SUPPLEMENTARY INFORMATION

Chemical bonding in Period II Homonuclear Diatomic Molecules: A comprehensive Relook

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Table ST1: Method and Basis Set Dependence of Be_2 bond distance

	*6-311G***	*aug-cc-pVDZ*	*aug-cc-pVTZ*	*aug-cc-pVQZ*
HF	6.389	6.922	6.921	6.920
B3LYP	2.492	2.503	2.482	2.482
M06-2X	2.747	2.754	2.743	-
PBEPBE	2.434	2.440	2.425	-
MP2	4.074	3.924	2.780	2.726
MP2(FULL)	2.917	3.867	2.451	2.609
CCSD(T)	-	2.501	2.532	2.501
CCSD(T)(FULL)	-	2.436	2.343	2.427

Atoms in Molecules Analysis:

Table ST2: Basis Set Dependence on Topological Properties of Li_2 Molecule.

DFT	***ρ(r)***	***∇²ρ***	***λ₁= λ₂***	***λ₃***	***|λ₁|/ λ₃***	***V***	***G***	***|V|/G***
6-311G++(d,p)	0.0137	0.00203	-0.0056	0.0132	0.424	-0.0063	0.0034	1.85
aug-cc-pVDZ	0.0128	0.01073	-0.0049	0.0205	0.239	-0.0060	0.0043	1.40
aug-cc-pVTZ	0.0137	0.00560	-0.0056	0.0169	0.331	-0.0062	0.0038	1.63
MP2								
6-311G++(d,p)	0.0132	0.00424	-0.0054	0.0150	0.360	-0.0064	0.0037	1.73
aug-cc-pVDZ	0.0125	0.01124	-0.0049	0.0210	0.233	-0.0060	0.0044	1.36
aug-cc-pVTZ	0.0129	0.00891	-0.0053	0.0195	0.272	-0.0062	0.0042	1.48
CCSD(T)								
6-311G++(d,p)	0.0132	0.00424	-0.0054	0.0150	0.360	-0.0064	0.0037	1.73
aug-cc-pVDZ	0.0125	0.01121	-0.0049	0.0210	0.233	-0.0060	0.0044	1.36
aug-cc-pVTZ	0.0129	0.00891	-0.0053	0.0195	0.272	-0.0062	0.0042	1.48

Table ST3: Basis Set Dependence on Topological Properties of Be_2 Molecule

DFT	***ρ(r)***	***∇²ρ***	***λ₁= λ₂***	***λ₃***	***|λ₁|/ λ₃***	***V***	***G***	***|V|/G***
6-311G++(d,p)	0.0342	-0.0337	-0.0237	0.0137	1.730	-0.0109	0.0012	9.08
aug-cc-pVDZ	0.0345	-0.0336	-0.0235	0.0134	1.754	-0.0112	0.0014	8.00
aug-cc-pVTZ	0.0351	-0.0374	-0.0260	0.0146	1.781	-0.0120	0.0013	9.23
MP2								
6-311G++(d,p)	0.0311	-0.0280	-0.0206	0.0131	1.573	-0.0108	0.0019	5.68
aug-cc-pVDZ	0.0312	-0.0270	-0.0206	0.0142	1.451	-0.0109	0.0021	5.19
aug-cc-pVTZ	0.0318	-0.0318	-0.0223	0.0135	1.652	-0.0117	0.0019	6.16
CCSD(T)								
6-311G++(d,p)	0.0311	-0.0280	-0.0206	0.0131	1.573	-0.0108	0.0019	5.68
aug-cc-pVDZ	0.0312	-0.0270	-0.0206	0.0142	1.451	-0.0109	0.0021	5.19
aug-cc-pVTZ	0.0318	-0.0311	-0.0223	0.0135	1.652	-0.0117	0.0019	6.16

Table ST4: Basis Set Dependence on Topological Properties of B_2 (Triplet) Molecule

