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 F12 methods.

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

TABLE I. 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.

		Dunning's basis set				
Molecule	Method	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	Exp.
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	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[b]
	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[b]
	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[b]
	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	

[a] Results from Ref. **?** .
[b] Results from Ref. **?** .