Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

H_2 binding to the active site of [NiFe] hydrogenase studied by multiconfigurational and coupled-cluster methods

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Table S1. Relative energies of the three H_2 adducts (kJ/mol), calculated with the CCSD(T) and DMRG-CASPT2 methods with and without the semi-core 3s3p correlation on model 1, using QM/MM structures optimised with the TPSS or B3LYP methods. The net effect is the difference of the energies obtained with and without the 3s3p correlation. The ^{1}**Ni-H$_2$** structures were used as the reference.

3s,3p correlation	Method	TPSS structures			B3LYP structures		
		^{1}Ni-H$_2$	**^{1}Fe-H$_2$**	**^{3}Fe-H$_2$**	**^{1}Ni-H$_2$**	**^{1}Fe-H$_2$**	**^{3}Fe-H$_2$**
without	CCSD(T)	0	24.7	-0.7	0	13.6	-19.9
	DMRG-CASPT2	0	18.6	-13.5	0	13.5	-21.3
with	CCSD(T)	0	18.1	4.1	0	8.9	-10.8
	DMRG-CASPT2	0	17.7	-4.6	0	15.8	-7.9
net effect	CCSD(T)	0	-6.6	4.8	0	-4.7	9.1
	DMRG-CASPT2	0	-0.9	8.9	0	2.3	13.4

Table S2. T_1, D_1, and %TAE diagnostics[1] of the CCSD(T) calculations on model 1. The following criteria have been suggested for the computation of reliable *d*-block energetic and spectroscopic properties using single-reference methods: $T_1 < 0.05$, $D_1 < 0.15$, and %TAE < 10. It can be seen that the T_1 values for the singlet structures and the D_1 values for all structures are above the limits, although %TAE is well below the limit for all complexes. However, as discussed before,[2] the non-dynamical correlation effects are situated on the Fe centre, which is constant in all complexes and does not affect the singlet–triplet energy difference.

Diagnostic	TPSS structures			B3LYP structures		
	^{1}Ni-H$_2$	**^{1}Fe-H$_2$**	**^{3}Fe-H$_2$**	**^{1}Ni-H$_2$**	**^{1}Fe-H$_2$**	**^{3}Fe-H$_2$**
T_1	0.060	0.057	0.044	0.059	0.055	0.046
D_1	0.369	0.380	0.201	0.369	0.366	0.193
%TAE(T)	6.1	5.8	4.9	5.8	5.5	5.6

Figure S1. Active natural orbitals and their occupation numbers resulting from the DMRG calculation of the ^{1}**Ni-H$_2$** state for model 1, optimised with the B3LYP method.

