Electronic Supplementary Material (ESI) for Chemical Science.

The three-center two-positron bond
Supplementary Information

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Table S1 Total energies (in E_h) of atomic, diatomic and triatomic species along with diatomic and triatomic equilibrium distances (in bohrs)

System	E(DMC)		E(Ref.)	
Ps	-		-0.25[a]	
Ps^-	-		-0.262005[1]	
Ps_2	-		-0.516004[2]	
H^-	-0.52759(4)		-0.52779(3)[3]	
PsH	-0.78919(4)		-0.78907(7)[3]	
Li^+	-7.27992(1)		-7.279910(5)[4]	
Li	-7.47801(2)		-7.47802(1)[5]	
System	E(DMC)	R(DMC)	E(Ref.)	R(Ref)
H_2^+	-		-0.602635[6]	2.00
H_2	-		-1.174476[7]	1.40
H_3^+ [b]	-1.346(4)	1.63(3)	-1.343426[8]	1.65
H_3^- [c]	-		-1.703511[9]	1.42, 6.07
Li_2^+	-14.80562(2)	5.90	-14.80562(1)[10]	5.877
Li_2	-14.99175(6)	5.05	-14.9952(1)[11]	5.051
Li_3^+ [b]	-22.3419(1)	5.645(7)	-	
Li_3^+ [d]	-22.31280(7)	5.937(7)	-	
$e^+[H_2^{2-}]$	-1.3403(1)	6.39(3)	-1.3403(1)[12]	6.4(4)
$2e^+[H_2^{2-}]$	-1.5885(1)	6.003(7)	-1.5888(1)[13]	6.0(4)
$2e^+[H_3^{3-}]$ [b]	-2.1652(2)	6.11(1)		
$2e^+[H_3^{3-}]$ [d]	-2.1401(4)	6.62(1)		

[a] Exact
[b] Singlet D_{3h} symmetry
[c] Singlet $C_{\infty v}$ symmetry
[d] Triplet $D_{\infty h}$ symmetry

Table S2 Total energies (in E_h), equilibrium distance (in Bohr) and force constant (in a.u.) of triatomic systems for D_{3h} symmetry calculated at VMC level

System	**E**	$\mathbf{r}_{eq}$	k_{ν_1}
$2e^-[H_3^{3+}]$ S	-1.347(4)	1.64(3)	0.56(6)
$2e^-[Li_3^{3+}]$ S	-22.3345(2)	5.687(10)	0.0248(4)
$2e^+[H_3^{3-}]$ S	-2.1489(1)	6.149(10)	0.0110(4)
$2e^-[Li_3^{3+}]$ T	-22.3105(2)	5.950(7)	0.0175(3)
$2e^+[H_3^{3-}]$ T	-2.1266(1)	6.78(2)	0.0085(6)

Table S3 Total energies (in E_h), equilibrium distance (in Bohr) and force constant (in a.u.) of triatomic systems for D_{3h} symmetry calculated at DMC level.

System	E	r_{eq}	k_{ν_1}	k_{ν_2}
$2e^-[H_3^{3+}]$ S	-1.346(4)	1.63(3)	0.57(5)	0.16(2)
$2e^-[Li_3^{3+}]$ S	-22.34190(10)	5.645(7)	0.0254(3)	0.0110(4)
$2e^+[H_3^{3-}]$ S	-2.1652(2)	6.11(1)	0.0114(4)	0.0047(7)
$2e^-[Li_3^{3+}]$ T	-22.31280(7)	5.937(7)	0.0168(2)	-
$2e^+[H_3^{3-}]$ T	-2.1401(4)	6.62(1)	0.0080(4)	-

Table S4 Potential energy curve (in Hartree) for $2e^+[H_3^{2-}]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.4	-2.060273	3.10E-04	-2.084490	1.46E-04
4.8	-2.070135	1.08E-04	-2.089042	1.38E-04
5.2	-2.072389	1.60E-04	-2.091617	1.40E-04
5.6	-2.074593	1.15E-04	-2.092395	1.52E-04
6.0	-2.075544	9.12E-05	-2.092527	1.77E-04
6.4	-2.075353	8.09E-05	-2.091662	2.24E-04
6.8	-2.074855	7.91E-05	-2.090231	1.24E-04
7.2	-2.073976	9.49E-05	-2.088270	1.49E-04

