

## Supporting Information

# Exploration of H<sub>2</sub> binding to the [NiFe]-hydrogenase active site with multiconfigurational density functional theory

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## 1 Studies with different $\mu$ values

A study of the  $\Delta E_{\text{H}_2}$  energy difference between the two investigated intermediates for different  $\mu$  values was conducted, first based on MP2–srDFT calculations on model 1. The resulting energy differences are given in Table S1. One notes that  $\Delta E_{\text{H}_2}$  decreases steadily with increasing  $\mu$ . Recalling that increasing  $\mu$  means moving correlation from the short-range DFT part to the long-range WFT part, a possible reason for these results could be that MP2 is inadequate to describe the energy difference in wave function theory. We therefore decided to calculate  $\Delta E_{\text{H}_2}$  also with CAS(14,14)-srPBE for the most relevant  $\mu$  values, and these

results are also reported in Table S1. These values clearly support our contention that MP2 is inadequate, while CAS(14,14) is sufficiently flexible and accurate to describe the transfer of correlation effects from the DFT part to the WFT part of the MC-srDFT model when  $\mu$  changes from 0.4 to 0.7. As a side remark, the variation in the CAS(14,14) natural orbital occupation numbers in Tables S2 and S3 as a function of the  $\mu$  value shows explicitly that the long-range correlation effects increase when  $\mu$  is increased.

From these results,  $\mu = 0.4-0.7$  all give reasonable  $\Delta E_{\text{H}_2}$  energy differences compared to DMRG(22,22)-CASPT2 and CCSD(T) values (cf. Table 1 in the paper). Previous studies (see paper for references) on smaller systems have found that 0.4 is optimal, our results here provide no reason for advocating another value. We therefore follow our earlier recommendation and use a value of  $\mu = 0.4$  in this study.

Table S1: The  $\Delta E_{\text{H}_2}$  energy difference (kJ/mol) for model 1 from MP2-srPBE and CAS(14,14)-srPBE calculations with B1 and various  $\mu$  values.

$\mu$	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3
MP2-srPBE	0.7	1.7	2.7	3.8	5.4	8.1	12.7	18.6
CAS(14,14)-srPBE				14.9	14.2	14.1	17.0	

We additionally investigated how the selection of the active space vary with different  $\mu$  values. In Tables S2 and S3, we have compiled occupation numbers of the relevant orbitals for several different  $\mu$ -values. For  $\mu = 1.0$ , the best CAS space would be either CAS(8,8) or CAS(14,14). The orbitals from a CAS(14,14)-srPBE calculations are shown in Figure 5. It can be seen that metal orbitals are missing in active space and the orbitals are somewhat different from the orbitals obtained with  $\mu = 0.4$ . This shows that care must be exercised in selecting orbitals based on different  $\mu$ -values.