DFT	*ρ(r)*	*$\nabla^2\rho$*	*$\lambda_1=\lambda_2$*	*λ_3*	*$\lvert\lambda_1\rvert/\lambda_3$*	*V*	*G*	*|V|/G*
6-311G++(d,p)	0.1321	-0.1983	-0.101	0.0038	26.579	-0.1901	0.0703	2.70
aug-cc-pVDZ	0.1281	+0.0431	-0.0818	0.2067	0.396	-0.2494	0.1301	1.92
aug-cc-pVTZ	0.1365	-0.1086	-0.1156	0.1226	0.943	-0.2438	0.1083	2.25
MP2								
6-311G++(d,p)	0.1204	0.0018	-0.0637	0.1291	0.493	-0.2262	0.1133	2.00
aug-cc-pVDZ	0.1172	0.1071	-0.0538	0.2147	0.251	-0.2334	0.1301	1.79
aug-cc-pVTZ	0.1236	0.0768	-0.0784	0.2336	0.336	-0.2538	0.1365	1.86
CCSD(T)								
6-311G++(d,p)	0.1204	0.0018	-0.0637	0.1291	0.493	-0.2262	0.1129	2.00
aug-cc-pVDZ	0.1172	0.1071	-0.0538	0.2147	0.251	-0.2334	0.1301	1.79
aug-cc-pVTZ	0.1236	0.0768	-0.0784	0.2336	0.336	-0.2538	0.1365	1.86

Table ST5: Basis Set Dependence on Topological Properties of C_2 Molecule

DFT	*ρ(r)*	*$\nabla^2\rho$*	*$\lambda_1=\lambda_2$*	*λ_3*	*$\lvert\lambda_1\rvert/\lambda_3$*	*V*	*G*	*|V|/G*
6-311G++(d,p)	0.2867	-0.3315	-0.1788	0.0260	6.877	-0.6233	0.2702	2.31
aug-cc-pVDZ	-	-	-	-	-	-	-	-
aug-cc-pVTZ	0.2969	+0.1963	-0.0947	+0.3856	0.245	-1.0031	+0.5261	1.91
MP2								
6-311G++(d,p)	0.2924	-0.4678	-0.2574	+0.0469	5.488	-0.5910	+0.2370	2.49
aug-cc-pVDZ	0.2833	-0.4152	-0.2444	+0.0735	3.325	-0.5408	+0.2185	2.48
aug-cc-pVTZ	0.3108	+0.0248	-0.2065	+0.4378	0.472	-1.0282	+0.5172	1.99
CCSD(T)								
6-311G++(d,p)	-	-	-	-	-	-	-	-
aug-cc-pVDZ	-	-	-	-	-	-	-	-
aug-cc-pVTZ	-	-	-	-	-	-	-	-

Table ST6: Basis Set Dependence on Topological Properties of N_2 Molecule

DFT	*ρ(r)*	*$\nabla^2\rho$*	*$\lambda_1=\lambda_2$*	*λ_3*	*$\lvert\lambda_1\rvert/\lambda_3$*	*V*	*G*	*|V|/G*
6-311G++(d,p)	0.6821	-2.5882	-1.7090	+0.8299	2.509	-1.8192	+0.5861	3.10
aug-cc-pVDZ	0.6606	-2.0244	-1.5847	+1.1451	1.384	-1.6008	+0.5474	2.92
aug-cc-pVTZ	0.7267	-3.4632	-2.0148	+0.5665	3.557	-2.1299	+0.6320	3.37
MP2								
6-311G++(d,p)	0.6372	-2.1834	-1.5426	+0.9018	1.711	-1.6601	+0.5571	2.98
aug-cc-pVDZ	0.6121	-1.6616	-1.4342	+1.2068	1.188	-1.4383	+0.5114	2.81
aug-cc-pVTZ	0.6805	-3.0149	-1.8407	+0.6664	2.762	-1.9517	+0.5990	3.26
CCSD(T)								
6-311G++(d,p)	0.6688	-2.5537	-1.6083	+0.6629	2.426	-1.7679	+0.5647	3.13
aug-cc-pVDZ	0.6401	-1.9387	-1.4955	+1.0522	1.421	-1.5168	+0.5160	2.94
aug-cc-pVTZ	0.7131	-3.4261	-1.9157	+0.4052	4.728	-2.0735	+0.6085	3.41

Table ST7: Basis Set Dependence on Topological Properties of O_2 (triplet) Molecule