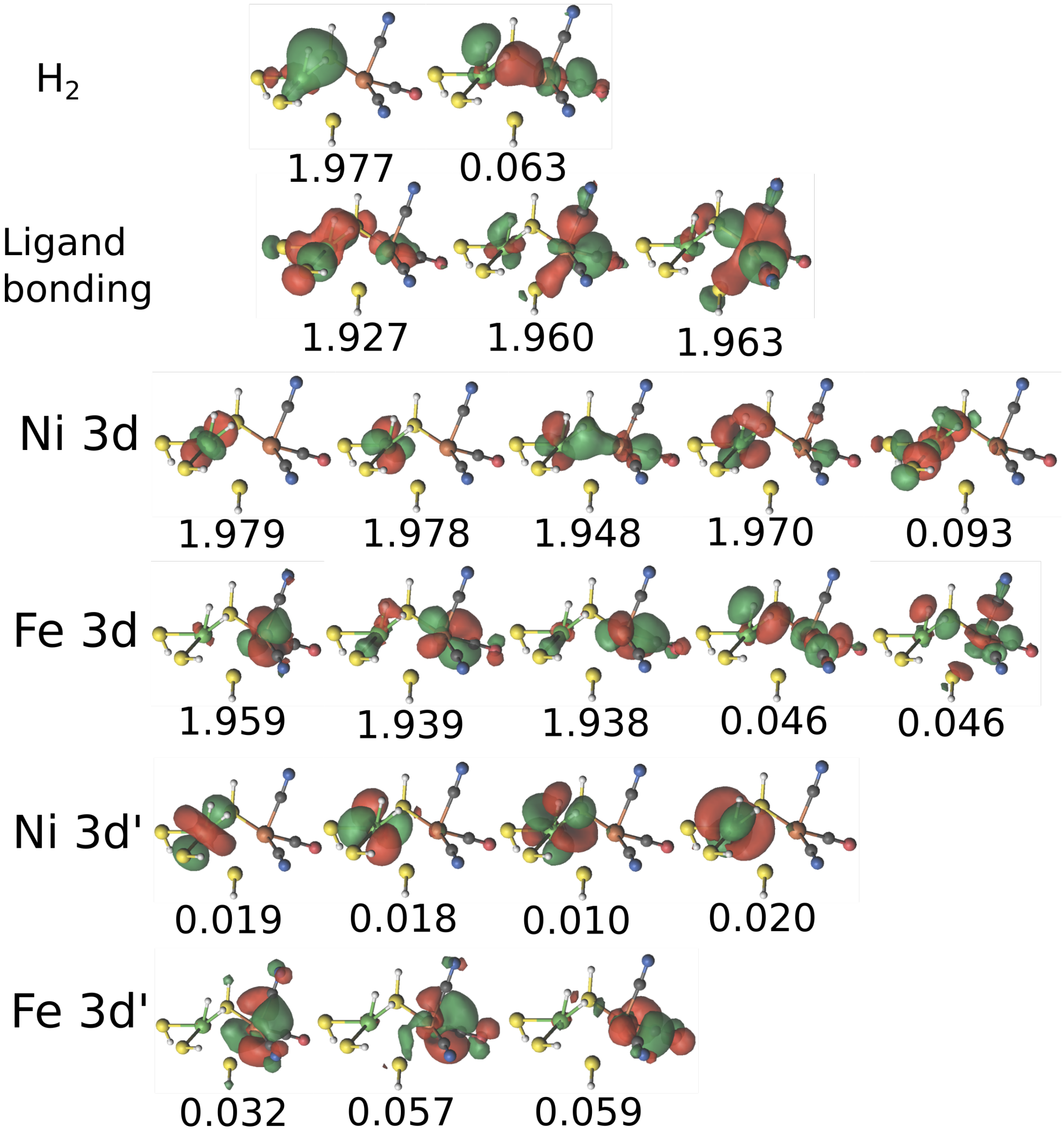


Figure S2. Active natural orbitals and their occupation numbers resulting from the DMRG calculation of singlet ^{1}**Fe-H$_2$** state for model 1, optimised with the B3LYP method.

