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

Supplementary Information

Prediction of proton affinities of organic molecules with the Any-Particle Molecular-Orbital second-order proton propagator approach

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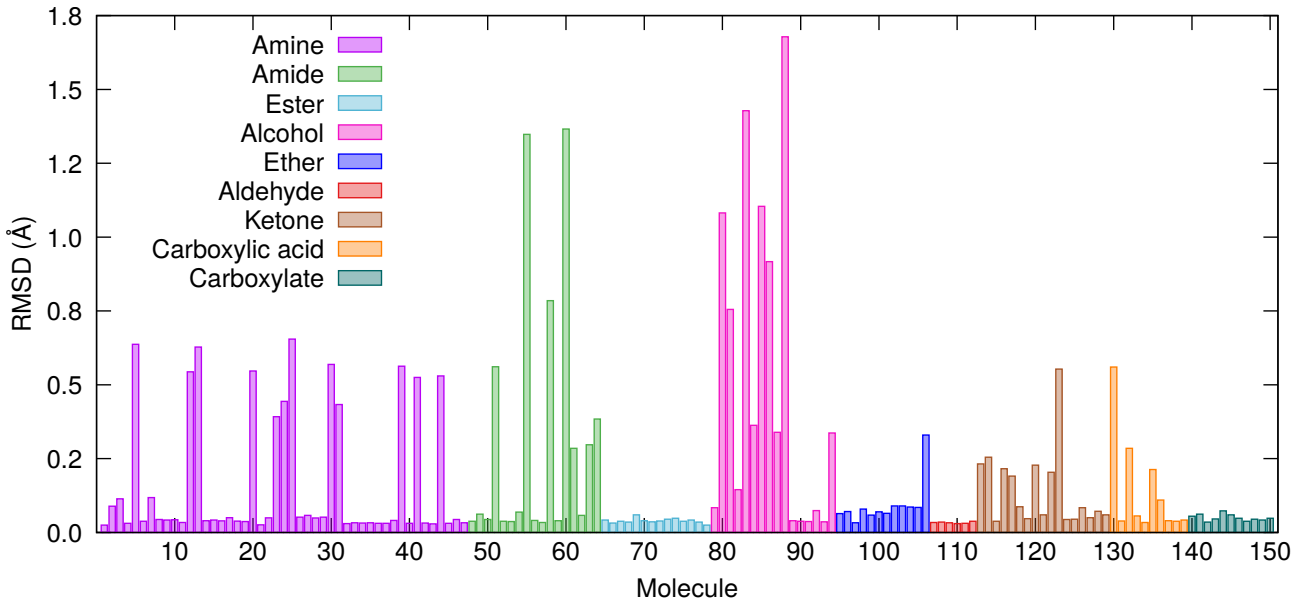

Figure S1: Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) structures for the 150 molecules.