DFT	*ρ(r)*	*$\nabla^2\rho$*	*$\lambda_1=\lambda_2$*	*λ_3*	*$\lvert\lambda_1\rvert/\lambda_3$*	*V*	*G*	*|V|/G*
6-311G++(d,p)	0.5395	-0.7650	-1.4931	+2.2212	0.672	-1.1265	+0.4676	2.41
aug-cc-pVDZ	0.5357	-0.9035	-1.4030	+1.9024	0.737	-1.1775	+0.4758	2.47
aug-cc-pVTZ	0.5386	-0.6575	-1.5204	+2.3834	0.638	-1.1234	+0.4795	2.34
MP2								
6-311G++(d,p)	0.5092	-0.5482	-1.3725	+2.1968	0.625	-1.0975	+0.4803	2.29
aug-cc-pVDZ	0.4921	-0.6268	-1.2512	+1.8757	0.667	-1.1017	+0.4725	2.33
aug-cc-pVTZ	0.5059	-0.3669	-1.3694	+2.3719	0.577	-1.0829	+0.4956	2.19
CCSD(T)								
6-311G++(d,p)	0.5295	-0.9367	-1.4629	+1.9390	0.754	-1.1081	+0.4370	2.54
aug-cc-pVDZ	0.5257	-1.0319	-1.3538	+1.6757	0.808	-1.1482	+0.4451	2.58
aug-cc-pVTZ	0.5249	-0.8862	-1.4977	+2.1092	0.710	-1.1479	+0.4632	2.48

Table ST8: Basis Set Dependence on Topological Properties of F_2 Molecule

DFT	*ρ(r)*	*$\nabla^2\rho$*	*$\lambda_1=\lambda_2$*	*λ_3*	*$\lvert\lambda_1\rvert/\lambda_3$*	*V*	*G*	*|V|/G*
6-311G++(d,p)	0.2674	+0.5937	-0.7095	+2.0127	0.353	-0.3865	+0.2675	1.44
aug-cc-pVDZ	0.2781	+0.5177	-0.7245	+1.9666	0.368	-0.4199	+0.2747	1.53
aug-cc-pVTZ	0.2964	+0.4591	-0.7281	+1.9153	0.380	-0.4644	+0.2896	1.60
MP2								
6-311G++(d,p)	0.2555	+0.6791	-0.6670	+2.0130	0.331	-0.3913	+0.2805	1.40
aug-cc-pVDZ	0.2519	+0.6519	-0.6247	+1.9013	0.329	-0.3913	+0.2771	1.41
aug-cc-pVTZ	0.2900	+0.5200	-0.7030	+1.9260	0.365	-0.4950	+0.3125	1.58
CCSD(T)								
6-311G++(d,p)	0.2461	+0.4722	-0.6152	+1.7026	0.361	-0.3216	+0.2198	1.46
aug-cc-pVDZ	0.2500	+0.4029	-0.6045	+1.6119	0.375	-0.3281	+0.2144	1.53
aug-cc-pVTZ	0.2973	+0.2002	-0.7250	+1.6502	0.439	-0.4648	+0.2575	1.81

Table ST9: Basis Set Dependence on Topological Properties of Ne_2 Molecule

DFT	*ρ(r)*	*$\nabla^2\rho$*	*$\lambda_1=\lambda_2$*	*λ_3*	*$\lvert\lambda_1\rvert/\lambda_3$*	*V*	*G*	*|V|/G*
6-311G++(d,p)	0.0019	+0.0147	-0.0021	+0.0188	0.112	-0.0016	+0.0026	0.62
aug-cc-pVDZ	0.0006	+0.0046	-0.0005	+0.0056	0.089	-0.0002	+0.0007	0.29
aug-cc-pVTZ	0.0009	+0.0060	-0.0008	+0.0076	0.105	-0.0006	+0.0011	0.55
MP2								
6-311G++(d,p)	0.0018	+0.0148	-0.0020	+0.0187	0.107	-0.0016	+0.0027	0.59
aug-cc-pVDZ	0.0011	+0.0104	-0.0012	+0.0127	0.094	-0.0007	+0.0017	0.41
aug-cc-pVTZ	0.0015	+0.0099	-0.0015	+0.0129	0.116	-0.0013	+0.0019	0.68
CCSD(T)								
6-311G++(d,p)	0.0016	+0.0146	-0.0019	+0.0184	0.103	-0.0016	+0.0026	0.62
aug-cc-pVDZ	0.0011	+0.0121	-0.0013	+0.0148	0.088	-0.0010	+0.0020	0.50
aug-cc-pVTZ	0.0021	+0.0131	-0.0022	+0.0175	0.126	-0.0019	+0.0026	0.73

Table ST10: Electron Density on atoms and NNA for Li_2, B_2, and C_2. (In case of C_2 wave function at CCSD/aug-cc-pVTZ level used for calculation.