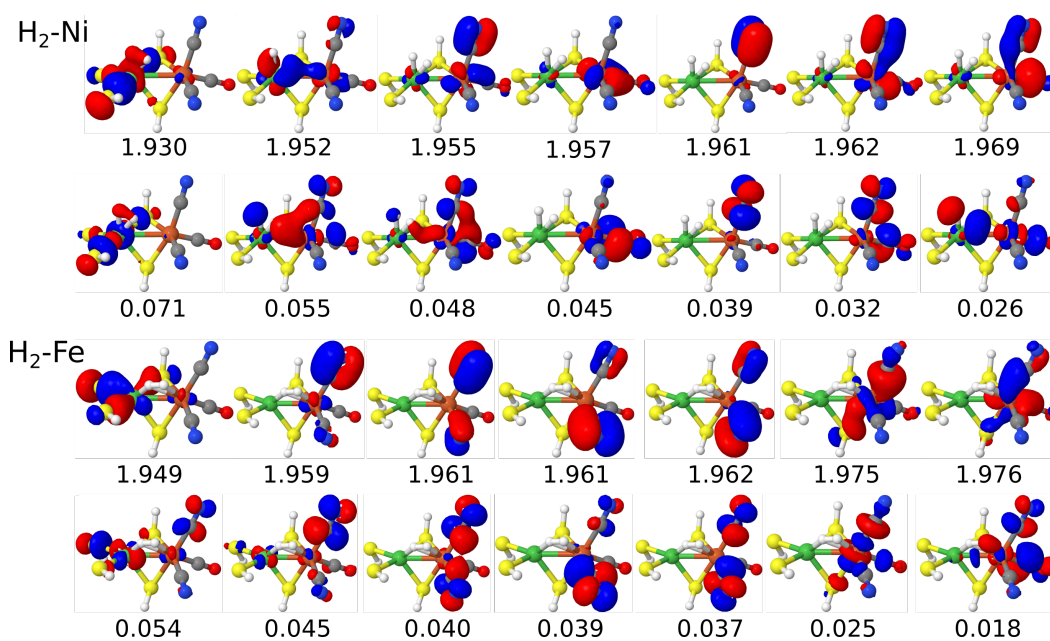


Figure S1: Active natural orbitals and their occupation numbers from a CAS(14,14)-srDFT calculation (started from the MP2 wavefunction) of model 1 with  $\mu = 1$

## Model 1

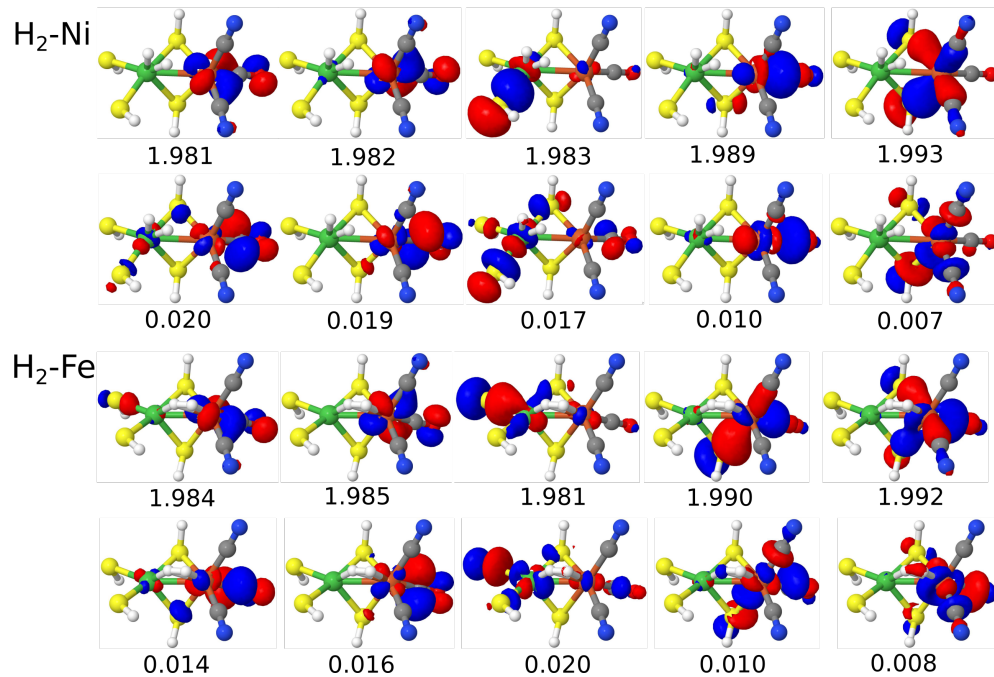


Figure S2: Active natural orbitals and their occupation numbers from a CAS(10,10)-srDFT calculation (started from the MP2 wavefunction) with  $\mu = 0.4$  for model 1



