Electronic Supporting Information

Experimental and theoretical investigations of magnetic exchange pathways in structurally diverse iron(III) Schiff-base complexes

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Table S1. The B3LYP/def2-TZVP calculated net Mulliken spin densities, the $<S^2>$ values and relative energies of broken-symmetry spin states for dimeric fragments of $K[FeL_2]\cdot H_2O$ (**1**) based on the experimental (X-ray) geometry.

$\{[FeL_2]\cdots K(H_2O)\cdots[FeL_2]\}^-$ of **1**			$\{[K(H_2O)FeL_2]\cdots[FeL_2K(H_2O)]\}$ of **1**		
	HS	BS		HS	BS
ρ(Fe1)	4.22	-4.22	ρ(Fe1)	4.22	-4.22
ρ(N1)	0.07	-0.07	ρ(N1)	0.06	-0.06
ρ(N2A)	0.06	-0.06	ρ(N2A)	0.08	-0.07
ρ(O4)	0.14	-0.14	ρ(O4)	0.11	-0.11
ρ(O1)	0.13	-0.13	ρ(O1)	0.12	-0.12
ρ(O2)	0.12	-0.12	ρ(O2)	0.12	-0.12
ρ(O3)	0.12	-0.12	ρ(O3)	0.16	-0.16
ρ(K1)	0.005	-0.0006			
ρ(O1')	0.13	0.13	ρ(O1')	0.12	0.12
ρ(O3')	0.11	0.11	ρ(O3')	0.16	0.16
ρ(O2')	0.13	0.13	ρ(O2')	0.12	0.12
ρ(O4')	0.15	0.15	ρ(O4')	0.11	0.11
ρ(N2A')	0.06	0.06	ρ(N2A')	0.08	0.07
ρ(N1')	0.06	0.06	ρ(N1')	0.06	0.06
ρ(Fe1')	4.21	4.21	ρ(Fe1')	4.22	4.22
$<S^2>$	30.02	5.02	$<S^2>$	30.02	5.02
$E_{BS} - E_{HS}$	-0.782 cm^{-1}		$E_{BS} - E_{HS}$	-2.913 cm^{-1}	

