

Ab initio and DFT benchmarking of tungsten nanoclusters and tungsten hydrides

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Abstract

We present several benchmark calculations comparing wave-function based methods and density functional theory for model systems containing tungsten. They include W₄ cluster as well as W₂, WH and WH₂ molecules.

Keywords: *Tungsten; ab initio; DFT; nanoclusters; benchmarking*

Formulation of the goal

Ma and Balasubramanian [1] obtained spectroscopic constants and potential energy curves of 15 electronic states of WH using the full second-order configuration-interaction (SOC) calculations. Relativistic-configuration-interaction (RCI) method was applied to estimate the spin-orbit effects. They observed that the spin-free ground state ${}^6\Sigma^+$ is dominated by single configuration and that the spin-orbit coupling does not contaminate the ground state of WH significantly. It is therefore tempting to exploit WH as a benchmark comparing CCSD(T) with various DFT versions at the spin-free level.

Balasubramanian and Ma investigated also the insertion of W into hydrogen molecule [2] and they have found for the lowest state (5B_2 WH₂) small spin-orbit effects on geometry, while more substantial on dissociation energy (with respect to the (7S) W + H₂ dissociation limit). They did not report the IR frequencies/intensities in their study. The first DFT study on higher tungsten hydrides including WH₂ was reported by Wang and Andrews [3]. They performed combined experimental (neon-matrix isolation of laser ablated W reacting with H₂) and theoretical study (using two density functionals: BPW91 and B3LYP). Analysis of their neon-matrix study revealed the band at 1832 cm⁻¹ which was identified as the anti-symmetric (b₂) stretching in WH₂.

Goal of this contribution is to provide benchmark calculations on selected properties of model systems containing tungsten, in particular, to compare the density functional data with wave-function based data. All large-scale simulations investigating properties of tungsten (e.g., in nuclear

fusion) are based on DFT data, hence such a benchmarks can be useful for judging the quality of the pertinent DFT predictions.

Methods

The calculations were performed on the local computer cluster Prašivá (Bratislava) and Calcul HPC cluster (Lille, France). We chose the W_2 , W_4 , WH, WH_2 as model structures of our study. For basic geometry optimization of all the studied species we used the Gaussian program package using DFT with several functionals: B3LYP, B3PW91, BLYP, LC-PW91PW91, M06L, PBE1PBE, PBEPBE, PVTZ-B3LYP, PVTZ-BLYP, PVTZ-LC-BLYP, PW91PW91, mPW-PW91, ω B97X; basis sets: PVDZ, PVTZ and also using several pseudopotentials. [4] For all the subsequent calculations we used the MOLCAS program package. [5]

After obtaining the optimized geometries we used the structural data for single point calculations applying Complete Active Space Perturbation Theory of 2nd order (CASPT2) and CCSDT as benchmarks for the above mentioned functionals. With the CASPT2 method we scanned a part of the potential surface by evenly expanding the cluster size. For this we used the ANO-RCC DZ and TZ basis sets and the scalar relativistic corrections were done via Douglas-Kroll-Hess transformation of the Dirac equation.

For the WH molecule the CCSD(T) potential energy curves were calculated. We made the Dunham analysis for WH and WD to obtain the spectroscopic constants for pertinent species. We used 6th to 8th polynomial to fit the potential. We used data from both CCSD(T) and the PBE functional in the fit. The PBE functional was chosen because of its implementation in both MOLCAS and GAUSSIAN. Both programs yielded very similar results and only the total energies were shifted by a constant.

In DFT calculations we also tested the effects of both semiempirical and ab initio dispersion corrections. The dispersion corrections were calculated either with standalone functionals already containing dispersion (B97D, w B97XD, B97D3) or adding a semi-empirical dispersion potential to the conventional Kohn-Sham DFT energy. Several schemes were constructed for these purposes from which we used the Grimme D3 method with a Becke-Johnson damping function. [6]

Results and discussion

The equilibrium distance in the W_2 molecule was obtained by scanning the energy as a function of distance. We used several functionals to get the equilibrium value. Results are collected in **Tab. 1**.

