Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Energy vs. density on paths toward exact density functionals

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Figure S1. PBE/aug-cc-pωCV5Z density near the nucleus of B^+, compared to the best exponential fit, showing the effect of Gaussian basis functions on the density.

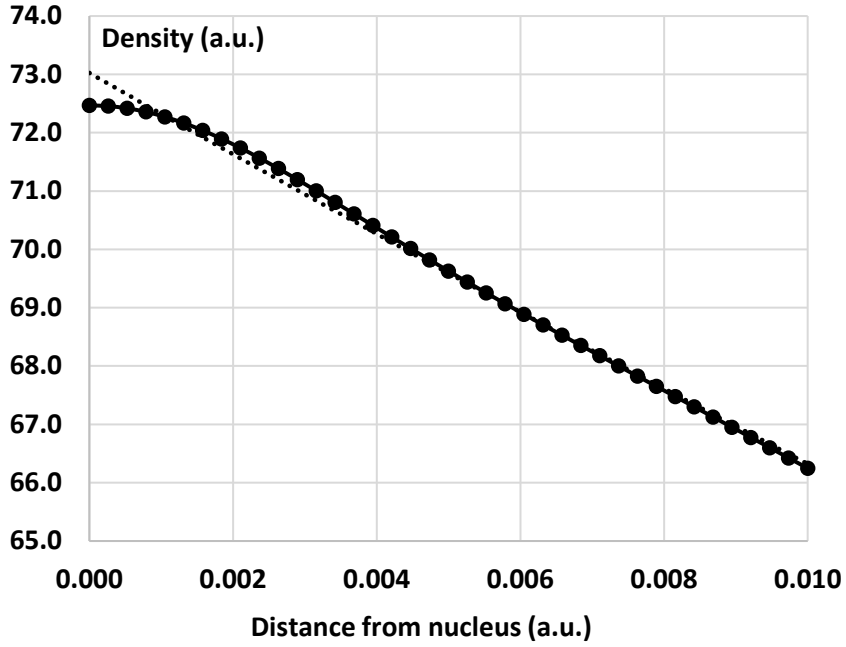

Figure S2. The six density difference plots of the four studied density functionals, B^{+} ion. (aug-cc-pωCV5Z)

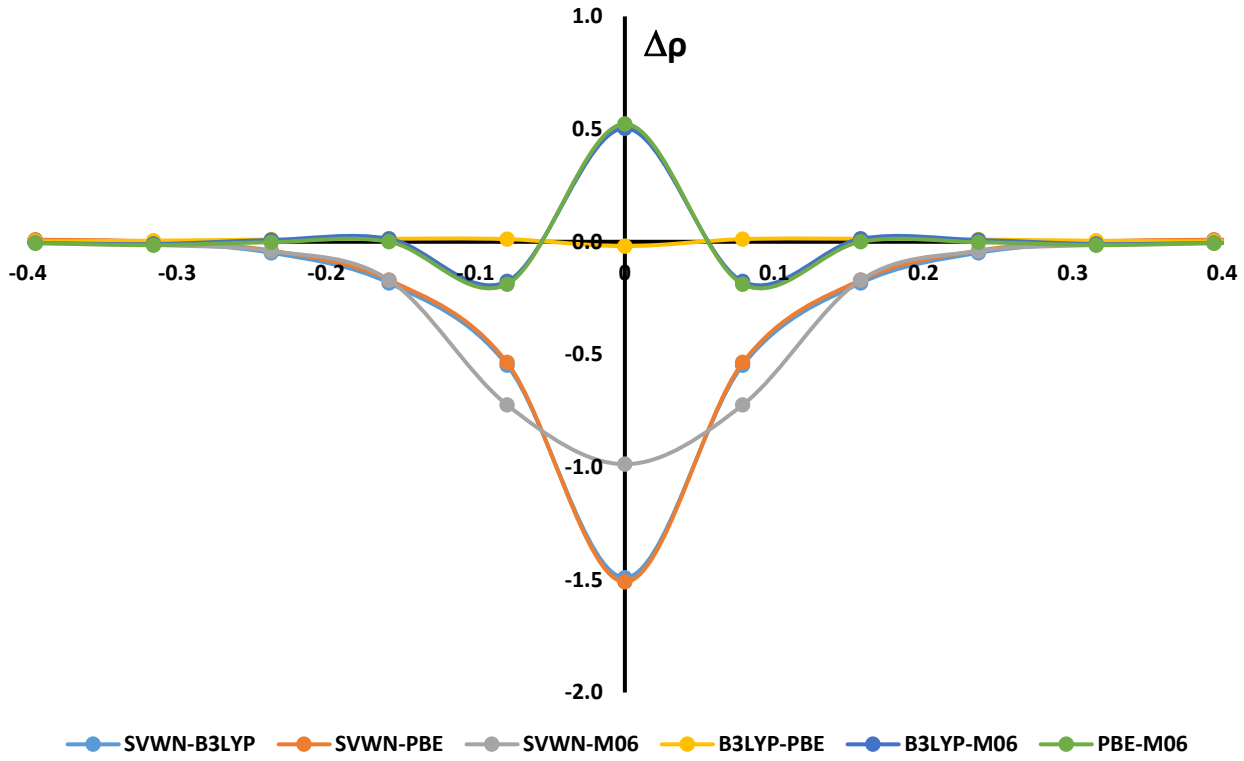

Figure S3. The six density difference plots of the four studied density functionals, B^{3+} ion. (aug-cc-pωCV5Z)

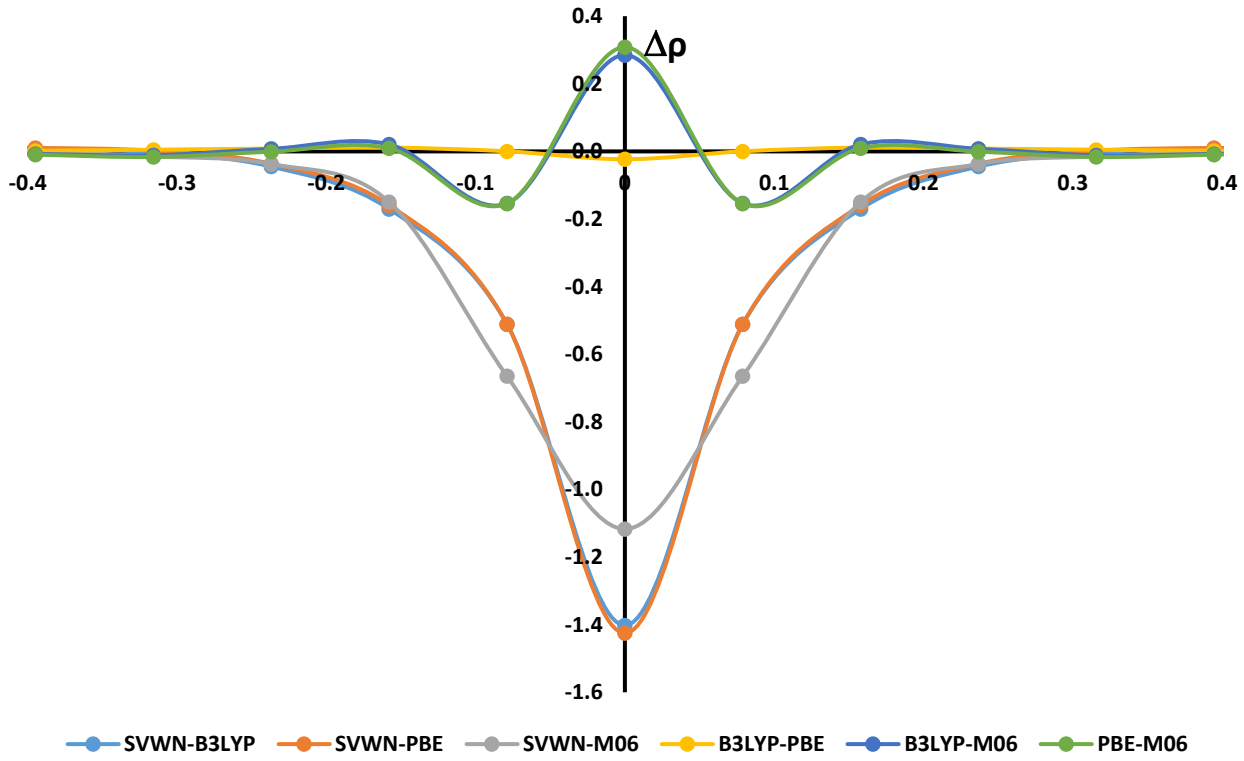

Figure S4. The six density difference plots of the four studied density functionals, C^{2+} ion. (aug-cc-pωCV5Z)