Diatoms	*R(D-D)*	*ρ(D)*	*R(D-BCP)*	*R(NNA-BCP)*	*ρ(NNA)*
Li_2	2.667	13.524	0.935	0.395	0.014
B_2	1.587	69.042	0.526	0.266	0.128
$*C_2$	1.247	122.014	0.446	0.177	0.319

R(D-D): Distance between diatoms (D), **ρ(D):** Electron density on the diatoms, **R(D-BCP):** Distance between BCP and atom, **R(NNA-BCP):** Distance between non-nuclear attractor and BCP , **ρ(NNA):** Electron density on non-nuclear attractor

Table ST11: Properties of Diatoms from atoms in molecules analysis. (In case of C_2 wave function at CCSD/aug-cc-pVTZ level used for calculation.

Diatoms	*Δρ(D)*	*ΔVol(D)*	*ΔESP(D)*
Li_2	-0.0108	-188.6638	0.0272
Be_2	-0.0365	-40.641	0.001
B_2	-0.0948	-61.566	0.0135
$*C_2$	-0.1518	-103.734	0.0419
N_2	-0.4061	-38.767	0.0673
O_2	-0.5882	-29.6879	0.0727
F_2	-0.0494	-20.6957	0.0494
Ne_2	-0.0054	-2.4548	0.0002

Δ Difference between (Diatom-Atom). Δρ(D) : Difference in electron density between diatom(D-D) and atom(D).

Table ST12: Ground and low lying electronic states (<10000 cm^{-1}) of B_2 and C_2.

B_2	*Electronic States (cm^{-1})*	*C_2*	*Electronic States (cm^{-1})*
$X\,^3\Sigma_g^-$ *(GS)*	0	$X^1\Sigma_g^+$ (GS)	0
$^5\Sigma_u$-	1833[a], 1826[b]	$a^3\Pi_u$	450[b], 716.2[c]
$A^3\Pi_u$	3380[a], 3374[b]	$b^3\Sigma_g^-$	5914[b], 6434.3[c]
$b^1\Delta_g$	4616[a], 4335[b]	$A^1\Pi_u$	7915[b], 8391.4[c]
$c^1\Sigma_g^+$	7319[a], 7205[b]	$c^3\Sigma_u^+$	9417[b], 9124.2[d]

Table ST13: Natural resonance theory (NRT) analysis for LiH and HF.

	Ionic	*Covalent*
LiH	84.6%	15.4%
HF	56.5%	43.5%

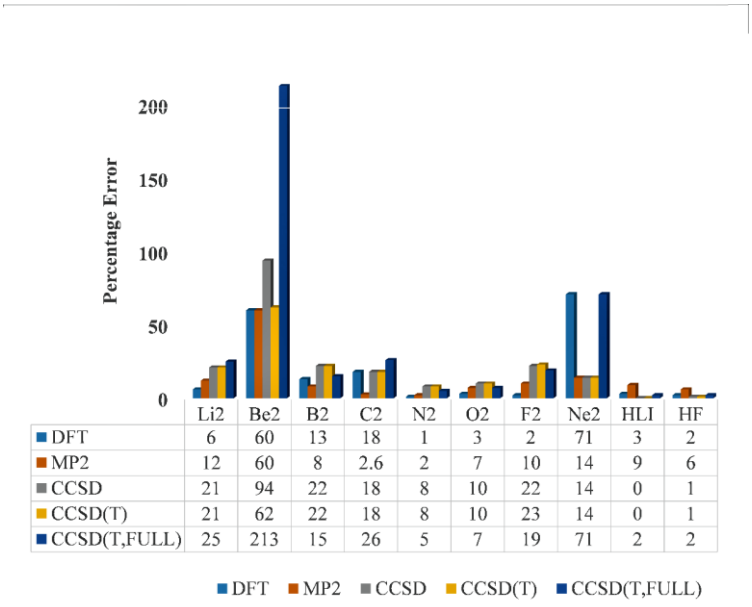

Figure SF1: Comparison of the percentage error of the diatoms dissociation energies.

