Supporting Information

Quantifying Electron Correlation of the Chemical Bond

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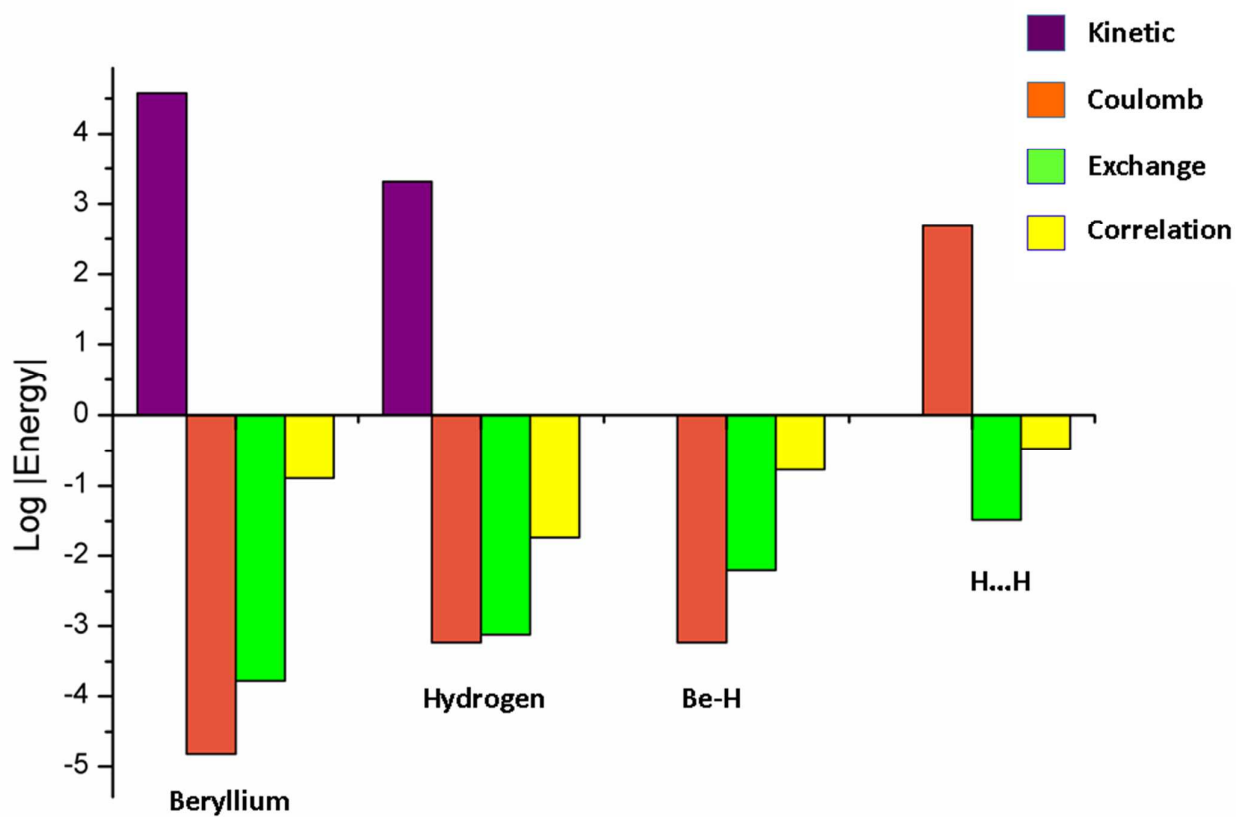# 1. Complete Topologically Partitioned Energy Fingerprints (MP2-IQA).

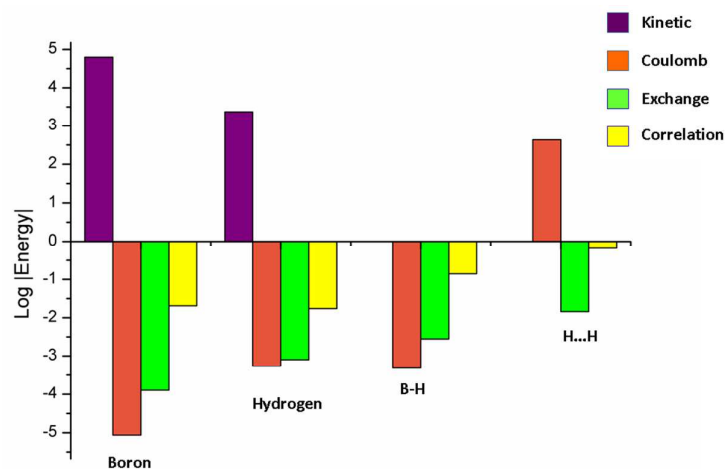**Figure S1.** The complete IQA fingerprint of BeH_2. The error of the total energy reconstruction is 6.9 kJmol^{-1}.

Figure S2. The complete IQA fingerprint of BH_3. The error of the total energy reconstruction is 2.6 kJmol^{-1}.

Figure S3. The complete IQA fingerprint of BH_4^-. The error of the total energy reconstruction is 14.1 kJmol^{-1}.

Figure S4. The difference in IQA energy components between BH_3 and BH_4^-. The energy contributions of BH_3 ("initial system") were subtracted from those of BH_4^- ("final system").

Figure S5. The complete IQA fingerprint of methane. The error of the total energy reconstruction is 3.6 kJmol^{-1}.

Figure S6. The complete IQA fingerprint of ammonia. The error of the total energy reconstruction is 1.3 kJmol^{-1}.
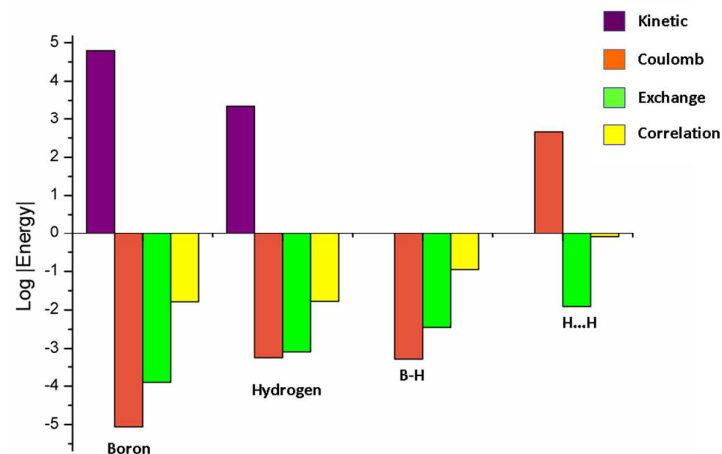

Figure S7. The complete IQA fingerprint of NH_4^+. The error of the total energy reconstruction is 4.6 kJmol^{-1}.
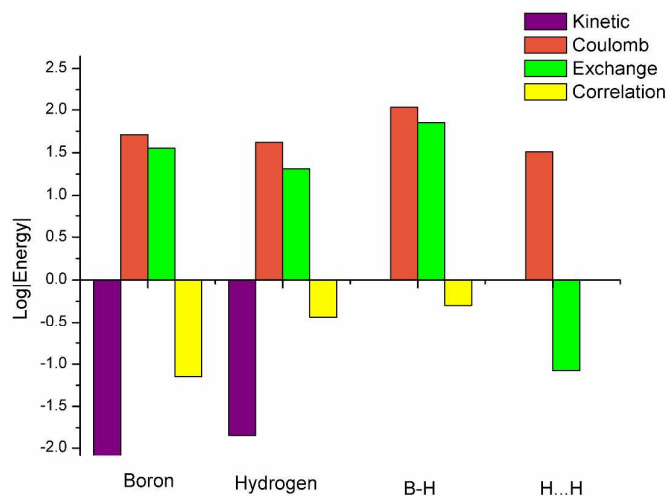