Table S1: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) amines.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Primary amines					
1	NH_3	204.0150	203.0074	1.0076	0.0250
2	$CHF_2CH_2NH_2$	208.0545	207.9932	0.0613	0.0890
3	$CH_2FCH_2NH_2$	213.1931	213.2649	-0.0718	0.1140
4	CH_3NH_2	214.8660	214.3026	0.5634	0.0310
5	(c-C_3H_5)NH_2	216.2000	216.4450	-0.2450	0.6370
6	$CH_3CH_2NH_2$	217.9732	217.9324	0.0408	0.0382
7	CH_2=(CH_3)CH_2NH_2	219.3000	218.7165	0.5835	0.1180
8	$CH_3(CH_2)_2NH_2$	219.3595	219.6320	-0.2725	0.0438
9	$CH_3(CH_2)_3NH_2$	220.2438	220.6167	-0.3729	0.0420
10	$CH_3(CH_2)_4NH_2$	220.7218	221.1563	-0.4345	0.0430
11	$(CH_3)_2CHNH_2$	220.7935	220.6698	0.1237	0.0339
12	$(CH_3)_2CHCH_2NH_2$	221.0325	221.4031	-0.3706	0.5440
13	(c-C_6H_{11})CH_2NH_2	221.5000	222.5515	-1.0515	0.6280
14	$CH_3(CH_2)_6NH_2$	221.5583	221.6314	-0.0731	0.0400
15	$CH_3(CH_2)_5NH_2$	221.6778	221.4423	0.2355	0.0420
16	$CH_3(CH_2)_7NH_2$	222.0124	221.7490	0.2634	0.0395
17	$CH_3CH_2(CH_3)CHNH_2$	222.2036	222.3947	-0.1911	0.0500
18	$CH_3(CH_2)_8NH_2$	222.2753	221.8274	0.4479	0.0385
19	$CH_3(CH_2)_9NH_2$	222.4000	221.6729	0.7271	0.0372
20	$(CH_3)_3CNH_2$	223.2553	224.3664	-1.1112	0.5465
21	(C_6H_{11})NH_2	223.3270	224.1381	-0.8112	0.0260
22	$CH_3CH_2C(CH_3)_2NH_2$	224.1396	224.6616	-0.5220	0.0494
Secondary amines					
23	$(CH_3)_2NH$	222.1560	221.9750	0.1810	0.3920
24	$CH_3CH_2NHCH_3$	225.1912	224.9844	0.2068	0.4440
25	$(CH_3)_2CHNHCH_3$	227.6052	227.2951	0.3100	0.6546
26	$(CH_3CH_2)_2NH$	227.6291	227.7126	-0.0835	0.0517
27	$CH(CH_3)_2NHCH_2CH_3$	229.4455	229.8365	-0.3910	0.0580
28	$(C_3H_7)_2NH$	229.9952	230.4776	-0.4823	0.0490
29	$(C_4H_9)_2NH$	231.4771	232.0688	-0.5917	0.0520
30	(s-C_4H_9)$_2$NH	234.3929	235.0229	-0.6299	0.5690
31	(t-C_4H_9)$_2$NH	236.1138	236.3189	-0.2051	0.4330
Tertiary amines					
32	$(CH_3)_3N$	226.7925	226.6356	0.1569	0.0300
33	$CH_3CH_2N(CH_3)_2$	229.5000	229.5505	-0.0505	0.0330
34	$(CH_3)_2$N(n-C_3H_7)	230.1000	230.8581	-0.7581	0.0320
35	$(CH_3)_2CHCH_2N(CH_3)_2$	231.5249	231.3838	0.1410	0.0330
36	$(C_4H_7)N(CH_3)_2$	231.6444	231.6490	-0.0047	0.0310
37	$(CH_3)_2CHN(CH_3)_2$	231.9790	231.7782	0.2008	0.0310
38	$(C_2H_5)_2NCH_3$	232.1000	232.1103	-0.0103	0.0410
39	(c-C_6H_{11})$CH_2N(CH_3)_2$	233.1740	232.3432	0.8308	0.5630
40	(s-C_4H_9)$(CH_3)_2N$	233.2457	233.2979	-0.0522	0.0310
41	$(C_2H_5)_2$N(C_3H_7)	233.9388	233.4109	0.5279	0.5250
42	(t-C_4H_9)$(CH_3)_2N$	234.1300	234.1788	-0.0488	0.0320
43	$(C_2H_5)_3N$	234.6558	234.0935	0.5623	0.0290
44	(t-C_5H_{11})$(CH_3)_2N$	234.8231	235.7562	-0.9331	0.5300
45	(c-C_6H_{11})$N(CH_3)_2$	235.0860	234.7254	0.3607	0.0310
46	$(C_3H_7)_3N$	236.9001	237.1191	-0.2190	0.0440
47	(n-C_4H_9)$_3$N	238.6472	239.1323	-0.4851	0.0330

Table S2: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) amides.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Amides					
48	$HCONH_2$	196.5000	195.4319	1.0681	0.0380
49	$HCONHCH_3$	203.4656	202.5231	0.9425	0.0620
50	CH_3CONH_2	206.4054	206.1921	0.2132	0.0440
51	$CH_3CH_2CONH_2$	209.4168	208.8441	0.5727	0.5610
52	n-C_3H_7NHCHO	209.9426	210.1194	-0.1768	0.0380
53	$(CH_3)_2CHCNH_2O$	209.9904	210.6936	-0.7032	0.0370
54	$(CH_3)_2CHCONH_2$	210.4000	211.1502	-0.7502	0.0690
55	$(CH_3)_2NCHO$	212.1176	210.4077	1.7099	1.3480
56	$CH_3CONHCH_2$	212.3566	211.4569	0.8997	0.0410
57	$(CH_3)_3CONH_2$	212.5000	213.4125	-0.9125	0.0340
58	$CH_3CONHC_2H_5$	214.6272	214.3096	0.3176	0.7850
59	$CH_3CON(CH_3)_2$	217.0172	218.1054	-1.0882	0.0400
60	$CH_3CH_2CH_2CON(CH_3)_2$	220.2916	219.9572	0.3344	1.3660
61	$C_3H_7CON(CH_3)_2$	220.7696	221.0226	-0.2530	0.2850
62	$CH_3CON(C_2H_5)_2$	221.1759	220.9626	0.2133	0.0580
63	$(CH_3)_3CCON(CH_3)_2$	221.5822	221.6706	-0.0884	0.2970
64	$(CH_3)_3CCH_2CON(CH_3)_2$	221.7256	222.6253	-0.8997	0.3840