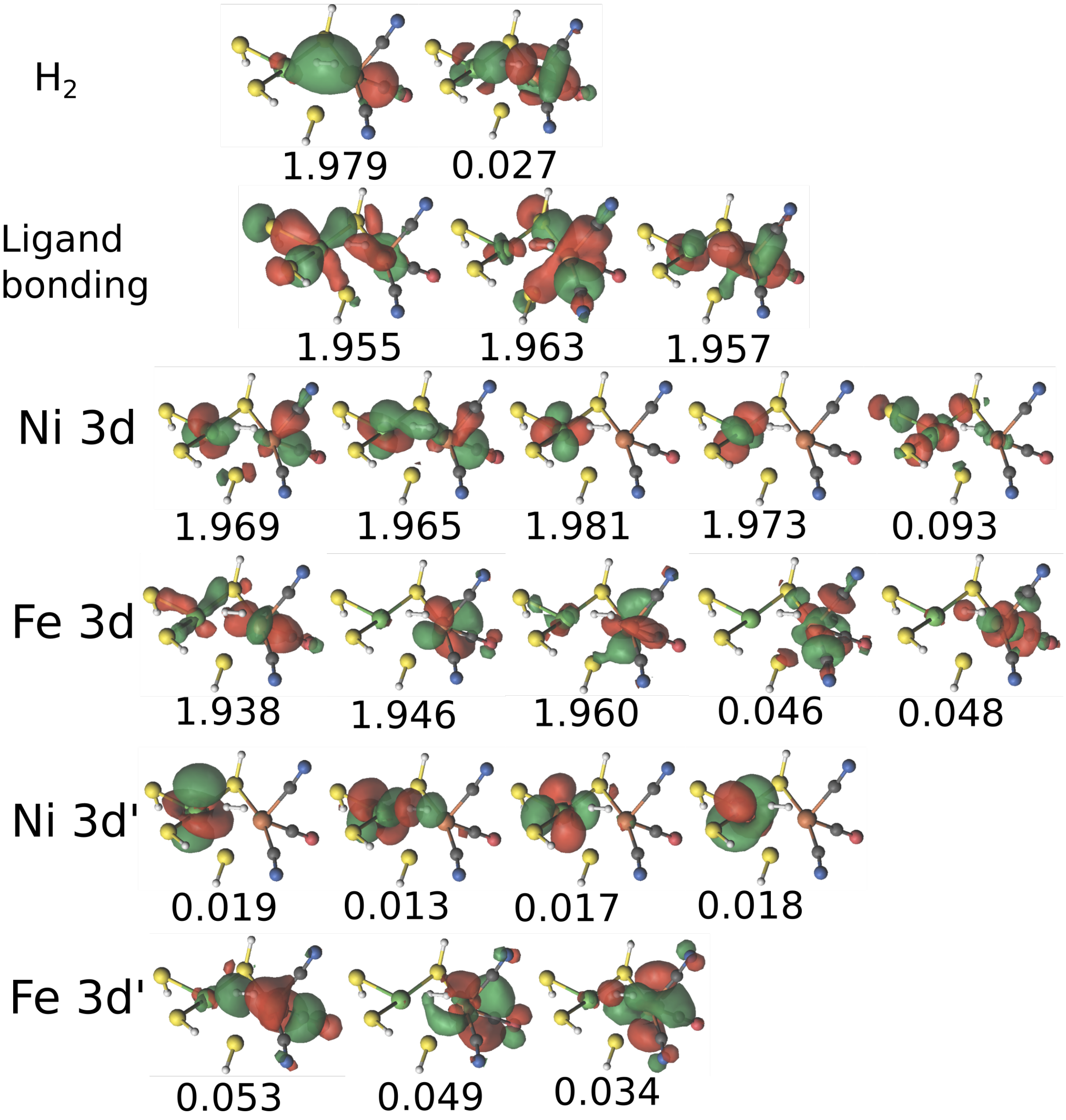
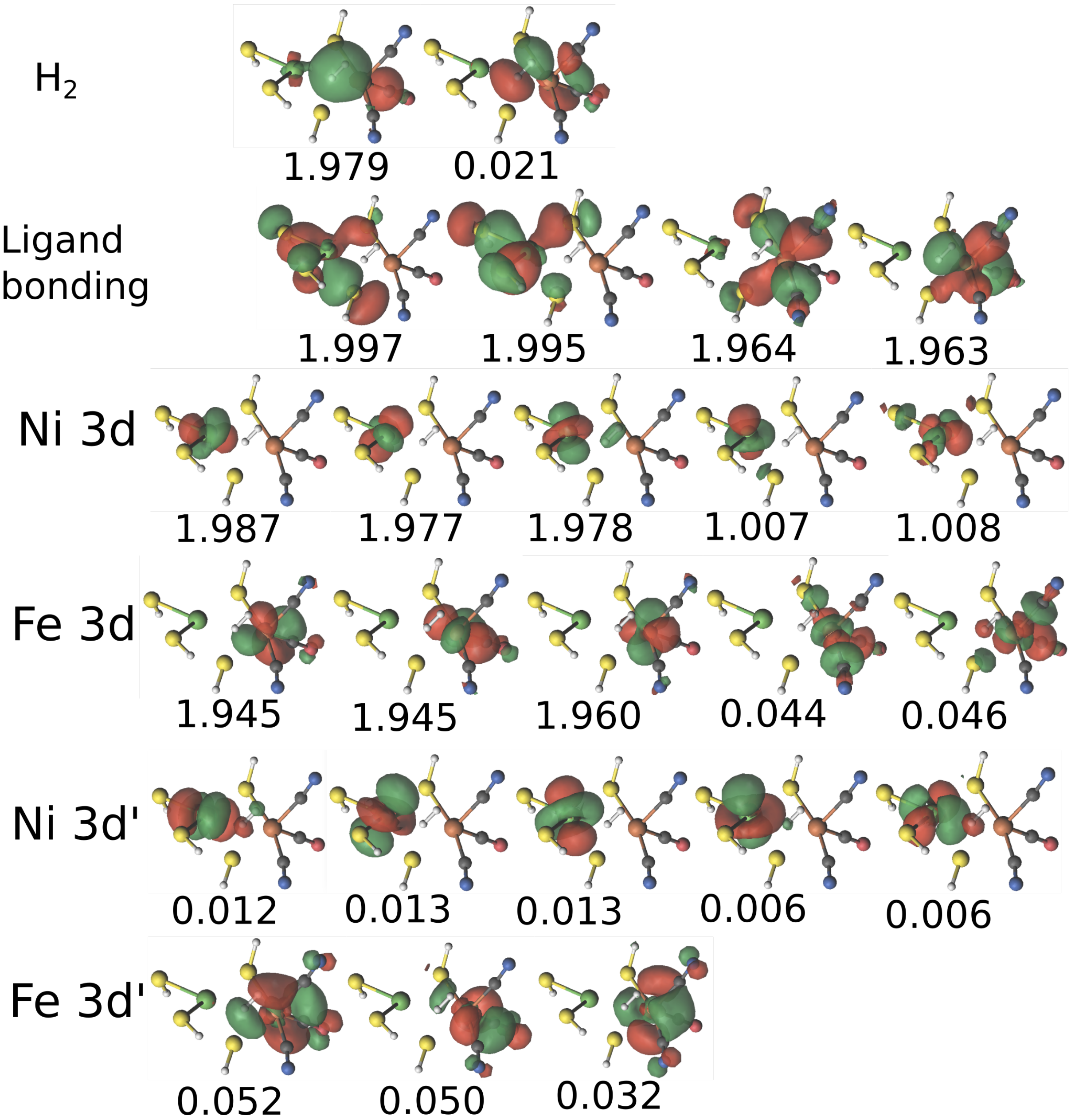


Figure S3. Active natural orbitals and their occupation numbers resulting from the DMRG calculation of the triplet ^{3}**Fe-H$_2$** state for model 1, optimised with the B3LYP method.



References

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2. Delcey, M. G.; Pierloot, K.; Phung, Q. M.; Vancoillie, S.; Lindh, R.; Ryde, U. Phys. Chem. Chem. Phys. 2014, 16, 7927-7938.