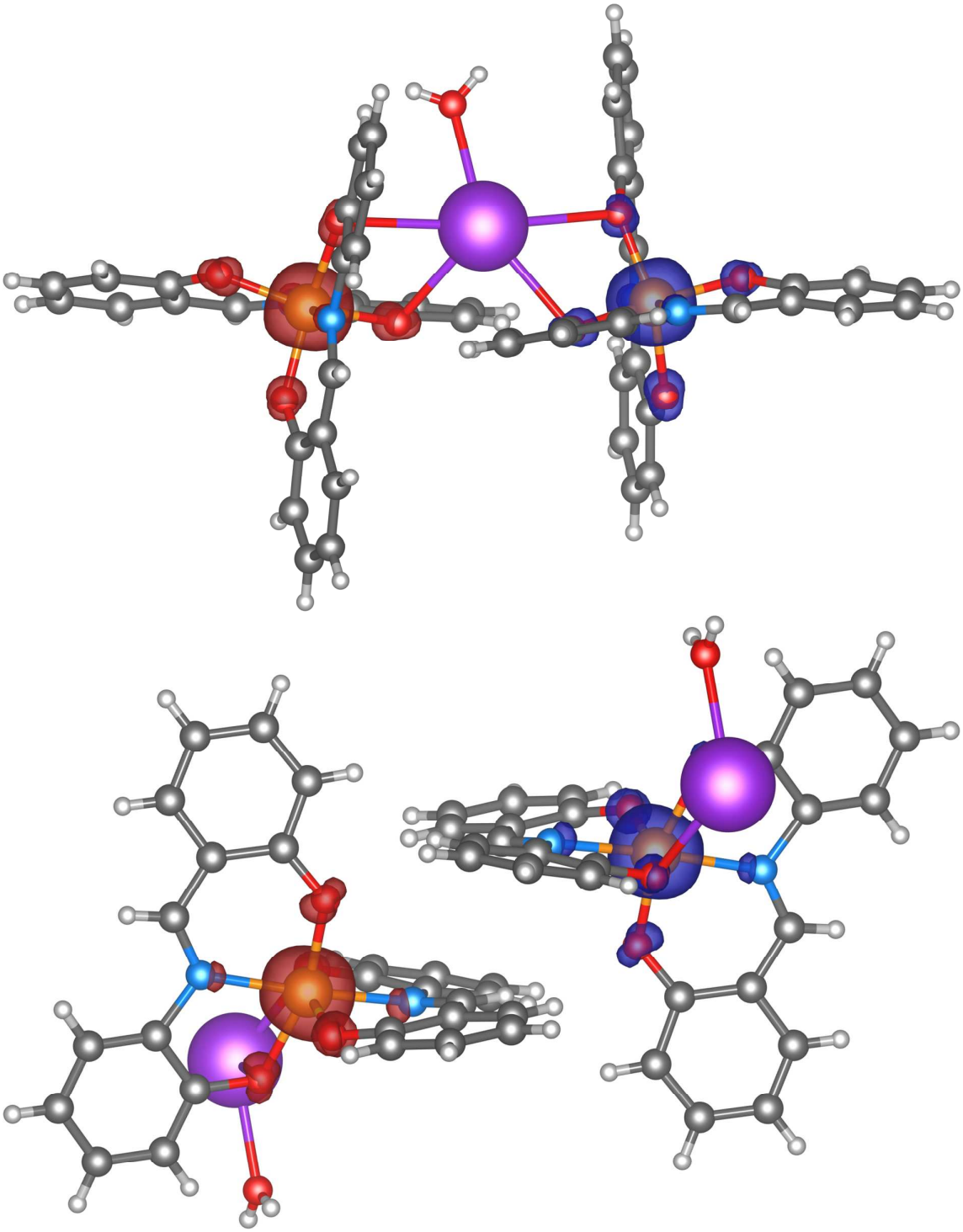

Fig. S1 The calculated spin density distribution for broken-symmetry spin state using B3LYP for the $\{[FeL_2]\cdots K(H_2O)\cdots[FeL_2]\}^-$ unit of **1** (top) and for $\{[K(H_2O)FeL_2]\cdots[FeL_2K(H_2O)]\}$ unit of **1** (bottom). Positive and negative spin densities are represented by dark blue and dark red surfaces, respectively. The isodensity surfaces are plotted with cutoff values of 0.02 ea_0^{-3}.

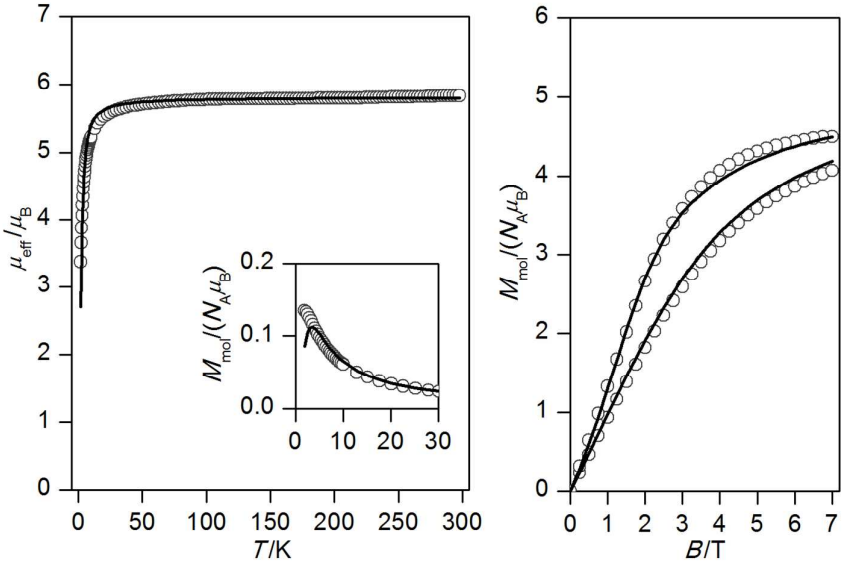

Fig. S2 The magnetic data for complex **1**. Left: the temperature dependence of the effective magnetic moment and molar magnetization measured at B = 0.1 T. Right: the isothermal magnetizations measured at T = 2.0 and 5 K. Empty circles – experimental data, full lines – calculated data using the Eq. (3) and J = −0.29(3) cm^{-1}, D = –1.2(2) cm^{-1} and g = 1.964(7). The data are scaled per one iron(III) centre.