Table S3: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) esters.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Esters					
65	$HCOOCH_3$	187.0219	186.5950	0.4270	0.0420
66	$HCO_2C_2H_5$	191.0611	191.4931	-0.4319	0.0320
67	HCO_2(n-C_3H_7)	192.3757	193.0105	-0.6348	0.0380
68	HCO_2(n-C_4H_9)	192.6386	193.3933	-0.7547	0.0350
69	$HCOOCH(CH_3)_2$	193.9053	195.7294	-1.8240	0.0600
70	$CH_3CO_2CH_3$	196.3671	196.5088	-0.1417	0.0400
71	$C_2H_5COOCH_3$	198.4225	197.6158	0.8068	0.0360
72	$CH_3COOCH_2CH_3$	199.7370	200.6667	-0.9296	0.0390
73	$C_3H_7COOCH_3$	199.9043	198.9694	0.9350	0.0450
74	i-$C_3H_7COOCH_3$	199.9521	198.9671	0.9851	0.0480
75	$C_3H_7COOCH_3$	199.9521	201.8105	-1.8583	0.0380
76	(c-C_3H_5)$COOCH_3$	201.2906	200.8166	0.4740	0.0420
77	t-$C_4H_9COOCH_3$	202.0076	201.6238	0.3839	0.0350
78	$CH_3CH{=}CHCOOCH_3$	203.4894	203.7523	-0.2628	0.0250

Table S4: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) alcohols.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Alcohols					
79	CH_2FCH_2OH	171.0325	170.8744	0.1582	0.0840
80	CHF_2CH_2OH	173.8528	172.4725	1.3803	1.0820
81	CH_3OH	180.2820	180.5668	-0.2848	0.7550
82	CH_3CH_2OH	185.5641	185.2321	0.3320	0.1450
83	$CH_3(CH_2)_2OH$	187.9780	187.4090	0.5690	1.4280
84	$CH_3(CH_2)_3OH$	188.6233	188.8250	-0.2016	0.3630
85	$(CH_3)_2CH_2OH$	189.6988	190.0610	-0.3622	1.1040
86	i-$CH_3(CH_2)_2OH$	189.7705	191.4539	-1.6833	0.9170
87	$CH_3(CH_2)_4OH$	190.0096	189.6252	0.3844	0.3390
88	$(CH_3)_3CCH_2OH$	190.1291	189.5860	0.5431	1.6780
89	$CH_3(CH_2)_5OH$	190.9656	190.0034	0.9622	0.0400
90	$CH_3(CH_2)_6OH$	190.9656	190.2340	0.7316	0.0380
91	$CH_3(CH_2)_7OH$	190.9656	190.3770	0.5886	0.0370
92	(c-C_5H_9)OH	191.0000	191.4147	-0.4147	0.0740
93	(c-C_6H_{11})CH_2OH	191.7065	191.5946	0.1119	0.0360
94	$CH_3CH_2CH(OH)CH_3$	194.7897	194.8554	-0.0657	0.3370

Table S5: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) ethers.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Ethers					
95	CH_3OCH_3	189.2925	189.1709	0.1217	0.0640
96	$CH_3CH_2OCH_3$	193.2600	193.9537	-0.6937	0.0710
97	n-$C_3H_7OCH_3$	194.7658	194.7401	0.0257	0.0330
98	$(C_4H_9)OCH_3$	196.0564	196.7902	-0.7338	0.0790
99	$(CH_3)_2CHOCH_3$	197.4904	199.3061	-1.8157	0.0590
100	$(C_2H_5)_2O$	197.9924	198.0447	-0.0524	0.0700
101	(c-C_6H_{11})CH_2OCH_3	199.2113	198.8910	0.3202	0.0650
102	$(C_3H_7)_2O$	200.2629	201.0242	-0.7613	0.0900
103	(c-C_6H_{11})OCH_3	200.8843	201.5569	-0.6726	0.0900
104	$(CH_3)_2CHOCH_2CH_3$	201.4101	202.5946	-1.1845	0.0860
105	$(C_4H_9)_2O$	203.6329	202.9359	0.6970	0.0850
106	(n-C_5H_{11})$_2O$	203.8002	204.8730	-1.0728	0.3300