Figure S8. The difference in IQA energy components between NH_3 and NH_4^+. The energy contributions of NH_3 ("initial system") were subtracted from those of NH_4^+ ("final system").
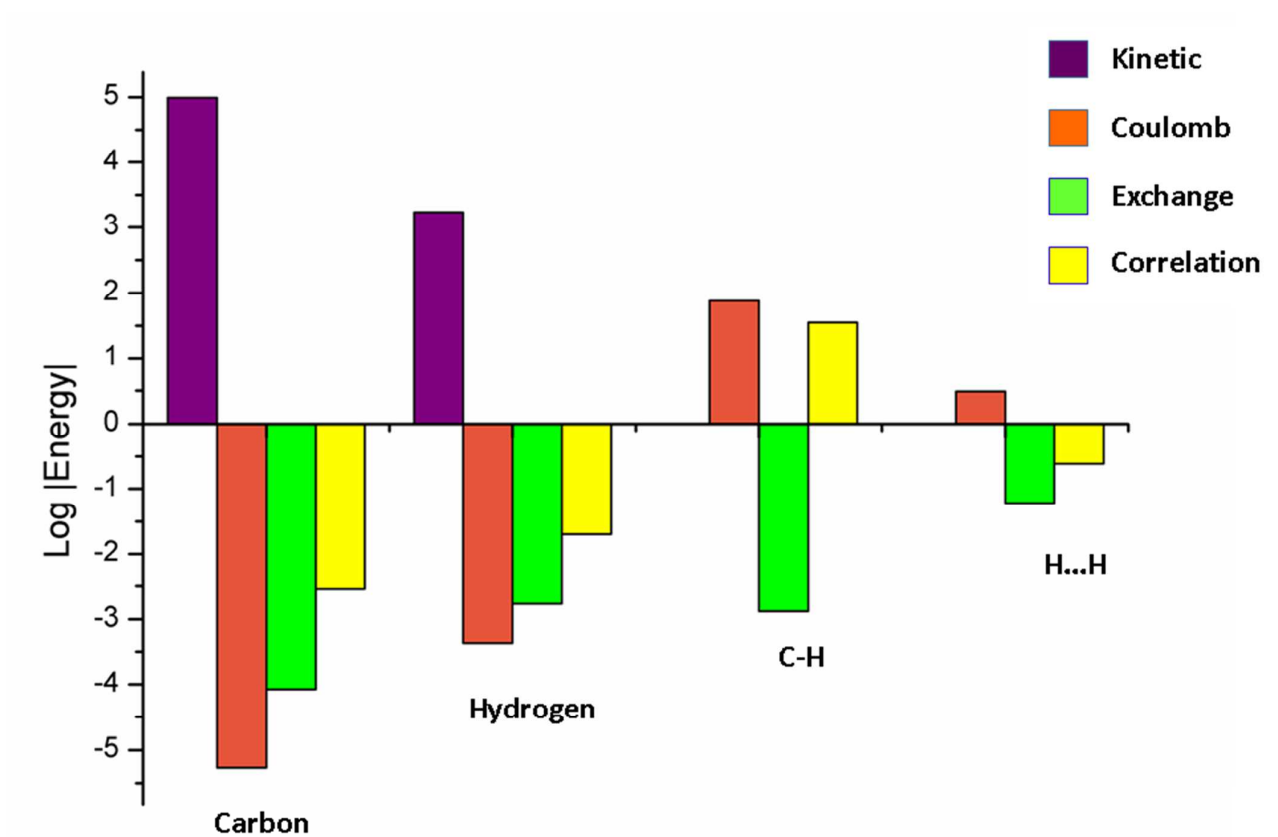
Figure S9. The complete IQA fingerprint of LiH. The error of the total energy reconstruction is 1.4 kJmol^{-1}.
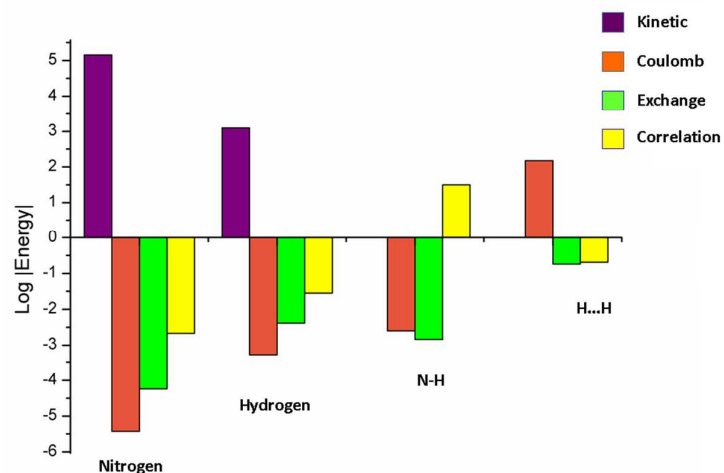

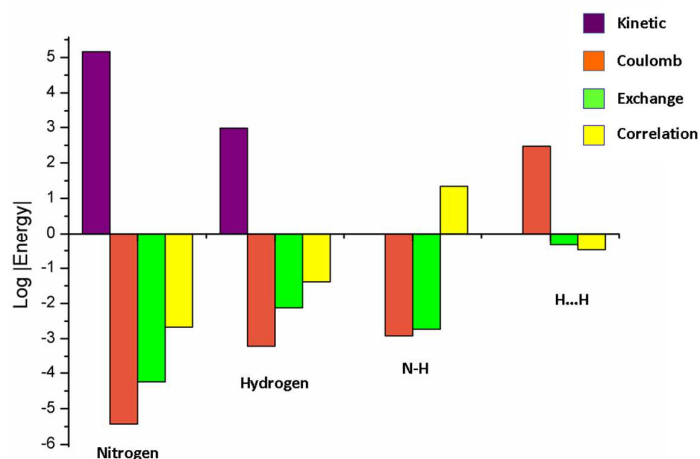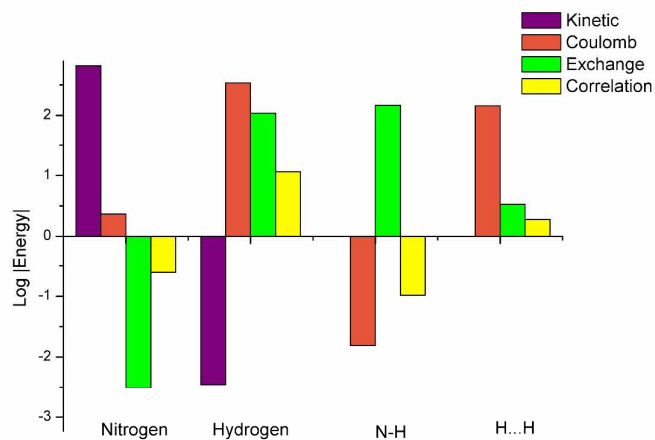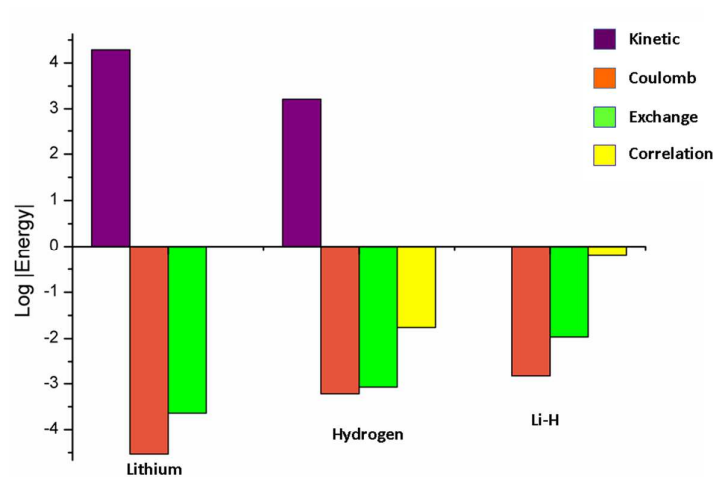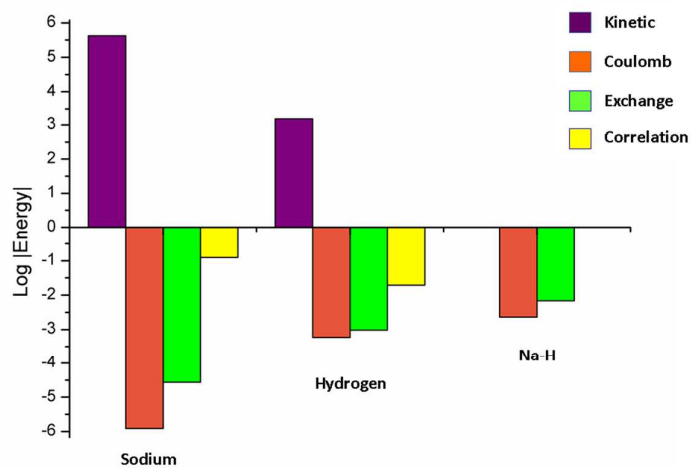**Figure S10.** The complete IQA fingerprint of NaH. The error of the total energy reconstruction is 4.5 kJmol^{-1}.
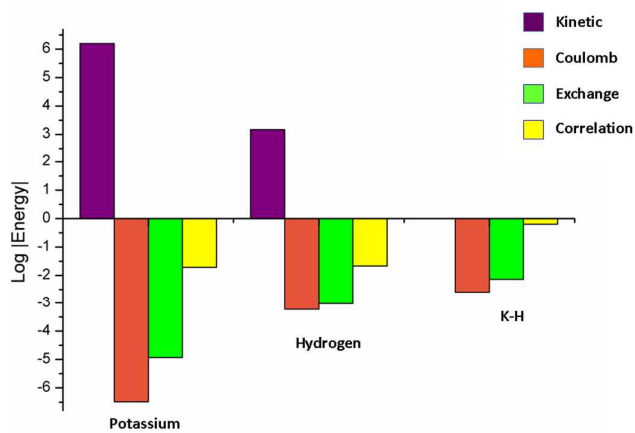

Figure S11. The complete IQA fingerprint of KH. The error of the total energy reconstruction is 1.0 kJmol^{-1}.