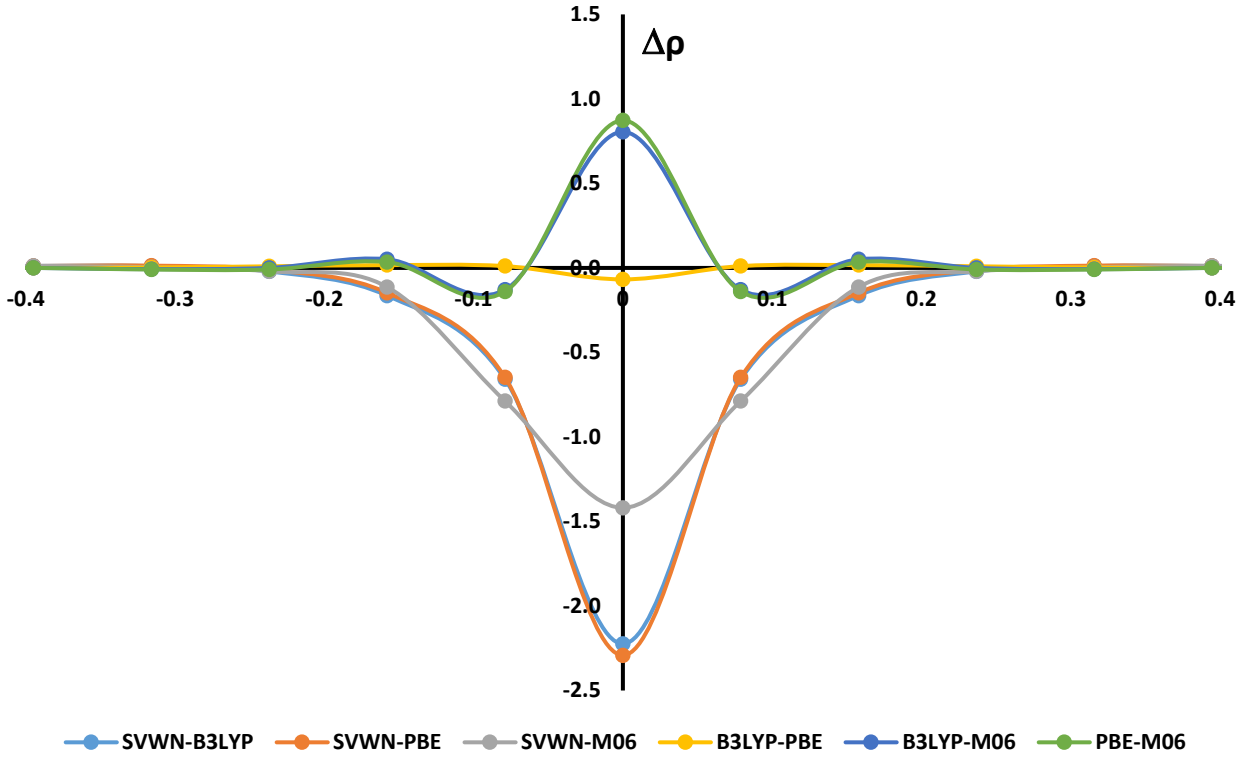

Figure S5. The six density difference plots of the four studied density functionals, C^{4+} ion. (aug-cc-pωCV5Z)

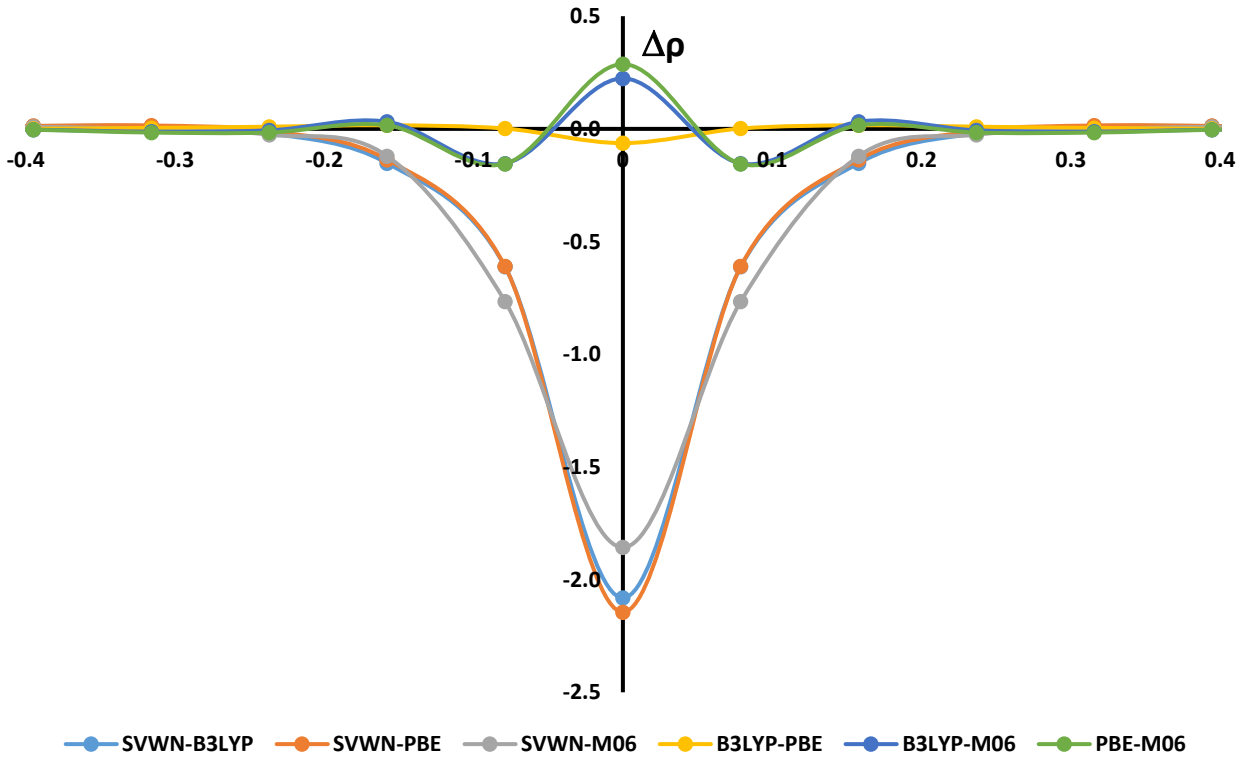

Figure S6. The six density difference plots of the four studied density functionals, N^{3+} ion. (aug-cc-pωCV5Z)

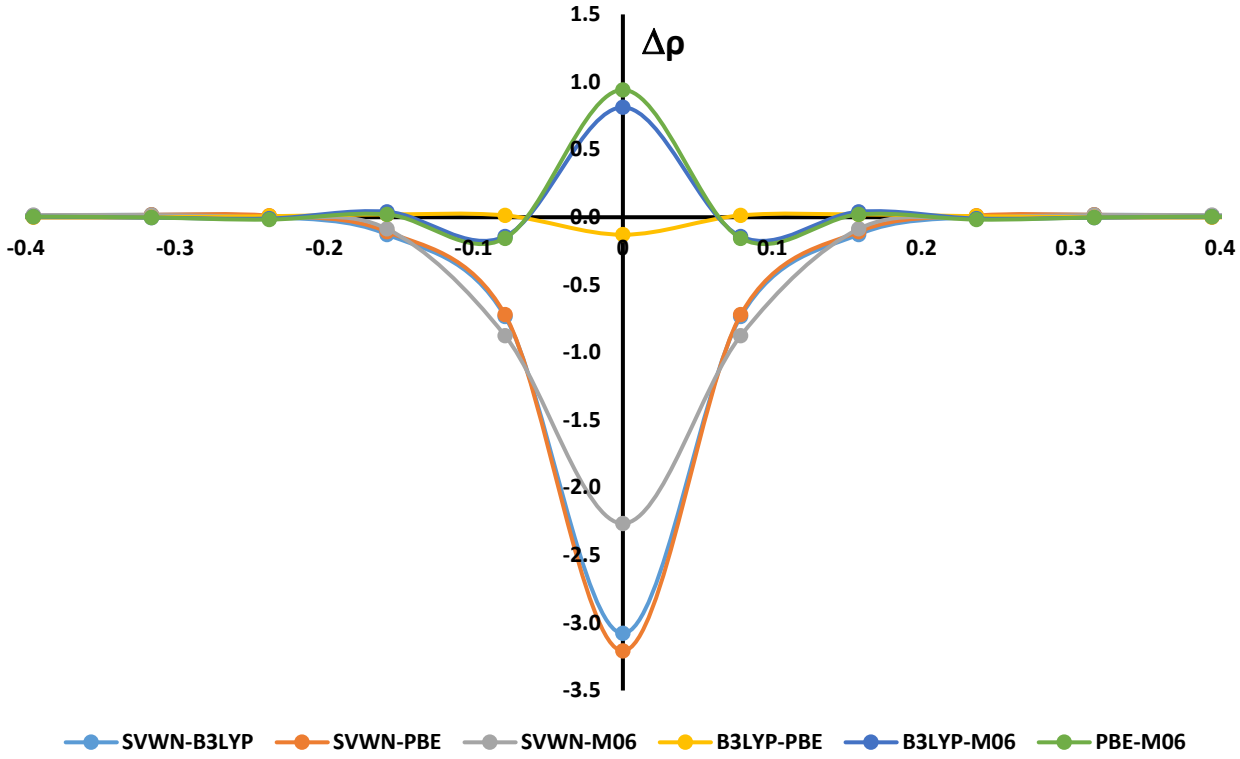

Figure S7. The six density difference plots of the four studied density functionals, N^{5+} ion. (aug-cc-pωCV5Z)

