-0.5120812442	2.8644010185
	H	0.8842691136	-0.5120812442	2.8644010185
	O	0.0000000000	-0.0005714796	-2.2186524355
	H	0.7623462884	-0.0034441125	-2.8055336404
	H	-0.7623462884	-0.0034441125	-2.8055336404
$H_3N\cdots NaCH_3$	CCSD(T)/AVTZ,NA=AWCVTZ ENERGY=-258.43608474			
	Na	-0.0000000000	0.0000000000	0.1298188327
	C	-0.0000000000	0.0000000000	2.4646681933
	H	1.0205721825	0.0000000000	2.8730365690
	H	-0.5102860913	0.8838414365	2.8730365690
	H	-0.5102860913	-0.8838414365	2.8730365690
	N	0.0000000000	0.0000000000	-2.3532292844
	H	0.9358407591	0.0000000000	-2.7495742095
	H	-0.4679203796	-0.8104618713	-2.7495742095
	H	-0.4679203796	0.8104618713	-2.7495742095

TableS2. Interatomic distances (Å) in the B···LiR complexes at CCSD(T)/AVTZ level.

Complex	*Li:Base dist.*	*LiF/H/C dist.*
LiF		1.591
OC···LiF	2.307	1.601
H_3P···LiF	2.647	1.606
H_2S···LiF		
HCN···LiF	2.067	1.613
H_2O···LiF	1.958	1.613
H_3N···LiF	2.075	1.617
LiH		1.610
OC···LiH	2.313	1.619
H_3P···LiH	2.649	1.626
H_2S···LiH	2.558	1.625
HCN···LiH	2.062	1.634
H_2O···LiH	1.944	1.633
H_3N···LiH	2.063	1.638
$LiCH_3$		1.986
OC···$LiCH_3$	2.314	1.993
H_3P···$LiCH_3$	2.652	2.000
H_2S···$LiCH_3$	2.562	1.999
HCN···$LiCH_3$	2.067	2.008
H_2O···$LiCH_3$	1.948	2.008
H_3N···$LiCH_3$	2.068	2.013

Table S3 Interatomic distances (Å) in the B···NaR complexes.

Complex	CCSD(T)/AVTZ, standard basis for Na		CCSD(T)/AVTZ*, (2s,2p) basis for Na	
	Na:Base dist.	*NaF/H/C dist.*	*Na:Base dist.*	*NaF/H/C dist.*
NaF		1.996		1.935
OC···NaF	2.758	2.006	2.705	1.943
H_3P···NaF	3.075	2.013	3.021	1.948
H_2S···NaF				
HCN···NaF	2.482	2.021	2.429	1.954
H_2O···NaF	2.493	2.023	2.321	1.953
H_3N···NaF	2.502	2.026	2.453	1.957
NaH		1.927		1.892
OC···NaH	2.816	1.937	2.776	1.903
H_3P···NaH	3.122	1.944	3.079	1.910
H_2S···NaH	3.034	1.944	2.991	1.910
HCN···NaH	2.507	1.954	2.461	1.920
H_2O···NaH	2.506	1.958	2.339	1.919
H_3N···NaH	2.517	1.958	2.474	1.924
$NaCH_3$		2.348		2.309
OC···$NaCH_3$	2.832	2.354	2.795	2.316
H_3P···$NaCH_3$	3.136	2.360	3.094	2.322
H_2S···$NaCH_3$	3.048	2.360	3.005	2.321
HCN···$NaCH_3$	2.517	2.368	2.470	2.330
H_2O···$NaCH_3$	2.546	2.377	2.347	2.330
H_3N···$NaCH_3$	2.525	2.373	2.483	2.334

* the aug-cc-pwCVTZ basis set used for Na.