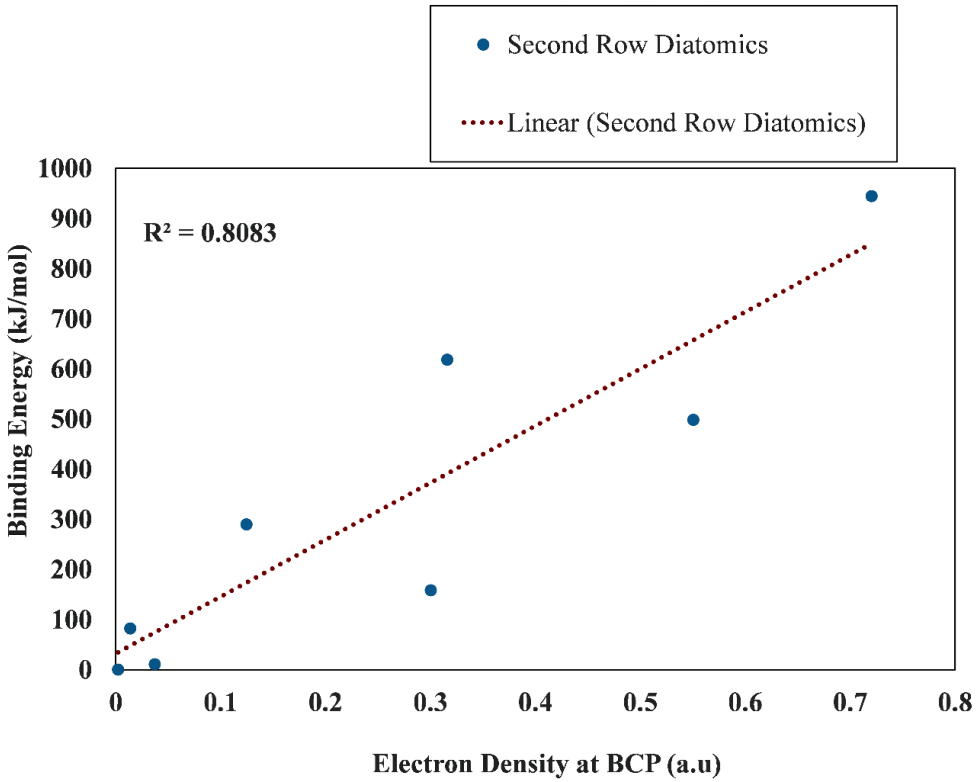

Figure SF2: Binding energy vs. Electron density for period 2 homonuclear diatoms.

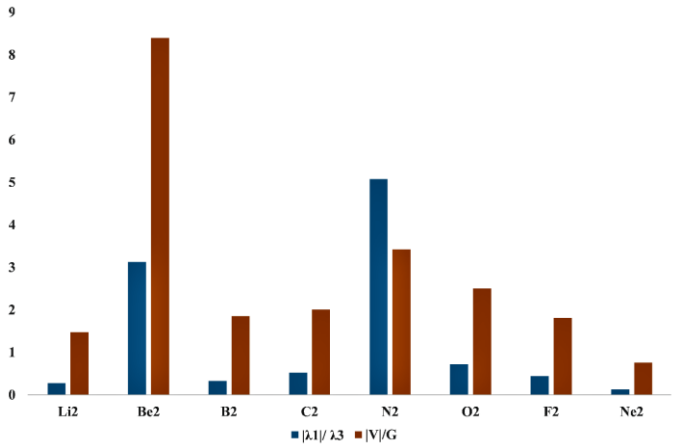

Figure SF3: $|\lambda_1|/\ \lambda_3$ and |V|/G ratio for homonuclear diatomic molecules. Range for the values are given in table 6. ($\lambda_1/\ \lambda_3$: First/third eigenvalue of Hessian matrix, V/G: Potential/Kinetic energy density)

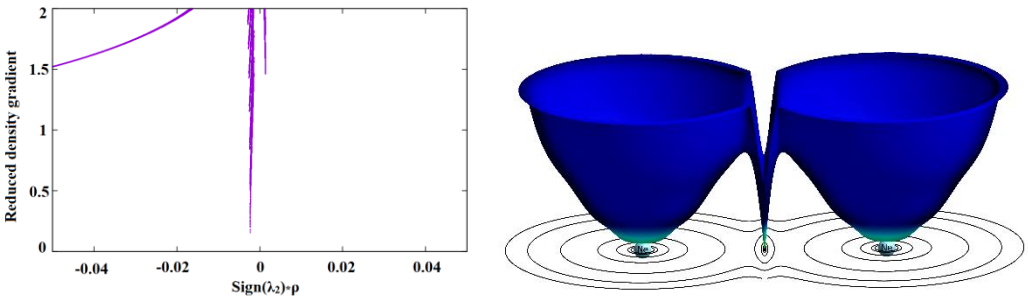

Figure SF4: Non-covalent index plot for Ne_2 (left) and superimposed contour plot and relief map of reduced density gradient (right) for Ne_2.