## Model 2

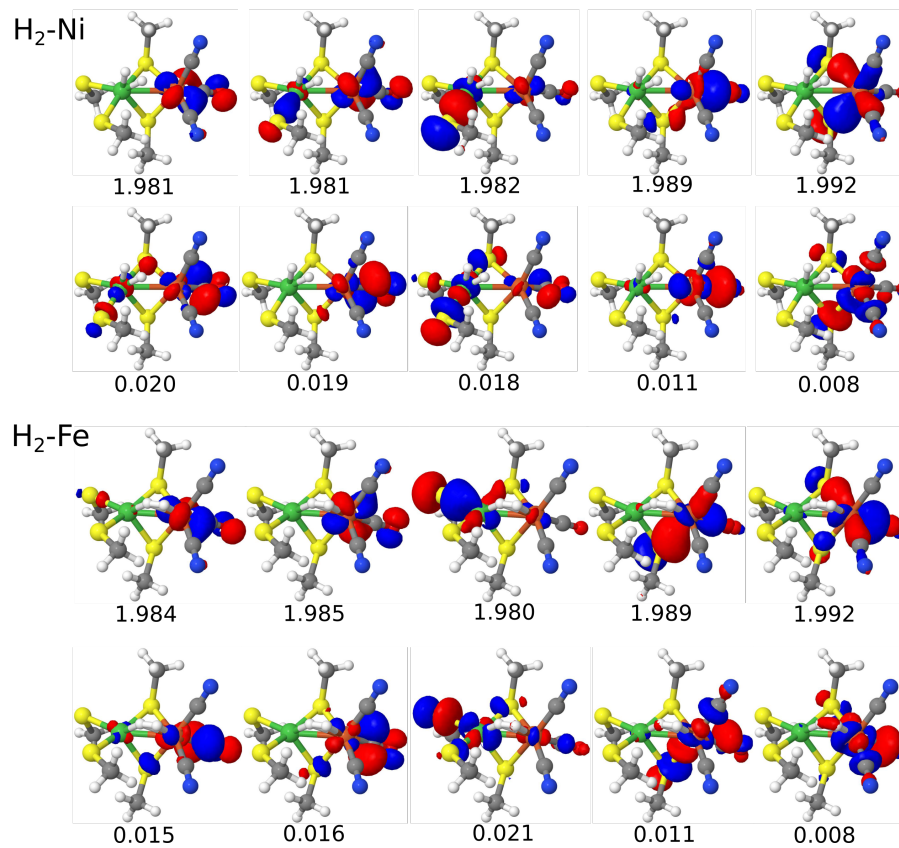


Figure S3: Active natural orbitals and their occupation numbers from a CAS(10,10)-srDFT calculation (started from the MP2 wavefunction) with  $\mu = 0.4$  for model 2

## Model 3

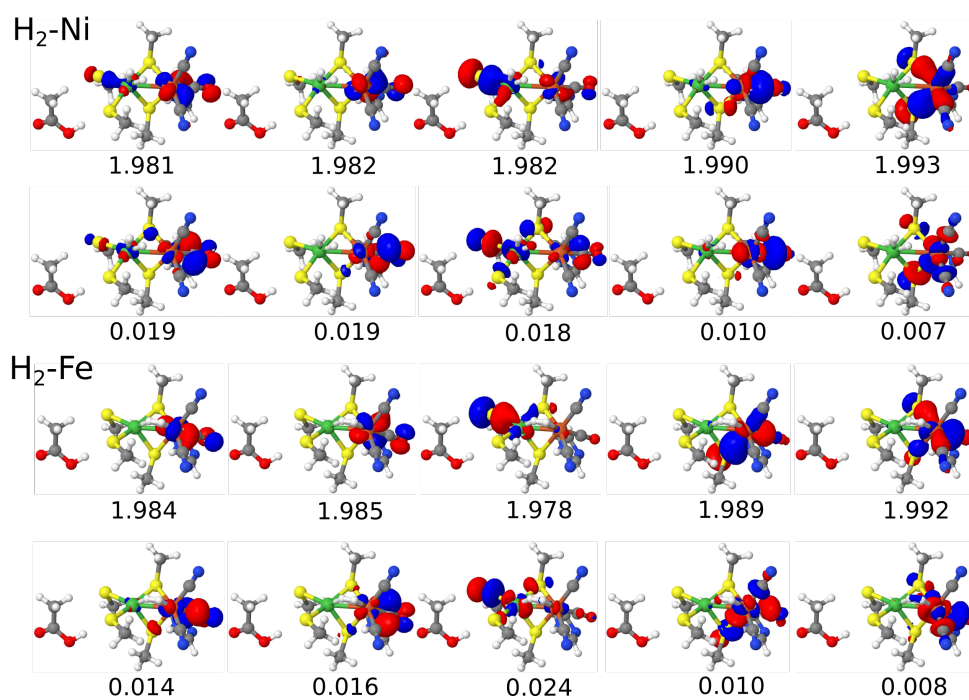


Figure S4: Active natural orbitals and their occupation numbers from a CAS(10,10)-srDFT calculation (started from the MP2 wavefunction) with  $\mu = 0.4$  for model 3