Table S6: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) aldehydes.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Aldehydes					
107	CH_2O	170.3872	167.0601	3.3271	0.0340
108	CH_3CHO	183.6759	183.9891	-0.3132	0.0350
109	CH_3CH_2CHO	187.8585	187.7296	0.1289	0.0330
110	n-C_3H_7CHO	189.4598	189.3784	0.0814	0.0300
111	n-C_4H_9CHO	190.3920	190.2593	0.1326	0.0310
112	$(CH_3)_2CHCOH$	190.5593	191.2533	-0.6940	0.0380

Table S7: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) ketones.

	Molecule (A)	Proton affinity (kcal mol^{-1})			RMSD
		PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	
Ketones					
113	$(CH_3)_2CO$	194.0727	193.9791	0.0936	0.2320
114	c-(C_4H_6)=O	194.6000	195.9000	-1.3000	0.2550
115	c-(C_5H_8)=O	196.8690	197.7311	-0.8621	0.0380
116	$CH_3COC_2H_5$	197.7294	196.6057	1.1237	0.2160
117	n-$C_3H_7COCH_3$	199.0201	198.0424	0.9777	0.1910
118	$(CH_3)_2CHCOCH_3$	199.8805	200.9757	-1.0952	0.0870
119	$(C_2H_5)_2CO$	200.0000	198.2684	1.7316	0.0470
120	$(CH_3)_3COCH_3$	200.7887	199.4099	1.3788	0.2280
121	$CH_3CH_2CH_2COCH_2CH_3$	201.5296	200.4569	1.0728	0.0600
122	4-$(CH_3)C_6H_9$=O	201.9359	203.9967	-2.0608	0.2040
123	$(C_3H_7)_2CO$	201.9598	199.6128	2.3470	0.5530
124	c-(C_8H_{14})=O	203.0115	203.9829	-0.9714	0.0440
125	(i-$C_3H_7)_2CO$	203.2266	204.2181	-0.9915	0.0450
126	c-(C_6H_{10})=O	203.6000	203.0812	0.5188	0.0840
127	(c-$C_3H_5)COCH_3$	204.3260	203.4433	0.8827	0.0500
128	c-(C_7H_{12})=O	204.5000	203.9414	0.5586	0.0720
129	(t-$C_4H_9)_2CO$	205.8556	205.4818	0.3738	0.0600

Table S8: Experimental (PA_{exp}) and calculated (PA_{PP2}) proton affinities, difference between PA_{exp} and PA_{PP2} values (ΔPA^{exp}_{PP2}), and Root-mean-square deviation (RMSD) between protonated (AH^+) and deprotonated (A) carboxylic acids.

		Proton affinity (kcal mol^{-1})			
	Molecule (A)	PA_{exp}	PA_{PP2}	ΔPA^{exp}_{PP2}	RMSD
Carboxylic acids					
130	HCOOH	177.3423	174.8708	2.4715	0.5600
131	CH_2FCOOH	182.9350	184.0744	-1.1394	0.0390
132	CH_3COOH	187.3088	186.9824	0.3264	0.2850
133	C_2H_5COOH	190.5354	191.4908	-0.9554	0.0560
134	$(CH_3)_2CCOOH$	195.1960	195.3420	-0.1460	0.0340
135	$c(C_4H_7)COOH$	195.4111	195.6487	-0.2376	0.2130
136	$c(C_5H_9)COOH$	195.4111	196.3013	-0.8902	0.1100
137	$(CH_3)_2CCHCOOH$	196.7017	197.3875	-0.6857	0.0400
138	$CH_3(CH)_2COOH$	196.8929	196.2483	0.6447	0.0380
139	$(c\text{-}C_6H_{11})COOH$	196.8929	195.9369	0.9560	0.0420
Carboxylate anions					
140	CF_3COO^-	322.6220	321.8195	0.8025	0.0550
141	CHF_2COO^-	330.2321	330.3197	-0.0876	0.0620
142	CH_3COCOO^-	333.4606	334.6183	-1.1577	0.0350
143	$ClCH_2COO^-$	336.2279	338.1673	-1.9394	0.0460
144	CH_2FCOO^-	339.2258	340.0145	-0.7887	0.0730
145	$Cl(CH_2)_2COO^-$	340.8401	341.6334	-0.7933	0.0600
146	$HCOO^-$	345.2217	345.0049	0.2168	0.0480
147	$CH_3(CH_2)_3COO^-$	346.1441	345.1271	1.0170	0.0380
148	$CH_3(CH_2)_2COO^-$	346.6053	344.4722	2.1331	0.0450
149	$CH_3CH_2COO^-$	347.5278	345.1525	2.3753	0.0420
150	CH_3COO^-	348.4502	350.7056	-2.2554	0.0480