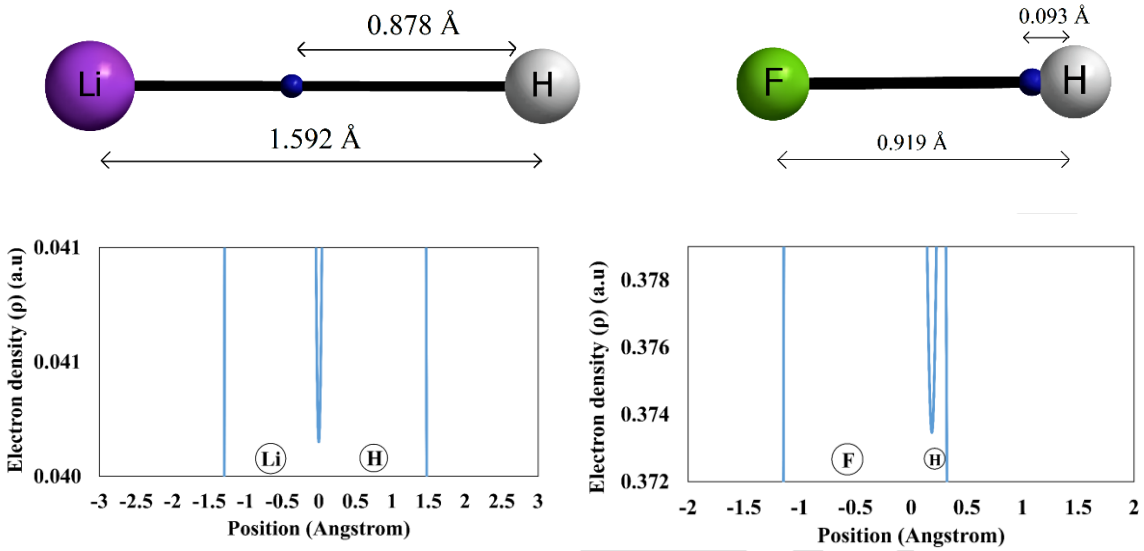

Figure SF5: Position of Bond critical point in LiH (top left) and HF (top right). Variation of the electron density (ρ) along the internuclear axis of LiH (bottom left) and HF (bottom right).

Diatoms	*1σ*	*2σ*	*3σ**		
LiH	**-2.446**	**-0.302**	-0.007		
	1σ	2σ	3σ	1π, 2π	
HF	**-26.299**	**-1.602**	**-0.768**	**-0.650**	-0.031

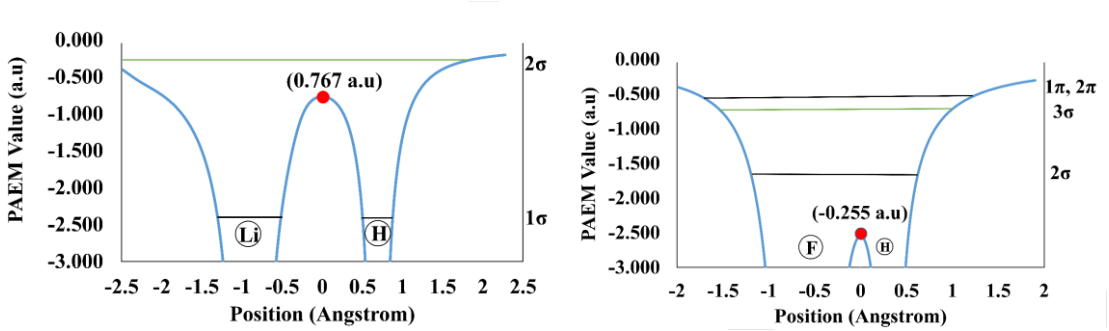

Figure SF6: Molecular orbitals and energy levels for LiH and HF. (Bold values are for filled orbital). Energies are in a.u. The PAEM-MO diagram along the line connecting two atoms: a) LiH molecule, b) HF molecule (Green line PAEM diagrams denotes major valence bonding orbital)