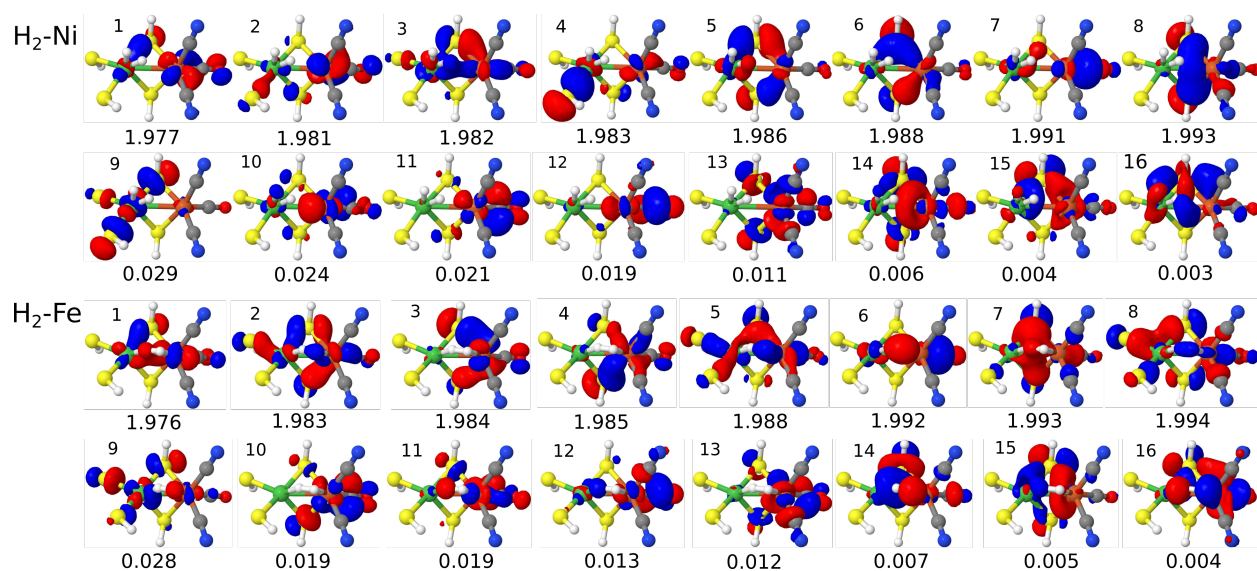


Figure S5: Active natural orbitals and their occupation numbers from a CAS(16,16)–srDFT calculation for model 1 (started from the MP2 wavefunction) with  $\mu = 0.4$