Table S2. The B3LYP/def2-TZVP calculated net Mulliken spin densities, the $<S^2>$ values and relative energies of broken-symmetry spin states for dimeric fragment of $Pr_3NH[FeL_2]$ (**2**) based on the experimental (X-ray) geometry.

$\{Pr_3NH[FeL_2]\cdots[FeL_2]Pr_3NH\}$ of **2**		
	HS	BS
ρ(Fe1)	4.22	-4.22
ρ(O1)	0.14	-0.14
ρ(N1A)	0.07	-0.07
ρ(O2)	0.11	-0.11
ρ(O3)	0.15	-0.15
ρ(N2A)	0.06	-0.06
ρ(O4)	0.10	-0.10
ρ(O4')	0.10	0.10
ρ(N2A')	0.06	0.06
ρ(O3')	0.15	0.15
ρ(O2)	0.11	0.11
ρ(N1A')	0.07	0.07
ρ(O1')	0.14	0.14
ρ(Fe1')	4.22	4.22
$<S^2>$	30.02	5.02
$E_{BS} - E_{HS}$	$-0.331\ cm^{-1}$	

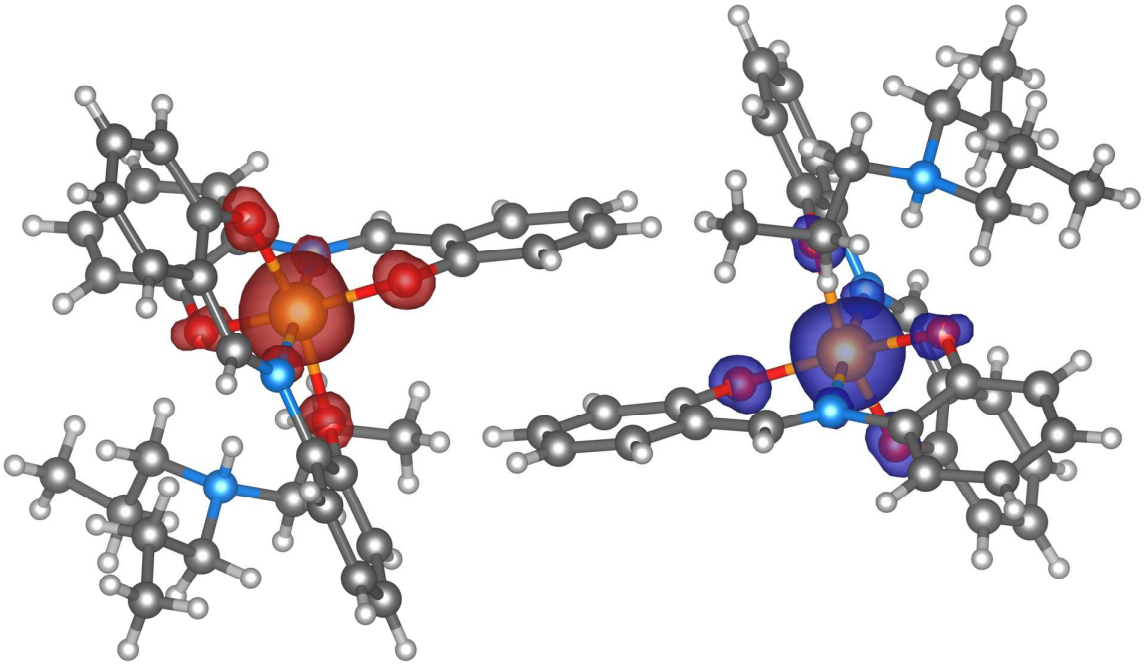

Fig. S3 The calculated spin density distribution for broken-symmetry spin state using B3LYP for the $\{Pr_3NH[FeL_2]\cdots[FeL_2]Pr_3NH\}$ unit of **2**. Positive and negative spin densities are represented by dark blue and dark red surfaces, respectively. The isodensity surfaces are plotted with cutoff values of 0.02 ea_0^{-3}.

