G2 Atomization Energies With Chemical Accuracy

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I. INTRODUCTION

II. THEORY

A. The DFT basis-set correction in a nutshell

The basis-set correction investigated here proposes to use the RSDFT formalism to capture a part of the short-range correlation effects missing in a finite one-electron basis-set. In a nutshell, this formalism relies on 1) the definition of a complementary density functional aiming at describing the correlation effects absent in a finite basis-set, 2) the definition of an *effective non divergent interaction* as the real-space representation of the coulomb operator projected in a finite basis-set, 3) the fit of such an effective interaction with a long-range interaction through the definition of a *range-separation parameter varying in space*, 4) the use of a correlation functional from RSDFT with a *multi-determinant* reference evaluated with the range-separation parameter varying in space. More details can be found in[?] .

1. Definition of basis-set dependent complementary functional

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III. RESULTS

A. The case of C_2 and the comparison with the F_{12} methods.

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TABLE I. Dissociation energy (D_e) in kcal/mol of the C_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F_{12}, CIPSI+LDA_{HF} and CIPSI+$LDA_{HF\text{-}val}$ (valence only interaction and density) in the Dunnng cc-pVXZ (VXZ) basis sets.

	FCIQMC	CIPSI	FCIQMC+F_{12}	CIPSI+LDA_{HF}	CIPSI+$LDA_{HF\text{-}val}$	CIPSI+PBE_{HF}	CIPSI+$PBE_{HF\text{-}val}$
V2Z	130.0	132.0	142.3	141.9	142.9	142.7	145.6
V3Z	139.9	140.3	145.3	142.8	145.5	142.7	146.7
V4Z	-	143.6	-	145.8	146.2	145.3	147.0
V5Z	-	144.3	-	145.1	146.1	144.9	146.5
				Estimated exact			
				146.9			

TABLE II. Dissociation energy (D_e) in kcal/mol of the N_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F_{12}, CIPSI+LDA_{HF} and CIPSI+$LDA_{HF\text{-}val}$ (valence only interaction and density) in the Dunnng cc-pVXZ (VXZ) basis sets.

	CIPSI	CIPSI+LDA_{HF}	CIPSI+$LDA_{HF\text{-}val}$	CIPSI+PBE_{HF}	CIPSI+$PBE_{HF\text{-}val}$
V2Z	200.9	216.3	218.2	222.3	225.8
V3Z	217.1	223.1	225.8	224.6	229.5
V4Z	223.5	227.9	228.8	227.7	230.3
V5Z	225.7	227.9	228.4	227.7	229.7
			Estimated exact		
			227.6		

TABLE III. Dissociation energy (D_e) in kcal/mol of the F_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F_{12}, CIPSI+LDA_{HF} and CIPSI+$LDA_{HF\text{-}val}$ (valence only interaction and density) in the Dunnng cc-pVXZ (VXZ) basis sets.

	CIPSI	CIPSI+LDA_{HF}	CIPSI+$LDA_{HF\text{-}val}$	CIPSI+PBE_{HF}	CIPSI+$PBE_{HF\text{-}val}$
V2Z	27.5	30.8	31.1	32.1	32.3
V3Z	35.4	37.0	37.5	37.5	37.8
V4Z	37.5	38.7	38.8	38.7	38.8
V5Z					
			Estimated exact		
			39.0		

TABLE IV. Dissociation energy (D_e) in kcal/mol of the O_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F_{12}, CIPSI+LDA_{HF} and CIPSI+$LDA_{HF\text{-}val}$ (valence only interaction and density) in the Dunnng cc-pVXZ (VXZ) basis sets.

	CIPSI	CIPSI+LDA_{HF}	CIPSI+$LDA_{HF\text{-}val}$	CIPSI+PBE_{HF}	CIPSI+$PBE_{HF\text{-}val}$
V2Z	105.3	111.8	112.5	115.0	117.3
V3Z	114.6	117.2	118.5	118.4	120.5
V4Z	118.0	120.0	120.2	120.2	121.2
V5Z					
			Estimated exact		
			120.4		