Selected topics of computational chemistry - Prof. Jen-Shiang K. Yu

Homework

0317033 謝明修

- Using the Segmented All-Electron Relativistically Contracted (SARC) Basis set to Calculate the ionization energy of Tungsten(W).

	Gaussian09 (B3LYP)	ORCA(B3LYP/G)		ORCA(B3LYP)	
	DKH2	DKH	ZORA	DKH	ZORA
W	-16126.91622	-16128.19828	-16616.30691	-16127.89555	-16616.00401
W^{+1}	-16126.62684	-16127.90838	-16616.01839	-16127.60863	-16615.71866
IE(eV)	7.874	7.889	7.851	7.808	7.765
Exp. (eV)			7.864		

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Homework

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- Calculate the antiferromagnetic properties.

ORCA	UKS 11-et	BS singlet Antiferro singlet	BS singlet UKS singlet	RKS Singlet
Mn-Mn (Å)	2.75	2.74	2.72	2.28
Mn-O (Å)	1.85	1.84	1.85	1.8
Spin Population Mn/Mn	4.86/4.86	3.99/-3.99	2.02/-2.02	0/0
S	5	0	0	0
S**2	30.078746	4.931103	2.871961	0
ideal S(S+1)	30	0	0	0
Deviation	0.078746	4.931103	2.871961	0
E(B3LYP/3-21G)	-2890.096819	-2890.103919	-2890.031785	-2889.917883
ΔE (kcal/mol)	4.5	0.0	45.3	116.7
E(antiferro coupling) cm^{-1}	1521.788			

G09	UKS 11-et	Antiferro singlet	UKS singlet	RKS Singlet
Mn-Mn (Å)	2.74	2.73	2.71	2.25
Mn-O (Å)	1.84	1.83	1.85	1.79
Spin Density Mn/Mn	4.85/4.85	3.91/-3.91	-2.07/2.07	0
E(B3LYP/3-21G)	-2890.864352	-2890.871215	-2890.798477	-2890.6846
delta E (kcal/mol)	4.3	0.0	45.6	117.1

Antiferromagnetic coupling constant

J1	-60.25
J2	-50.21
J3	-59.96

The orbitals are plotted and printed at the website:
http://ukko.life.nctu.edu.tw/~u0317033/Selected_topics_of_computational_chemistry/week4/HW.html

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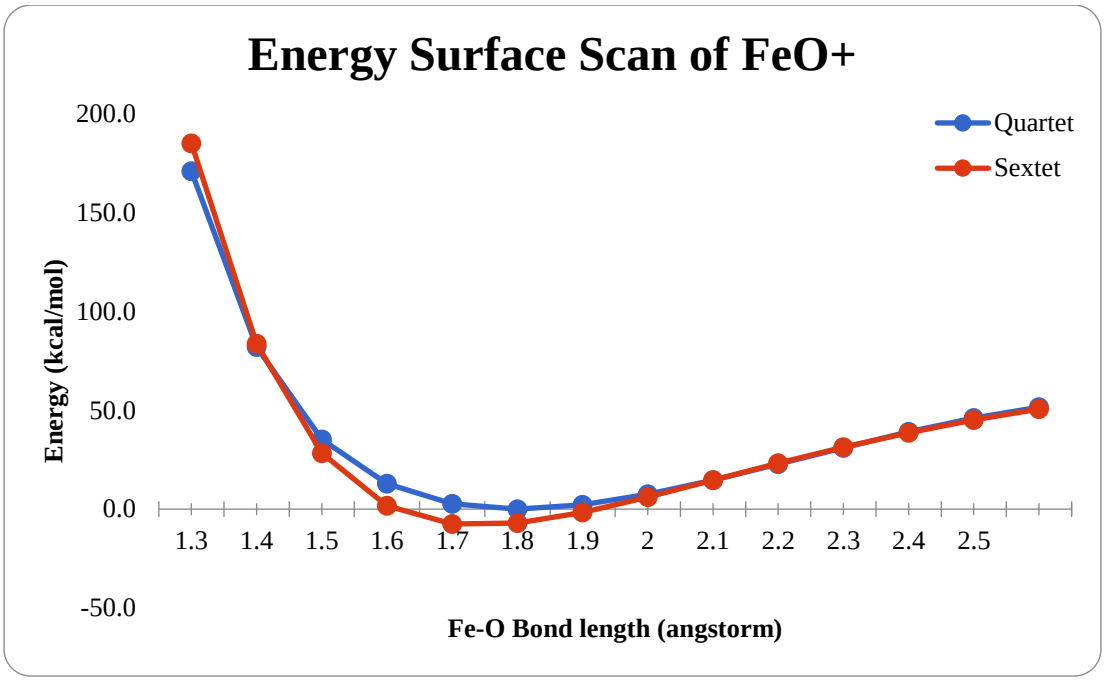
Homework