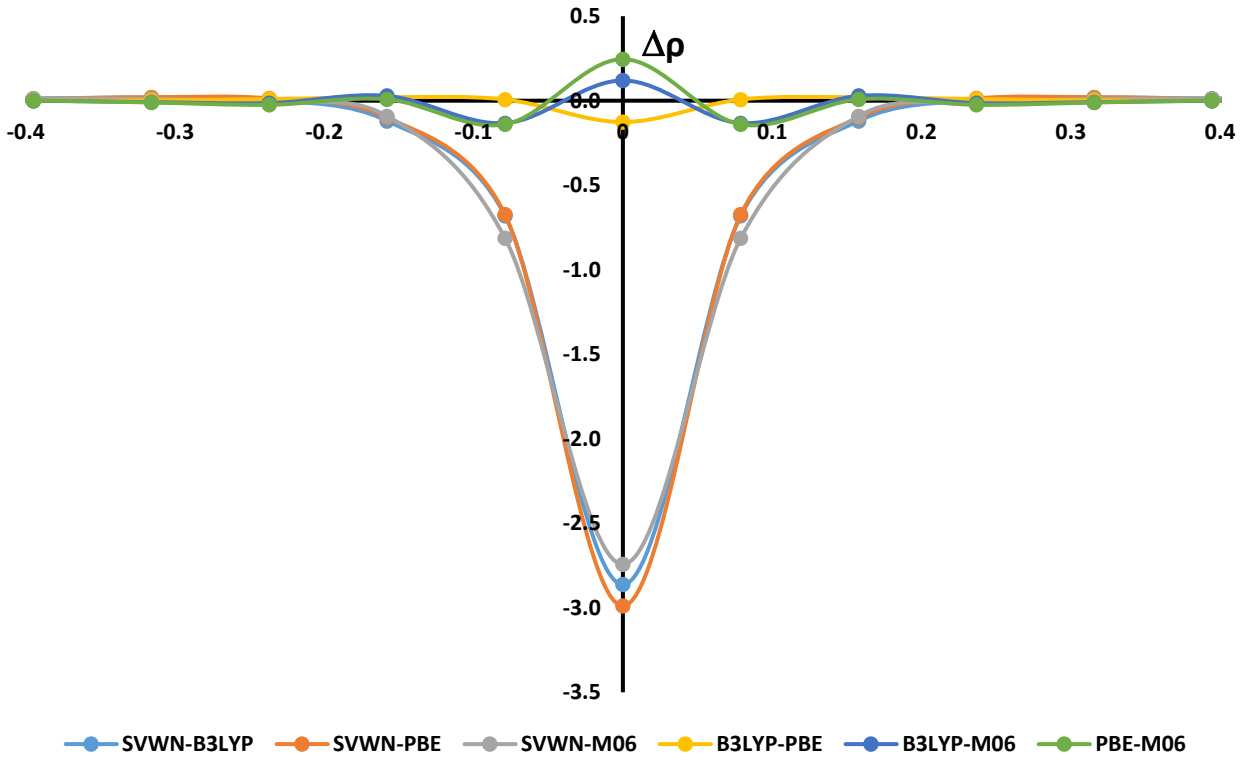

Figure S8. The six density difference plots of the four studied density functionals, O^{4+} ion. (aug-cc-pωCV5Z)

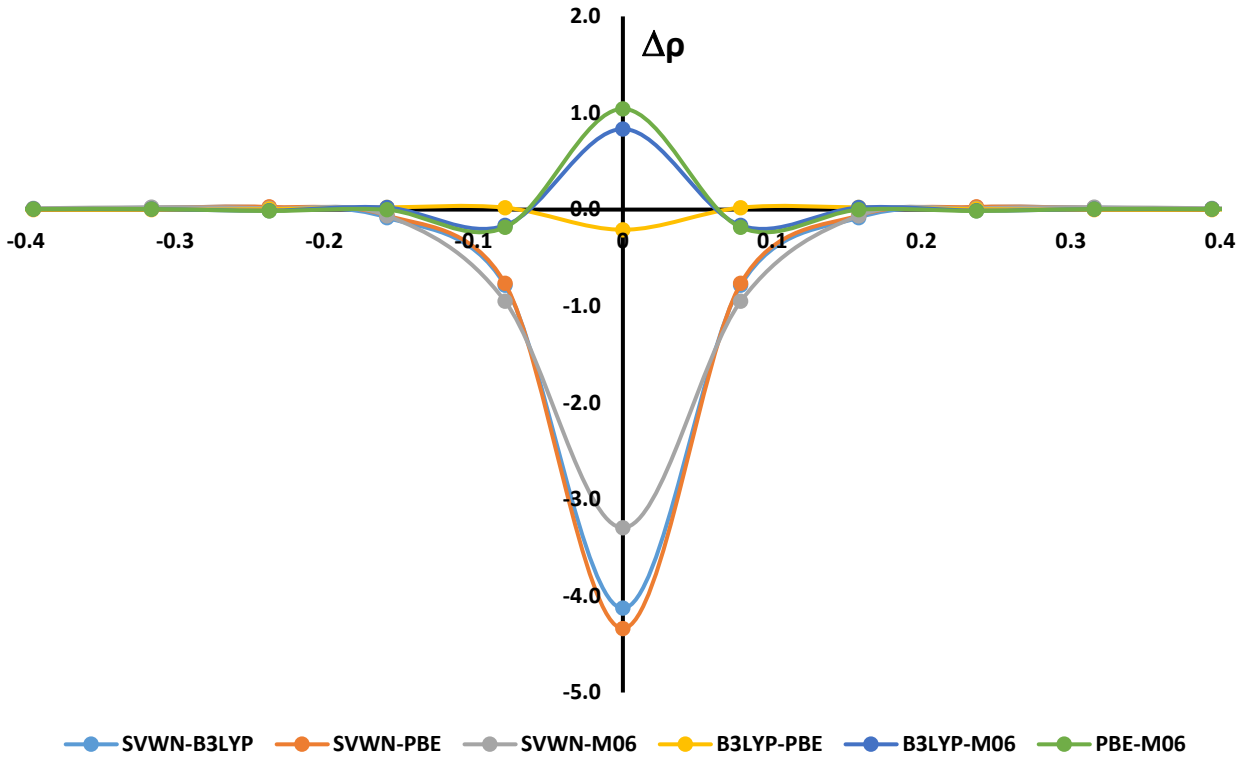

Figure S9. The six density difference plots of the four studied density functionals, O^{6+} ion. (aug-cc-pωCV5Z)

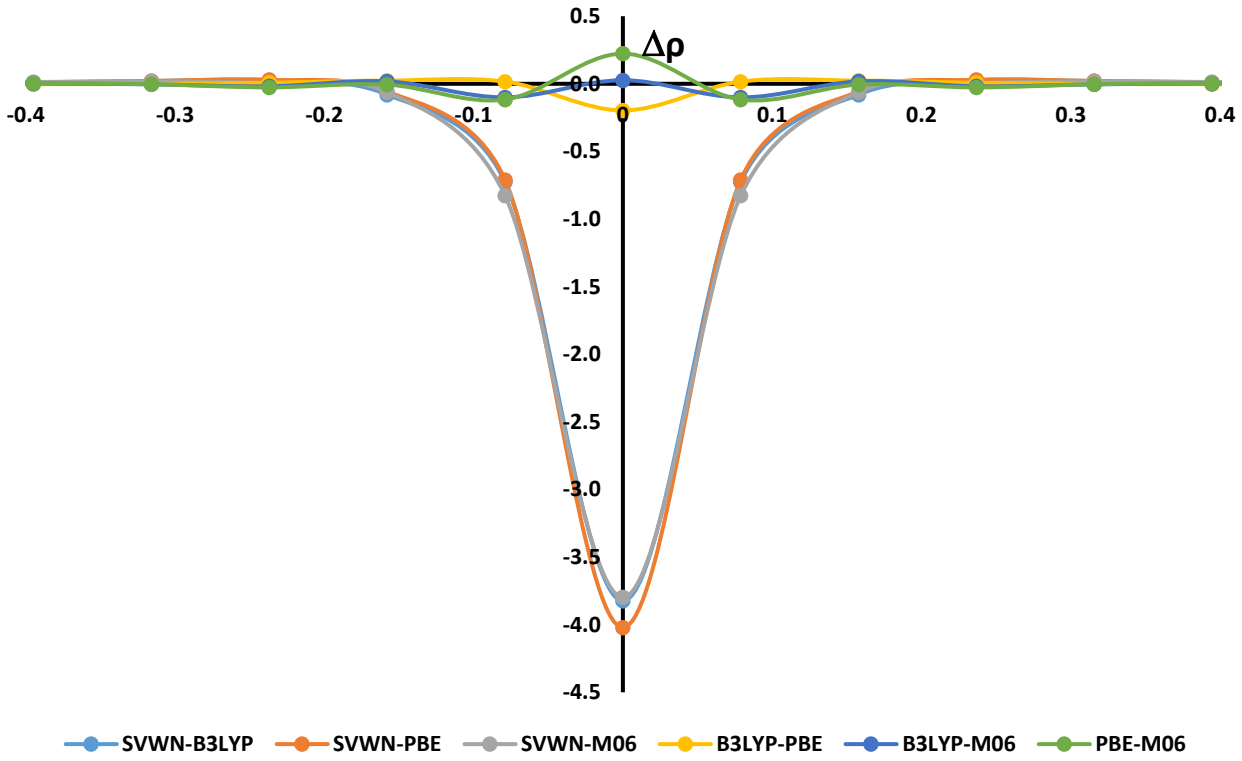

Figure S10. The six density difference plots of the four studied density functionals, F^{5+} ion. (aug-cc-pωCV5Z)

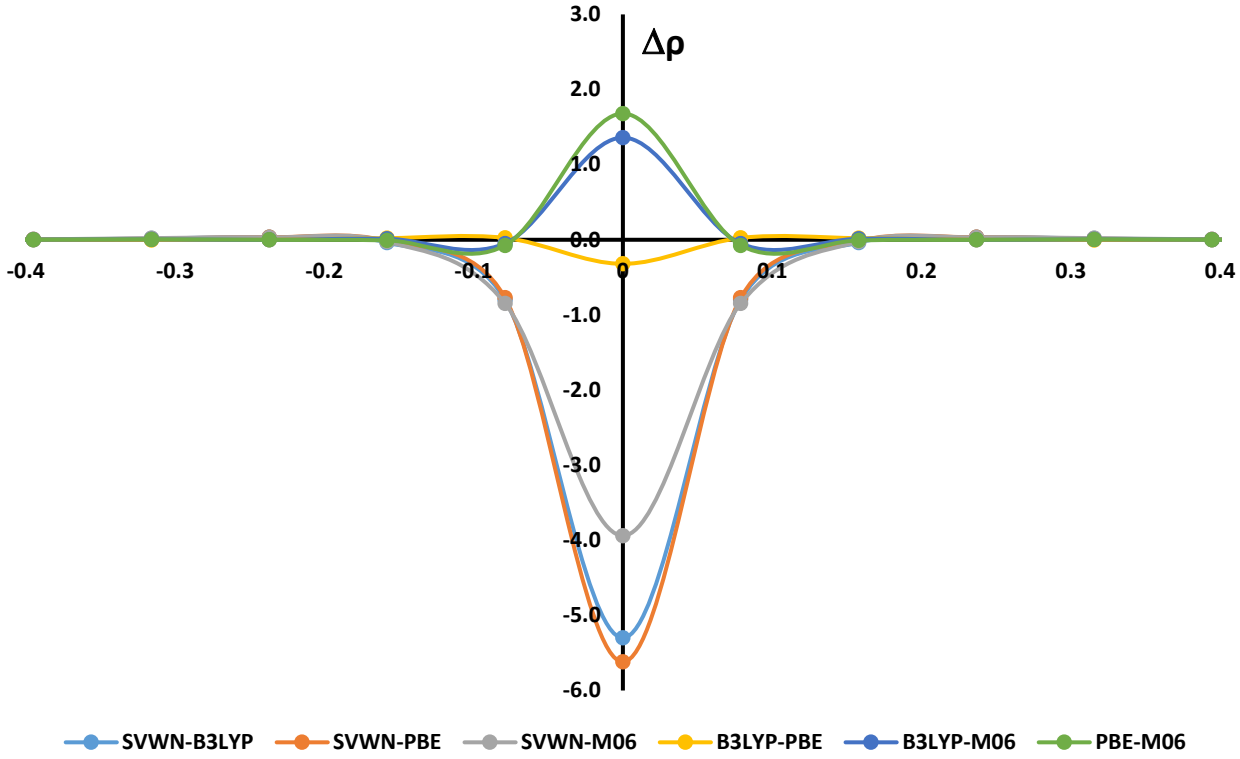

Figure S11. The six density difference plots of the four studied density functionals, F^{7+} ion. (aug-cc-pωCV5Z)

