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Supporting Information

On the nature of the two-positron bond: Evidence for a novel bond type

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R_{HH}	MC-HF	MC-HF	VMC	DMC
	aug-cc-pVTZ	aug-cc-pVQZ		
3.2	-1.273450	-1.275147		
3.6	-1.287555	-1.289003		
4.0	-1.299544	-1.300855		
4.4	-1.309134	-1.310377		
4.8	-1.316450	-1.317666		
5.2	-1.321790	-1.323002		
5.6	-1.325519	-1.326738	-1.58090(2)	-1.5882(1)
5.7			-1.58120(2)	-1.5884(1)
5.8			-1.58149(2)	-1.5886(1)
5.9			-1.58165(2)	-1.5887(1)
6.0	-1.328008	-1.329237	-1.58178(2)	-1.5887(1)
6.1			-1.58180(2)	-1.5887(1)
6.2			-1.58181(2)	-1.5887(1)
6.3			-1.58178(2)	-1.5886(1)
6.4	-1.329587	-1.330830	-1.58166(2)	-1.5884(1)
6.8	-1.330528	-1.331792		
7.2	-1.331043	-1.332332		
7.6	-1.331292	-1.332603		
8.0	-1.331389	-1.332710		
8.1	-1.331398	-1.332720		
8.2	-1.331404	-1.332725		
8.3	-1.331407	-1.332727		
8.4	-1.331408	-1.332725		
8.5	-1.331406	-1.332720		
8.6	-1.331403	-1.332713		
8.7	-1.331398	-1.332705		
8.8	-1.331393	-1.332696		
9.2	-1.331367	-1.332651		
9.6	-1.331337	-1.332607		
10.0	-1.331308	-1.332568		
10.4	-1.331277	-1.332537		
10.8	-1.331247	-1.332512		
11.2	-1.331218	-1.332490		
11.6	-1.331190	-1.332470		
12.0	-1.331164	-1.332453		

Table S2 Total energy of the singlet electronic spin state of $\left[H^-, e^+, H^-\right]$ system as a function of the inter-proton distance computed at the MC-HF/[auc-cc-pVTZ:auc-cc-pVTZ], VMC and DMC levels of theory. The statistical error of the last digit of the QMC results is given in parentheses. All values are given in atomic units.

R_{HH}	MC-HF	VMC	DMC
	auc-cc-pVTZ		
3.2	-1.111312		
3.6	-1.123523		
4.0	-1.135653		
4.4	-1.146367		
4.8	-1.155217		
5.2	-1.162160		
5.6	-1.167326		
5.7	-1.168361		
5.8	-1.169300		
5.9	-1.170146	-1.33533(2)	-1.3399(1)
6.0	-1.170902	-1.33559(2)	-1.3401(1)
6.1	-1.171570	-1.33577(2)	-1.3403(1)
6.2	-1.172153	-1.33591(2)	-1.3404(1)
6.3	-1.172654	-1.33600(2)	-1.3405(1)
6.4	-1.173075	-1.33600(2)	-1.3404(1)
6.5	-1.173418	-1.33600(2)	-1.3404(1)
6.6	-1.173687	-1.33595(2)	-1.3404(1)
6.7	-1.173884	-1.33586(2)	-1.3402(1)
6.8	-1.174011	-1.33567(2)	-1.3401(1)
6.9	-1.174071	-1.33551(2)	-1.3398(1)
7.0	-1.174068		
7.1	-1.174003		
7.2	-1.173881		
7.6	-1.172887		
8.0	-1.171278		
8.4	-1.169314		
8.8	-1.167221		
9.2	-1.165157		
9.6	-1.163210		
10.0	-1.161418		
10.4	-1.159786		
10.8	-1.158307		
11.2	-1.156969		
11.6	-1.155761		
12.0	-1.154671		

Table S3 Vibrational energy levels of $\left[H^-, e^+, H^-\right]$ and $\left(PsH\right)_2$ based on their respective ground-state potential energy curves obtained at the DMC level of theory given in atomic units.

Level	$\left[H^-, e^+, H^-\right]$	$\left(PsH\right)_2$
0	-1.3394	-1.5876
1	-1.3373	-1.5855
2	-1.3354	-1.5836
3	-1.3335	-1.5818
4	-1.3316	-1.5805
5	-1.3299	-1.5793
6	-1.3282	
7	-1.3267	
8	-1.3252	
9	-1.3237	

Table S4 Total energy of PsH system computed at the MC-HF/[auc-cc-pVTZ:auc-cc-pVTZ] and MC-HF/[auc-cc-pVQZ:auc-cc-pVQZ] levels of theory while the exact value is from [G. Ryzhikh, J. Mitroy *J. Phys. B* **1999**, 32, 4051]. All values are in atomic units.