2. Methods, Geometries and Results of IQA Correlation Calculations.

Table S1. The molecules or ions studied, along with the level of theory employed, the MORPHY Gauss-Legendre grid and the determined bond correlation energy. The electronic state is singlet unless indicated otherwise by (D) and (T) for doublets and triplets, respectively.

System [MPx-N°cores][a]	Basis Set[b]	Grid[c]	X-Y Bond Correlation[d]
LiH[MP2-1]	6-311G(d,p)	30-15-27	Li-H = -1.6
LiH [MP2-1]	Uncon-6-311++G(2d,2p)+P-	30-15-27	Li-H = -2.1
LiH[MP2-0]	Uncon-6-311++G(2d,2p)+P	30-15-27	Li-H = -4.5
NaH[MP2-0]	6-31G(d,p)	30-15-27	Na-H = -0.1
NaH[MP2-0]	6-31G(d,p)	40-20-36	Na-H = +0.3
NaH[MP2-0]	Uncon-6-31G(d,p)	30-15-27	Na-H = -0.4
NaH[MP2-0]	Uncon-6-31G(d,p)	40-20-36	Na-H = -0.1
KH[MP2-9]	6-31G(d,p)	20-10-18	K-H = +5.3
KH[MP2-5]	6-31G(d,p)	20-10-18	K-H = -1.3
KH[MP2-1]	6-31G(d,p)	20-10-18	K-H = -1.3
KH[MP2-0]	6-31G(d,p)	30-15-27	K-H = -0.9
KH[MP2-9]	Uncon-6-31G(d,p)-SP	30-15-27	K-H = +2.1
KH[MP2-5]	Uncon-6-31G(d,p)-SP	30-15-27	K-H = -1.5
KH[MP2-1]	Uncon-6-31G(d,p)-SP	30-15-27	K-H = -1.5
KH[MP2-0]	Uncon-6-31G(d,p)-SP	40-20-36	K-H = -1.5
BeH_2[MP2-1]	6-31G(d,p)	40-20-36	Be-H = -4.2
BeH_2[MP2-0]	Uncon-6-31G(d,p)+S	40-20-36	Be-H = -6.0
BeH_2[MP2-0]	Uncon-6-31G(d,p)+S	40-20-36	H...H = -3.0
MgH_2[MP2-1]	6-31G(d,p)	40-20-36	Mg-H = -1.6
MgH_2[MP2-1]	6-31G(d,p)	40-20-36	H...H = -0.5
AlH_3[MP2-1]	6-31G(d,p)	30-15-27	Al-H = -3.8
AlH_3[MP2-1]	6-31G(d,p)	30-15-27	H...H = -0.6
AlH_4^-[MP2-1]	6-31G(d,p)	30-15-27	Al-H = -5.5
AlH_4^-[MP2-1]	6-31G(d,p)	30-15-27	H...H = -1.0
PH_3[MP2-1]	6-31G(d,p)	30-15-27	P-H = -2.1
PH_3[MP2-1]	6-31G(d,p)	30-15-27	H...H = -0.9
PH_4^+[MP2-1]	6-31G(d,p)	30-15-27	P-H = -4.0
PH_4^+[MP2-1]	6-31G(d,p)	30-15-27	H...H = -0.3
SiH_4[MP2-1]	6-31G(d,p)	30-15-27	Si-H = -6.7
SiH_4[MP2-1]	6-31G(d,p)	30-15-27	H...H = -0.7
BH_3[MP2-1]	6-31G(d,p)	30-15-27	B-H (aver) = -7.3
BH_3[MP2-1]	6-31G(d,p)	30-15-27	H...H (aver) = -1.5
BH_2F[MP2-1]	6-31G(d,p)	30-15-27	B-H = -7.5
BH_2F[MP2-1]	6-31G(d,p)	30-15-27	B-F = -5.2
BH_4^-[MP2-1]	6-31G(d,p)	40-20-36	B-H (aver) = -9.1
BH_4^-[MP2-1]	6-31G(d,p)	40-20-36	H...H (aver) = -1.2
NaF[MP2-1]	6-31G(d,p)	30-15-27	Na-F = +1.2
NaCl[MP2-1]	6-31G(d,p)	30-15-27	Na-Cl= -1.5
MgF2[MP2-1]	6-31G(d,p)	30-15-27	Mg-F = +1.1
MgF2[MP2-1]	6-31G(d,p)	30-15-27	F...F = -0.2

BeO[MP2-1]	6-31G(d,p)	30-15-27	Be=O = +2.1
MgO[MP2-1]	6-31G(d,p)	30-15-27	Mg=O = +56.0
CaO[MP2-1]	6-31G(d,p)	30-15-27	Ca=O = +68.6
HF[MP2-1]	6-31G(d,p)	40-20-36	H-F = +1.2
H_2S[MP2-1]	6-31G(d,p)	50-25-45	S-H = +12.0
H_2S[MP2-1]	6-31G(d,p)	50-25-45	H...H = -1.6
H_2O[MP2-1]	6-31G(d,p)	50-25-45	O-H = +13.3
H_2O[MP2-1]	6-31G(d,p)	50-25-45	O-H = +13.3
H_2O[MP2-1]	6-31G(d,p)	50-25-45	H...H = -3.6
H_2O[MP3-1]	6-31G(d,p)	50-25-45	O-H = +4.4
H_2O[MP4(SDQ)-1]	6-31G(d,p)	50-25-45	O-H = +4.8
OH^-[MP2-1]	6-31G(d,p)	30-15-27	O-H = +21.4
NH_3[MP2-1]	6-31G(d,p)	50-25-45	N-H = +31.5
NH_3 [MP2-1]	6-31G(d,p)	50-25-45	H...H = - 4.9
NH_3[MP3-1]	6-31G(d,p)	40-20-36	N-H = +20.4
NH_3[MP4(SDQ)-1]	6-31G(d,p)	40-20-36	N-H(aver) = +20.7
NH_4^+[MP2-1]	6-31G(d,p)	40-20-36	N-H(aver) = +21.9
NH_4^+[MP2-1]	6-31G(d,p)	40-20-36	H...H(aver) = -3.0
CH_4[MP2-1]	6-31G(d,p)	40-20-36	C-H = +35.6
CH_4[MP2-1]	6-31G(d,p)	40-20-36	H...H = +4.1
CH_4[MP3-1]	6-31G(d,p)	40-20-36	C-H = +26.3
CH_4[MP4(SDQ)- 1]	6-31G(d,p)	40-20-36	C-H = +26.0
C_3H_3(D)[MP2-1]	6-31G(d,p)	20-10-18	C-H = +30.7
C_3H_3(D)[MP2-1]	6-31G(d,p)	20-10-18	C-C = +59.2
C_3H_3(D)[MP2-1]	6-31G(d,p)	20-10-18	C=C = +146.7
CH_3(D)[MP2-1]	6-31G(d,p)	20-10-18	C-H = +31.5
CH_2(T)[MP2-1]	6-31G(d,p)	20-10-18	C-H = +31.5
H_2NO(D)[MP2-1]	6-31G(d,p)	20-10-18	N-H = +34,4
H_2NO(D)[MP2-1]	6-31G(d,p)	20-10-18	N=O= +119.0
N_2[MP2-2]	6-31G(d,p)	40-20-36	N≡N = +400.1
O_2(S)[MP2-2]	6-31G(d,p)	40-20-36	O=O = +292.3
O_2(T)[MP2-2]	6-31G(d,p)	40-20-36	O=O = +250.6
O_2^-(D)[MP2-2]	6-31G(d,p)	40-20-36	O=O = +151.6
FO(D)[MP2-2]	6-31G(d,p)	40-20-36	F-O = +292.3
F_2[MP2-2]	6-31G(d,p)	40-20-36	F-F = +86.9
F_2^-(D)[MP2-2]	6-31G(d,p)	40-20-36	F-F = +5.1
H_2[MP2-0]	11s6p	30-15-27	H-H = +21.1
H_2*[MP2-0][e]	11s6p	40-20-36	H-H = +21.2
CO[MP2-2]	6-31G(d,p)	40-20-36	C-O = +43.0
CN-[MP2-2]	6-31G(d,p)	40-20-36	C≡N = +98.9
CN(D)[MP2-2]	6-31G(d,p)	30-15-27	C≡N = +100.9
NO-[MP2-2]	6-31G(d,p)	40-20-36	N=O = +309.9
NO(D)[MP2-2]	6-31G(d,p)	40-20-36	N=O = +214.1
NO_2(D)[MP2-2]	6-31G(d,p)	40-20-36	N=O = +171.2
NO_2(D)[MP2-2]	6-31G(d,p)	40-20-36	O...O = +28.4
SO_2[MP2-2]	6-31G(d,p)	40-20-36	S=O = +35.7
SO_2[MP2-2]	6-31G(d,p)	40-20-36	O...O = +24.5
OF_2[MP2-2]	6-31G(d,p)	40-20-36	O-F = +94.6