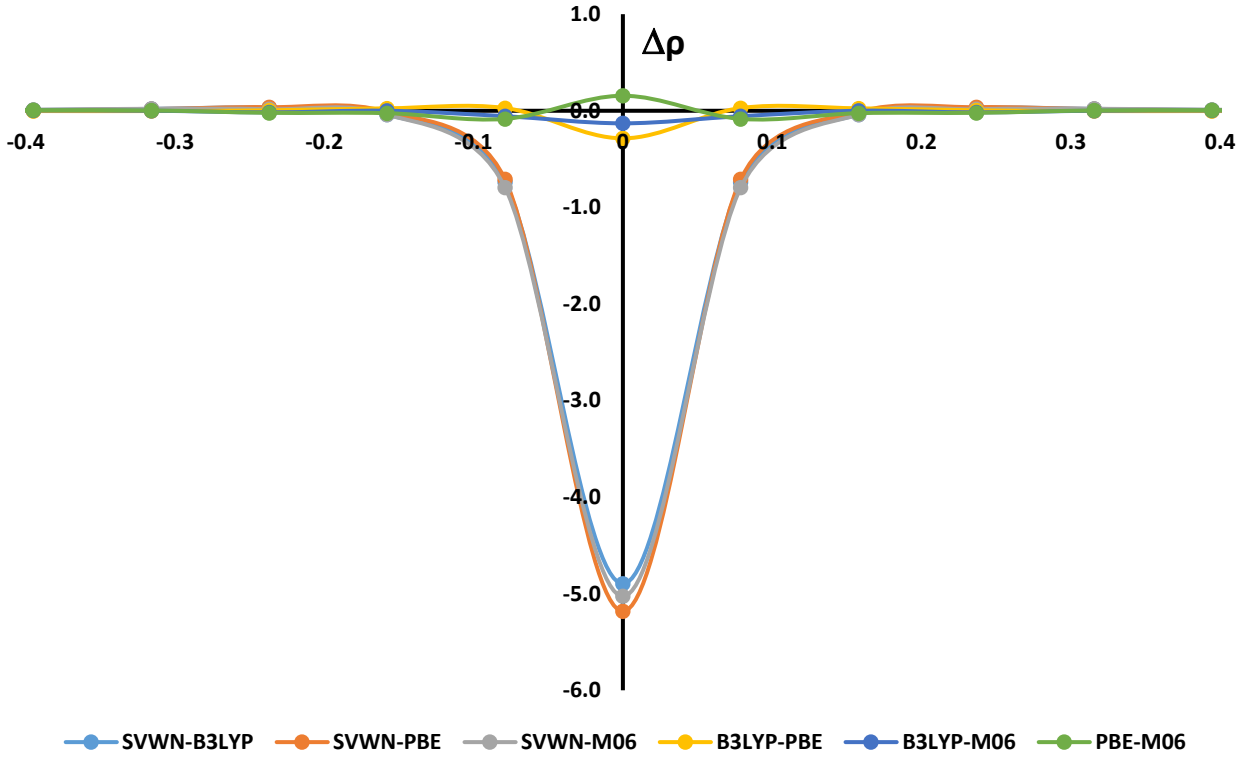

Figure S12. The six density difference plots of the four studied density functionals, Ne^{6+} ion. (aug-cc-pωCV5Z)

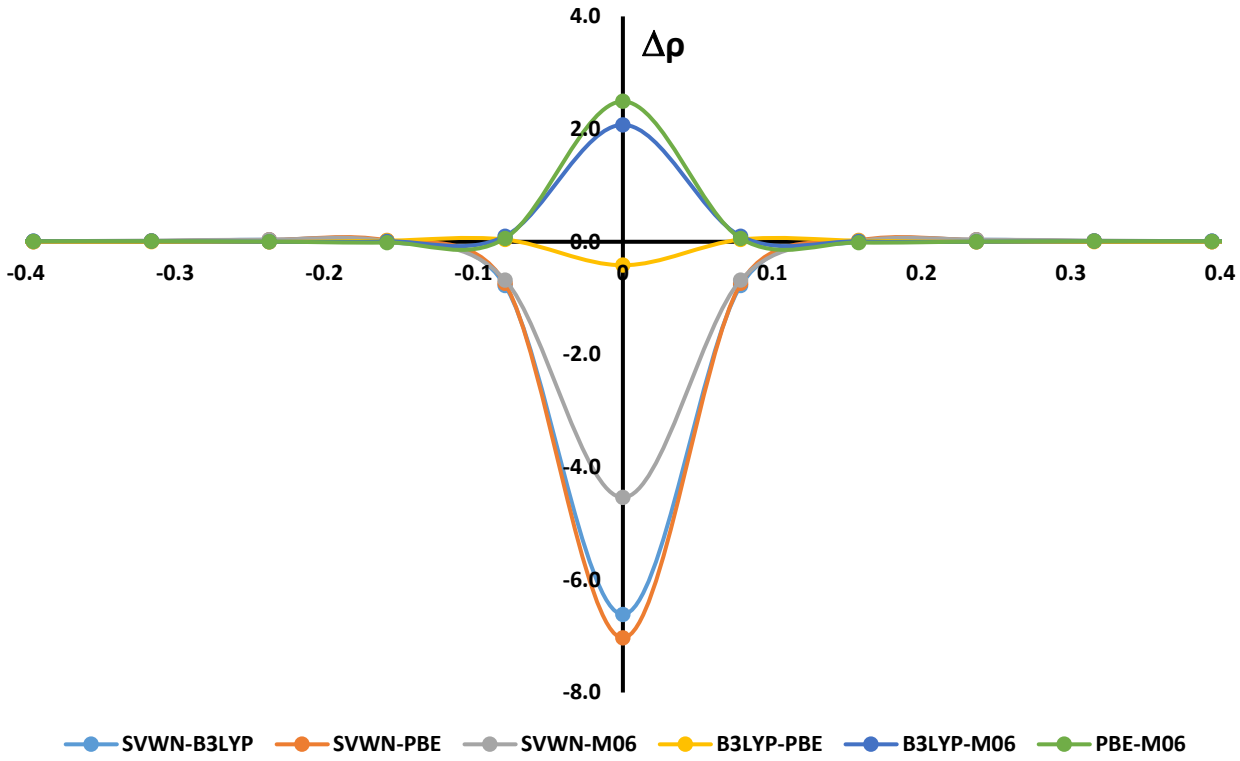

Figure S13. The six density difference plots of the four studied density functionals, Ne^{8+} ion. (aug-cc-pωCV5Z)

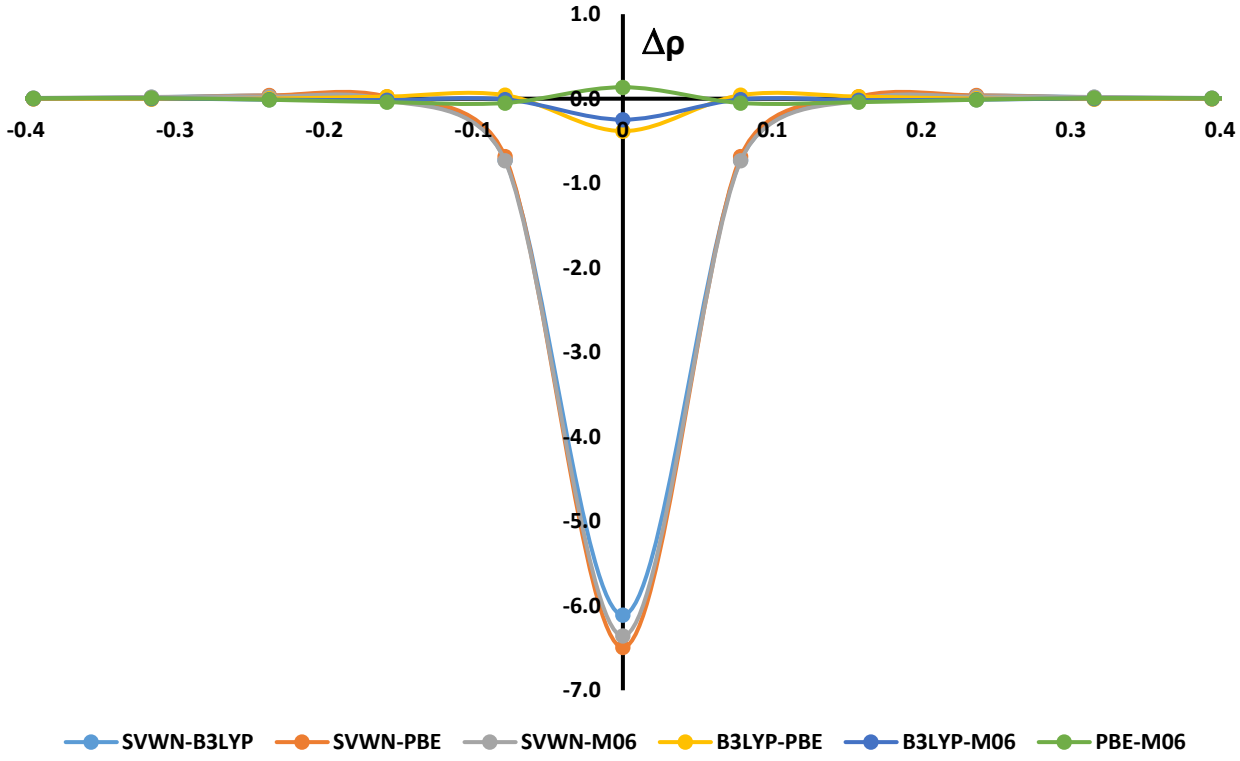

Figure S14. Average $\Delta E_D' = E(\rho)-E(\rho')$ in kJ/mol for two test sets: (A) Top: B3LYP, PBE, SVWN, and M06; (B) bottom: PBE, M06-2X, PBE0, and SVWN, using the other three functional's densities as trial densities. The functionals represent very different densities in terms of previous ranking for these systems[1]. The computed energies are the experimentally known double ionization potentials discussed in the main text. Despite the energies being many eVs, these changes in densities affect the computed energies by only < 1.5 kJ/mol, i.e. the density variations manifest below chemical accuracy; such systems are referred to as "practically normal".