	MC-HF	MC-HF	Exact
	auc-cc-pVTZ	auc-cc-pVQZ	
E	-0.665519	-0.666175	-0.789196

Table S5 TC-IQA terms computed at the MC-HF/[aug-cc-pVTZ:aug-cc-pVTZ] level of theory at 6.0 Bohr inter-nuclear distance for the singlet positronic and electronic spin states of $(PsH)_2$ system. All values are given in atomic units.

E_{intra}

$T_{\text{e}}\left(\Omega_{k=1,2}\right)$	$V_{\text{e-nuc}}\left(\Omega_{k=1,2}\right)$	$V_{\text{ee}}^{\text{cl}}\left(\Omega_{k=1,2}\right)$	$V_{\text{ee}}^{\text{xc}}\left(\Omega_{k=1,2}\right)$	
0.6142	-1.5609	0.9515	-0.4683	
$T_{\text{p}}\left(\Omega_{k=1,2}\right)$	$V_{\text{p-nuc}}\left(\Omega_{k=1,2}\right)$	$V_{\text{ep}}^{\text{cl}}\left(\Omega_{k=1,2}\right)$	$V_{\text{pp}}^{\text{cl}}\left(\Omega_{k=1,2}\right)$	$V_{\text{pp}}^{\text{xc}}\left(\Omega_{k=1,2}\right)$
0.0655	0.3399	-0.6081	0.1236	-0.1040

E_{inter}

$V_{\text{e-nuc}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{e-nuc}}\left(\Omega_2,\Omega_1\right)$	$V_{\text{nuc-nuc}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{ee}}^{\text{cl}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{ee}}^{\text{xc}}\left(\Omega_1,\Omega_2\right)$	
-0.3273	-0.3273	0.1667	0.6432	-0.0123	
$V_{\text{ep}}^{\text{cl}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{ep}}^{\text{cl}}\left(\Omega_2,\Omega_1\right)$	$V_{\text{p-nuc}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{p-nuc}}\left(\Omega_2,\Omega_1\right)$	$V_{\text{pp}}^{\text{cl}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{pp}}^{\text{xc}}\left(\Omega_1,\Omega_2\right)$
-0.3050	-0.3050	0.1549	0.1549	0.1457	-0.0232

Table S6 TC-IQA terms computed at the MC-HF/[aug-cc-pVTZ:aug-cc-pVTZ] level of theory at 8.4 Bohr inter-nuclear distance for the singlet positronic and electronic spin states of $(PsH)_2$ system. All values are given in atomic units.

E_{intra}

$T_{\text{e}}\left(\Omega_{k=1,2}\right)$	$V_{\text{e-nuc}}\left(\Omega_{k=1,2}\right)$	$V_{\text{ee}}^{\text{cl}}\left(\Omega_{k=1,2}\right)$	$V_{\text{ee}}^{\text{xc}}\left(\Omega_{k=1,2}\right)$	
0.6011	-1.5448	0.9368	-0.4667	
$T_{\text{p}}\left(\Omega_{k=1,2}\right)$	$V_{\text{p-nuc}}\left(\Omega_{k=1,2}\right)$	$V_{\text{ep}}^{\text{cl}}\left(\Omega_{k=1,2}\right)$	$V_{\text{pp}}^{\text{cl}}\left(\Omega_{k=1,2}\right)$	$V_{\text{pp}}^{\text{xc}}\left(\Omega_{k=1,2}\right)$
0.0652	0.3285	-0.5872	0.1182	-0.1129

E_{inter}

$V_{\text{e-nuc}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{e-nuc}}\left(\Omega_2,\Omega_1\right)$	$V_{\text{nuc-nuc}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{ee}}^{\text{cl}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{ee}}^{\text{xc}}\left(\Omega_1,\Omega_2\right)$	
-0.2373	-0.2373	0.1190	0.4730	-0.0028	
$V_{\text{ep}}^{\text{cl}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{ep}}^{\text{cl}}\left(\Omega_2,\Omega_1\right)$	$V_{\text{p-nuc}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{p-nuc}}\left(\Omega_2,\Omega_1\right)$	$V_{\text{pp}}^{\text{cl}}\left(\Omega_1,\Omega_2\right)$	$V_{\text{pp}}^{\text{xc}}\left(\Omega_1,\Omega_2\right)$
-0.2309	-0.2309	0.1158	0.1158	0.1129	-0.0052

