Electronic Supplementary Information

Wavefunction theory and density functional theory analysis of ground and excited states of TaB and WB

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Table S1. Excitation energies (T_e, cm^{-1}) for lowest states of Ta at the MRCI level under the cc-pVQZ-PP (60ECP) basis set and experimental excitation energies.

State	MRCI/CAS(5,9)[a]	Experiment[b]
$a^4F_{3/2}$	0	0.00
$a^4F_{5/2}$	2014	2010.10
$a^4F_{7/2}$	4131	3963.92
$a^4F_{9/2}$	5804	5621.04
$a^4P_{3/2}$	6559	6068.91
$a^4P_{1/2}$	6774	6049.42
$a^4P_{5/2}$	10112	9253.43
$a^2G_{7/2}$	10465	9705.38
$a^6D_{3/2}$	10748	9975.81
$a^6D_{1/2}$	10846	9758.97
$a^2G_{9/2}$	11399	10690.32

[a]The active space consists of 6s, 5d, and 6p orbitals of Ta.

[b]Experimental excitation energies of Ta were obtained from A. Kramida, Y. Ralchenko and J. Reader, NIST Atomic Spectra Database (Version 5.3). National Institute of Standards and Technology, Gaithersburg, MD. http://physics.nist.gov/asd.

Table S2. Bond length (r_e, Å), excitation energy (T_e, cm^{-1}), harmonic vibrational frequency (ω_e, cm^{-1}), anharmonicity ($\omega_e x_e$, cm^{-1}), and % compositions of the low-lying $\Omega = 0^+, 0^-, 1, 2, 1, 0^+, 0^-, 2$, and 1 spin-orbit states of TaB at MRCI.

Ω	r_e	T_e	ω_e	$\omega_e x_e$	Composition[a]
0^+	2.118	0	519	2.3	56.192% $1^5\Delta$, 30.7% $1^3\Pi$, 4.556% $2^3\Pi$, 7.395% $1^1\Sigma^+$, 1.098% $1^3\Sigma^-$
0^-	2.139	341	533	7.1	80.802% $1^5\Delta$, 16.968% $1^3\Pi$, 2.132% $2^3\Pi$
1	2.124	1238	423	1.8	76.844% $1^5\Delta$, 19.909% $1^3\Pi$, 2.056% $1^3\Sigma^+$
2	2.111	1926	433	-6.6	53.594 $1^3\Pi$, 44.793% $1^5\Delta$
1	2.014	2147	569	42.9	91.634% $1^3\Pi$, 7.596% $1^5\Delta$
0^+	2.086	2745	495	-3.2	99.96% $1^5\Pi$
0^-	2.024	3017	573	21.7	77.718% $1^5\Pi$, 12.173% $1^3\Sigma^+$, 7.700% $2^3\Pi$, 1.540% $1^5\Delta$
2	2.095	3434	627	8.5	57.616% $1^3\Pi$, 36.697% $1^5\Delta$
1	2.057	3599	563	-0.2	42.939% $1^3\Pi$, 39.982% $1^5\Delta$, 11.500% $1^5\Phi$, 2.190% $1^3\Sigma^-$, 1.243% $1^1\Pi$

[a]Only dominant compositions are listed.

Table S3. Dissociation energy with respect to Ta(^{4}F)+B(^{2}P) fragments (D_e, kcal/mol), bond distance (r_e, Å), harmonic vibrational frequency (ω_e, cm^{-1}), and anharmonicity ($\omega_e x_e$, cm^{-1}) of the $1^3\Pi$ electronic state of TaB under various exchange-correlation functionals.