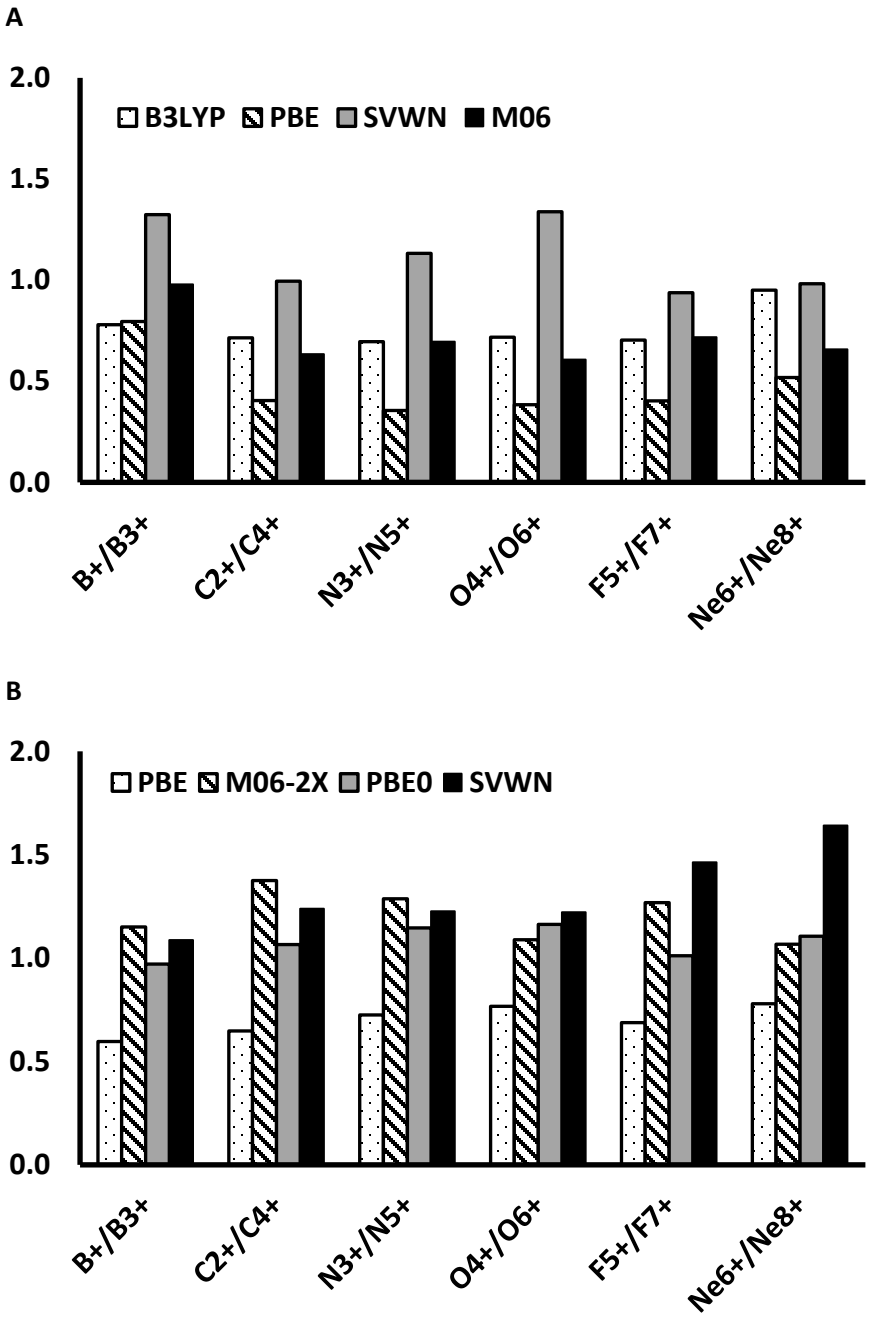

Figure S15. Difference between the ionization potentials computed by a given density functional using its own density and other densities: A) M06; B) B3LYP; C) PBE; D) SVWN.

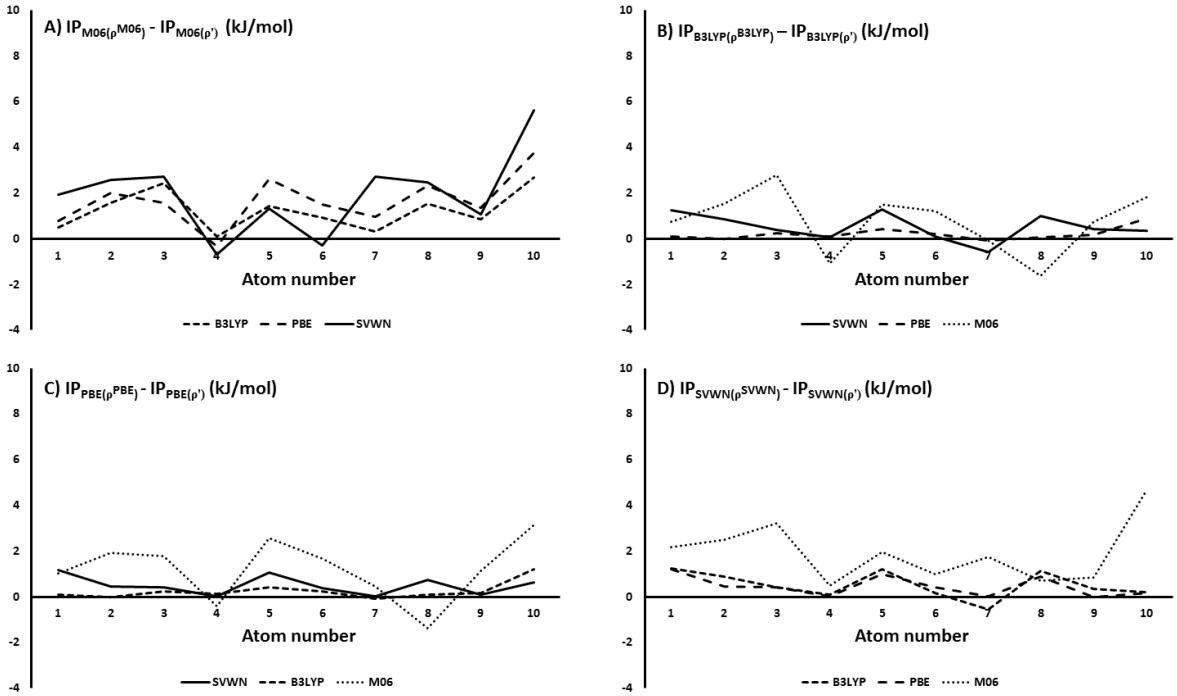

Table S1. Computed B3LYP and PBE energies (a.u.) of ions similar to those studied previously[1,2] (aug-cc-pωCV5Z basis set). The IP values refer to the energy of removing both 2s electrons in kJ/mol. Experimental data from NIST[3].

	B3LYP			PBE			*Experiment (NIST)*
	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP	
B^{+}/B^{3+}	-24.3298	-22.0132	6082.30	-24.2934	-21.9820	6068.65	***6086.9***
C^{2+}/C^{4+}	-36.5024	-32.3792	10825.34	-36.4610	-32.3442	10808.71	***10843.3***
N^{3+}/N^{5+}	-51.1753	-44.7448	16883.32	-51.1303	-44.7063	16866.41	***16920.3***
O^{4+}/O^{6+}	-68.3483	-59.1104	24253.99	-68.3006	-59.0686	24238.68	***24316.4***
F^{5+}/F^{7+}	-88.0210	-75.4758	32937.47	-87.9713	-75.4308	32925.06	***33032.3***
Ne^{6+}/Ne^{8+}	-110.1936	-93.8411	42933.43	-110.1422	-93.7930	42924.89	***43068.7***

Table S2. Computed SVWN and M06 energies (a.u.) of ions similar to those studied previously[1,2] (aug-cc-pωCV5Z basis set). The IP values refer to the energy of removing both 2s electrons in kJ/mol.

	SVWN			M06		
	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP
B^{+}/B^{3+}	-24.0382	-21.7432	6025.72	-24.3340	-22.0492	5998.70
C^{2+}/C^{4+}	-36.1300	-32.0395	10739.70	-36.5087	-32.4265	10717.78
N^{3+}/N^{5+}	-50.7211	-44.3342	16768.75	-51.1843	-44.8034	16753.11
O^{4+}/O^{6+}	-67.8112	-58.6282	24109.87	-68.3598	-59.1802	24101.01
F^{5+}/F^{7+}	-87.4003	-74.9213	32763.70	-88.0353	-75.5567	32762.41
Ne^{6+}/Ne^{8+}	-109.4886	-93.2137	42729.73	-110.2103	-93.9331	42735.76

Table S3. Computed PBE, B3LYP, and M06 energies (a.u.) using the optimized SVWN densities of ions similar to those studied previously[1,2] (aug-cc-pωCV5Z basis set). The IP values refer to the energy of removing both 2s electrons in kJ/mol.