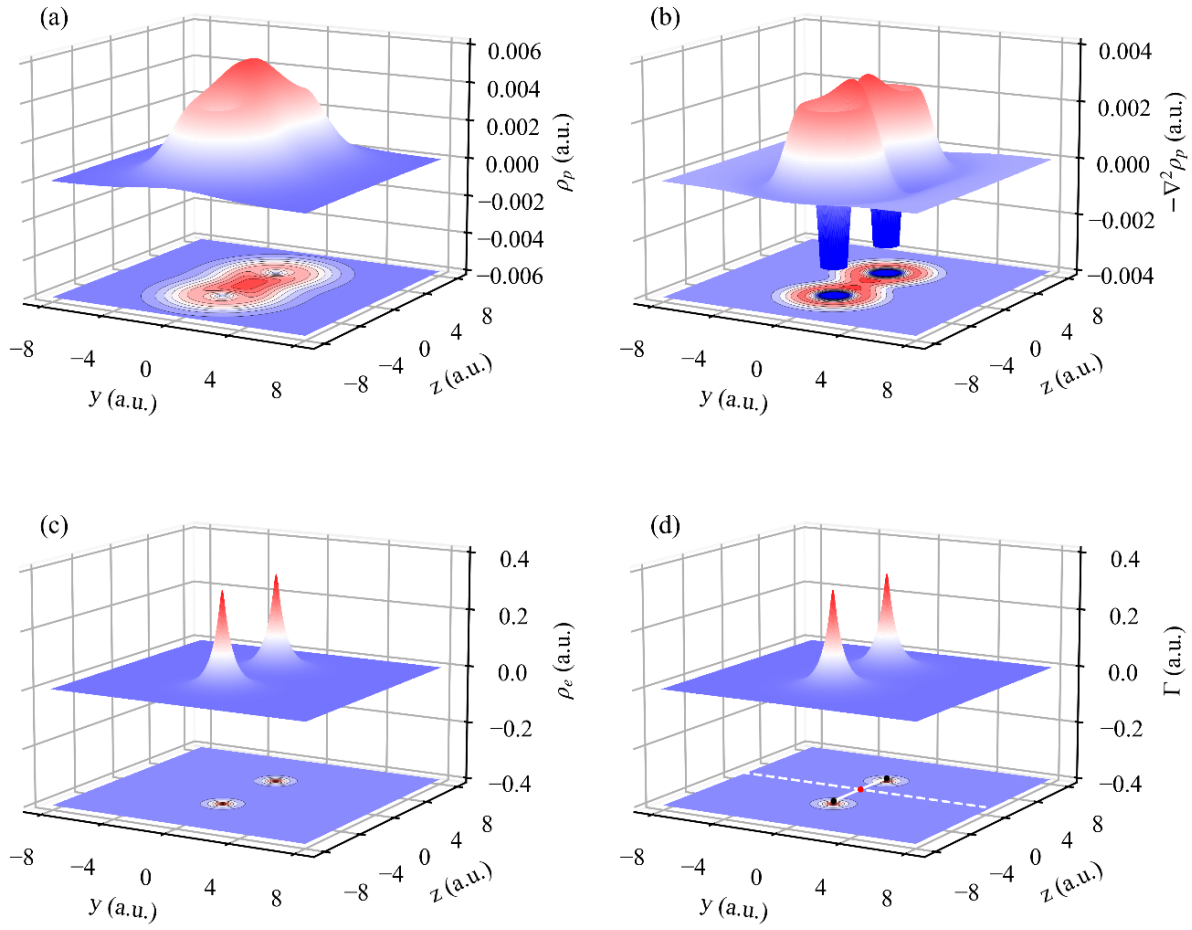

Fig. S1 Relief maps of (a) the one-positron density, (b) the Laplacian of the one-positron density, (c) the one-electron density, and (d) the Gamma density of $(PsH)_2$. The protons are 6.0 Bohr apart, placed at (0.0, 0.0, 3.0) and (0.0, 0.0, -3.0) in the coordinate system. The black and red spheres in panel (d) are the (3, -3) and (3, -1) CPs of the Gamma density, respectively, while the solid white lines are the gradient paths connecting the (3, -3) and (3, -1) CPs. The dashed white line is the intersection of the zero-flux surface and the yz plane, which acts as the boundary of the AIM.