Tab. 1. W_2 geometries and binding energies at different levels of theory

Method	cc-pvdz-PP		cc-pvtz-PP		Energy [eV]	
	Interatomic distance [Å]	Deviation from reference [7] [%]	Interatomic distance [Å]	Deviation from reference [7] [%]	cc-pvdz-PP	cc-pvtz-PP
wB97XD	1.9704	1.97	1.9569	2.64	-3.512	-
M06L	2.0008	0.45	1.9852	1.23	-4.516	-4.201
M06X	1.9534	2.81	1.9389	3.53	-2.268	-2.674
B97D	2.0094	0.02	1.9958	0.70	-4.847	-4.930

When compared with the theoretical benchmark of 2.010Å [7, 8], we see that these functionals give overall reasonable results even though they slightly overestimate bond strength. As we can see no significant differences between the results and the theoretical reference were observed for all of the studied methods. This could be mainly caused by the fact that in diatomic molecules the main contribution to the energy comes from the covalent bond and the dispersion effects have only a very small to no significance. The overall agreement at the PVDZ level is most probably caused by a compensation of errors. However all DFT methods underestimate the R_e with respect to the CASPT2 result. This can be caused by the use of pseudopotential basis in DFT which treat relativistic effects in an averaged way.

The optimization of W_4 yielded a regular tetrahedron structure with the interatomic distance around 2.4Å. The results are collected in **Tab. 2**.

Tab. 2. W_4 geometries and binding energies at different levels of theory

Method	Interatomic distance [Å]		$\Delta E[W_4-2W_2]^a$ [eV]	
	cc-pvdz-PP	cc-pvtz-PP	cc-pvdz-PP	cc-pvtz-PP
DK-CCSD(T) ^b	2.4631	2.4304	-122.391	-140.076
BLYP	2.4542	2.4504	-119.664 (-2.727)	-117.612 (-22.464)
B3LYP	2.4217	2.4169	-132.705 (-10.314)	-129.6 (-10.503)
B3PW91	2.4026	2.4806	-156.546 (-34.182)	-152.874 (-12.798)
PW91PW91	2.4265	2.4223	-150.12 (-27.729)	-147.825 (-7.749)
mPW91PW91	2.4272	2.4231	-147.825 (-25.434)	-145.395 (-5.319)
PBEPBE	2.4250	2.4210	-151.173 (-28.809)	-148.689 (-8.613)
PBE1PBE	2.3951	2.4731	-166.752 (-44.361)	-162.756 (-22.68)
M062X	2.3686	2.3638	-156.465 (-34.101)	-152.118 (-12.042)
M06L	2.4264	2.4273	-151.308 (-28.944)	-146.367 (-6.291)
LC-BLYP	2.3692	2.3952	-180.198 (-57.807)	-143.667 (-3.591)
LC- ω PBE	2.3673	2.4461	-197.397 (-75.006)	-192.375 (-52.299)

LC-PW91PW91	2.3497	2.3761	-211.869 (-89.505)	-170.478
B97X	2.3853	2.4090	-156.249 (-33.858)	-120.501
B97XD	2.4196	2.4145	-113.778 (-8.586)	-109.593

^a δE with respect to CCSD(T) binding energy is in parentheses;

^b for DK-CCSD(T) we used ANO-RCC-VDZP and ANO-RCC-VTZP basis sets

The energies for the WH molecule were obtained in a similar manner as for W_2 with the addition of a CCSD(T) benchmark calculation. The resulting potential energy curve is depicted on **Fig. 1**.

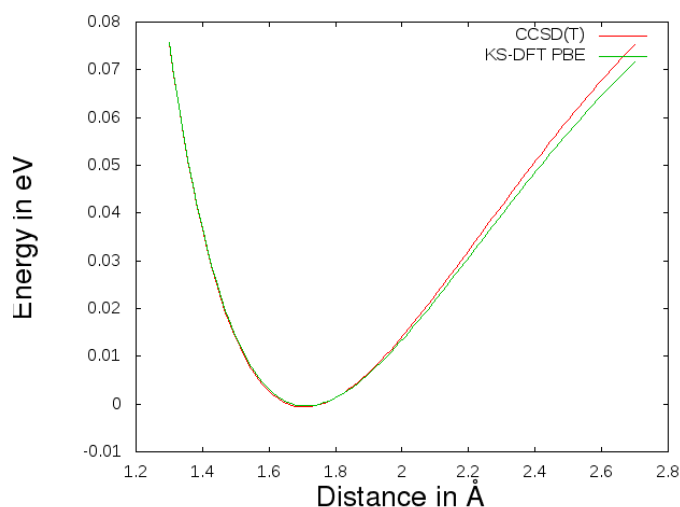


Fig. 1. Potential energy of WH as a function of distance

We can see that DFT with PBE functional is reasonably accurate and differ from the benchmark by underestimating the energy at greater interatomic distances. The infrared spectroscopic constants are summarized in the **Tab. 3.** for WH and **Tab. 4.** for WD.