	PBE(SVWN)			B3LYP(SVWN)			M06(SVWN)		
	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP
B^{+}/B^{3+}	-24.2920	-21.9808	6067.93	-24.3283	-22.0119	6081.62	-24.3312	-22.0469	5997.38
C^{2+}/C^{4+}	-36.4595	-32.3430	10807.96	-36.5008	-32.3779	10824.60	-36.5061	-32.4243	10716.77
N^{3+}/N^{5+}	-51.1288	-44.7050	16865.60	-51.1737	-44.7435	16882.52	-51.1818	-44.8012	16752.17
O^{4+}/O^{6+}	-68.2990	-59.0673	24237.79	-68.3466	-59.1091	24253.13	-68.3574	-59.1780	24100.35
F^{5+}/F^{7+}	-87.9696	-75.4295	32924.12	-88.0193	-75.4744	32936.57	-88.0327	-75.5546	32761.41
Ne^{6+}/Ne^{8+}	-110.1405	-93.7917	42923.91	-110.1919	-93.8397	42932.50	-110.2078	-93.9309	42734.88

Table S4. Computed SVWN, B3LYP, and M06 energies (a.u.) using the optimized PBE densities of ions similar to those studied previously[1,2] (aug-cc-pωCV5Z basis set). The IP values refer to the energy of removing both 2s electrons in kJ/mol.

	SVWN(PBE)			B3LYP(PBE)			M06(PBE)		
	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP
B^{+}/B^{3+}	-24.0368	-21.7420	6025.00	-24.3296	-22.0131	6081.93	-24.3328	-22.0482	5998.04
C^{2+}/C^{4+}	-36.1285	-32.0383	10738.95	-36.5022	-32.3791	10825.06	-36.5079	-32.4257	10718.01
N^{3+}/N^{5+}	-50.7195	-44.3330	16767.94	-51.1751	-44.7447	16883.10	-51.1837	-44.8026	16753.56
O^{4+}/O^{6+}	-67.8096	-58.6269	24108.96	-68.3481	-59.1103	24253.80	-68.3592	-59.1794	24101.56
F^{5+}/F^{7+}	-87.3987	-74.9200	32762.74	-88.0209	-75.4757	32937.34	-88.0346	-75.5560	32762.65
Ne^{6+}/Ne^{8+}	-109.4869	-93.2124	42728.76	-110.1934	-93.8410	42933.31	-110.2096	-93.9323	42736.07

Table S5. Computed SVWN, PBE, and M06 energies (a.u.) using the optimized B3LYP densities of ions similar to those studied previously[1,2] (aug-cc-pωCV5Z basis set). The IP values refer to the energy of removing both 2s electrons in kJ/mol.

	SVWN(B3LYP)			PBE (B3LYP)			M06(B3LYP)		
	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP
B^{+}/B^{3+}	-24.0367	-21.7419	6025.04	-24.2932	-21.9819	6068.30	-24.3328	-22.0484	5997.75
C^{2+}/C^{4+}	-36.1285	-32.0382	10738.96	-36.4608	-32.3441	10808.44	-36.5078	-32.4259	10717.12
N^{3+}/N^{5+}	-50.7195	-44.3329	16767.96	-51.1302	-44.7062	16866.19	-51.1835	-44.8028	16752.43
O^{4+}/O^{6+}	-67.8095	-58.6269	24109.00	-68.3004	-59.0685	24238.51	-68.3590	-59.1797	24100.40
F^{5+}/F^{7+}	-87.3986	-74.9199	32762.80	-87.9711	-75.4307	32924.92	-88.0344	-75.5563	32761.50
Ne^{6+}/Ne^{8+}	-109.4868	-93.2123	42728.80	-110.1421	-93.7929	42924.78	-110.2095	-93.9326	42734.98

Table S6. Computed B3LYP, PBE, and SVWN energies (a.u.) using the optimized M06 densities of ions similar to those studied previously[1,2] (aug-cc-pωCV5Z basis set). The IP values refer to the energy of removing both 2s electrons in kJ/mol.

	B3LYP(M06)			PBE(M06)			SVWN(M06)		
	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP	$X^{(n)+}$	$X^{(n+2)+}$	IP
B^{+}/B^{3+}	-24.3285	-22.0124	6081.01	-24.2919	-21.9810	6067.34	-24.0350	-21.7409	6023.15
C^{2+}/C^{4+}	-36.5013	-32.3786	10824.23	-36.4601	-32.3433	10808.53	-36.1273	-32.0373	10738.20
N^{3+}/N^{5+}	-51.1744	-44.7443	16882.25	-51.1296	-44.7055	16866.45	-50.7183	-44.3321	16766.96
O^{4+}/O^{6+}	-68.3473	-59.1099	24252.88	-68.2998	-59.0678	24238.59	-67.8082	-58.6261	24107.62
F^{5+}/F^{7+}	-88.0202	-75.4753	32936.38	-87.9705	-75.4300	32924.93	-87.3978	-74.9191	32762.76
Ne^{6+}/Ne^{8+}	-110.1925	-93.8407	42931.63	-110.1413	-93.7923	42924.41	-109.4860	-93.2115	42728.68

Table S7. Experimental ionization potentials and ground states of atoms and ions from NIST.

ATOM	Exp. IP/eV	STATE X	STATE X^+
H	13.60	$^2S^1/_2$	
He	24.59	$^1S_0$	$^2S_{1/2}$
Li	5.39	$^2S^1/_2$	$^1S_0$
Be	9.32	$^1S_0$	$^2S_{1/2}$
B	8.30	$^2P°^1/_2$	$^1S_0$
C	11.26	$^3P_0$	$^2P°_{1/2}$
N	14.53	$^4S°^3/_2$	$^3P_0$
O	13.62	$^3P_2$	$^4S°_{3/2}$
F	17.42	$^2P°^3/_2$	$^3P_2$
Ne	21.56	$^1S_0$	$^2P°_{3/2}$

Table S8. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms (in kJ/mol), computed using CCSD(T) and CCSD, aug-cc-pV5Z basis set.

ATOM	CCSD(T)			CCSD		
	X	X+	IP	X	X+	IP
H	-0.5000	0.0000	**1312.74**	-0.5000	0.0000	**1312.74**
He	-2.9032	-1.9999	**2371.50**	-2.9032	-1.9999	**2371.50**
Li	-7.4600	-7.2622	**519.15**	-7.4599	-7.2622	**519.07**
Be	-14.6463	-14.3042	**898.23**	-14.6458	-14.3042	**896.82**
B	-24.6298	-24.3255	**799.01**	-24.6279	-24.3249	**795.64**
C	-37.8195	-37.4060	**1085.58**	-37.8167	-37.4043	**1082.81**
N	-54.5627	-54.0284	**1402.58**	-54.5594	-54.0262	**1399.85**
O	-75.0372	-74.5384	**1309.40**	-75.0329	-74.5362	**1304.06**
F	-99.7000	-99.0607	**1678.73**	-99.6946	-99.0577	**1672.20**
Ne	-128.9004	-128.1074	**2082.13**	-128.8939	-128.1037	**2074.66**

Table S9. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms kJ/mol), computed using B3LYP and PBE functionals, aug-cc-pV5Z basis set.

ATOM	B3LYP			PBE		
	X	X+	IP	X	X+	IP
H	-0.4991	0.0000	**1310.26**	-0.5000	0.0000	**1312.71**
He	-2.9081	-1.9949	**2397.62**	-2.8929	-1.9937	**2360.75**
Li	-7.4825	-7.2786	**535.44**	-7.4620	-7.2567	**539.00**
Be	-14.6593	-14.3276	**871.05**	-14.6298	-14.2992	**868.05**
B	-24.6479	-24.3297	**835.39**	-24.6120	-24.2932	**837.04**
C	-37.8402	-37.4192	**1105.43**	-37.7985	-37.3743	**1113.55**
N	-54.5818	-54.0464	**1405.79**	-54.5354	-53.9943	**1420.76**
O	-75.0712	-74.5556	**1353.91**	-75.0146	-74.4978	**1356.73**
F	-99.7421	-99.0947	**1699.95**	-99.6756	-99.0269	**1703.26**
Ne	-128.9422	-128.1483	**2084.27**	-128.8658	-128.0700	**2089.26**

Table S10. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms kJ/mol), computed using SVWN and M06 functionals, aug-cc-pV5Z basis set.

ATOM	SVWN			M06		
	X	X+	IP	X	X+	IP
H	-0.4787	0.0000	**1256.74**	-0.5002	0.0000	**1313.25**
He	-2.8348	-1.9417	**2344.93**	-2.9102	-1.9996	**2390.90**
Li	-7.3439	-7.1427	**528.11**	-7.4859	-7.2908	**512.06**
Be	-14.4471	-14.1154	**870.93**	-14.6609	-14.3325	**862.23**
B	-24.3560	-24.0381	**834.49**	-24.6425	-24.3325	**813.85**
C	-37.4701	-37.0404	**1128.22**	-37.8305	-37.4145	**1092.34**
N	-54.1365	-53.5852	**1447.62**	-54.5789	-54.0373	**1421.95**
O	-74.5310	-74.0163	**1351.17**	-75.0651	-74.5576	**1332.58**
F	-99.1144	-98.4545	**1732.62**	-99.7399	-99.0950	**1693.17**
Ne	-128.2329	-127.4176	**2140.53**	-128.9512	-128.1549	**2090.93**

Table S11. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms kJ/mol), computed using SWN densities but other functionals, aug-cc-pV5Z basis set.