OF_2[MP2-2]	6-31G(d,p)	40-20-36	F...F = -13.6
$HF^0...F^1-F^2$[MP2-3]	6-31G(d,p)	30-15-27	$H-F^0$ = +1.4
$HF^0...F^1-F^2$[MP2-3]	6-31G(d,p)	30-15-27	$H...F^1$ = -0.3
$HF^0...F^1-F^2$[MP2-3]	6-31G(d,p)	30-15-27	$H...F^2$ = -0.2
$HF^0...F^1-F^2$[MP2-3]	6-31G(d,p)	30-15-27	$F^0...F^1$ = -1.7
$HF^0...F^1-F^2$[MP2-3]	6-31G(d,p)	30-15-27	$F^0...F^2$ = +0.3
$HF^0...F^1-F^2$[MP2-3]	6-31G(d,p)	30-15-27	F^1-F^2 = +87.3
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	H^2-O^1 = +13.4
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	H^6-O^4 = +8.4
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	H^5-O^4 = +13.7
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$H^6...O^1$ = -2.3
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$H^2...H^3$ = -3.3
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$H^5...H^6$ = -2.8
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$O^1...O^4$ = +1.9
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$H^3...H^6$ = -0.06
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$O^4...H^3$ = -0.57
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$O^1...H^5$ = -0.33
$H^3H^2O^1...H^6O^4H^5$[MP2-2]	6-31G(d,p)	50-25-45	$H^5...H^3$ = -0.01
$H^4-F^3...H^2-F^1$[MP2-2]	6-31G(d,p)	30-15-27	H^4-F^3 = +2.4
$H^4-F^3...H^2-F^1$[MP2-2]	6-31G(d,p)	30-15-27	H^1-F^2 = +0.75
$H^4-F^3...H^2-F^1$[MP2- 2]	6-31G(d,p)	30-15-27	$F^3...H^2$ = -1.7
$H^4-F^3...H^2-F^1$[MP2- 2]	6-31G(d,p)	30-15-27	$F^3...F^1$ = +0.38
$H^4-F^3...H^2-F^1$[MP2- 2]	6-31G(d,p)	30-15-27	$H^4...H^2$ = -0.08
$H^4-F^3...H^2-F^1$[MP2- 2]	6-31G(d,p)	30-15-27	$H^4...F^1$ = -0.45
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	H^2-O^1 = +18.7
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	H^5-F^4 = +2.9
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	$O^1...H^5$ = -1.8
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	$H^2...H^3$ = -3.5
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	$O^1...F^4$ = +1.6
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	$H^2...H^5$ = -1.5
$H^2H^3O^1...H^5F^4$[MP2-2][f]	6-31G*	40-20-36	$H^2...F^4$ = -0.61
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$O^2...H^1$ = +6.3
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$O^2...H^4$ = +13.5
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$N^3...H^5$ = +30.6
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$N^3...H^1$ = -2.2
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$H^1...H^4$ = -2.4
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$H^5...H^6$ = -4.5
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$N^3...O^2$ = +2.4
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$H^1...H^5$ = -0.04
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$N^3...H^4$ = -0.12
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$O^2...H^5$ = -0.31
$H^5H^6H^7N^3...H^1O^2H^4$[MP2-2]	6-31G(d,p)	40-20-36	$H^7...H^4$ = -0.02
$H_2...H_2$ (a)[MP2-0]	6-31G(d,p)	40-20-36	H...H = -0.39
$H_2...H_2$ (b)[MP2-0]	6-31G(d,p)	40-20-36	H...H = -0.09
$H_2...H_2$ (c)[MP2-0]	6-31G(d,p)	40-20-36	H...H = -0.95
$H_2...H_2$ (d)[MP2-0]	6-31G(d,p)	40-20-36	H...H = -0.004
$H_2...H_2$ (e)[MP2-0]	6-31G(d,p)	40-20-36	H...H = -0.26
$(He...He)_2$[MP2-0]	6-311G+(d,p)	40-20-36	He...He = -0.04

(He...He)$_2$[MP2-0]	6-311G+(d,p)	40-20-36	(He...He)$_2$ = -0.013
LiHe$^+$[MP2-0]	6-311G(d,p)	40-20-36	Li-He = -0.2
HeH$^+$[MP2-0]	6-311G(d,p)	40-20-36	He-H = -2.0

(a) The molecule under consideration and, in brackets, the level of Møller-Plesset (MP) perturbation used, together with the number of core orbitals (-n) excluded from the perturbation calculations.

(b) The default basis set used is 6-31G(d,p) unless stated otherwise. In addition, some of these employed basis sets were uncontracted and are designated by "uncon". Also, a few of the atomic orbital basis sets were modified by the addition or removal of functions, which are designated by +S, –SP or +P. These designations have the following meaning:

- +S: diffuse *S* function added to the standard 6-31G(d,p) basis set of *H* with an exponent of 0.0537592529.
- –SP: the SP shell of exponent 0.716801 was removed from the uncontracted K 6-31G(d,p) basis set due to linear dependency.
- +P: the Uncon-6-311++G(2d,2p)+P basis set and the 11s6p basis set are for LiH and H$_2$, respectively, and are fully specified in Sections 3.1 and 3.3.

(c) The Gauss-Legendre grid was employed. For the hydrogen-bonded complexes this represents the grid on the heavy atom. The grid for hydrogen was the 10-5-9 grid.

(d) The bond and its correlation energy. The average (aver) bond correlation energy is given for symmetry-equivalent bonds, which turned out not to be exactly symmetrical due to the numerical quadrature or the numerical imprecision in the geometry optimization procedure. For example, the bond correlation energies of BH$_3$ with the 30-15-27 grid are -7.16, -7.26 and -7.41 kJmol^{-1}, which average to -7.3 kJmol^{-1}. For other molecules with symmetry equivalent bonds, where no averaging is given, the bond correlation energies were the same to one decimal place (i.e. 0.1 kJmol^{-1}).

(e) The data given for H$_2$ dimers later in this table does not include the H-H bond correlation energy but only the through-space values. This entry gives the H-H bond correlation determined for these complexes, but with a somewhat larger basis set.

(f) Numerical problems in the program MORPHY prevented the use of the 6-31G(d,p) basis set.

Table S2. The level of theory used to determine the geometry and the error in reproducing the GAUSSIAN09 MP2 energy.

System	Geometry determined at:	Geometry (Å)	MORPHY energy error[a] (in kJmol^{-1})
LiH	MP2/6-311G(d,p)	1.598	0.5
LiH	MP2/6-311G(d,p)	1.598	-0.8
LiH	MP2/6-311G(d,p)	1.598	0.4
NaH	MP2/6-31G(d,p) [5 cores]	1.908	5.2
KH (contracted)	MP2/6-31G(d,p) [5 cores]	2.297	-0.4
KH (uncontracted)	MP2/6-31G(d,p) [5 cores]	2.297	7.1
BeH_2	MP2/6-31G(d,p)	1.326	0.9
BeH_2	MP2/uncon-6-31G(d,p)+S	Be-H = 1.319 / H...H = 2.653	1.4
MgH_2	MP2/6-31G(d,p)	Mg-H = 1.708 / H...H = 3.415	0.8
AlH_3	MP2/6-31G(d,p)	Al-H = 1.578 / H...H = 2.772	0.9
AlH_4^-	MP2/6-31G(d,p)	Al-H = 1.628 / H...H = 2.659	1.3
PH_3	MP2/6-31G(d,p)	P-H = 1.402 / H...H = 2.063	0.1
PH_4^+	MP2/6-31G(d,p)	P-H = 1.384 / H...H = 2.260	4.2
SiH_4	MP2/6-31G(d,p)	Si-H = 1.468 / H...H = 2.398	4.2
BH_3	MP2/6-31G(d,p)	B-H = 1.185 / H...H = 2.205	-3.8
BH_2F	MP2/6-31G(d,p)	B-H = 1.578 / B-F = 2.772	-9.7
BH_4^-	MP2/6-31G(d,p)	B-H= 1.231 / H...H = 2.010	-3.6
NaF	MP2/6-31G(d,p)	Na-F = 1.920	2
NaCl	MP2/6-31G(d,p)	Na-Cl = 2.393	1.9
MgF_2	MP2/6-31G(d,p)	Mg-F = 1.747 / F...F = 3.949	3.9
BeO	MP2/6-31G(d,p)	1.356	0.9
MgO	MP2/6-31G(d,p)	1.734	1.5
CaO	MP2/6-31G(d,p)	2.042	1.3
HF	MP2/6-31G(d,p)	0.921	-1.5
H_2S	MP2/6-31G(d,p)	H-S = 1.328 / H...H = 1.924	5.0
H_2O	MP2/6-31G(d,p)	O-H = 0.961 / H...H = 1.515	-1.5
H_2O	MP3/6-31G(d,p)	0.961	-2.3
H_2O	MP4/6-31G(d,p)	0.961	-2.2
NH_3	MP2/6-31G(d,p)	N-H = 1.012 / H...H = 1.618	-2.6