Table S4 Complete list of D_e^{CBS} values used, Fitted and Residuals

Complex	D_e^{CBS} /kJ mol^{-1}	D_e (Fitted) /kJ mol^{-1}	Residuals /kj mol^{-1}
OC···LiF	27.11	25.63	1.48
H_3P···LiF	37.49	36.66	0.83
HCN···LiF	62.22	62.98	-0.76
H_2O···LiF	68.87	69.04	-0.17
H_3N···LiF	81.76	81.86	-0.10
OC···LiH	28.15	26.75	1.40
H_3P···LiH	38.56	38.26	0.30
H_2S···LiH	40.39	39.81	0.58
HCN···LiH	64.77	65.73	-0.96
H_2O···LiH	71.95	72.06	-0.11
H_3N···LiH	85.43	85.44	-0.01
OC···$LiCH_3$	26.82	25.76	1.06
H_3P···$LiCH_3$	36.84	36.85	-0.01
H_2S···$LiCH_3$	38.74	38.34	0.40
HCN···$LiCH_3$	62.54	63.30	-0.76
H_2O···$LiCH_3$	69.16	69.40	-0.24
H_3N···$LiCH_3$	82.55	82.28	0.27
OC···NaF	19.44	19.97	-0.53
H_3P···NaF	29.25	28.56	0.69
HCN···NaF	50.74	49.07	1.67
H_2O···NaF	53.48	53.80	-0.32
H_3N···NaF	62.63	63.79	-1.16
OC···NaH	14.75	17.26	-2.51
H_3P···NaH	23.6	24.68	-1.08
H_2S···NaH	25.06	25.68	-0.62
HCN···NaH	43.38	42.40	0.98
H_2O···NaH	46.97	46.48	0.49
H_3N···NaH	55.5	55.11	0.39
OC···$NaCH_3$	13.31	16.29	-2.98
H_3P···$NaCH_3$	21.81	23.29	-1.48
H_2S···$NaCH_3$	23.32	24.24	-0.92
HCN···$NaCH_3$	40.9	40.01	0.89
H_2O···$NaCH_3$	44.57	43.87	0.70
H_3N···$NaCH_3$	52.76	52.01	0.75

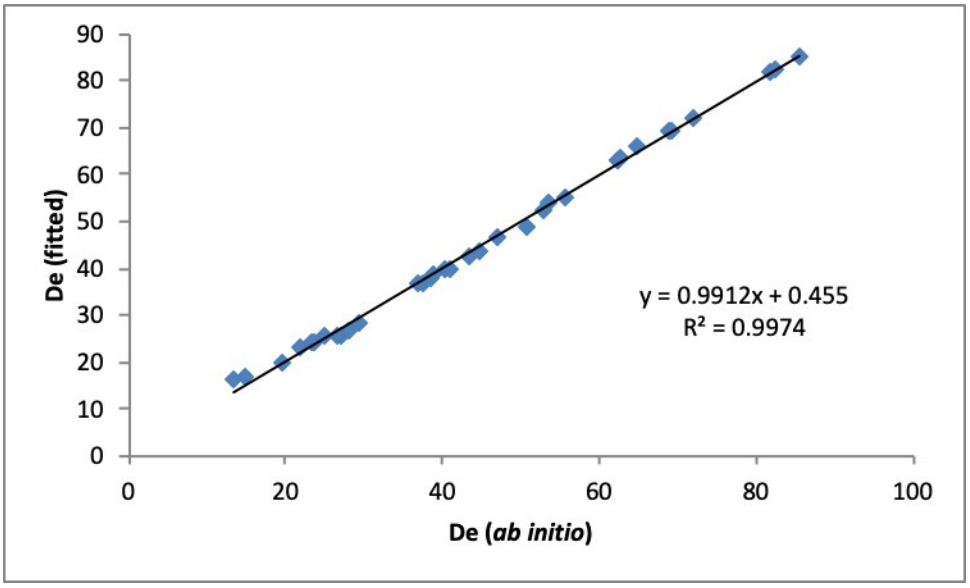
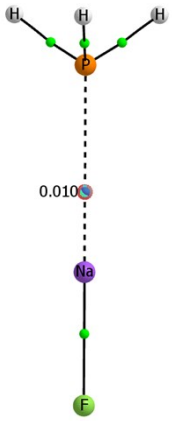
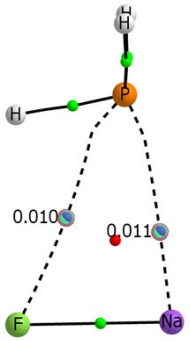
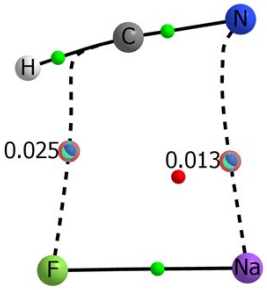
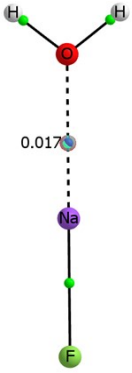
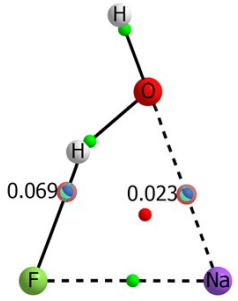
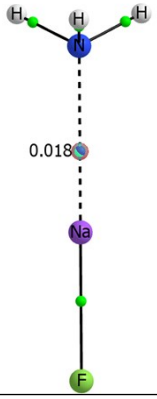
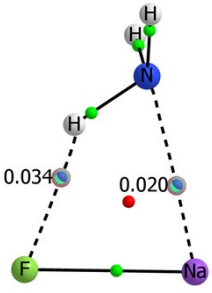