ATOM	PBE(SVWN)			B3LYP(SVWN)			M06(SVWN)		
	X	X+	IP	X	X+	IP	X	X+	IP
H	-0.4996	0.0000	**1311.6**	-0.4986	0.0000	**1309.1**	-0.4995	0.0000	**1311.4**
He	-2.8922	-1.9932	**2360.3**	-2.9072	-1.9943	**2396.7**	-2.9084	-1.9988	**2388.3**
Li	-7.4609	-7.2558	**538.6**	-7.4813	-7.2776	**535.0**	-7.4830	-7.2894	**508.3**
Be	-14.6286	-14.2980	**868.1**	-14.6579	-14.3262	**871.0**	-14.6586	-14.3313	**859.2**
B	-24.6102	-24.2920	**835.6**	-24.6459	-24.3282	**834.1**	-24.6385	-24.3308	**807.8**
C	-37.7964	-37.3725	**1112.9**	-37.8381	-37.4171	**1105.3**	-37.8272	-37.4123	**1089.3**
N	-54.5333	-53.9922	**1420.6**	-54.5798	-54.0441	**1406.3**	-54.5727	-54.0344	**1413.3**
O	-75.0121	-74.4956	**1356.1**	-75.0687	-74.5534	**1353.0**	-75.0615	-74.5552	**1329.3**
F	-99.6732	-99.0246	**1703.0**	-99.7395	-99.0923	**1699.4**	-99.7341	-99.0906	**1689.5**
Ne	-128.8639	-128.0680	**2089.8**	-128.9400	-128.1460	**2084.7**	-128.9479	-128.1512	**2091.5**

Table S12. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms (in kJ/mol), computed using PBE densities but other functionals, aug-cc-pV5Z basis set.

ATOM	SVWN(PBE)			B3LYP(PBE)			M06(PBE)		
	X	X+	IP	X	X+	IP	X	X+	IP
H	-0.4782	0.0000	**1255.5**	-0.4990	0.0000	**1310.2**	-0.4999	0.0000	**1312.5**
He	-2.8341	-1.9411	**2344.5**	-2.9080	-1.9948	**2397.6**	-2.9093	-1.9994	**2388.9**
Li	-7.3428	-7.1418	**527.7**	-7.4824	-7.2786	**535.2**	-7.4844	-7.2906	**509.1**
Be	-14.4459	-14.1142	**870.9**	-14.6592	-14.3274	**870.9**	-14.6604	-14.3327	**860.2**
B	-24.3541	-24.0367	**833.5**	-24.6475	-24.3295	**834.9**	-24.6400	-24.3327	**806.6**
C	-37.4681	-37.0385	**1127.8**	-37.8398	-37.4189	**1105.2**	-37.8286	-37.4140	**1088.4**
N	-54.1344	-53.5831	**1447.6**	-54.5815	-54.0460	**1405.8**	-54.5750	-54.0361	**1414.8**
O	-74.5285	-74.0142	**1350.3**	-75.0709	-74.5552	**1353.9**	-75.0637	-74.5568	**1330.9**
F	-99.1121	-98.4522	**1732.6**	-99.7420	-99.0946	**1699.7**	-99.7367	-99.0933	**1689.2**
Ne	-128.2308	-127.4153	**2141.0**	-128.9423	-128.1484	**2084.2**	-128.9514	-128.1540	**2093.8**

Table S13. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms (in kJ/mol), computed using B3LYP densities but other functionals, aug-cc-pV5Z basis set.

ATOM	SVWN (B3LYP)			PBE (B3LYP)			M06 (B3LYP)		
	X	X+	IP	X	X+	IP	X	X+	IP
H	-0.4782	0.0000	**1255.5**	-0.5000	0.0000	**1312.6**	-0.4991	0.0000	**1310.3**
He	-2.8339	-1.9411	**2344.1**	-2.8928	-1.9937	**2360.7**	-2.9095	-1.9995	**2389.3**
Li	-7.3427	-7.1417	**527.7**	-7.4619	-7.2567	**538.7**	-7.4843	-7.2907	**508.3**
Be	-14.4457	-14.1140	**870.8**	-14.6297	-14.2991	**868.0**	-14.6604	-14.3325	**860.8**
B	-24.3540	-24.0366	**833.3**	-24.6117	-24.2932	**836.2**	-24.6404	-24.3327	**807.9**
C	-37.4679	-37.0383	**1128.0**	-37.7980	-37.3741	**1113.1**	-37.8290	-37.4142	**1089.0**
N	-54.1345	-53.5829	**1448.2**	-54.5350	-53.9939	**1420.6**	-54.5754	-54.0364	**1415.2**
O	-74.5284	-74.0143	**1350.0**	-75.0143	-74.4975	**1356.8**	-75.0644	-74.5573	**1331.3**
F	-99.1119	-98.4521	**1732.3**	-99.6754	-99.0268	**1702.9**	-99.7373	-99.0937	**1689.7**
Ne	-128.2306	-127.4152	**2140.9**	-128.8660	-128.0703	**2089.3**	-128.9522	-128.1543	**2094.9**

Table S14. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms (in kJ/mol), computed using M06 densities but other functionals, aug-cc-pV5Z basis set.

ATOM	B3LYP(M06)			PBE(M06)			SVWN(M06)		
	X	X+	IP	X	X+	IP	X	X+	IP
H	-0.4988	0.0000	**1309.5**	-0.4996	0.0000	**1311.7**	-0.4778	0.0000	**1254.6**
He	-2.9074	-1.9947	**2396.1**	-2.8920	-1.9935	**2358.8**	-2.8330	-1.9408	**2342.4**
Li	-7.4813	-7.2784	**532.7**	-7.4610	-7.2563	**537.3**	-7.3412	-7.1412	**525.0**
Be	-14.6589	-14.3267	**872.1**	-14.6294	-14.2986	**868.5**	-14.4449	-14.1133	**870.4**
B	-24.6469	-24.3293	**833.8**	-24.6107	-24.2930	**834.0**	-24.3529	-24.0359	**832.5**
C	-37.8389	-37.4184	**1104.2**	-37.7968	-37.3733	**1111.7**	-37.4669	-37.0375	**1127.2**
N	-54.5808	-54.0454	**1405.8**	-54.5339	-53.9930	**1420.1**	-54.1328	-53.5821	**1445.9**
O	-75.0698	-74.5550	**1351.6**	-75.0125	-74.4952	**1358.2**	-74.5268	-74.0124	**1350.5**
F	-99.7409	-99.0937	**1699.1**	-99.6737	-99.0255	**1701.9**	-99.1101	-98.4505	**1731.8**
Ne	-128.9409	-128.1474	**2083.3**	-128.8639	-128.0689	**2087.3**	-128.2273	-127.4136	**2136.4**

Table S15. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms (in kJ/mol), computed using B3LYP and PBE functionals, def-TZVP basis set.

ATOM	B3LYP			PBE		
	X	X+	IP	X	X+	IP
H	-0.4988	0.0000	**1309.51**	-0.4996	0.0000	**1311.74**
He	-2.9059	-1.9933	**2396.12**	-2.8906	-1.9921	**2358.97**
Li	-7.4824	-7.2785	**535.32**	-7.4619	-7.2566	**538.98**
Be	-14.6581	-14.3264	**870.86**	-14.6283	-14.2977	**867.93**
B	-24.6463	-24.3283	**834.93**	-24.6101	-24.2915	**836.54**
C	-37.8382	-37.4173	**1104.84**	-37.7960	-37.3722	**1112.73**
N	-54.5790	-54.0435	**1405.88**	-54.5322	-53.9912	**1420.35**
O	-75.0669	-74.5523	**1351.01**	-75.0097	-74.4943	**1353.03**
F	-99.7363	-99.0898	**1697.35**	-99.6691	-99.0218	**1699.64**
Ne	-0.4988	0.0000	**1309.51**	-0.4996	0.0000	**1311.74**

Table S16. Electronic energies for atoms and ions (in a.u.) and ionization potentials (IP) for atoms (in kJ/mol), computed using SVWN and M06 functionals, def-TZVP basis set.

ATOM	SVWN			M06		
	X	X+	IP	X	X+	IP
H	-0.4783	0.0000	**1255.90**	-0.4999	0.0000	**1312.41**
He	-2.8326	-1.9402	**2342.98**	-2.9082	-1.9990	**2386.98**
Li	-7.3438	-7.1427	**527.88**	-7.4861	-7.2911	**512.08**
Be	-14.4457	-14.1142	**870.31**	-14.6596	-14.3316	**861.19**
B	-24.3539	-24.0365	**833.54**	-24.6407	-24.3314	**812.16**
C	-37.4674	-37.0381	**1127.15**	-37.8279	-37.4123	**1091.05**
N	-54.1329	-53.5817	**1446.99**	-54.5765	-54.0342	**1423.70**
O	-74.5256	-74.0124	**1347.36**	-75.0612	-74.5552	**1328.50**
F	-99.1074	-98.4488	**1729.30**	-99.7345	-99.0911	**1689.47**
Ne	-128.2241	-127.4090	**2140.11**	-128.9457	-128.1492	**2091.12**

Table S17. Errors in computed ionization potentials (in kJ/mol) with two basis sets as specified.

	aug-cc-pV5Z				**def-TZVP**			
	B3LYP	PBE	SVWN	M06	B3LYP	PBE	SVWN	M06
H	1.81	-0.64	55.34	-1.18	2.57	0.33	56.18	-0.34
He	-25.25	11.62	27.43	-18.54	-23.75	13.39	29.38	-14.62
Li	-15.21	-18.77	-7.88	8.17	-15.09	-18.75	-7.65	8.15
Be	28.46	31.46	28.58	37.28	28.65	31.58	29.20	38.33
B	-34.73	-36.38	-33.84	-13.20	-34.28	-35.89	-32.89	-11.51
C	-18.96	-27.08	-41.74	-5.87	-18.37	-26.26	-40.68	-4.58
N	-3.44	-18.41	-45.27	-19.59	-3.53	-17.99	-44.64	-21.34
O	-39.94	-42.76	-37.20	-18.61	-37.04	-39.07	-33.40	-14.54
F	-18.88	-22.18	-51.55	-12.10	-16.28	-18.57	-48.22	-8.40
Ne	-3.58	-8.56	-59.83	-10.23	-4.26	-8.14	-59.41	-10.42

Table S18. Average basis set sensitivity, calculated as the difference in absolute errors in IPs computed with aug-cc-pV5Z and def-TZVP. Units of kJ/mol.