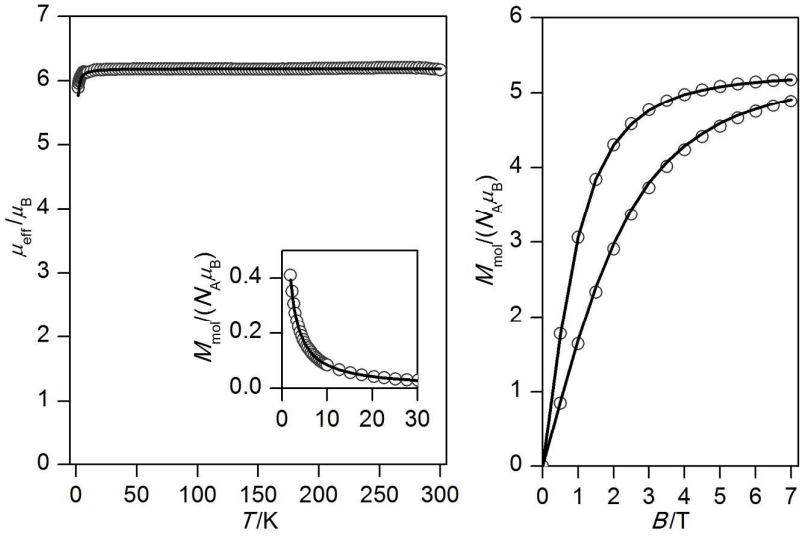

Fig. S4 The magnetic data for complex $(Pr_3NH)[FeL_2]\cdot H_2O$ (**2**). Left: The temperature dependence of the effective magnetic moment and molar magnetization measured at B = 0.1 T. Right: The isothermal magnetizations measured at T = 2.0 and 4.6 K. Empty circles – experimental data, full lines – calculated data using the Eq. (4) and J = −0.038(5) cm^{-1}, D = +0.53(8) cm^{-1} and g = 2.091(2). The data are scaled per one iron(III) centre.

Table S3. The B3LYP/def2-TZVP calculated net Mulliken spin densities, the $<S^2>$ values and relative energies of broken-symmetry spin states for dimeric fragment of $[FeL(bpyO_2)(CH_3OH)][FeL_2]$ (**3**) based on the experimental (X-ray) geometry.

{$[FeL(bpyO_2)(CH_3OH)]\cdots [FeL_2]$} of **3**		
	HS	BS
ρ(Fe1)	4.21	4.21
ρ(N1)	0.07	0.07
ρ(N2)	0.07	0.07
ρ(O1)	0.15	0.15
ρ(O2)	0.08	0.07
ρ(O3)	0.14	0.14
ρ(O4)	0.13	0.13
ρ(H9B)	0.002	-0.002
ρ(O9)	0.06	-0.06
ρ(O8)	0.07	0.06
ρ(O7)	0.05	-0.05
ρ(O6)	0.18	-0.18
ρ(O5)	0.15	-0.15
ρ(N3)	0.07	-0.07
ρ(Fe2)	4.20	-4.20
$<S^2>$	30.02	5.02
E_{BS} - E_{HS}	-7.990 cm^{-1}	