NH_3	MP3/6-31G(d,p)	1.012	-4.2
NH_3	MP4/6-31G(d,p)	1.012	-6.2
NH_4^+	MP2/6-31G(d,p)	1.023	-5.2
CH_4	MP2/6-31G(d,p)	C-H= 1.085 H...H = 1.772	-4.1
CH_4	MP3/6-31G(d,p)	1.085	-4.1
CH_4	MP4/6-31G(d,p)	1.085	-4.9
$C_3H_3(D)$	MP2/6-31G(d,p)	C-H= 1.090 C-C = 1.464 C=C = 1.322	33.6
$CH_3(D)$	MP2/6-31G(d,p)	1.074	5.4
$CH_2(T)$	MP2/6-31G(d,p)	1.174	4.2
H_2NO	MP2/6-31G(d,p)	N-H = 1.013 N=O = 1.273	15.7
N_2	MP2/6-31G(d,p)	1.131	-2.5
$O_2(S)$	MP2/6-31G(d,p)	1.275	-2.7
$O_2(T)$	MP2/6-31G(d,p)	1.247	-2.1
$O_2^-(D)$	MP2/6-31G(d,p)	1.381	-2.2
FO(D)	MP2/6-31G(d,p)	1.344	-2
F_2	MP2/6-31G(d,p)	1.421	-0.9
$F_2^-(D)$	MP2/6-31G(d,p)	1.892	-0.4
H_2	MP2/11s6p	0.735	0.005
CO	MP2/6-31G(d,p)	1.139	-2
NO^-	MP2/6-31G(d,p)	1.118	-1.5
NO(D)	MP2/6-31G(d,p)	1.143	1.6
NO_2	MP2/6-31G(d,p)	N=O = 1.217	20.7
CN^-	MP2/6-31G(d,p)	1.201	-1.2
CN(D)	MP2/6-31G(d,p)	1.125	-4.2
SO_2	MP2/6-31G(d,p)	1.477	9.8
OF_2	MP2/6-31G(d,p)	1.423	5.5
$HF^0...F^1-F^2$	MP2/6-31G(d,p)	$H-F^0$ = 0.922 F^1-F^2 = 1.424 $H...F^1$ = 2.380 $H...F^2$ = 3.570 $F^0...F^1$ = 2.527 $F^0...F^2$ = 3.893	-4.3
$H^3H^2O^1...H^6O^4H^5$	MP2/6-31G(d,p)	H^2-O^1 = 0.963 H^6-O^4 = 0.960 H^5-O^4 = 0.967 $H^6...O^1$ = 1.965 $H^2...H^3$ = 1.519 $H^5...H^6$ = 1.520 $O^1...O^4$ = 2.912 $H^3...H^6$ = 2.310 $O^4...H^3$ = 3.152 $O^1...H^5$ = 3.414 $H^5...H^3$ = 3.773	-3.54
$H^4-F^3...H^2-F^1$	MP2/6-31G(d,p)	H^4-F^3 = 0.918	-2.42

System	Method	Distances	Error
		H^1-F^2 = 0.917	
		F^3...H^2 = 1.840	
		F^3...F^1 = 2.709	
		H^4...H^2 = 2.263	
		H^4...F^1 = 2.981	
$H^2H^3O^1$...H^5F^4	MP2/6-31G*	H^2-O^1 = 0.971	-1.94
		H^5-F^4 = 0.948	
		O^1...H^5 = 1.749	
		H^2...H^3 = 1.539	
		O^1...F^4 = 2.686	
		H^2...H^5 = 2.243	
		H^2...F^4 = 3.089	
$H^5H^6H^7N^3$...$H^1O^2H^4$	MP2/6-31G(d,p)	O^2...H^1 = 0.973	-6.2
		O^2...H^4 = 0.960	
		N^3...H^5 = 1.013	
		N^3...H^1 = 1.992	
		H^1...H^4 = 1.522	
		H^5...H^6 = 1.625	
		N^3...O^2 = 2.963	
		H^1...H^5 = 2.667	
		N^3...H^4 = 3.368	
		O^2...H^5 = 3.617	
		H^7...H^4 = 3.795	
H_2...H_2 (a)	MP2/6-31G(d,p)	H...H = 3.337	0.06
H_2...H_2 (b)	MP2/6-31G(d,p)	H...H = 3.530	2.36
H_2...H_2 (c)	MP2/6-31G(d,p)	H...H = 3.329	4.3
H_2...H_2 (d)	MP2/6-31G(d,p)	H...H = 4.080	5.1
H_2...H_2 (e)	MP2/6-31G(d,p)	H...H = 3.922	0.27
(He...He)$_2$	MP2/6-311G+(d,p)	He...He = 3.045	-0.27
LiHe$^+$	MP2/6-311G(d,p)	1.972	0.4
HeH$^+$	MP2/6-311G(d,p)	0.785	0.02

(a) Where several grids were employed the error is calculated with the largest grid used for that system, as given in Table S1.

3. Basis Sets and General Discussion of H_2, LiH, KH, NaH and BeH_2.

3.1 H_2

The 11s6p basis of *H* is the S and P basis functions of the uncontracted aug-cc-pV6Z basis set for hydrogen. In GAUSSIAN09 format it is

```
H 0
S  1 1.00      0.000000000000
     0.1776775560D+04  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.2540177120D+03  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.5469803900D+02  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.1501834400D+02  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.4915078000D+01  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.1794924000D+01  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.7107160000D+00  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.3048020000D+00  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.1380460000D+00  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.6215700000D-01  0.1000000000D+01
 S  1 1.00      0.000000000000
     0.1890000000D-01  0.1000000000D+01
 P  1 1.00      0.000000000000
     0.8649000000D+01  0.1000000000D+01
 P  1 1.00      0.000000000000
     0.3430000000D+01  0.1000000000D+01
 P  1 1.00      0.000000000000
     0.1360000000D+01  0.1000000000D+01
 P  1 1.00      0.000000000000
     0.5390000000D+00  0.1000000000D+01
 P  1 1.00      0.000000000000
     0.2140000000D+00  0.1000000000D+01
 P  1 1.00      0.000000000000
     0.6700000000D-01  0.1000000000D+01
****
```

This basis for H_2 was chosen to give a reasonable description of H_2. The uncontracted aug-cc-pV6Z basis set gives an HF energy of -1.13366 Hartrees for H_2 while the 11s6p basis employed here gives a HF energy of -1.13360 Hartrees. The MP2 energies associated with these basis sets are -0.03070841933 Hartrees for the 11s6p basis, while for uncontracted aug-cc-pV6Z the energy is -0.03398252384 Hartrees. As the aug-cc-pV6Z basis set is very large and these two sets of numbers are close, we conclude that the 11s6p basis set is adequate for H_2. For the individual H atom the exact energy is 0.5 Hartrees while our 11s6p basis gives an energy of -0.4999993 Hartrees, an error of less than 10^{-6} Hartree. This observation again confirms that the

basis set is very good. The grid employed (40-20-36) in MORPHY reproduced the GAUSSIAN09 MP2 correlation energy to within 0.01 kJmol^{-1}, which is considerably smaller than the bond correlation energy of +21.2 kJmol^{-1}. This, along with the accuracy of the wavefunction, confirms the positive bond correlation is not an artefact of the methodological approach but is a genuine result.

3.2 The inclusion of core orbitals into the MP2 wavefunction

There is an additional point of interest with group IA (H, Li, Na and K) concerning the choice of orbitals to include in the correlation calculation for molecules containing Li, Na and K. The 1s orbital of Li is lower in energy (-2.45144 au) than the 2s orbital of F (-1.57766 au) at the HF/6-31G(d,p) level but they differ by less than one Hartree and one includes the 2s of F in the correlation calculation of Hydrogen Fluoride. Should the 1s of Li be included in the correlated wavefunction of LiH? If one includes the core orbital of LiH what should one do about NaH or KH where there are more core orbitals? Which of these should be included? To a certain extent this question is related to the problem in pseudo-potential studies where one has to consider which orbitals to include in the core. Thus for some elements small core and large core pseudo-potentials are known[1]. We shall return to this subject again in our discussion of NaH and KH, where there is the possibility of four different core orbital situations.