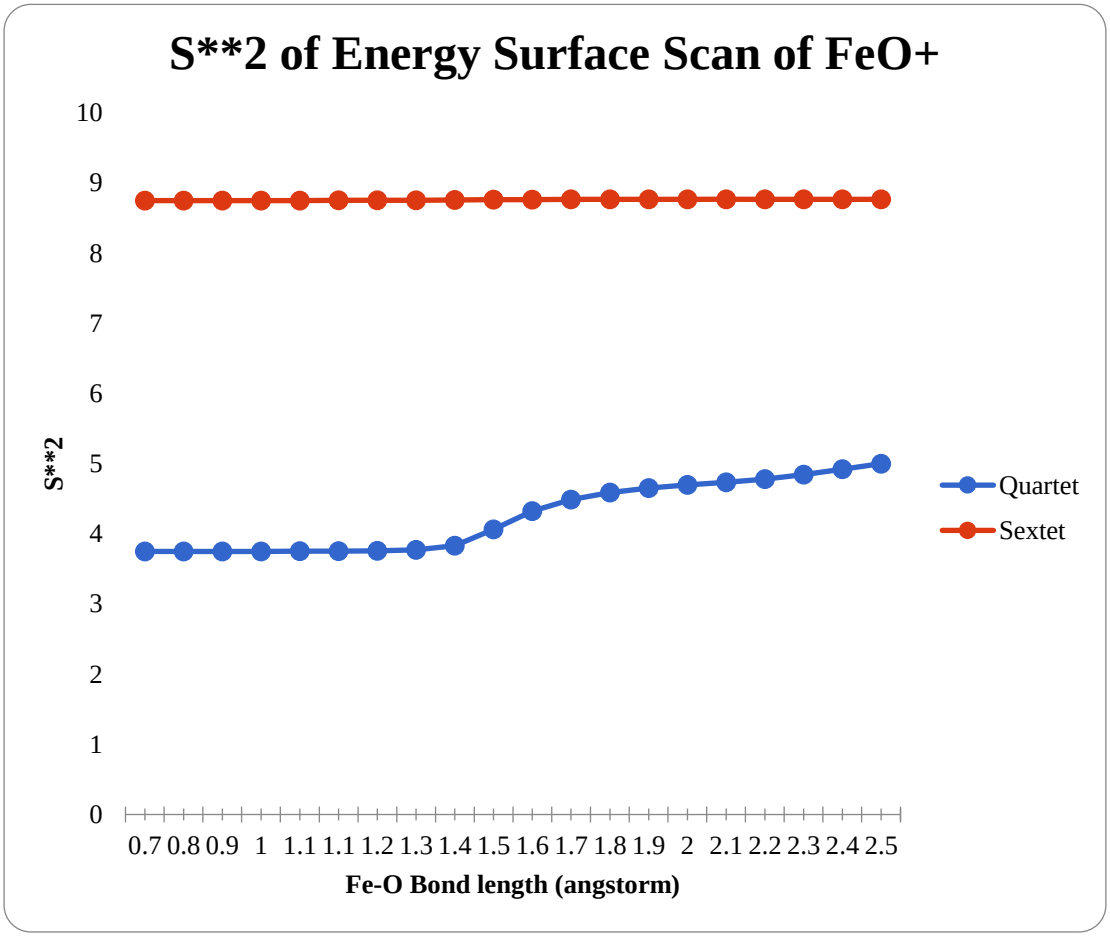
0317033 謝明修

- Calculate the Minimum Energy Crossing Point (MECP) of FeO^+.

