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. Here, we briefly explain the working equations and notations needed for this work, and we encourage the interested reader to find the detailed formal derivation of the theory in[?] .

B. The very basics

Consider a basis-set incomplete $\mathcal{B}$ for which we assume to have accurate approximations of both the FCI density $n_{\Psi^{\mathcal{B}}_{\text{FCI}}}$ and energy $E^{\mathcal{B}}_{\text{FCI}}$. According to equation (15) of[?] , one can approximate the exact ground state energy E_0 as

$$E_0 \approx E^{\mathcal{B}}_{\text{FCI}} + \bar{E}^{\mathcal{B}}[n_{\Psi^{\mathcal{B}}_{\text{FCI}}}] \tag{1}$$

where $\bar{E}^{\mathcal{B}}[n]$ is the complementary density functional defined in equation (8) of[?] , which aims at correcting the basis-set error introduced by the incompleteness of $\mathcal{B}$.

Such a functional is not universal as it depends on the basis set $\mathcal{B}$ used. The exact form of this functional is of course not known and we approximate it in two-steps. First, we define a real-space representation of the coulomb interaction truncated in $\mathcal{B}$, which is then fitted with a long-range interaction thanks to a range-separation parameter $\mu(r)$ varying in space (see **??**). Then, we choose a specific class of short-range density functionals, namely the short-range correlation functionals with multi-determinantal reference introduced by Toulouse *et al*[?] , that we evaluate with the range-separation parameter $\mu(r)$ varying in space at the FCI density $n_{\Psi^{\mathcal{B}}_{\text{FCI}}}$ (see **??**).

C. Definition of a real-space representation of the coulomb operator truncated in a basis-set $\mathcal{B}$

One of the consequences of the use of an incomplete basis-set $\mathcal{B}$ is that the wave function does not present a cusp near the electron coalescence point, which means that all derivatives of the wave function are continuous. As the exact electronic cusp originates from the divergence of the coulomb interaction at the electron coalescence point, a cusp-free wave function could also come from a non-divergent electron-electron interaction. Therefore, the use of a finite basis-set $\mathcal{B}$ can be thought as a cutting of the divergence of the coulomb interaction at the electron coalescence point.

The present paragraph briefly describes how to obtain an effective interaction $W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ which:

- is non-divergent at the electron coalescence point as long as a finite-basis set $\mathcal{B}$ is used
- tends to the regular $1/r_{12}$ interaction in the limit of a complete basis set $\mathcal{B}$.

1. General definition of an effective interaction for the basis set $\mathcal{B}$

Consider the coulomb operator projected in the basis-set $\mathcal{B}$

$$\hat{W}^{\mathcal{B}}_{\text{ee}} = \frac{1}{2} \sum_{ijkl \in \mathcal{B}} V_{ij}^{kl} \; \hat{a}^\dagger_k \hat{a}^\dagger_l \hat{a}_j \hat{a}_i, \tag{2}$$

where the indices run over all orthonormal spin-orbitals in $\mathcal{B}$ and V_{ij}^{kl} are the usual coulomb two-electron integrals. Consider now the expectation value of $\hat{W}^{\mathcal{B}}_{\text{ee}}$ over a general wave function $\Psi^{\mathcal{B}}$ belonging to the $N-$electron Hilbert space spanned by the basis set $\mathcal{B}$. After a few mathematical work (see appendix A of[?] for a detailed derivation), such an expectation value can be rewritten as an integral over $\mathbb{R}^6$:

$$\left\langle \Psi^{\mathcal{B}} \middle| \hat{W}^{\mathcal{B}}_{\text{ee}} \middle| \Psi^{\mathcal{B}} \right\rangle = \frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2), \tag{3}$$

where the function $f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ is defined as:

$$f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \sum_{ijklmn \in \mathcal{B}} V_{ij}^{kl} \; \Gamma_{kl}^{mn}[\Psi^{\mathcal{B}}] \; \phi_n(\mathbf{X}_2)\phi_m(\mathbf{X}_1)\phi_i(\mathbf{X}_1)\phi_j(\mathbf{X}_2), \tag{4}$$

$\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}]$ is the two-body density matrix of $\Psi^{\mathcal{B}}$

$$\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] = \left\langle \Psi^{\mathcal{B}} \middle| \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_n \hat{a}_m \middle| \Psi^{\mathcal{B}} \right\rangle, \tag{5}$$

and $\mathbf{X}$ collects the space and spin variables.

$$\mathbf{X} = (\mathbf{r}, \sigma) \qquad \mathbf{r} \in \mathbb{R}^3, \; \sigma = \pm\frac{1}{2}$$
$$\int \text{d}\mathbf{X} = \sum_{\sigma=\pm\frac{1}{2}} \int_{\mathbb{R}^3} \text{d}\mathbf{r}. \tag{6}$$

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Then, consider the expectation value of the exact coulomb operator over $\Psi^{\mathcal{B}}$

$$\left\langle \Psi^{\mathcal{B}} \right| \hat{W}_{\text{ee}} \left| \Psi^{\mathcal{B}} \right\rangle = \frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \, \frac{1}{r_{12}} n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) \; . \quad (7)$$

where $n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ is the two-body density associated to $\Psi^{\mathcal{B}}$. Because $\Psi^{\mathcal{B}}$ belongs to $\mathcal{B}$, such an expectation value coincides with the expectation value of $\hat{W}^{\mathcal{B}}_{\text{ee}}$ and therefore one can write:

$$\left\langle \Psi^{\mathcal{B}} \right| \hat{W}^{\mathcal{B}}_{\text{ee}} \left| \Psi^{\mathcal{B}} \right\rangle = \left\langle \Psi^{\mathcal{B}} \right| \hat{W}_{\text{ee}} \left| \Psi^{\mathcal{B}} \right\rangle, \quad (8)$$

which can be rewritten as:

$$\begin{aligned} &\iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) \; n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) \\ = &\iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; \frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \; n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2). \end{aligned} \quad (9)$$

where we introduced $W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$

$$W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \frac{f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)}{n^{(2)}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)}, \quad (10)$$

which is the effective interaction in the basis set $\mathcal{B}$.

III. RESULTS

A. The case of C_2 and the comparison with the F12 methods.

TABLE I. 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	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.

		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	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. ? .