3.3 LiH

The LiH basis sets, designated uncon-6-311++G(2d,2p)+P, are the standard 6-311++G(2d,2p) basis sets uncontracted and with the addition of p-functions to provide core polarization functions for some of the core s-functions of Li and in GAUSSIAN09 format are

```
   H 0
 S  1 1.00     0.000000000000
    0.3386500000D+02 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.5094790000D+01 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.1158790000D+01 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.3258400000D+00 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.1027410000D+00 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.3600000000D-01 0.1000000000D+01
 P  1 1.00     0.000000000000
    0.1500000000D+01 0.1000000000D+01
 P  1 1.00     0.000000000000
    0.3750000000D+00 0.1000000000D+01
****
   Li 0
 S  1 1.00     0.000000000000
    0.9004600000D+03 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.1344330000D+03 0.1000000000D+01
 S  1 1.00     0.000000000000
    0.3043650000D+02 0.1000000000D+01
 SP  1 1.00     0.000000000000
    0.8626390000D+01 0.1000000000D+01 0.1000000000D+01
```

```
SP 1 1.00      0.000000000000
    0.2483320000D+01 0.1000000000D+01 0.1000000000D+01
S  1 1.00      0.000000000000
    0.3031790000D+00 0.1000000000D+01
SP 1 1.00      0.000000000000
    0.4868900000D+01 0.1000000000D+01 0.1000000000D+01
SP 1 1.00      0.000000000000
    0.8569240000D+00 0.1000000000D+01 0.1000000000D+01
SP 1 1.00      0.000000000000
    0.2432270000D+00 0.1000000000D+01 0.1000000000D+01
SP 1 1.00      0.000000000000
    0.6350700000D-01 0.1000000000D+01 0.1000000000D+01
SP 1 1.00      0.000000000000
    0.2436830000D-01 0.1000000000D+01 0.1000000000D+01
SP 1 1.00      0.000000000000
    0.7400000000D-02 0.1000000000D+01 0.1000000000D+01
D  1 1.00      0.000000000000
    0.4000000000D+00 0.1000000000D+01
D  1 1.00      0.000000000000
    0.1000000000D+00 0.1000000000D+01
****
```

For numerical reasons in MORPHY we had to use the 6-311G(d,p) basis set on Li rather than the 6-31G(d,p) basis set, which we mostly used for other elements considered in this work. Additionally, to maintain a balanced basis we employed the same basis on H. However, given the small size of LiH, we additionally used the larger basis (uncon-6-311++G(2d,2p)+P) to look at the effect of additional polarization functions (2d and 2p), as well as the effect of core polarization functions (addition p-functions) and diffuse functions (++). By comparing the HF energy given by this basis set (-7.98653 Hartrees) to that of the very large uncontracted aug-cc-pV5Z basis (-7.98734 Hartrees) we see that they are within 0.001 Hartrees of each other and thus the basis set employed here is reasonably close to the basis set limit. The results of the IQA analysis of this system indicate, unlike for H_2, a negative and small bond correlation energy. The effect of including the Lithium 1s-orbital in the MP2 wavefunction is to double the bond correlation energy over the MP2 wavefunction without the 1S-orbital included (i.e. -0.00172 and -0.00078 Hartrees, respectively for the uncon-6-311++G (2d,2p)+P basis set). Clearly core orbitals effects cannot be neglected for group 1A elements in correlation calculations.

One additional point is that for all reasonable grids, we always obtain a negative bond correlation energy, whichever basis set we use (i.e. 6-311G(d,p) or uncon-6-311++G(2d,2p)+P). Moreover, for the 30-15-27 Gauss-Legendre grids, the error in the energy produced by these grids, compared to the MP2 value from GAUSSIAN09, is always less than the bond correlation energy. Thus the sign of the bond correlation energy is unlikely to change with an increase in the grid size.

3.4 X-H bonds Across a Row of the Periodic Table.

Having considered LiH in some detail we now consider the rest of its period of the periodic table namely (BeH_2, BH_3, CH_4, NH_3, H_2O and HF). Our interest in these molecules is to see how correlation affects the bonds as we traverse a period. The key points, which we have observed before[2], are firstly that *most of the correlation energy resides in the atoms that make up a given bond*, although its value is not particularly large for hydrogen. The correlation energy of the actual bond or bonds is much smaller than that of the heavy atom making up one end of the bond. Secondly, *the bond correlation energy can be positive or negative.* About half way across the period its sign changes from stabilizing to destabilizing (moving from left to right), implying HF theory over-describes bonds in the later part of the period and under-describes

them in the earlier part. The observation that the sign of the bond correlation energy changes between BH_3 and CH_4 could be due to the fact that they have a different number of electrons, with BH_3 not obeying the octet rule, while CH_4 does. To investigate this question further we looked at a related boron compound that is iso-electronic with CH_4 and, in addition, has the same number of bonds, namely BH_4^-. The change from negative bond correlation energy to positive is still found in going from BH_4^- to CH_4. Thus electron deficiency is not determining the sign. In addition, as mentioned in the main text, we modelled BH_4^- with the geometry and basis set of CH_4 and did not determine a change to the sign either.

So next we considered if the H basis is perhaps unable to describe the hydridic character of the H. To investigate this potential basis set effect we chose to study BeH_2, whose hydrogens have a larger electronic charge than the hydrogens in BH_3, and thus any basis set defect in H is likely to be more noticeable. The basis is given in Section 3.6. This calculation should be better able to describe both the Be and H atoms. By including the cores we aimed to eliminate any effect that might arise from the cores being closer to the valence level in BeH_2 than in CH_4, which might have given rise to the sign change observed for the bond correlation energy. Despite these two changes (basis set and core correlation) the determined bond correlation energy was still negative, confirming that this is a genuine result.

3.5 NaH and KH

These two hydrides show a dependence on the grid size for the sign of the bond correlation energy. Ultimately this fact is due to the small size of the bond correlation energy and the numerical error involved in describing it. Thus for NaH (6-31G(d,p) and no frozen cores in the MP2 wavefunction), using the 30-15-27 grid, the bond correlation energy is -0.1 kJmol^{-1}, while for the grid 40-20-36 this energy is 0.3 kJmol^{-1}. These grids reproduce the MP2 energy to -0.5 and < 0.1 kJmol^{-1} for the smaller and larger grid, respectively. For the 30-15-27 grid, clearly the error in the total correlation energy is more than the bond correlation energy (-0.5 and -0.1 kJmol^{-1}, respectively), thus the reliability of the sign of the bond correlation energy can only be ascertained once the error in the grid determined energy is less than magnitude of the bond correlation energy.

For KH four different "frozen core situations" are possible (i.e. (i) none, (ii) 1s frozen, (iii) 1s, 2s and 2p frozen, and (iv) 1s, 2s, 2p, 3s and 3p frozen). In addition to the question of the number of core orbitals to use for KH, we have used two basis sets. As the 2PDM is used in its primitive form by the program MORPHY there is no advantage from the point of view of efficiency to using a contracted basis set. The time consuming part of the calculations occur in MORPHY and not in GAUSSIAN09 and thus employing an uncontracted basis gives additional flexibility to the wavefunction and hence, a better description of the electronic state under consideration, but only costs a small time penalty. These uncontracted basis sets also allows the SCF procedure to give virtual orbitals in the region of the core and thus provide orbitals suitable to correlate the core. In the contracted 6-31G(d,p) basis each core orbital is represented by one basis function and hence the SCF procedure produces only one orbital for each core orbital. Hence none of the core orbitals have correlating orbitals in that region of space where they physically reside, and any correlation calculation involving core orbitals has only virtual valence orbitals to correlate them, which is a less than an ideal situation. The two basis sets thus employed are 6-31G(d,p) and its uncontracted form but the uncontracted form has a linear dependency in the basis, and hence an SP-shell with exponent 0.716801 was removed.