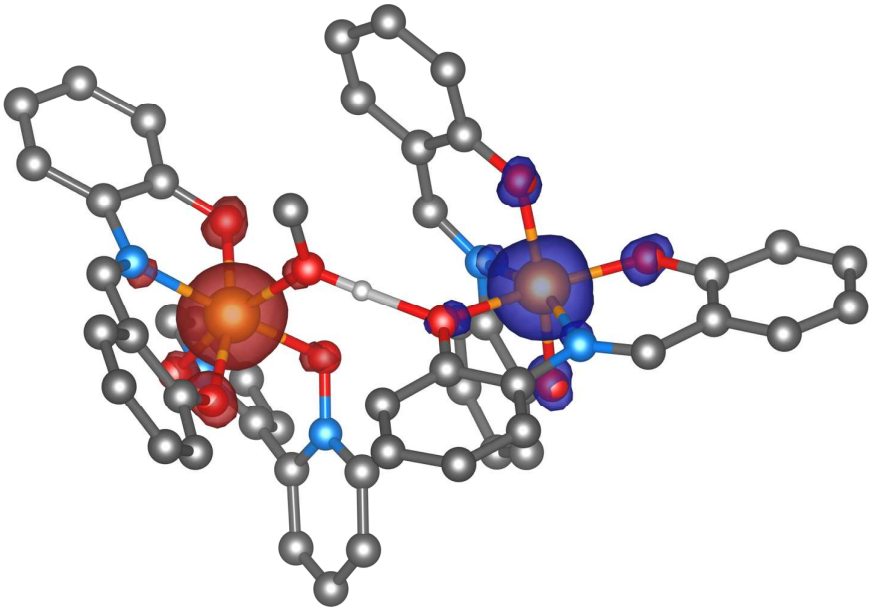

Fig. S5 The calculated spin density distribution for broken-symmetry spin state using B3LYP for the {$[FeL(bpyO_2)(CH_3OH)]\cdots[FeL_2].CH_3OH$} unit of **3**. Positive and negative spin densities are represented by dark blue and darkred surfaces, respectively. The isodensity surfaces are plotted with cutoff values of 0.02 ea_0^{-3}. Only hydrogen atoms involved in hydrogen bonding is shown.

Table S4. The B3LYP/def2-TZVP calculated net Mulliken spin densities, the $<S^2>$ values and relative energies of broken-symmetry spin states for dimeric fragment of $[Fe_2L_3(CH_3OH)].2CH_3OH.H_2O$ (**4**) based on the experimental (X-ray) geometry.

{$[Fe_2L_3(CH_3OH)]$} of **4**		
	HS	BS
ρ(Fe1)	4.22	-4.21
ρ(N1A)	0.07	-0.07
ρ(O1)	0.19	-0.19
ρ(O2)	0.15	-0.15
ρ(O3)	0.03	-0.03
ρ(O4)	0.15	0.01
ρ(O5)	0.15	-0.02
ρ(O6)	0.17	0.17
ρ(O7)	0.18	0.18
ρ(N3)	0.08	0.08
ρ(N2)	0.07	0.06
ρ(Fe2)	4.20	4.19
$<S^2>$	30.02	4.99
$E_{BS} - E_{HS}$	-206.991 cm^{-1}	

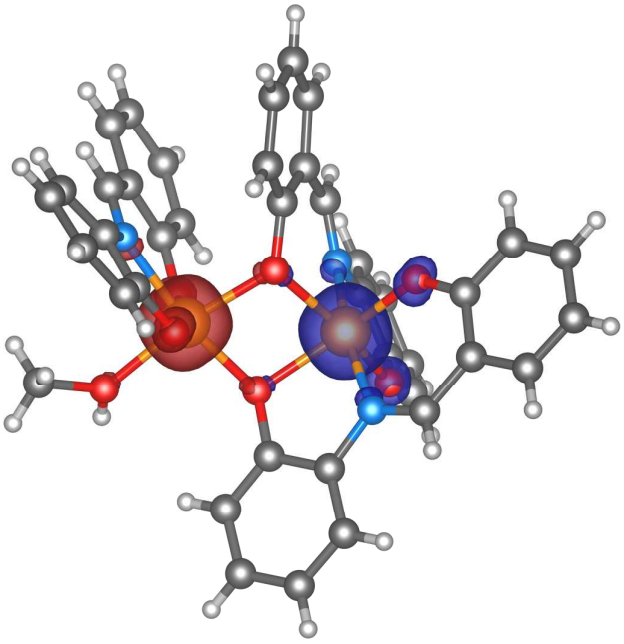

Fig. S6 The calculated spin density distribution high spin state and broken-symmetry state using B3LYP for the $[Fe_2L_3(CH_3OH)]$ unit of **4**. Positive and negative spin densities are represented by dark blue and green surfaces, respectively. The isodensity surfaces are plotted with cutoff values of 0.02 ea_0^{-3}.