Family of functional	DFA	D_e	r_e	ω_e	$\omega_e x_e$
GGA	BP86	77.87	1.990	706	6.6
	BLYP	68.35	2.003	682	6.9
	PBE	80.36	1.988	721	3.6
MGGA	TPSS	72.76	1.999	704	5.1
	MN15-L	69.10	2.007	751	4.3
global GGA Hybrid	B3LYP	61.13	1.980	697	3.5
	B3P86	70.34	1.967	723	3.4
	B3PW91	68.66	1.970	719	3.2
	PBE0	68.62	1.965	727	3.4
MGGA Hybrid	TPSSh	62.81	1.923	674	2.6
	M06	72.49	1.949	721	3.9
	M06-2X	66.15	1.948	741	4.7
	MN15	71.48	1.959	724	3.9
RSH	LRC-ωPBE	59.13	1.862	844	4.6
	CAM-B3LYP	56.02	1.959	725	3.7
	ωB97X	56.98	1.954	732	3.7

Table S4. % DFT errors of dissociation energy (D_e), bond distance (r_e), harmonic vibrational frequency (ω_e), and anharmonicity ($\omega_e x_e$) of the $1^3\Pi$ electronic state of TaB. The DFT errors are calculated with respect to the MRCI values.

Family of functional	DFA	D_e	r_e	ω_e	$\omega_e x_e$
GGA	BP86	24.9	-1.1	6.5	78.4
	BLYP	9.6	-0.4	2.9	86.5
	PBE	28.8	-1.2	8.7	-2.7
MGGA	TPSS	16.7	-0.6	6.2	37.8
	MN15-L	10.8	-0.2	13.3	16.2
Global GGA Hybrid	B3LYP	-2.0	-1.6	5.1	-5.4
	B3P86	12.8	-2.2	9.0	-8.1
	B3PW91	10.1	-2.1	8.4	-13.5
	PBE0	10.0	-2.3	9.7	-8.1
MGGA Hybrid	TPSSh	0.7	-4.4	1.7	-29.7
	M06	16.2	-3.1	8.7	5.4
	M06-2X	6.1	-3.2	11.8	27.0
	MN15	14.6	-2.6	9.2	5.4
RSH	LRC-ωPBE	-5.2	-7.5	27.3	24.3
	CAM-B3LYP	-10.2	-2.6	9.4	0.0
	ωB97X	-8.6	-2.9	10.4	0.0

Table S5. Excitation energies (cm^{-1}) for lowest states of W at the MRCI level under the cc-pVQZ-PP (60ECP) basis set and experimental excitation energies.

State	MRCI/CAS(6,9)[a]	Experiment[b]
$^5D_0$	0	0
$^5D_1$	1212	1670.29
$^5D_2$	2987	3325.53
$^7S_3$	3210	2951.29
$^5D_3$	4646	4830.33
$^5D_4$	5873	6219.33

[a]The active space consists of 6s, 5d, and 6p orbitals of W.

[b]Experimental excitation energies of Ta were obtained from A. Kramida, Y. Ralchenko and J. Reader, *NIST Atomic Spectra Database (Version 5.3).* National Institute of Standards and Technology, Gaithersburg, MD. http://physics.nist.gov/asd.

Table S6. % compositions and vertical excitation energies (VEE, cm^{-1}) of the low-lying spin-orbit states of WB under MRCI at r_e = 1.971 Å.

Ω	VEE	Composition[a]
7/2	0	91.010% $1^6\Pi$, 8.713% $1^4\Delta$
5/2	63	82.101% $1^6\Pi$, 13.792% $1^4\Delta$, 2.025% $1^4\Pi$
3/2	78	63.251% $1^6\Pi$, 24.818% $1^4\Delta$, 5.483% $1^4\Pi$
1/2	113	41.954% $1^4\Delta$, 38.518% $1^6\Pi$, 11.907% $1^4\Pi$, 2.374% $1^2\Sigma^+$
1/2	790	46.145% $1^6\Pi$, 29.166% $1^4\Pi$, 8.736% $1^4\Delta$, 8.384% $1^2\Sigma^+$
1/2	1317	51.682% $1^6\Pi$, 6.717% $1^6\Sigma^+$, 14.249% $1^4\Delta$, 15.352% $1^4\Pi$
3/2	1340	92.885% $1^6\Pi$, 3.666% $1^6\Sigma^+$

[a]Only dominant compositions are listed.

