

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 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	38.7	38.8
			Estimated exact		
			38.2 ^a		

TABLE II. Dissociation energy (D_e) in kcal/mol of the C_2 , O_2 , N_2 and F_2 molecules computed with various methods and basis sets.

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) ^a
	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	146.1	143.9	145.9	145.12	
	exFCI+PBE (FC)	147.7	146.3	146.4	146.0	
	exFCI+PBE-on-top	142.7	142.7	145.3	144.9	
	exFCI+PBE-on-top(FC)	143.3	144.7	145.7	145.6	
N_2	exFCI	200.9	217.1	223.5	225.7	228.5 ^b
	exFCI+LDA	216.3	223.1	227.9	227.9	
	exFCI+LDA(FC)	218.2	225.8	228.8	228.4	
	exFCI+PBE	225.3	225.6	228.2	227.9	
	exFCI+PBE (FC)	228.6	228.1	228.9	228.6	
	exFCI+PBE-on-top	222.3	224.6	227.7	227.7	
	exFCI+PBE-on-top(FC)	224.8	226.7	228.3	228.3	
O_2	exFCI	105.3	114.6	118.0	119.1	120.2 ^b
	exFCI+LDA	111.8	117.2	120.0	119.9	
	exFCI+LDA(FC)	112.5	118.5	120.2	120.2	
	exFCI+PBE	115.9	118.4	120.1	119.9	
	exFCI+PBE (FC)	117.5	119.5	120.4	120.3	
	exFCI+PBE-on-top	115.0	118.4	120.2		
	exFCI+PBE-on-top(FC)	116.1	119.4	120.5		
F_2	exFCI	27.5	35.4	37.5	38.0	38.2 ^b
	exFCI+LDA	30.8	37.0	38.7	38.7	
	exFCI+LDA(FC)	31.1	37.5	38.8	38.8	
	exFCI+PBE	33.3	37.8	38.8	38.7	
	exFCI+PBE (FC)	33.9	38.2	39.0	38.8	
	exFCI+PBE-on-top	32.1	37.5	38.7	38.7	
	exFCI+PBE-on-top(FC)	32.4	37.8	38.8	38.8	

^a Results from Ref. ? .

^b Results from Ref. ? .