

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 in².

1. Definition of basis-set dependent complementary functional

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III. RESULTS

A. The case of C₂ and the comparison with the F12 methods.

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TABLE I. Dissociation energy (D_e) in kcal/mol of the C_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F12, CIPSI+LDA_{HF} and CIPSI+LDA_{HF-val} (valence only interaction and density) in the Dunning cc-pVXZ (VXZ) basis sets. ^a Results from Ref²

Molecule	Method	Dunning's basis set				Exp.
		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	
C ₂	FCIQMC	130.0(1)	139.9(3)	143.3(2)		146.9(5)
	FCIQMC+F12	142.3	145.3			
	exFCI	132.0	140.3	143.6	144.3	
	exFCI+LDA	141.9	142.8	145.8	146.2	
	exFCI+LDA(FC)	142.9	145.5	146.2	146.1	
	exFCI+PBE	142.7	142.7	145.3	144.9	
	exFCI+PBE(FC)	143.3	144.7	145.7	145.6	
O ₂	exFCI	105.3	114.6	118.0		120.2
	exFCI+LDA	111.8	117.2	120.0		
	exFCI+LDA(FC)	112.5	118.5	120.2		
	exFCI+PBE	115.0	118.4	120.2		
	exFCI+PBE(FC)	116.1	119.4	120.5		
N ₂	exFCI	200.9	217.1	223.5	225.7	228.5
	exFCI+LDA	216.3	223.1	227.9	227.9	
	exFCI+LDA(FC)	218.2	225.8	228.8	228.4	
	exFCI+PBE	222.3	224.6	227.7	227.7	
	exFCI+PBE(FC)	224.8	226.7	228.3	228.3	
F ₂	exFCI	27.5	35.4	37.5	38.0	38.2
	exFCI+LDA	30.8	37.0	38.7	38.7	
	exFCI+LDA(FC)	31.1	37.5	38.8	38.8	
	exFCI+PBE	32.1	37.5	38.7		
	exFCI+PBE(FC)	32.4	37.8	38.8	38.8	

TABLE II. Dissociation energy (D_e) in kcal/mol of the C_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F12, CIPSI+LDA_{HF} and CIPSI+LDA_{HF-val} (valence only interaction and density) in the Dunning cc-pVXZ (VXZ) basis sets. ^a Results from Ref²

	FCIQMC	CIPSI	FCIQMC+F12	CIPSI+LDA _{HF}	CIPSI+LDA _{HF-val}	CIPSI+PBE _{HF}	CIPSI+PBE _{HF-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 III. Dissociation energy (D_e) in kcal/mol of the N_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F12, CIPSI+LDA_{HF} and CIPSI+LDA_{HF-val} (valence only interaction and density) in the Dunning cc-pVXZ (VXZ) basis sets. ^a Results from Ref² taking into account the ZPE correction.

	CIPSI	CIPSI+LDA _{HF}	CIPSI+LDA _{HF-val}	CIPSI+PBE _{HF}	CIPSI+PBE _{HF-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 IV. Dissociation energy (D_e) in kcal/mol of the F_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F12, CIPSI+LDA_{HF} and CIPSI+LDA_{HF-val} (valence only interaction and density) in the Dunning cc-pVXZ (VXZ) basis sets. ^a Results from Ref² taking into account the ZPE correction.

	CIPSI	CIPSI+LDA _{HF}	CIPSI+LDA _{HF-val}	CIPSI+PBE _{HF}	CIPSI+PBE _{HF-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	38.0	38.7	38.8		38.8
			Estimated exact		
			38.2 ^a		

TABLE V. Dissociation energy (D_e) in kcal/mol of the O_2 molecule computed using FCIQMC, CIPSI, FCIQMC+F12, CIPSI+LDA_{HF} and CIPSI+LDA_{HF-val} (valence only interaction and density) in the Dunning cc-pVXZ (VXZ) basis sets. ^a Results from Ref² taking into account the ZPE correction.

	CIPSI	CIPSI+LDA _{HF}	CIPSI+LDA _{HF-val}	CIPSI+PBE _{HF}	CIPSI+PBE _{HF-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		