

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.

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.

	FCIQMC	CIPSI	FCIQMC+F ₁₂	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	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				