Table S5 Potential energy curve (in Hartree) for $e^+[H_3^-]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.4	-1.752080	3.14E-04	-1.777169	1.12E-04
4.8	-1.766600	1.13E-04	-1.780472	9.55E-05
5.2	-1.770521	1.19E-04	-1.782728	7.86E-05
5.6	-1.773680	1.08E-04	-1.784643	9.21E-05
6.0	-1.775935	1.69E-04	-1.786088	6.02E-05
6.4	-1.778397	1.18E-04	-1.786910	6.99E-05
6.8	-1.779746	1.03E-04	-1.787773	6.86E-05
7.2	-1.781522	1.00E-04	-1.788336	5.98E-05

Table S6 Potential energy curve (in Hartree) for $e^+[H_3^{2-}]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.4	-1.823325	2.64E-04	-1.839220	1.22E-04
4.8	-1.828656	8.75E-05	-1.843064	8.53E-05
5.2	-1.832172	7.46E-05	-1.845263	1.10E-04
5.6	-1.833944	1.07E-04	-1.846903	9.25E-05
6.0	-1.834647	8.87E-05	-1.847079	1.02E-04
6.4	-1.834363	8.24E-05	-1.846709	9.50E-05
6.8	-1.833510	7.79E-05	-1.845503	1.13E-04
7.2	-1.831198	1.54E-04	-1.844356	9.08E-05

Table S7 Potential energy curve (in Hartree) for H_3^- in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.8	-1.540921	6.39E-05	-1.548103	7.02E-05
5.2	-1.539070	7.60E-05	-1.545813	7.25E-05
5.6	-1.537844	8.19E-05	-1.544120	6.45E-05
6.0	-1.536943	6.66E-05	-1.542198	5.99E-05
6.4	-1.535647	6.70E-05	-1.540654	6.30E-05
6.8	-1.534728	5.68E-05	-1.539143	5.01E-05
7.2	-1.533880	5.94E-05	-1.537910	4.50E-05

Table S8 Potential energy curve (in Hartree) for the positronic singlet $2e^+[H_3^{3-}]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.4	-2.124223	1.14E-04	-2.143440	1.23E-04
4.8	-2.135587	1.16E-04	-2.153232	1.47E-04
5.2	-2.142887	1.15E-04	-2.159849	1.44E-04
5.6	-2.146867	1.15E-04	-2.163421	1.67E-04
6.0	-2.148783	1.12E-04	-2.165047	1.34E-04
6.4	-2.148563	1.12E-04	-2.164726	9.51E-05
6.8	-2.146737	1.09E-04	-2.162819	1.31E-04
7.2	-2.143985	1.07E-04	-2.159856	1.46E-04
7.6	-2.140169	1.01E-04	-2.156644	1.35E-04

Table S9 Potential energy curve (in Hartree) for the positronic triplet $2e^+[H_3^{3-}]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
5.2	-2.113935	1.10E-04	-2.129561	2.15E-04
5.6	-2.119879	9.09E-05	-2.134930	1.69E-04
6.0	-2.123521	9.99E-05	-2.138353	2.14E-04
6.4	-2.125958	1.04E-04	-2.139902	3.38E-04
6.8	-2.126640	7.43E-05	-2.139849	3.52E-04
7.2	-2.125796	8.89E-05	-2.139030	4.96E-04
7.6	-2.124226	9.50E-05	-2.137341	5.59E-04
8.0	-2.122099	9.37E-05	-2.135430	6.40E-04