Figure S1. De (*ab initio*) vs. De (fitted) values (Table S5), kJ mol^{-1}.

Figure S2. Molecular graph of H_3P:NaF, HCN:NaF, H_2O:NaF, H_3N:NaF and H_2O:NaH Type I and II complexes.

	Type I	Type II
$H_3P\cdots NaF$		
HCN⋯NaF		
$H_2O\cdots NaF$		
$H_3N\cdots NaF$		

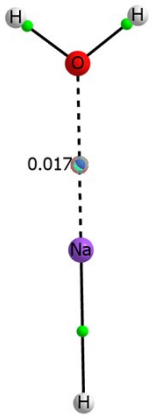
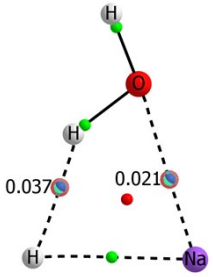
$H_2O\cdots NaH$		

Table S5. SAPT charge transfer [SAPT2+(3)/awCVTZ] terms for Type I and Type II complexes B···NaR at the CCSD(T)/awCVTZ optimised geometry.

Complex	SAPT charge transfer (kJ mol^{-1})	
	Type I	Type II
H_3P···NaF	0.78	–1.09
HCN···NaF	–0.59	–5.38
H_2O···NaF	–0.29	–18.24
H_3N···NaF	0.23	–6.41
H_2O···NaH	–0.72	–17.10

Table S6. SAPT decomposition [SAPT2+(3)δMP2/AVTZ] of the interaction energy (I.E.) calculated for complexes B···LiR at the CCSD(T)/AVTZ geometry. The so-called Chemist's Grouping has been used to group the SAPT terms into electrostatic (E_{elec}), exchange-repulsion (E_{exch}), induction (E_{ind}) and dispersion (E_{disp}).