Table S7. Dissociation energy with respect to W(^{7}S)+B(^{2}P) fragments (D_e, kcal/mol), bond distance (r_e, Å), harmonic vibrational frequency (ω_e, cm^{-1}), and anharmonicity ($\omega_e x_e$, cm^{-1}) of the $1^6\Pi$ and $1^4\Delta$ electronic states of WB under various exchange-correlation functionals.

Family of functional	DFA	$1^6\Pi$				$1^4\Delta$[a]			
		D_e	r_e	ω_e	$\omega_e x_e$	D_e	r_e	ω_e	$\omega_e x_e$
GGA	BP86	75.79	1.960	739	4.3	70.44	1.861	849	3.6
	BLYP	74.65	1.960	728	4.1	73.19	1.868	834	3.5
	PBE	75.72	1.958	740	4.4	69.14	1.858	853	3.6
MGGA	TPSS	71.45	1.966	726	4.7	64.95	1.863	847	3.7
	MN15-L	62.46	1.978	693	6.4	-	-	-	-
global GGA Hybrid	B3LYP	66.91	1.954	736	5.2	63.87	1.853	853	3.8
	B3P86	68.38	1.946	744	5.3	61.81	1.844	858	4.0
	B3PW91	64.15	1.952	727	5.5	56.06	1.848	863	4.2
	PBE0	64.65	1.951	721	5.6	55.96	1.845	859	3.7
MGGA Hybrid	TPSSh	67.60	1.962	718	3.7	60.33	1.857	857	6.7
	M06	71.02	1.932	775	4.6	-	-	-	-
	MN15	69.60	1.930	782	5.8	63.63	1.836	865	3.8
RSH	LRC-ωPBE	57.59	1.944	684	6.0	48.86	1.828	653	4.8
	CAM-B3LYP	63.54	1.941	735	6.1	60.27	1.838	871	4.6
	ωB97X	68.18	1.932	755	6.4	68.43	1.832	867	5.0

[a] Due to convergence issues the DFT MN15-L and M06 results of $1^4\Delta$ are not listed.

Table S8. % DFT errors of dissociation energy (D_e), bond distance (r_e), harmonic vibrational frequency (ω_e), and anharmonicity ($\omega_e x_e$) of the $1^6\Pi$ electronic state of WB. The DFT errors are calculated with respect to the MRCI values.

Family of functional	DFA	D_e	r_e	ω_e	$\omega_e x_e$
GGA	BP86	19.7	-0.6	2.9	7.5
	BLYP	17.9	-0.6	1.4	2.5
	PBE	19.6	-0.7	3.1	10.0
MGGA	TPSS	12.8	-0.3	1.1	17.5
	MN15-L	-1.4	0.4	-3.5	60.0
Global GGA Hybrid	B3LYP	5.7	-0.9	2.5	30.0
	B3P86	8.0	-1.3	3.6	32.5
	B3PW91	1.3	-1.0	1.3	37.5
	PBE0	2.1	-1.0	0.4	40.0
MGGA Hybrid	TPSSh	6.8	-0.5	0.0	-7.5
	M06	12.2	-2.0	7.9	15.0
	MN15	9.9	-2.1	8.9	45.0
RSH	LRC-ωPBE	-9.0	-1.4	-4.7	50.0
	CAM-B3LYP	0.3	-1.5	2.4	52.5
	ωB97X	7.7	-2.0	5.2	60.0

Table S9. % DFT errors of dissociation energy (D_e), bond distance (r_e), harmonic vibrational frequency (ω_e), and anharmonicity ($\omega_e x_e$) of the $1^4\Delta$ electronic state of WB. The DFT errors are given with respect to the MRCI values.