  1. Do the 'Energy Surface Scan' of Fe—O bond length

	B3LYP/TZVP					
	Quartet			Sextet		
Bond length(Å)	(a.u)	(kcal/mol)	S**2	(a.u)	(kcal/mol)	S**2
0.6	-1329.963861	5424.9	3.750355	-1329.544131	5688.3	8.750794
0.7	-1333.885601	2964.0	3.750449	-1333.567819	3163.4	8.751009
0.8	-1335.892409	1704.7	3.750705	-1335.6693	1844.7	8.751363
0.9	-1337.008064	1004.7	3.75115	-1336.862024	1096.3	8.751716
1	-1337.677114	584.8	3.751967	-1337.587208	641.2	8.752219
1.1	-1338.088812	326.5	3.753734	-1338.038427	358.1	8.753184
1.2	-1338.336758	170.9	3.758083	-1338.314271	185.0	8.754833
1.3	-1338.478466	82.0	3.771168	-1338.475824	83.6	8.757179
1.4	-1338.55291	35.3	3.833738	-1338.564003	28.3	8.760009
1.5	-1338.588643	12.8	4.065438	-1338.606323	1.7	8.763036
1.6	-1338.604733	2.7	4.323783	-1338.6211	-7.5	8.765957
1.7	-1338.609107	0.0	4.489401	-1338.62041	-7.1	8.768228
1.8	-1338.605646	2.2	4.589723	-1338.611724	-1.6	8.769422
1.9	-1338.597203	7.5	4.65337	-1338.599377	6.1	8.769862
2	-1338.585822	14.6	4.69791	-1338.58573	14.7	8.769997
2.1	-1338.572971	22.7	4.735071	-1338.57213	23.2	8.770054
2.2	-1338.559672	31.0	4.780322	-1338.559301	31.3	8.770005
2.3	-1338.546888	39.0	4.842509419	-1338.547658	38.6	8.769747
2.4	-1338.535796	46.0	4.921700877	-1338.537356	45.0	8.769189
2.5	-1338.526933	51.6	5.000892336	-1338.528466	50.6	8.76831


Energy Surface Scan of FeO+
200.0
150.0
100.0
50.0
0.0
-50.0
Energy (kcal/mol)
1.3 1.4 1.5 1.6 1.7 1.8 1.9 2 2.1 2.2 2.3 2.4 2.5
Fe-O Bond length (angstorm)
Quartet
Sextet


S**2 of Energy Surface Scan of FeO+
10
9
8
7
6
5
4
3
2
1
0
S**2
0.7 0.8 0.9 1 1.1 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2 2.1 2.2 2.3 2.4 2.5
Fe-O Bond length (angstorm)
Quartet
Sextet

2. Calculate the MECP of around 1.4Å and 2.2Å

	B3LYP/aug-TZVP	
	Around 1.4 Å	Around 2.2 Å
Quartet Single Point	-1338.556334	-1338.562836
Sextet Single Point	-1338.567794	-1338.562279
MECP		
Energy	-1338.582274	-1338.556778
Final ΔE of two surface	-0.000000841	0.000000063
F—O (Å)	1.43	2.25

3. Fit the Morse potential:

Though it is not successful, see http://ukko.life.nctu.edu.tw/~u0317033/Selected_topics_of_computational_chemistry/Morse_fit.html

Selected topics of computational chemistry - Prof. Jen-Shiang K. Yu
Homework

0317033 謝明修

- Calculate the 'singlet to singlet', 'singlet to triplet' and 'singlet to doublet' excitation energy of formaldehyde at SAC-CI/D95(d) with Rydberg function.

  The assigned character is the orbital number. (The MO has some problems with Rydberg function which cannot be distinguished clearly.)

Singlet -> Singlet

		Excitation energy		Oscillator strength	
State	Character	SAC-CI(eV)	Exp.(eV)	SAC-CI	Exp.
$1A_1$	Ground state	0.00			
$2A_1$	8->11	7.72	8.14	0.0390	0.017
$3A_1$	7->16 7->14	10.21		0.1711	
$4A_1$	8->15	9.32	10.7	0.0303	
$5A_1$	7->10	11.92		0.0222	
$6A_1$	7->16 7->14	13.43		0.0088	
$1A_2$	8->16	3.95	4.1, 4.2		
$2A_2$	8->10	7.92			
$3A_2$	8->14	9.39			
$4A_2$	5->16	10.56			
$1B_1$	6->16	9.34		0.0017	
$2B_1$	7->9	10.72	10.7	0.0450	
$3B_1$	7->12	11.69	11.6-11.9	0.0337	
$4B_1$	7->13	13.07		0.0088	
$1B_2$	8->9	6.76	7.091, 7.13	0.0180	0.028
$2B_2$	8->12	7.66	7.97, 8.00	0.0325	0.032
$3B_2$	8->13	9.08		0.0103	
$4B_2$	8->17	10.06		0.0123	