Table S3 gives a summary of our results. If we included only the valence orbital in the correlation calculation (contracted basis) we obtained a positive correlation bond energy (3.3 or 2.6 kJmol^{-1}), but on explicitly including the 3s and 3p orbitals as well as the valence orbital then a small grid (10-5-9) gave the bond correlation energy as 0.1 kJmol^{-1}, while a larger one (20-10-18) gave a value with a change of sign of -0.6 kJmol^{-1}. Interestingly, the error in the correlation energy produced by MORPHY for the MP2 energy involving **one orbital only** is less than the bond correlation energy (1.22 and 1.7 kJmol^{-1}, for the smaller and larger grids, respectively). Thus the values of 3.3 or 2.6 kJmol^{-1} are unlikely to change sign with improvement of the grid. However, as we have just seen, including the 3s and 3p orbitals significantly reduces the bond correlation energies implying these orbitals need to be included in the wavefunction. The

effect of including core orbitals, other than the 3s and 3p, on the bond correlation energy is minimal for the contracted basis set (Table S3). The error in MORPHY's determination of the total correlation energy is usually less than the bond correlation energy for valence-only MP2 wavefunctions. However, once core orbitals are included in the wavefunction this is generally no longer true, but there are two exceptions. The first is the value of the bond correlation energy of -0.9 kJmol^{-1} (Table S3, grid 30-15-27, 6-31G(d,p) (0 cores)), where the error in the total correlation is -0.4 kJmol^{-1}. Thus the value of -0.9 kJmol^{-1} is unlikely to change sign with improvement of the grid. The second is the bond correlation energy of -1.5 kJmol^{-1} (Table S3, **Uncon-**6-31G(d,p)-SP (5 cores)), which has a total correlation energy error of -0.6 kJmol^{-1}. For the MP2 wavefunction with the uncontracted basis sets that include the core orbitals 1s, or 1s, 2s and 2p, a compact grid is needed to describe this region of electron density close to the nucleus accurately and hence there is a rather large error in the total correlation energy (e.g. 7.1 kJmol^{-1} for the **Uncon-**6-31G(d,p)-SP (0 cores) with a 40-20-36 grid).

Table S3. The bond correlation energies for KH in kJmol^{-1}. All results obtained with an uncontracted basis set are marked in bold.

Basis set (and N^o cores)	Grid and bond correlation		Grid and bond correlation	
	Grid: 10-5-9	Grid: 20-10-18	Grid: 30-15-27	Grid: 40-20-36
6-31G(d,p) (9 cores)	3.3	2.6		
6-31G(d,p) (5 cores)	0.1	-0.6		
6-31G(d,p) (1 cores)	0.1	-0.6		
6-31G(d,p) (0 cores)	0.1	-0.6	-0.9	
Uncon-6-31G(d,p)-SP (9 cores)	**3.0**	**2.3**	**2.1**	
Uncon-6-31G(d,p)-SP (5 cores)	**-0.6**	**-1.3**	**-1.5**	
Uncon-6-31G(d,p)-SP (1 cores)	**-0.6**	**-1.4**	**-1.5**	
Uncon-6-31G(d,p)-SP (0 cores)	**-0.6**	**-1.4**	**-1.5**	**-1.5**

3.6 BeH₂

The basis sets used for BeH$_2$ are the uncontracted 6-31G(d,p) for Be and H with an additional diffuse s-function on H of exponent 0.05375925290. In GAUSSIAN09 format these are

```
   H 0
S  1 1.00      0.000000000000
   0.1873113696D+02  0.1000000000D+01
S  1 1.00      0.000000000000
   0.2825394365D+01  0.1000000000D+01
S  1 1.00      0.000000000000
   0.6401216923D+00  0.1000000000D+01
S  1 1.00      0.000000000000
   0.1612777588D+00  0.1000000000D+01
S  1 1.00      0.000000000000
   0.5375925290D-01  0.1000000000D+01
P  1 1.00      0.000000000000
   0.1100000000D+01  0.1000000000D+01
****
   Be 0
S  1 1.00      0.000000000000
   0.1264585690D+04  0.1000000000D+01
S  1 1.00      0.000000000000
   0.1899368060D+03  0.1000000000D+01
S  1 1.00      0.000000000000
   0.4315908900D+02  0.1000000000D+01
S  1 1.00      0.000000000000
   0.1209866270D+02  0.1000000000D+01
S  1 1.00      0.000000000000
   0.3806323220D+01  0.1000000000D+01
S  1 1.00      0.000000000000
   0.1272890300D+01  0.1000000000D+01
SP  1 1.00      0.000000000000
   0.3196463098D+01  0.1000000000D+01  0.1000000000D+01
SP  1 1.00      0.000000000000
   0.7478133038D+00  0.1000000000D+01  0.1000000000D+01
SP  1 1.00      0.000000000000
   0.2199663302D+00  0.1000000000D+01  0.1000000000D+01
SP  1 1.00      0.000000000000
   0.8230990070D-01  0.1000000000D+01  0.1000000000D+01
D  1 1.00      0.000000000000
   0.4000000000D+00  0.1000000000D+01
****
```

The results of the use of this basis set are given in Tables S1 and S2 under the entry labelled MP2/uncon-6-31G(d,p)+S. By comparison with the smaller 6-31G(d,p) basis set, the larger one has more bond correlation energy (-4.2 to -6.0 kJmol^{-1}, respectively), although the larger one also includes the core orbitals and, as we have seen for KH, this lowers the bond correlation energy. Our study of BeH$_2$ is intended to decide if the hydrogen basis set could not describe the second row hydrides LiH, BeH$_2$ and BH$_3$, and if this issue actually caused the sign of the bond correlation energy to be negative. Extending the H basis by a diffuse function and including the core orbital of Be had no effect on the sign of the correlation energy, as the results for LiH also indicate.

A referee raised some concerns about calculations involving Be, in that dynamic correlation effects are expected to be important for this element. Unfortunately, at this moment in time our computer codes are not interfaced to a program that explicitly takes such effects into account. However, it is notable that we have experienced some numerical problems with Be-containing molecules, which in all probability reflects this referee's concerns. Unpublished results on BeO involving three orders of perturbation theory give bond correlation energies that are both positive and negative (i.e. MP2: 0.3 kJmol^{-1}, MP3: -15.9 kJmol^{-1} and MP4(SDQ): -8.9 kJmol^{-1}).

As a final comment we mention that the values for the bond correlations (i.e. Be-O and Be-H) turned out to be sensitive to the grid size, even to the extent that their sign may alternate with grid size until it stabilises.

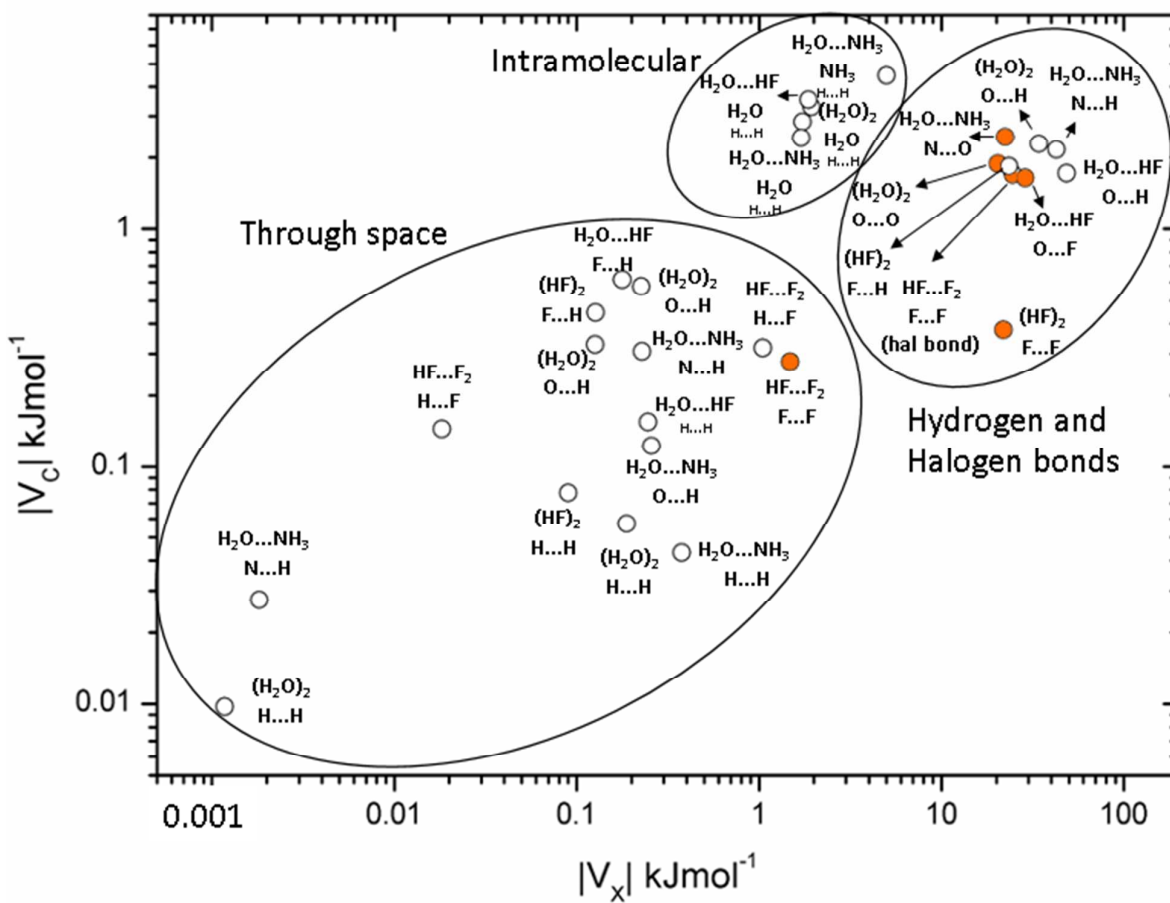**4. Additional Plots relating V_c to V_X and internuclear Distance.**