Complex	SAPT term / (kJ mol^{-1})				
	E_{elec}	E_{exch}	E_{ind}	E_{disp}	I.E.
OC···LiF	–28.02	17.25	–14.42	–1.47	–26.66
H_3P···LiF	–39.79	23.75	–21.12	–1.99	–39.16
H_2S···LiF	---	---	---	---	---
HCN···LiF	–69.83	28.47	–19.14	–1.94	–62.44
H_2O···LiF	–77.69	31.79	–20.21	–1.81	–67.92
H_3N···LiF	–103.12	46.98	–22.67	–2.27	–81.08
OC···LiH	–28.67	18.10	–14.45	–2.06	–27.09
H_3P···LiH	–40.58	25.37	–21.43	–2.94	–39.57
H_2S···LiH	–42.09	26.81	–20.26	–3.64	–39.18
HCN···LiH	–70.54	29.77	–19.85	–2.61	–63.23
H_2O···LiH	–79.66	33.66	–21.31	–2.43	–69.74
H_3N···LiH	–105.86	49.53	–23.51	–3.14	–82.98
OC···$LiCH_3$	–28.05	18.04	–13.42	–2.39	–25.83
H_3P···$LiCH_3$	–39.48	25.10	–20.01	–3.36	–37.75
H_2S···$LiCH_3$	–40.70	26.16	–18.70	–3.97	–37.20
HCN···$LiCH_3$	–68.48	29.18	–18.68	–3.05	–61.03
H_2O···$LiCH_3$	–77.48	33.18	–20.21	–2.82	–67.33
H_3N···$LiCH_3$	–103.01	48.74	–22.28	–3.56	–80.10

Table S7. SAPT decomposition [SAPT2+(3)δMP2/awCVTZ] of the interaction energy (I.E.) calculated for Type I complexes B···NaR at the CCSD(T)/awCVTZ optimised geometry. The so-called Chemist's Grouping has been used to group the SAPT terms into electrostatic (E_{elec}), exchange-repulsion (E_{exch}), induction (E_{ind}) and dispersion (E_{disp}) contributions.

Complex	SAPT term / (kJ mol^{-1})				
	E_{elec}	E_{exch}	E_{ind}	E_{disp}	I.E.
OC···NaF	–20.73	12.74	–7.06	–2.78	–17.83
H_3P···NaF	–33.25	20.31	–12.51	–3.45	–28.90
H_2S···NaF	---	---	---	---	---
HCN···NaF	–58.58	23.38	–9.44	–4.37	–49.02
H_2O···NaF	–62.66	25.62	–9.70	–4.49	–51.23
H_3N···NaF	–81.97	37.60	–9.99	–5.05	–59.41
OC···NaH	–19.79	14.19	–5.59	–3.77	–14.96
H_3P···NaH	–31.11	21.68	–10.34	–4.92	–24.70
H_2S···NaH	–32.75	22.36	–8.87	–5.33	–24.60
HCN···NaH	–55.23	26.73	–8.86	–5.80	–43.17
H_2O···NaH	–60.72	29.77	–9.40	–5.88	–46.22
H_3N···NaH	–78.62	41.11	–9.54	–6.68	–53.73
OC···$NaCH_3$	–19.41	15.43	–4.37	–4.36	–12.72
H_3P···$NaCH_3$	–30.40	22.83	–8.71	–5.73	–22.00
H_2S···$NaCH_3$	–31.99	23.50	–7.26	–6.07	–21.81
HCN···$NaCH_3$	–53.79	28.37	–7.92	–6.67	–40.00
H_2O···$NaCH_3$	–59.37	31.51	–8.45	–6.65	–42.96
H_3N···$NaCH_3$	–76.55	42.46	–8.48	–7.54	–50.11

Table S8. SAPT decomposition [SAPT2+(3)δMP2/awCVTZ] of the interaction energy (I.E.) calculated for Type II complexes B···NaR at the CCSD(T)/awCVTZ optimised geometry. The so-called Chemist's Grouping has been used to group the SAPT terms into electrostatic (E_{elec}), exchange-repulsion (E_{exch}), induction (E_{ind}) and dispersion (E_{disp}) contributions.

Complex	SAPT term / (kJ mol^{-1})				
	E_{elec}	E_{exch}	E_{ind}	E_{disp}	I.E.
H_3P···NaF	–44.67	45.18	–17.92	–12.89	–30.29
HCN···NaF	–109.89	101.86	–38.43	–22.76	–69.22
H_2O···NaF	–189.49	197.42	–79.28	–33.81	–105.17
H_3N···NaF	–136.20	119.49	–36.31	–23.37	–76.39
H_2O···NaH	–156.56	169.44	–55.05	–30.38	–72.55