Singlet -> Triplet

		Excitation energy	
State	Character	SAC-CI(eV)	Exp. (eV)
$1A_1$	7->16	6.00	6.0, 5.6-6.2
$2A_1$	8->11	7.65	
$3A_1$	8->15	9.25	
$4A_1$	7->10	11.76	
$1A_2$	8->16	3.53	3.5, 3.3-3.6
$2A_2$	8->10	7.93	
$3A_2$	5->16	10.19	
$4A_2$	8->14	9.35	
$1B_1$	6->16	8.47	8.5
$2B_1$	7->9	10.65	
$3B_1$	7->12	11.52	
$4B_1$	8->9	6.60	7.09, 6.7-7.0
$1B_2$	8->12	7.52	7.92
$2B_2$	8->13	8.98	
$3B_2$	8->17	9.91	

Singlet -> Doublet (Ionization energy)

		Excitation energy	
State	Character	SAC-CI(eV)	Exp. (eV)
$1A_1$	6	15.62	16.2
$2A_1$	4	21.17	21.15
$3A_1$	3	31.92	
$1B_1$	7	14.28	14.5
$1B_2$	8	10.27	10.9
$2B_2$	5	16.96	17

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Homework

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- Calculate the excitation energy of formaldehyde using CFour/ACESII program and compare the results with SAC-CI.

Without Rydberg Functions

	CCSD/PVDZ(a.u.)	EOM-CCSD(eV)	SAC-CI/D95(d)(eV)
$1A_1$	-114.2128476	0.000	0.000
$2A_1$	-113.845093	10.007	10.238
$3A_1$	-113.7962177	11.337	12.828
$4A_1$	-113.6958286	14.069	15.082
$1B_1$	-113.8653717	9.455	3.992
$2B_1$	-113.7653106	12.178	10.595
$3B_1$	-113.6477476	15.377	13.921
$1B_2$	-113.8994978	8.527	9.374
$2B_2$	-113.7867221	11.596	14.272
$3B_2$	-113.6650017	14.908	13.608
$1A_2$	-114.0626343	4.088	10.121
$2A_2$	-113.8166084	10.782	10.361
$3A_2$	-113.6984765	13.997	16.400

Add Rydberg functions

	CCSD/PVDZ(a.u.)	EOM-CCSD(eV)	SAC-CI/D95(d)(eV)	Exp. (eV)
$1A_1$	-114.2182948	0.000	0.000	
$2A_1$	-113.9292884	7.864	7.716	8.14
$3A_1$	-113.8704517	9.465	10.206	
$4A_1$	-113.8398943	10.297	9.322	10.7
$1B_1$	-113.8704964	9.464	9.342	
$2B_1$	-113.8223597	10.774	10.720	10.7
$3B_1$	-113.7857453	11.770	11.687	11.6-11.9
$1B_2$	-113.9640728	6.918	6.756	7.091, 7.13
$2B_2$	-113.9296694	7.854	7.655	7.97, 8.00
$3B_2$	-113.8774138	9.276	9.076	
$1A_2$	-114.0680656	4.088	3.952	4.1, 4.2
$2A_2$	-113.920588	8.101	7.919	
$3A_2$	-113.8667522	9.566	9.390	

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Homework

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- Optimize the geometry of [HCO]• radical at different levels.

	QCISD/cc-pVTZ	SAC-CI/cc-pVTZ				EOM-CCSD/PVTZ	Exp.
		Anion Doublet		Cation Doublet			
		Direct	Non Direct	Direct	Non Direct		
∠HCO	124.79	125.11	125.11	124.81	124.90	123.77	124.4
H-C(Å)	1.119	1.111	1.111	1.110	1.109	1.104	1.119
C-O(Å)	1.178	1.170	1.169	1.174	1.172	1.175	1.175