	B3LYP	PBE	SVWN	M06
H	0.75	0.97	0.84	0.84
He	1.50	1.77	1.95	3.92
Li	0.12	0.02	0.23	0.02
Be	0.19	0.12	0.62	1.05
B	0.46	0.50	0.95	1.69
C	0.59	0.82	1.07	1.29
N	0.09	0.41	0.63	1.75
O	2.90	3.69	3.81	4.08
F	2.60	3.61	3.33	3.70
Ne	0.69	0.42	0.42	0.19
Average	0.99	1.23	1.38	1.85

Table S19. Computed electronic energies of the water molecule and water cation (in units of a.u.), and the ionization potential in units of kJ/mol, aug-cc-pV5Z basis set.

E(B3LYP), H_2O	E(B3LYP), H_2O^+	**IP(B3LYP) kJ/mol**	E(PBE), H_2O	E(PBE), H_2O^+	**IP(PBE) kJ/mol**
-76.4369	-75.9746	**1213.83**	-76.3884	-75.9235	**1220.53**
E(SVWN), H_2O	E(SVWN), H_2O^+	**IP(SVWN) kJ/mol**	E(M06), H_2O	E(M06), H_2O^+	**IP(M06) kJ/mol**
-75.9134	-75.4354	**1255.16**	-76.4342	-75.9700	**1218.76**

Table S20. Computed electronic energies of the water molecule and water cation (in units of a.u.), and the ionization potential in units of kJ/mol, aug-cc-pV5Z basis set, for PBE, B3LYP, and M06 using SVWN densities as trial densities.

PBE(SVWN)			**B3LYP(SVWN)**			**M06(SVWN)**		
E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**
-76.3861	-75.9209	**1221.3**	-76.4344	-75.97194	**1214.08**	-76.4297	-75.9667	**1215.82**

Table S21. Computed electronic energies of the water molecule and water cation (in units of a.u.), and the ionization potential in units of kJ/mol, aug-cc-pV5Z basis set, for SVWN, B3LYP, and M06 using PBE densities as trial densities.

SVWN(PBE)			**B3LYP(PBE)**			**M06(PBE)**		
E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**
-75.9111	-75.4328	**1255.87**	-76.4368	-75.9743	**1214.14**	-76.4325	-75.9685	**1218.28**

Table S22. Computed electronic energies of the water molecule and water cation (in units of a.u.), and the ionization potential in units of kJ/mol, aug-cc-pV5Z basis set, for SVWN, PBE, and M06 using B3LYP densities as trial densities.

SVWN(B3LYP)			PBE(B3LYP)			M06(B3LYP)		
E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**
-75.9110	-75.4328	**1255.39**	-76.3884	-75.9234	**1220.87**	-76.4327	-75.9688	**1217.98**

Table S23. Computed electronic energies of the water molecule and water cation (in units of a.u.), and the ionization potential in units of kJ/mol, aug-cc-pV5Z basis set, for B3LYP, PBE, and SVWN using M06 densities as trial densities.

B3LYP(M06)			PBE(M06)			SVWN(M06)		
E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**	E_{el} H_2O	E_{el} H_2O^+	**IP kJ/mol**
-76.4343	-75.9726	**1212.13**	-76.3858	-75.9214	**1219.28**	-75.9081	-75.4314	**1251.70**

Table S24. Computed zero point energies from TPSSh/def2-TZVPP geometry optimization and numerically computed frequencies.

	ZPE (a.u.)	ZPE (kJ/mol)
NaCl	0.0007976	2.09
N2	0.0053607	14.07
HF	0.0090684	23.81
CO	0.0048478	12.73
O2	0.0035435	9.30

Table S25. Computed bond dissociation energies (aug-cc-pV5Z basis, in kJ/mol), corrected for enthalpy and ZPE. Experimental values from the 2014 CRC Handbook of Chemistry and Physics[4].

	CCSD(T)	CCSD	B3LYP	PBE	SVWN	M06	EXP.
NaCl	423.8	414.5	383.2	392.0	431.9	427.5	412.1
N_2	937.5	895.8	939.5	1005.9	1103.2	920.5	944.9
HF	569.0	559.6	558.1	571.1	655.3	566.1	569.7
CO	1075.1	1040.5	1052.3	1113.3	1237.8	1073.9	1076.6
O_2	493.2	457.3	506.3	593.4	722.5	497.0	498.5
MAE	***5.3***	***27.8***	***15.6***	***42.8***	***129.8***	***9.5***	

Table S26. Computed electronic energies and D_e (not corrected for ZPE) of diatomic molecules, aug-cc-pV5Z basis set. B3LYP, PBE, and CCSD(T).

	B3LYP		**PBE**		**CCSD(T)**	
	Energy (a.u.)	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE(kJ/mol)**	**Energy (a.u.)**	**BDE(kJ/mol)**
NaCl	-622.5210	**385.3**	-622.2917	**394.1**	-621.9901	**425.9**
N_2	-109.5268	**953.6**	-109.4593	**1019.9**	-109.4878	**951.6**
HF	-100.4628	**581.9**	-100.4022	**595.0**	-100.4258	**592.8**
CO	-113.3171	**1065.0**	-113.2419	**1126.0**	-113.2710	**1087.9**
O_2	-150.3389	**515.6**	-150.2587	**602.7**	-150.2657	**502.5**

Table S27. Computed electronic energies and D_e (not corrected for ZPE) of diatomic molecules, aug-cc-pV5Z basis set. SVWN, M06, and CCSD.

	SVWN		**M06**		**CCSD**	
	Energy (a.u.)	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE(kJ/mol)**	**Energy (a.u.)**	**BDE(kJ/mol)**
NaCl	-620.2719	**434.0**	-622.5693	**429.6**	-621.9756	**416.6**
N_2	-108.6986	**1117.3**	-109.5137	**934.6**	-109.4654	**909.9**
HF	-99.8518	**679.1**	-100.4647	**589.9**	-100.4168	**583.4**
CO	-112.4774	**1250.6**	-113.3095	**1086.6**	-113.2507	**1053.2**
O_2	-149.3407	**731.8**	-150.3231	**506.3**	-150.2434	**466.6**

Table S28. Electronic energies of diatomic molecules for PBE, B3LYP, and M06 computed using SVWN densities.

	PBE		B3LYP		M06	
	Energy (a.u.)	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**
NaCl	-622.2895	**393.93**	-622.5178	**384.67**	-622.5684	**423.78**
N_2	-109.4551	**1019.71**	-109.5224	**952.40**	-109.5077	**937.13**
HF	-100.3998	**596.26**	-100.4603	**583.57**	-100.4572	**583.90**
CO	-113.2379	**1126.90**	-113.3124	**1064.49**	-113.3026	**1086.40**
O_2	-150.2542	**603.22**	-150.3334	**514.07**	-150.3150	**507.08**

Table S29. Electronic energies of diatomic molecules for SVWN, B3LYP, and M06 computed using PBE densities.

	SVWN		B3LYP		M06	
	Energy (a.u.)	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**
NaCl	-620.2691	**433.84**	-622.5204	**384.68**	-622.5733	**426.80**
N_2	-108.6946	**1117.53**	-109.5261	**953.15**	-109.5114	**936.49**
HF	-99.8495	**680.83**	-100.4626	**582.07**	-100.4601	**583.89**
CO	-112.4735	**1251.77**	-113.3162	**1064.20**	-113.3068	**1088.80**
O_2	-149.3362	**732.59**	-150.3378	**514.02**	-150.3196	**507.31**

Table S30. Electronic energies of diatomic molecules for SVWN, PBE, and M06 computed using B3LYP densities.

	SVWN		**PBE**		**M06**	
	Energy (a.u.)	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**
NaCl	-620.2685	**433.49**	-622.2914	**393.61**	-622.5748	**428.61**
N_2	-108.6942	**1116.27**	-109.4585	**1019.22**	-109.5110	**932.53**
HF	-99.8494	**681.07**	-100.4019	**595.00**	-100.4607	**583.46**
CO	-112.4727	**1250.34**	-113.2410	**1125.26**	-113.3073	**1087.14**
O_2	-149.3354	**730.82**	-150.2578	**601.46**	-150.3195	**503.52**

Table S31. Electronic energies of diatomic molecules for SVWN, B3LYP, and PBE computed using M06 densities.

	SVWN		**B3LYP**		**PBE**	
	Energy (a.u.)	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**	**Energy (a.u.)**	**BDE (kJ/mol)**
NaCl	-620.2624	**430.49**	-622.5178	**385.65**	-622.2875	**392.85**
N_2	-108.6922	**1119.87**	-109.5237	**950.28**	-109.4565	**1019.77**
HF	-99.8463	**678.79**	-100.4607	**580.43**	-100.3995	**593.85**
CO	-112.4694	**1248.81**	-113.3137	**1063.01**	-113.2380	**1125.30**
O_2	-149.3333	**734.22**	-150.3357	**514.36**	-150.2558	**605.50**

Table S32. Computed Co-C bond dissociation energies (kJ/mol) of 5'-deoxyadenosylcobalamin (def2-TZVPP basis, not corrected for zero-point energies).

	E(B3LYP)	E(PBE)	E(SVWN)	E(M06)
ρ_{B3LYP}	65.9	123.1	199.2	121.1
ρ_{PBE}	69.5	119.8	200.8	117.0
ρ_{SVWN}	67.3	120.6	200.0	119.0
ρ_{M06}	68.2	117.1	198.1	102.4
SENSITIVITY (MAD from native)	2.4	3.9	1.2	8.3

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[3] **2017**.

[4] W. M. Haynes, *CRC Handbook of Chemistry and Physics*, CRC Press, **2014**.