Table S9: Mean absolute error ($|\Delta|$), mean absolute deviation (MAD) and maximum absolute deviation (AD_{max}). Values in kcal mol^{-1}.

Functional group	$\|\Delta\|$	MAD	AD_{max}
Amine (47)	0.3831	0.2464	1.1112
Alcohol (16)	0.5484	0.3281	1.6833
Amide (17)	0.6555	0.3617	1.7099
Ether (12)	0.6793	0.3673	1.8157
Ester (14)	0.7750	0.3841	1.8583
Aldehyde (6)	0.7795	0.8492	3.3271
Ketone (17)	1.0788	0.4100	2.3470
Carboxylic acid (10)	0.8453	0.4372	2.4715
Carboxylate (11)	1.2333	0.6854	2.3753
Total	0.6797	0.4522[a]	3.3271

[a] Average mean absolute deviation.

Table S10: Adiabatic gas phase proton affinities calculated for selected molecules.

		Energy (hartree)		Proton affinity (kcal mol^{-1})			Absolute error (kcal mol^{-1})			
	Molecule	ΔE_{el} [a]	ΔZPE [a]	PA_{ad} [b]	PA_{PP2}	PA_{exp}	ΔPA_{ad}^{exp}	ΔPA_{PP2}^{exp}	ΔPA_{PP2}^{ad}	RMSD (Å)
1	NH_3	-0.3371	0.0156	203.2209	203.0074	204.0150	0.7941	1.0076	0.2135	0.0250
2	$CHF_2CH_2NH_2$	-0.3441	0.0149	208.0182	207.9932	208.0545	0.0363	0.0613	0.0250	0.0890
3	$CH_2FCH_2NH_2$	-0.3520	0.0152	212.8169	213.2649	213.1931	0.3762	-0.0718	-0.3044	0.1140
4	CH_3NH_2	-0.3548	0.0155	214.4214	214.3026	214.8660	0.4446	0.5634	0.1188	0.0310
5	c-$(C_3H_5)NH_2$	-0.3534	0.0149	213.8938	216.4450	216.2000	2.3062	-0.2450	-2.0612	0.6370
6	$CH_3CH_2NH_2$	-0.3597	0.0153	217.5695	217.9324	217.9732	0.4037	0.0408	-0.3629	0.0382
7	$CH_2{=}(CH_3)CH_2NH_2$	-0.3605	0.0150	218.2802	218.7165	219.3000	1.0198	0.5835	-0.4363	0.1180
8	$CH_3(CH_2)_2NH_2$	-0.3616	0.0154	218.7127	219.6320	219.3595	0.6468	-0.2725	-0.3743	0.0438
9	$CH_3(CH_2)_3NH_2$	-0.3628	0.0154	219.4754	220.6167	220.2438	0.7684	-0.3729	-0.3955	0.0420
10	$CH_3(CH_2)_4NH_2$	-0.3634	0.0154	219.8625	221.1563	220.7218	0.8593	-0.4345	-0.4248	0.0430
11	$(CH_3)_2CHNH_2$	-0.3627	0.0150	219.6342	220.6698	220.7935	1.1593	0.1237	-1.0356	0.0339
12	$(CH_3)_2CHCH_2NH_2$	-0.3633	0.0153	219.8806	221.4031	221.0325	1.1519	-0.3706	-0.7813	0.5440
13	c-$(C_6H_{11})CH_2NH_2$	-0.3672	0.0152	222.3699	222.5515	221.5000	-0.8699	-1.0515	0.1816	0.6280
14	$CH_3(CH_2)_6NH_2$	-0.3640	0.0154	220.2225	221.6314	221.5583	1.3358	-0.0731	-1.2627	0.0400
15	$CH_3(CH_2)_5NH_2$	-0.3637	0.0154	220.0834	221.4423	221.6778	1.5944	0.2355	-1.3589	0.0420
16	$CH_3(CH_2)_7NH_2$	-0.3641	0.0154	220.3109	221.7490	222.0124	1.7015	0.2634	-1.4381	0.0395
17	$CH_3CH_2(CH_3)CHNH_2$	-0.3649	0.0149	221.1175	222.3947	222.2036	1.0861	-0.1911	-0.8950	0.0500
18	$CH_3(CH_2)_8NH_2$	-0.3653	0.0152	221.1821	221.8274	222.4000	1.2179	0.5726	-0.6453	0.0372
20	$(CH_3)_3CNH_2$	-0.3667	0.0149	222.1975	224.3664	223.2553	1.0577	-1.1112	0.0534	0.5465
21	$(C_6H_{11})NH_2$	-0.3673	0.0152	222.4564	224.1381	223.3270	0.8705	-0.8112	-0.0594	0.0260
22	$CH_3CH_2C(CH_3)_2NH_2$	-0.3688	0.0148	223.5898	224.6616	224.1396	0.5497	-0.5220	-0.0277	0.0494
88	$(CH_3)_3CCH_2OH$	-0.3109	0.0129	188.5206	189.5860	190.1291	1.6085	0.5431	-1.0654	1.6780
107	CH_2O	-0.2797	0.0144	167.9753	167.0601	170.3872	2.4119	3.3271	0.9152	0.0340
107 CCSD(T)	CH_2O	-0.2839[c]	0.0144[c]	170.6268[c]	167.0601	170.3872	**-0.2396**	3.3271	3.0875	0.0340
122	4-$(CH_3)C_6H_9(=O)$	-0.3280	0.0134	198.9387	203.9967	201.9359	2.9973	-2.0608	-0.9365	0.2040
123	$(C_3H_7)_2CO$	-0.3284	0.0132	199.2876	199.6128	201.9598	2.6723	2.3470	-0.3253	0.5530
130	HCOOH	-0.2901	0.0134	175.1430	174.8708	177.3423	2.1992	2.4715	0.2722	0.5600
130 CCSD(T)	HCOOH	-0.2945[c]	0.0134[c]	177.8705[c]	174.8708	177.3423	**-0.5283**	2.4715	1.9432	0.5600
148	$CH_3(CH_2)_2COO^-$	-0.5621	0.0140	345.4585	344.4722	346.6053	1.1468	2.1331	0.9863	0.0450
149	$CH_3CH_2COO^-$	-0.5629	0.0139	345.9894	345.1525	347.5278	1.5383	2.3753	0.8369	0.0420
150	CH_3COO^-	-0.5637	0.0139	346.4993	350.7056	348.4502	1.9509	-2.2554	0.3045	0.0480
150 CCSD(T)	CH_3COO^-	-0.5683[c]	0.0139[c]	349.3800[c]	350.7056	348.4502	**-0.9298**	-2.2554	1.3256	0.5600