Table S10 Potential energy curve (in Hartree) for the electronic singlet $2e^-[Li_3^{3+}]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.8	-22.320278	2.47E-04	-22.329433	7.25E-05
5.2	-22.330751	2.14E-04	-22.338943	5.71E-05
5.6	-22.334513	1.71E-04	-22.341941	6.80E-05
6.0	-22.333354	3.16E-04	-22.340373	6.50E-05
6.4	-22.329877	2.25E-04	-22.336641	6.15E-05
6.8	-22.324713	2.42E-04	-22.331058	7.34E-05
7.2	-22.318883	2.38E-04	-22.324738	6.36E-05
7.6	-22.311375	2.12E-04	-22.317742	4.81E-05

Table S11 Potential energy curve (in Hartree) for the electronic triplet $2e^-[Li_3^{3+}]$ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
4.8	-22.294029	2.68E-04	-22.296798	3.50E-05
5.2	-22.304349	1.80E-04	-22.306955	3.38E-05
5.6	-22.309206	2.18E-04	-22.311635	3.50E-05
6.0	-22.310410	2.18E-04	-22.312654	3.70E-05
6.4	-22.309026	2.01E-04	-22.311312	3.37E-05
6.8	-22.305786	2.38E-04	-22.308146	3.33E-05
7.2	-22.301491	2.25E-04	-22.304029	3.25E-05
7.6	-22.297133	1.79E-04	-22.299412	3.10E-05

Table S12 Potential energy curve (in Hartree) for H_3^+ in D_{3h} symmetry

R/Bohr	VMC	±	DMC	±
0.8	-0.821350	6.89E-05	-0.821701	1.19E-05
0.9	-1.004019	6.56E-05	-1.004152	3.73E-06
1.0	-1.127085	7.61E-05	-1.127251	1.13E-05
1.1	-1.210251	5.78E-05	-1.210496	3.62E-06
1.2	-1.265961	5.00E-05	-1.266223	1.44E-05
1.4	-1.325071	4.21E-05	-1.325250	2.94E-06
1.6	-1.343060	3.87E-05	-1.343246	1.04E-05
1.8	-1.339360	3.94E-05	-1.339473	2.98E-06
2.0	-1.323952	3.23E-05	-1.324112	1.06E-05
2.2	-1.302710	3.18E-05	-1.302802	2.79E-06
2.4	-1.278603	2.56E-05	-1.278797	1.03E-05
2.6	-1.253832	2.43E-05	-1.253946	2.21E-06
2.8	-1.229235	2.67E-05	-1.229398	9.39E-06
3.2	-1.183429	2.45E-05	-1.183601	9.93E-06
4.8	-1.062555	1.75E-05	-1.063170	2.03E-05
5.2	-1.046507	2.16E-05	-1.046961	1.53E-05
5.6	-1.034108	2.07E-05	-1.034581	1.45E-05
6.0	-1.024797	2.51E-05	-1.025332	1.60E-05
6.4	-1.017976	2.29E-05	-1.018502	1.57E-05
6.8	-1.013012	1.84E-05	-1.013440	2.06E-05
7.2	-1.009327	2.40E-05	-1.009663	2.03E-05

Table S13 Potential energy curve (in Hartree) for $2e^+[H_3^{2-}]$ in C_{2v} symmetry as a function of the internal angle θ (in degrees) while fixing one of the internuclear distances to R=6.1 bohr

Angle θ	R_3	VMC	±	DMC	±
20	2.14	-2.152772	3.90E-04	-2.162633	1.02E-03
25	2.66	-2.090512	2.89E-04	-2.115209	2.66E-04
30	3.18	-2.079752	2.85E-04	-2.101476	1.49E-04
35	3.70	-2.047689	8.17E-05	-2.096023	4.00E-04
40	4.21	-2.032580	9.46E-05	-2.092927	3.01E-04
50	5.20	-2.022538	1.16E-04	-2.089545	3.18E-04
60	6.15	-2.018736	9.51E-05	-2.087508	3.19E-04
70	7.05	-2.018641	1.66E-04	-2.087092	3.22E-04
80	7.91	-2.018582	1.33E-04	-2.086885	2.49E-04