Tab. 3. ${}^6\Sigma^+$ WH spectroscopic constants

Method	R_e [Å]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]	D_e [eV]
Emission spectroscopy [9]	1.79 ± 0.02	531 ± 62	-	-
Spin-free SOCI/RECP [1]	1.7270	1897	-	2.69
DK-CCSD(T)/ANO-RCC-VTZP	1.7042	1933	29.6	-
DK-CCSD(T)/ANO-RCC-VQZP	1.7063	1928	28.8	-
DK-CCSD(T)/ANO-RCC-Large	1.7064	1925	28.9	-

Tab. 4. ${}^6\Sigma^+$ WD spectroscopic constants

Method	R_e [Å]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]	D_e [eV]
DK-CCSD(T)/ANO-RCC-VTZP	1.7057	1365.3	15.19	-
DK-CCSD(T)/ANO-RCC-VQZP	1.7036	1370.2	15.19	-
DK-CCSD(T)/ANO-RCC-Large	1.7058	1366.2	14.74	-

As we can see, all theoretical methods yielded smaller R_e and larger ω_e . This indicates that an experimental re-investigation might be warranted.

By taking our reference result of 1944 cm^{-1} and rescale it with a factor of 0.95 (which is used for harmonic stretching modes) we obtain 1846 cm^{-1} which is in good agreement with the experimental value of 1832 cm^{-1} . [3] All the valence modes in DFT and a_1 representation exhibit almost identical deviation from the experimental reference and can be considered as acceptable methods for calculating spectroscopic properties.

Tab. 5. 5B_2 WH_2 geometries, vibrational frequencies, and infrared intensities at different levels of theory

Method	W-H Distance [Å]	HWH Angle [deg]	Frequencies [cm^{-1}]
CASPT2/ANO-RCC-Large	1.7072	111.2	1944($a_1,176$),1928($b_2,246$),683($a_1,91$)
BLYP	1.7192	112.4	1882($a_1,45$), 1864($b_2,162$), 27($a_1,34$)
B3LYP	1.7150	113.4	1913($a_1,61$), 1896($b_2,215$), 48($a_1,43$)
B3PW91	1.7095	113.8	1931($a_1,57$), 1916($b_2,211$), 58($a_1,48$)
PW91PW91	1.7104	112.3	1916($a_1,38$),1901($b_2,147$), 633($a_1,38$)
mPW91PW91	1.7110	112.8	1911($a_1,40$),1896($b_2,155$), 638($a_1,38$)
PBEPBE	1.7120	112.1	1909($a_1,39$),1894($b_2,149$), 32($a_1,39$)
PBE1PBE	1.7095	113.3	1935($a_1,59$), 1921($b_2,216$), 54($a_1,51$)
M062X	1.6973	111.9	1981($a_1,43$),1946($b_2,166$), 23($a_1,50$)
M06L	1.7169	112.2	1904($a_1,60$), 1877($b_2,223$), 78($a_1,39$)
LC-BLYP	1.7196	116.2	1949($a_1,88$), 1930($b_2,308$), 54($a_1,61$)
LC- ω PBE	1.7166	116.1	1948($a_1,87$), 1929($b_2,316$), 68($a_1,65$)
LC-PW91PW91	1.7112	116.0	1971($a_1,80$), 1955($b_2,300$), 62($a_1,69$)
Ne-matrix IR spectrum [3]	-	-	1832(a_1)

Conclusions

In this investigation we calculated interatomic distances, and other infrared spectroscopic data. The benchmarks show that most of the used functionals are quite reliable to describe such systems. We have also shown that for these cases dispersion has only a negligible effect. We have provided a benchmark for the harmonic frequencies of both WH and WH_2 and in the case of WH_2 also a comparison to a set of functionals.

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