Family of functional	DFA	D_e	r_e	ω_e	$\omega_e x_e$
GGA	BP86	17.4	-0.8	3.2	9.1
	BLYP	22.0	-0.4	1.3	6.1
	PBE	15.2	-1.0	3.6	9.1
MGGA	TPSS	8.3	-0.7	2.9	12.1
Global GGA Hybrid	B3LYP	6.5	-1.2	3.6	15.2
	B3P86	3.0	-1.7	4.3	21.2
	B3PW91	-6.6	-1.5	4.9	27.3
	PBE0	-6.7	-1.7	4.4	12.1
MGGA Hybrid	TPSSh	0.5	-1.0	4.1	103.0
	MN15	6.1	-2.1	5.1	15.2
RSH	LRC-ωPBE	-18.6	-2.6	-20.7	45.5
	CAM-B3LYP	0.5	-2.0	5.8	39.4
	ωB97X	14.1	-2.3	5.3	51.5

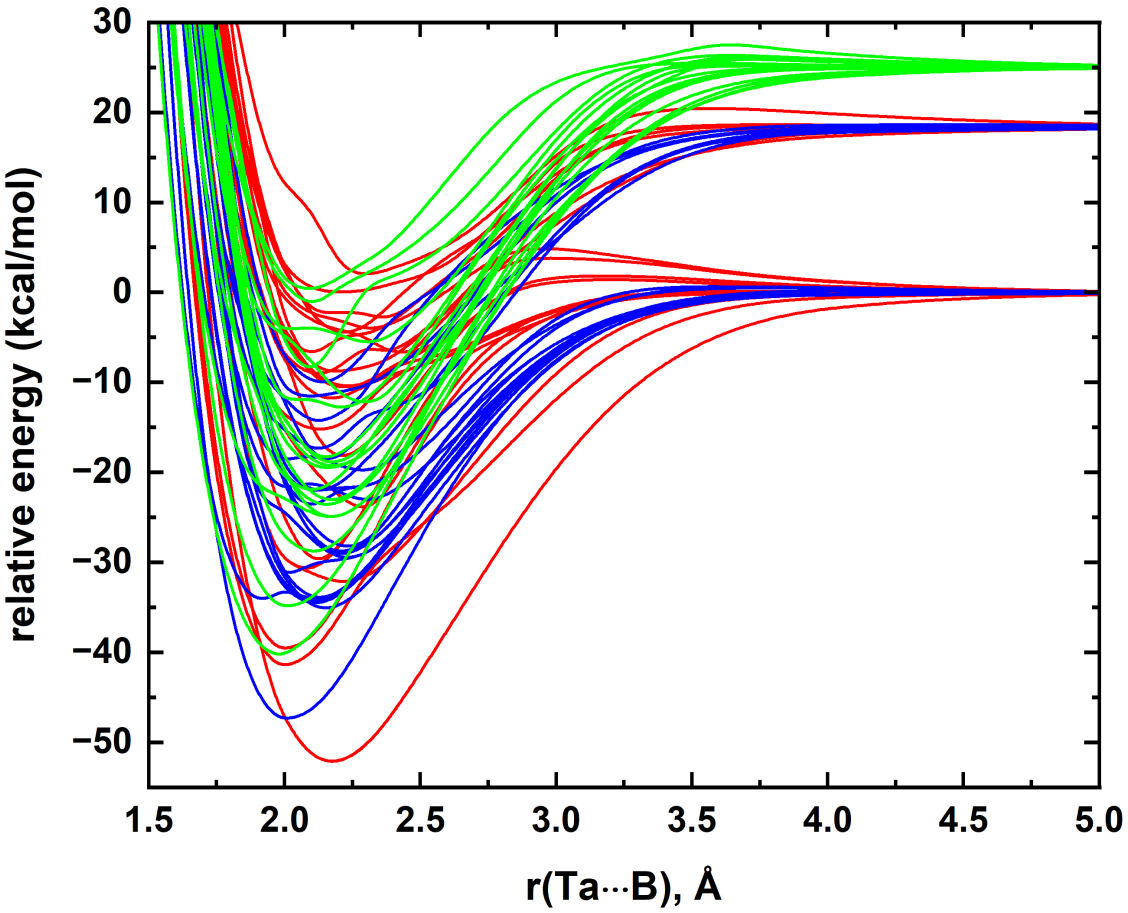

Figure S1. CASSCF PECs of TaB as a function of Ta···B distance [r(Ta···B), Å]. Quintet, triplet, and singlet spin PECs are shown in red, blue, and green respectively.

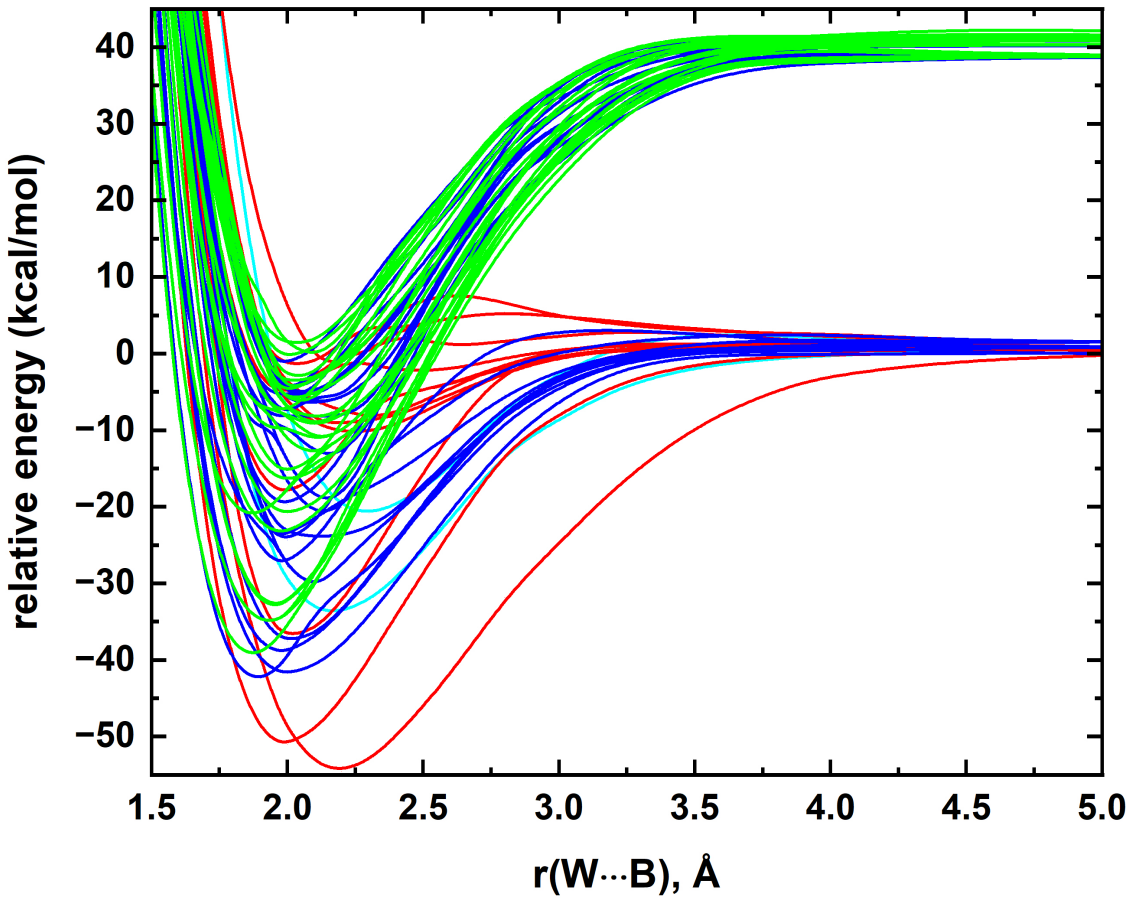

Figure S2. Studied CASSCF PECs of WB as a function of W···B distance [r(W···B), Å]. Octet, sextet, quartet, and doublet spin PECs are shown in cyan, red, blue, and green respectively.

