G2 Atomization Energies With Chemical Accuracy

Bathélemy Pradines,[1] Anthony Scemama,[1] Julien Toulouse,[2] Pierre-François Loos,[1, a)] and Emmanuel Giner[2]
[1)] *Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France*
[2)] *Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Sorbonne Université, CNRS, Paris, France*

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

The

III. RESULTS

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

[a)] Corresponding author: loos@irsamc.ups-tlse.fr

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. [a] Results from Ref[?]

	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	143.3
V3Z	139.9	140.3	145.3	142.8	145.5	142.7	144.7
V4Z	-	143.6	-	145.8	146.2	145.3	145.7
V5Z	-	144.3	-	145.1	146.1	144.9	145.6
			Estimated exact [a]				
			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. [a] Results from Ref[?] taking into account the ZPE correction.

	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	224.8
V3Z	217.1	223.1	225.8	224.6	226.7
V4Z	223.5	227.9	228.8	227.7	228.3
V5Z	225.7	227.9	228.4	227.7	228.3
			Estimated exact		
			228.5[a]		

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. [a] Results from Ref[?] taking into account the ZPE correction.

	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	32.4
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		
			38.2[a]		

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. [a] Results from Ref[?] taking into account the ZPE correction.

	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	116.1
V3Z	114.6	117.2	118.5	118.4	119.4
V4Z	118.0	120.0	120.2	120.2	120.5
V5Z					
			Estimated exact		
			120.2 [a]		