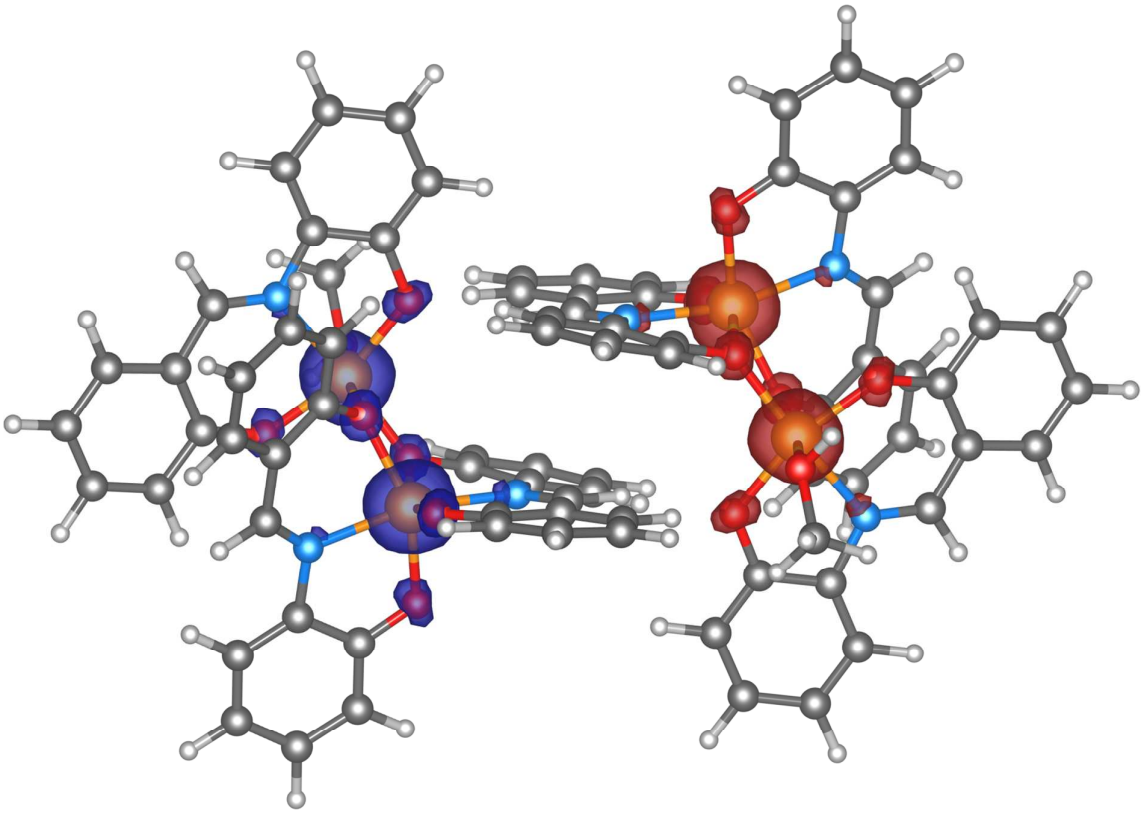

Fig. S7 The calculated spin density distribution for broken-symmetry spin state BS12 using B3LYP for the $\{[Fe_2L_3(CH_3OH)]\}_2$ unit of **4**. Positive and negative spin densities are represented by dark blue and dark red surfaces, respectively. The isodensity surfaces are plotted with cutoff values of 0.02 $e a_0^{-3}$.