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 from the description of the WFT in a finite basis set. Here, we briefly explain the working equations and notations needed for this work, and the interested reader can find the detailed formal derivation of the theory in[?] .

B. The very basics

Consider an incomplete basis-set $\mathcal{B}$ 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 an incomplete 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 $\mathcal{B}$

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

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 $\mathbb{R}^6$:

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

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 $\Psi^{\mathcal{B}}$

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

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

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

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

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

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 $\hat{W}^{\mathcal{B}}_{\text{ee}}$

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

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 $\mathcal{B}$.

As already discussed in? , such an effective interaction is symmetric, *a priori* non translational nor rotational invariant if the basis set $\mathcal{B}$ does not have such symmetries and is necessary *finite* at the electron coalescence point for an incomplete basis set $\mathcal{B}$. Also, as demonstrated in the appendix B of? , $W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ tends to the regular coulomb interaction $1/r_{12}$ for all points in $\mathbb{R}^6$ in the limit of a complete basis set $\mathcal{B}$.

2. *Definition of a valence effective interaction*

As the average inter electronic distances are very different between the valence electrons and the core electrons, it can be advantageous to define an effective interaction taking into account only for the valence electrons which are the most important in most of the chemical processes.

According to (10) and (11), the effective interaction is defined by the expectation value of the coulomb operator over a wave function $\Psi^{\mathcal{B}}$. Therefore, to define an effective interaction accounting only for the valence electrons, one needs to define a function $f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ satisfying

$$\left\langle \Psi^{\mathcal{B}} \middle| \hat{W}^{\mathcal{B}_{\text{val}}}_{\text{ee}} \middle| \Psi^{\mathcal{B}} \right\rangle = \frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \, f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2), \quad (11)$$

where $\hat{W}^{\mathcal{B}_{\text{val}}}_{\text{ee}}$ is the valence coulomb operator defined as

$$\hat{W}^{\mathcal{B}_{\text{val}}}_{\text{ee}} = \frac{1}{2} \sum_{ijkl \, \in \, \mathcal{B}_{\text{val}}} V_{ij}^{kl} \, \hat{a}^{\dagger}_k \hat{a}^{\dagger}_l \hat{a}_j \hat{a}_i, \quad (12)$$

$\mathcal{B}_{\text{val}}$ is a given set of molecular orbitals associated to the valence space which will be defined later on. Following the spirit of (13), the function $f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ can be defined as

$$\begin{aligned} f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \sum_{(ij) \, \in \, \mathcal{B}} \ \sum_{(klmn) \, \in \, \mathcal{B}_{\text{val}}} V_{ij}^{kl} \, \Gamma_{kl}^{mn}[\Psi^{\mathcal{B}}] \\ \phi_n(\mathbf{X}_2)\phi_m(\mathbf{X}_1)\phi_i(\mathbf{X}_1)\phi_j(\mathbf{X}_2). \end{aligned} \quad (13)$$

It is important to notice the difference between the set of orbitals for the indices (i, j), which span the full set of MOs within $\mathcal{B}$, and the (k, l, m, n), which span only the valence space $\mathcal{B}_{\text{val}}$. With such a definition, one can show (see annex) that $f^{\text{val}}_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)$ fulfills (**??**) and tends to the exact interaction $1/r_{12}$ in the limit of a complete basis set $\mathcal{B}$, whatever the choice of subset $\mathcal{B}_{\text{val}}$.

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)	143.0	145.4	146.4	146.0	
	exFCI+PBE	146.1	143.9	145.9	145.12	
	exFCI+PBE (FC)	147.4	146.1	146.4	145.9	
	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)	217.8	225.9	228.1	228.5	
	exFCI+PBE	225.3	225.6	228.2	227.9	
	exFCI+PBE (FC)	227.6	227.8	228.4	228.5	
	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)	112.4	118.5	120.2	120.3	
	exFCI+PBE	115.9	118.4	120.1	119.9	
	exFCI+PBE (FC)	117.2	119.4	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)	33.7	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. ? .