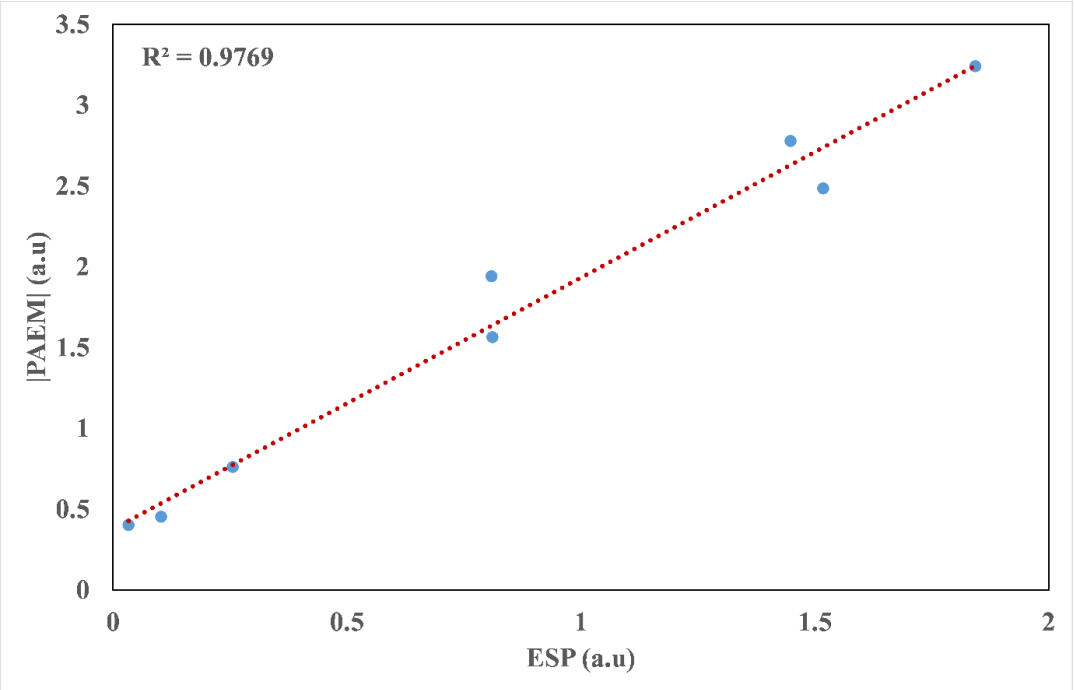

Figure SF7: Correlation plot between |PAEM| and ESP for homonuclear diatomics of period 2.

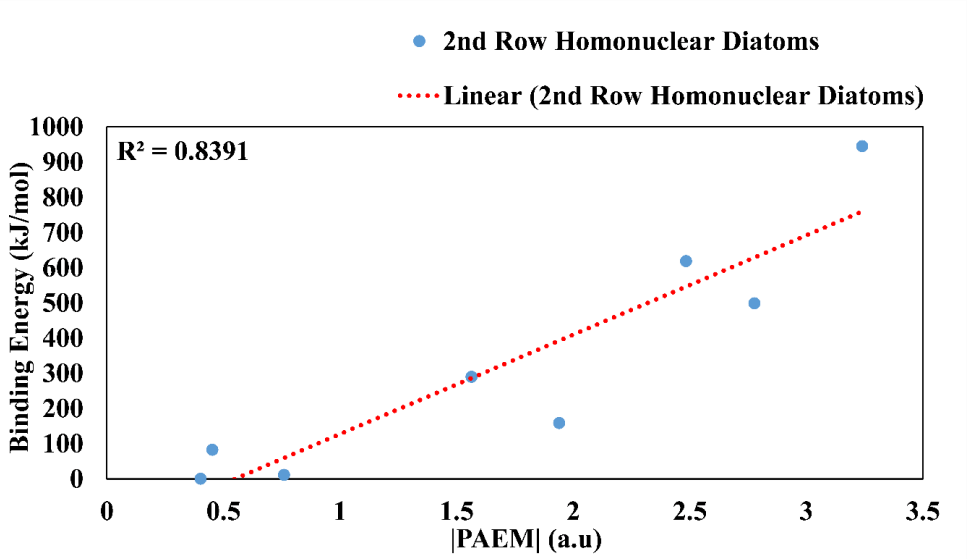

Figure SF8: Correlation plot between binding energy vs. |PAEM| for homonuclear diatomics of period 2.

Reference 79: Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.