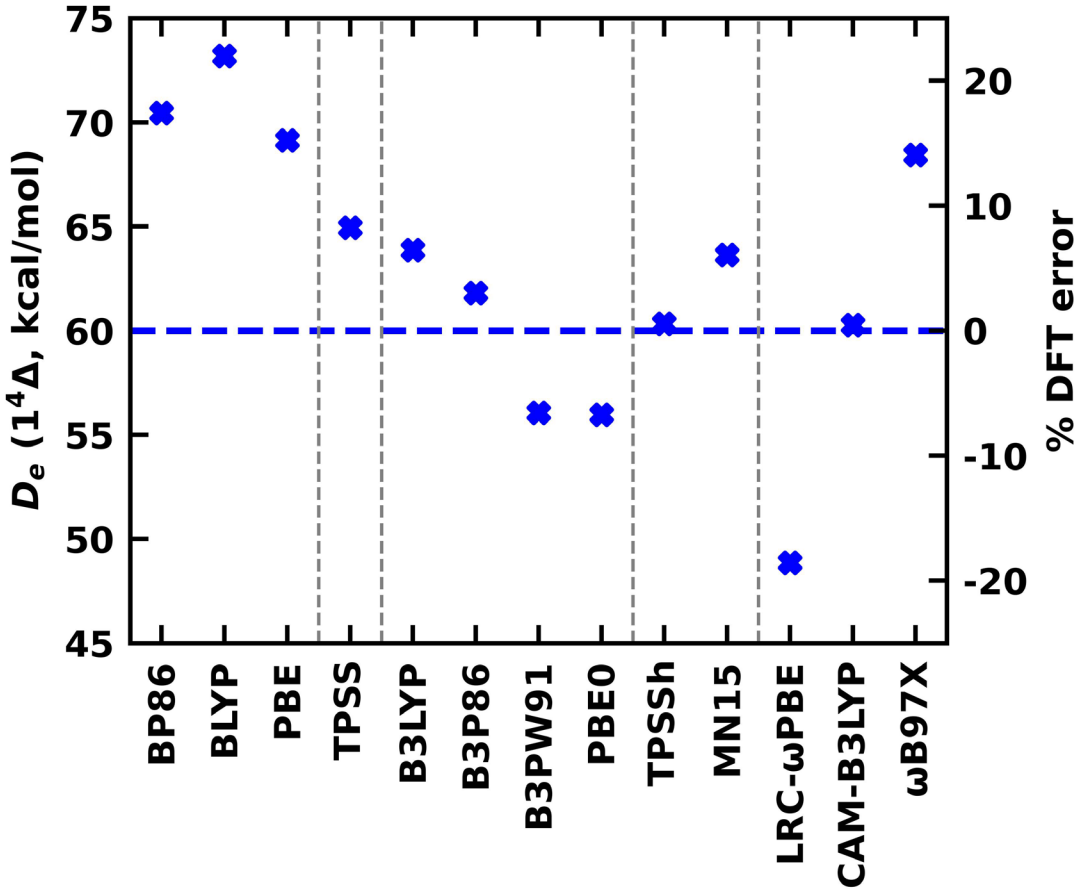

Figure S3. Dissociation energy (D_e, kcal/mol) of WB($1^4\Delta$) obtained at various density functional approximations (blue cross marks). The families of density functionals are separated with vertical gray dashed lines and ordered by the rung on Jacob's ladder (left to right: GGA, MGGA, global GGA hybrid, MGGA hybrid, and RSH). The horizontal blue dashed line represents the MRCI D_e.