[a] ΔE_{el}= $E(AH^+)$ - E(A) and ΔZPE= $ZPE(AH^+)$ - ZPE(A). MP2/6-311++G(2d,2p)

[b] PA^{ad}= -ΔE_{el} - ΔZPE + $\frac{5}{2}RT$. ($\frac{5}{2}RT$=1.4812 kcal mol^{-1})

[c] CCSD(T)/6-311++G(2d,2p)

1 Theory appendix

Here we summarize the generalized any particle propagator theory and explain how it is employed to calculate proton binding energies of molecular systems.

1.1 APMO/HF theory

The molecular Hamiltonian, H^{TOT}, includes contributions from classical and quantum particles, such that:

$$H^{TOT} = -\sum_{i}^{N^Q} \frac{1}{2M_i}\nabla_i^2 + \sum_{i}^{N^Q}\sum_{j>i}^{N^Q} \frac{Q_i Q_j}{r_{ij}} + \sum_{i}^{N^Q}\sum_{j}^{N^C} \frac{Q_i Q_j}{r_{ij}} + \sum_{i}^{N^C}\sum_{j>i}^{N^C} \frac{Q_i Q_j}{r_{ij}} \quad , \tag{1}$$

where Q_i is the charge of the particle i, and N^Q and N^C are the number of quantum and classical particles, respectively.