Table S14 Potential energy curve (in Hartree) for $e^+[H_3^{2-}]$ in C_{2v} symmetry as a function of the internal angle θ (in degrees) while fixing one of the internuclear distances to R=6.1 bohr

Angle θ	R_3	**VMC**	$\pm$	**DMC**	$\pm$
20	2.14	-1.906276	3.60E-04	-1.910344	2.43E-04
25	2.66	-1.862379	6.80E-05	-1.873857	8.22E-05
30	3.18	-1.852850	8.93E-05	-1.863797	9.40E-05
35	3.70	-1.847789	1.08E-04	-1.859888	8.31E-05
40	4.21	-1.845121	7.63E-05	-1.856901	1.04E-04
50	5.20	-1.838761	1.32E-04	-1.851839	9.61E-05
60	6.15	-1.834154	1.22E-04	-1.847309	1.02E-04
70	7.05	-1.835532	9.99E-05	-1.846307	1.10E-04
80	7.91	-1.835666	1.04E-04	-1.847058	9.57E-05

Table S15 Potential energy curve (in Hartree) for $e^+[H_3^-]$ in C_{2v} symmetry as a function of the internal angle θ (in degrees) while fixing one of the internuclear distances to R=6.1 bohr

Angle θ	R_3	**VMC**	$\pm$	**DMC**	$\pm$
20	2.14	-1.908521	7.24E-05	-1.913757	5.16E-05
25	2.66	-1.862696	7.40E-05	-1.868503	6.98E-05
30	3.18	-1.799373	1.73E-04	-1.828375	1.23E-04
35	3.70	-1.803534	8.20E-05	-1.811682	6.27E-05
40	4.21	-1.790276	8.11E-05	-1.800972	7.85E-05
50	5.20	-1.782268	2.09E-04	-1.794755	1.99E-04
60	6.15	-1.783209	1.34E-04	-1.793528	2.62E-04
70	7.05	-1.781331	3.33E-04	-1.792499	1.73E-04
80	7.91	-1.778940	8.52E-05	-1.793478	1.97E-04

Table S16 Potential energy curve (in Hartree) for $[H_3^-]$ in C_{2v} symmetry as a function of the internal angle θ (in degrees) while fixing one of the internuclear distances to R=6.1 bohr

Angle θ	R_3	**VMC**	$\pm$	**DMC**	$\pm$
20	2.14	-1.649986	6.38E-05	-1.651792	2.89E-05
25	2.66	-1.604368	4.96E-05	-1.606617	3.39E-05
30	3.18	-1.568879	5.86E-05	-1.572085	4.50E-05
35	3.70	-1.546772	1.30E-04	-1.556130	5.95E-05
40	4.21	-1.543869	7.77E-05	-1.548743	5.20E-05
50	5.20	-1.538636	7.83E-05	-1.544087	6.23E-05
60	6.15	-1.535500	5.76E-05	-1.541480	8.02E-05
70	7.05	-1.535484	6.07E-05	-1.540173	6.09E-05
80	7.91	-1.534719	1.48E-04	-1.541791	7.13E-05

Table S17 Potential energy curve (in Hartree) for $2e^+[H_3^{3-}]$ in C_{2v} symmetry as a function of the internal angle θ (in degrees) while fixing two of the internuclear distances to R=6.1 bohr

Angle θ	R_3	**VMC**	$\pm$	**DMC**	$\pm$
20	2.14	-2.138950	1.26E-04	-2.174117	5.44E-04
25	2.66	-2.114563	1.17E-04	-2.141195	2.46E-04
30	3.18	-2.117330	1.13E-04	-2.138720	1.71E-04
35	3.70	-2.126270	1.20E-04	-2.145415	1.36E-04
40	4.21	-2.135539	9.17E-05	-2.153423	1.26E-04
50	5.20	-2.145800	9.90E-05	-2.163058	1.17E-04
60	6.15	-2.149130	1.22E-04	-2.165092	1.12E-04
70	7.05	-2.146746	1.41E-04	-2.163734	1.23E-04
80	7.91	-2.143824	8.35E-05	-2.160592	1.25E-04

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