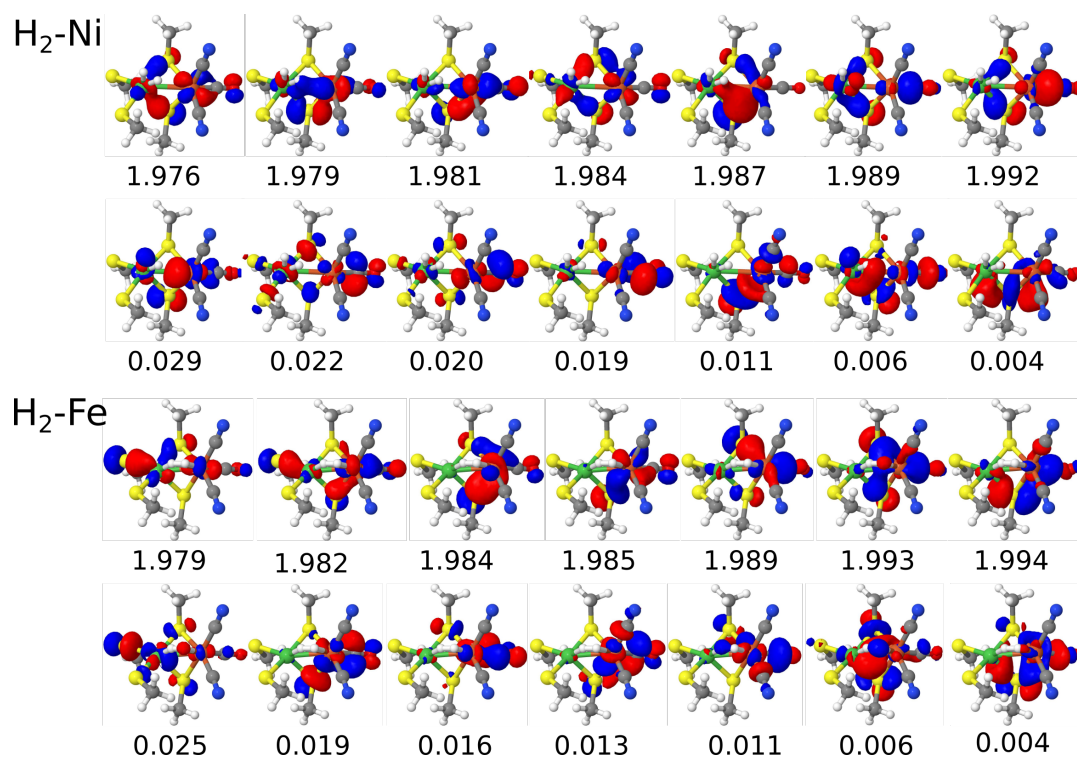


Figure S6: Active natural orbitals and their occupation numbers from CAS(14,14)-srPBE calculation on model 2.

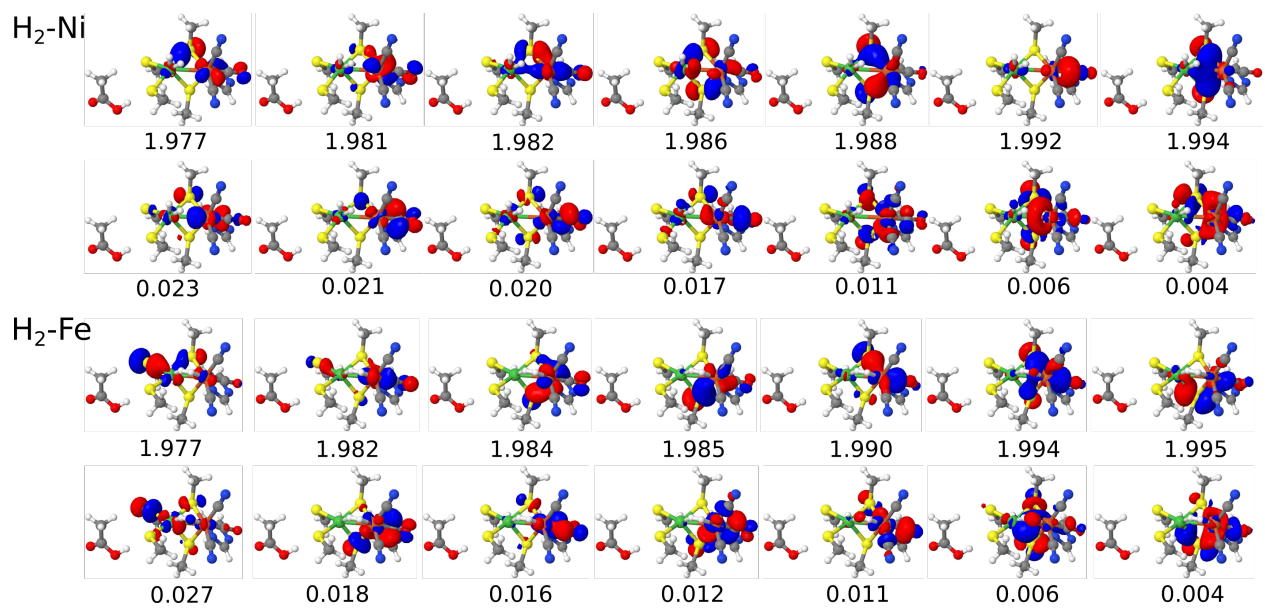


Figure S7: Active natural orbitals and their occupation numbers from CAS(14,14)-srPBE calculation on model 3.

Table S2: MP2–srPBE and CAS–srPBE natural orbital occupation numbers for  $\text{H}_2\text{-Ni}$