At the APMO/HF level the molecular wavefunction, Ψ_0, is approximated as a product of single-configurational wavefunctions, Φ^α, for different types of quantum species α:

$$\Psi_0 = \prod_{\alpha}^{N^Q} \Phi^\alpha. \tag{2}$$

Each Φ^α is represented in terms of molecular orbitals (MO), ψ_i^α. These ψ_i^α are obtained by solving the

equations

$$f^{\alpha}(i)\psi_i^{\alpha} = \varepsilon_i^{\alpha}\psi_i^{\alpha}, \quad \forall i, \alpha. \tag{3}$$

Each f^{α}(i) is an effective one-particle Fock operator for the quantum species α written as

$$f^{\alpha}(i) = h^{\alpha}(i) + {Q_{\alpha}}^2 \sum_{j\in\alpha}[J_j^{\alpha} \mp K_j^{\alpha}] + \sum_{\beta\neq\alpha}^{N^Q} Q_{\alpha} \sum_{j\in\beta} Q_{\beta} J_j^{\beta}. \tag{4}$$

In the above equation $h^{\alpha}(i)$ is the one–particle core Hamiltonian,

$$h^{\alpha}(i) = -\frac{\nabla_i^2}{2M_{\alpha}} + \sum_{j}^{N^C} \frac{Q_j^C Q_{\alpha}}{r_{ij}} \tag{5}$$

and J^{α} and K^{α} are Coulomb and exchange operators defined as,

$$J_j^{\alpha}(1)\psi_i^{\alpha}(1) = \left[\int d\mathbf{r}_2 \psi_j^{\alpha *}(2)\frac{1}{r_{12}}\psi_j^{\alpha}(2)\right]\psi_i^{\alpha}(1), \tag{6}$$

$$K_j^{\alpha}(1)\psi_i^{\alpha}(1) = \left[\int d\mathbf{r}_2 \psi_j^{\alpha *}(2)\frac{1}{r_{12}}\psi_i^{\alpha}(2)\right]\psi_j^{\alpha}(1). \tag{7}$$

The sign preceding the exchange operator in Eq. 4 is chosen depending on the bosonic (positive) or fermionic (negative) nature of the α particles. In practice, all the quantum nuclei species are treated as fermions in the highest spin state.

1.2 APMO propagator theory

Here we summarize the APMO propagator theory. Details can be found in References[1,2]. For a system comprising N^Q fermionic species $\{\alpha, \beta, ...\}$, the one-particle Green function for species α can be written as:

$$\mathbf{G}^{\alpha}(\omega^{\alpha}) = (\mathbf{a}^{\alpha}|(\omega^{\alpha}\hat{I} - \hat{H})^{-1}\mathbf{a}^{\alpha}) \tag{8}$$

where $\mathbf{a}^{\alpha}$ contains all the single annihilation operators for the α species, $\{a_i^{\alpha}, a_a^{\alpha}\}$. The parameter ω^{α} has energy units and take the values of the binding energies for particles of the α species. The superoperators, $\hat{I}$ and $\hat{H}$, are defined as follows:

$$\hat{I}A = A \tag{9}$$

$$\hat{H}A = [A, H^{TOT}]_{-} = A\,H^{TOT} - H^{TOT}\,A \tag{10}$$

where H^{TOT} stands for the APMO Hamiltonian in its second quantized form. By applying Löwdin's inner projection technique with an appropriate superoperator space $\mathbf{h}^{\alpha}$, Eq(10) can be rewritten as[1]

follows:

$$\mathbf{G}^{\alpha}(\omega^{\alpha}) = (\mathbf{a}^{\alpha}|\mathbf{h}^{\alpha})(\mathbf{h}^{\alpha}|(\omega^{\alpha}\hat{I} - \hat{H})\mathbf{h}^{\alpha})^{-1}(\mathbf{h}^{\alpha}|\mathbf{a}^{\alpha}) \tag{11}$$

The super-operator space, $\mathbf{h}^{\alpha}$, is defined in such a way that it changes the number of α particles by one, while conserving the number of particles of the other species:

$$\begin{aligned}
\mathbf{h}^{\alpha} =& \{\mathbf{a}^{\alpha}\} \cup \{\mathbf{f}^{\alpha}_{\mathbf{3}}\} \cup \{\mathbf{f}^{\alpha}_{\mathbf{5}}\} \cup \ldots \\
\mathbf{h}^{\alpha} =& \{\mathbf{a}^{\alpha}\} \cup \{\mathbf{f}^{\alpha\alpha\alpha}_{\mathbf{3}}, \mathbf{f}^{\beta\alpha\beta}_{\mathbf{3}}, \mathbf{f}^{\gamma\alpha\gamma}_{\mathbf{3}} \ldots\} \cup \{\mathbf{f}^{\alpha}_{\mathbf{5}}\} \cup \ldots \\
\mathbf{h}^{\alpha} =& \{a_a, a_i\} \cup \{a_i^{\dagger}a_a a_b, a_a^{\dagger}a_i a_j, a_I^{\dagger}a_a a_A, a_A^{\dagger}a_i a_I, a_{\Gamma}^{\dagger}a_i a_{\Lambda}, a_{\Lambda}^{\dagger}a_a a_{\Gamma}, \ldots\} \cup \{\mathbf{f}^{\alpha}_{\mathbf{5}}\} \cup \ldots
\end{aligned} \tag{12}$$

The projection space, $\mathbf{h}^{\alpha}$, is partitioned into a primary space, $\mathbf{a}^{\alpha\dagger} = \{a_a^{\alpha\dagger}, a_i^{\alpha\dagger}\}$ and a complementary space, $\mathbf{f}^{\alpha}$. The latter space contains operators associated to ionizations of an α particle coupled to excitations of any type of particle in the system. Using this partition, the propagator matrix can be rearranged and subsequently transformed into the expression

$$\mathbf{G}^{\alpha^{-1}}(\omega^{\alpha}) = (\mathbf{a}^{\alpha}|(\omega^{\alpha}\hat{I} - \hat{H})|\mathbf{a}^{\alpha}) - (\mathbf{a}^{\alpha}|\hat{H}|\mathbf{f}^{\alpha})(\mathbf{f}^{\alpha}|(\omega^{\alpha}\hat{I} - \hat{H})|\mathbf{f}^{\alpha})^{-1}(\mathbf{f}^{\alpha}|\hat{H}|\mathbf{a}^{\alpha}) \tag{13}$$

which can also be presented as a Dyson-like equation:

$$\mathbf{G}^{\alpha^{-1}}(\omega^\alpha) = \mathbf{G}_{\mathbf{0}}^{\alpha^{-1}}(\omega^\alpha) - \Sigma^\alpha(\omega^\alpha) \tag{14}$$

with

$$\mathbf{G}_{\mathbf{0}}^{\alpha}(\omega^\alpha)_{pq} = \frac{\delta_{pq}}{\omega^\alpha - \epsilon_p^\alpha}. \tag{15}$$

where ϵ_p^α is the energy of the p-th canonical Hartree-Fock orbital of the α species. The self-energy matrix for the α species, $\Sigma^\alpha(\omega^\alpha)$, is defined by Eq.(14). To obtain working equations for computing the values of ω^α, we apply two approximations. First, we approximate the APMO wavefunction using pertubation theory with the Hartree-Fock wavefunction as the reference wavefunction. Second, we truncate the operator space (Eq. (12)). Approximations to second and third order can be obtained by truncating $\mathbf{f}^\alpha$ to $\mathbf{f}_{\mathbf{3}}^{\alpha}$.

In addition, we can also neglect the off-diagonal terms of the self-matrix. Within this approximation, the Dyson equation takes the form

$$\omega_p^\alpha = \varepsilon_p^\alpha + \Sigma_{pp}^\alpha(\omega_p^\alpha) \tag{16}$$

where ε_p^α is the p^{th} canonical orbital energy for the α species. The relaxation and correlation effects missing in the Koopmans's approximation ($\omega_p^\alpha = \varepsilon_p^\alpha$) are included via the energy dependent self–energy term, $\Sigma_{pp}^\alpha(\omega_p^\alpha)$. $\Sigma_{pp}^\alpha(\omega_p^\alpha)$ can be further decomposed into intraspecies and interspecies contributions:

$$\Sigma_{pp}^\alpha(\omega^\alpha) = \Sigma_{pp}^{\alpha,\alpha}(\omega^\alpha) + \sum_{\beta\neq\alpha}^{N^Q} \Sigma_{pp}^{\alpha,\beta}(\omega^\alpha) \tag{17}$$

In a system comprised of quantum protons and electrons, the self-energy for protons contains a proton-proton ($\alpha - \alpha$) term and proton-electron ($\alpha - \beta$) term.

References

[1] J. Romero, E. Posada, R. Flores-Moreno and A. Reyes, *J. Chem. Phys.*, 2012, **137**, 074105.

[2] M. Díaz-Tinoco, J. Romero, J. V. Ortiz, A. Reyes and R. Flores-Moreno, *J. Chem. Phys.*, 2013, **138**, 194108.