Figure S12. The absolute value of interatomic correlation *versus* the absolute interatomic exchange for molecular complexes. Positive values for correlation are marked in orange.
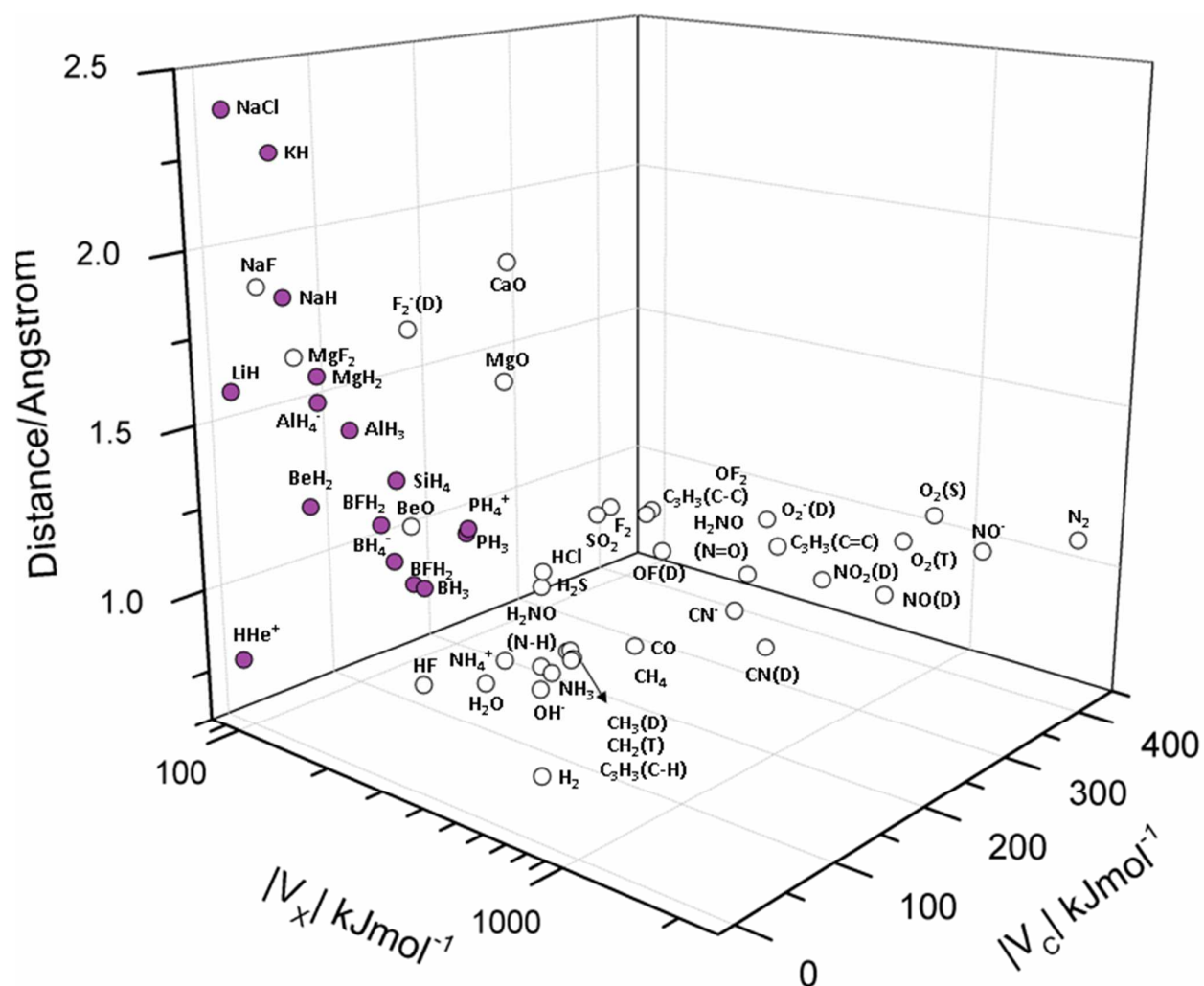
Figure S13. 3D plot of bond distance as a function of absolute bond correlation energy and absolute bond exchange energy for the several different molecular systems studied. Negative values of correlation energies are marked in purple.
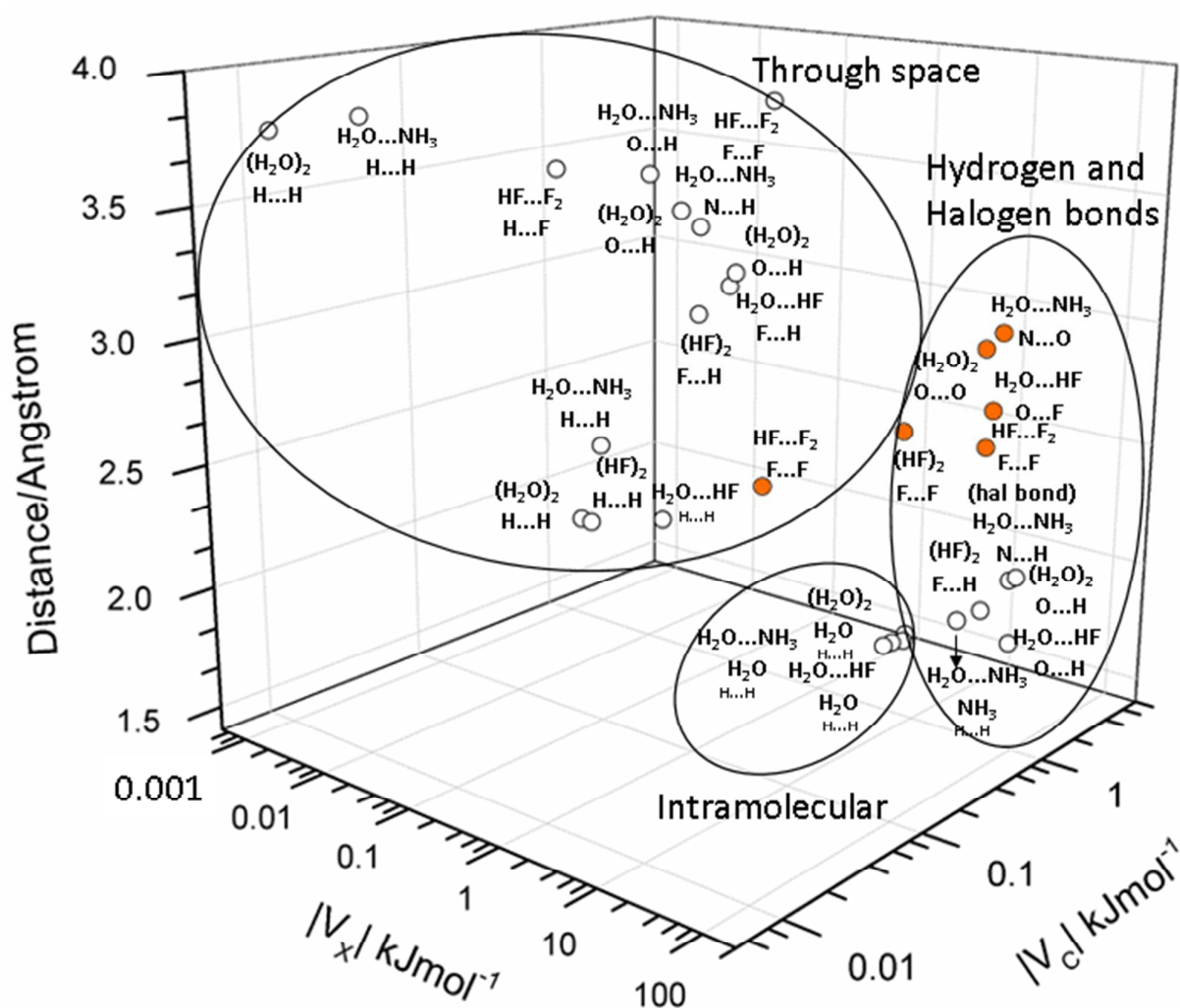
Figure S14. 3D plot of interatomic distance as a function of absolute interatomic correlation energy and absolute interatomic exchange energy for the several different molecular complexes. Positive values of correlation energies are marked in orange.

References

1. Stoll, H., B. Metz, and M. Dolg, *Relativistic energy-consistent pseudopotentials—Recent developments.,* J.Comput.Chem., **23,** 767-778 (2002).

2. McDonagh, J.L., M.A. Vincent, and P.L.A. Popelier, *Partitioning Dynamic Electron Correlation Energy: Viewing Møller-Plesset Correlation Energies Through Interacting Quantum Atom (IQA) Energy Partitioning,* Chem.Phys.Lett., **662,** 228-234 (2016).