$\mu$		occupation numbers								
1.0	MP2	1.964	1.964	1.962	1.961	1.960	1.959	1.958	1.957	1.949
		0.046	0.043	0.042	0.041	0.033	0.033	0.030	0.030	0.026
0.9	MP2	1.966	1.966	1.966	1.964	1.964	1.962	1.961	1.959	1.950
		0.048	0.040	0.039	0.037	0.031	0.031	0.029	0.027	0.025
0.8	MP2	1.971	1.969	1.969	1.969	1.966	1.966	1.965	1.961	1.952
		0.048	0.037	0.036	0.033	0.030	0.029	0.025	0.023	0.023
0.7	MP2	1.974	1.974	1.972	1.972	1.970	1.969	1.968	1.965	1.957
		0.046	0.033	0.032	0.029	0.028	0.027	0.021	0.020	0.020
	CAS(14,14)	2	2	1.987	1.978	1.977	1.966	1.965	1.964	1.945
0.6	MP2	1.979	1.978	1.977	1.976	1.974	1.973	1.971	1.970	1.964
		0.042	0.028	0.028	0.026	0.024	0.023	0.017	0.017	0.016
	CAS(14,14)	2	2	1.990	1.982	1.981	1.971	1.970	1.969	1.954
0.5	MP2	1.984	1.982	1.981	1.980	1.978	1.977	1.976	1.975	1.973
		0.034	0.024	0.023	0.022	0.020	0.017	0.013	0.013	0.012
	CAS(14,14)	2	2	1.992	1.986	1.985	1.977	1.975	1.974	1.966
0.4	MP2	1.989	1.987	1.987	1.986	1.984	1.983	1.983	1.982	1.980
		0.025	0.019	0.017	0.016	0.014	0.012	0.010	0.009	0.008
	CAS(14,14)	2	2	1.992	1.990	1.988	1.983	1.982	1.981	1.978
0.3	MP2	1.994	1.993	1.992	1.992	1.991	1.990	1.990	1.989	1.987
		0.016	0.013	0.010	0.009	0.008	0.006	0.006	0.005	0.005
	CAS(16,16)	2	1.993	1.991	1.988	1.986	1.983	1.982	1.981	1.977

Table S3: MP2–srPBE and CAS–srPBE natural occupation numbers for  $\text{H}_2\text{--Fe}$

$\mu$		occupation numbers								
1.0	MP2	1.965	1.964	1.962	1.961	1.960	1.959	1.958	1.956	1.954
		0.043	0.042	0.041	0.038	0.033	0.030	0.030	0.029	0.027
0.9	MP2	1.967	1.967	1.966	1.964	1.963	1.963	1.962	1.958	1.955
		0.041	0.039	0.038	0.037	0.031	0.029	0.028	0.026	0.026
0.8	MP2	1.971	1.970	1.970	1.969	1.967	1.965	1.965	1.960	1.957
		0.041	0.036	0.035	0.033	0.029	0.026	0.025	0.024	0.023
0.7	MP2	1.975	1.974	1.974	1.973	1.971	1.969	1.968	1.964	1.960
		0.041	0.032	0.031	0.029	0.027	0.024	0.021	0.020	0.019
	CAS(14,14)	2	2	1.988	1.986	1.976	1.974	1.971	1.969	1.950
		0.053	0.030	0.029	0.027	0.024	0.014	0.009	0	0
0.6	MP2	1.979	1.979	1.978	1.976	1.975	1.972	1.972	1.968	1.966
		0.038	0.028	0.026	0.025	0.024	0.021	0.017	0.017	0.016
	CAS(14,14)	2	2	1.990	1.988	1.980	1.978	1.975	1.972	1.957
		0.046	0.027	0.025	0.023	0.020	0.012	0.007	0	0
0.5	MP2	1.984	1.984	1.982	1.981	1.979	1.978	1.977	1.975	1.973
		0.033	0.023	0.021	0.021	0.019	0.017	0.013	0.013	0.012
	CAS(14,14)	2	2	1.992	1.991	1.984	1.982	1.979	1.977	1.967
		0.037	0.023	0.021	0.018	0.016	0.008	0.005	0	0
0.4	MP2	1.989	1.988	1.987	1.986	1.985	1.984	1.982	1.982	1.981
		0.025	0.018	0.016	0.014	0.014	0.012	0.010	0.009	0.008
	CAS(14,14)	2	2	1.994	1.994	1.993	1.988	1.984	1.983	1.979
			0.020	0.019	0.017	0.012	0.010	0.004	0.004	0
	CAS(16,16)	2	1.994	1.993	1.992	1.988	1.985	1.984	1.983	1.976
		0.028	0.019	0.019	0.013	0.012	0.007	0.005	0.004	0
0.3	MP2	1.994	1.993	1.993	1.992	1.992	1.991	1.989	1.989	1.989
		0.016	0.011	0.010	0.008	0.007	0.006	0.006	0.005	0.005