

# A density-based basis-set correction for weak and strong correlation

## I. SIZE CONSISTENCY OF THE BASIS-SET CORRECTION

### A. Sufficient condition for size consistency

The basis-set correction is expressed as an integral in real space

$$\begin{aligned} \bar{E}^{\mathcal{B}}[n, \zeta, n_2, \mu] = \\ \int d\mathbf{r} n(\mathbf{r}) \bar{\epsilon}_{\text{c,md}}^{\text{sr,PBE}}(n(\mathbf{r}), \zeta(\mathbf{r}), s(\mathbf{r}), n_2(\mathbf{r}), \mu(\mathbf{r})), \end{aligned} \quad (1)$$

where all the local quantities  $n(\mathbf{r}), \zeta(\mathbf{r}), s(\mathbf{r}), n_2(\mathbf{r}), \mu(\mathbf{r})$  are obtained from the same wave function  $\Psi$ . In the limit of two non-overlapping and non-interacting dissociated fragments  $A + B$ , this integral can be rewritten as the sum of the integral over the region  $\Omega_A$  and the integral over the region  $\Omega_B$

$$\begin{aligned} \bar{E}_{A+B}^{\mathcal{B}}[n, \zeta, n_2, \mu] = \\ \int_{\Omega_A} d\mathbf{r} n(\mathbf{r}) \bar{\epsilon}_{\text{c,md}}^{\text{sr,PBE}}(n(\mathbf{r}), \zeta(\mathbf{r}), s(\mathbf{r}), n_2(\mathbf{r}), \mu(\mathbf{r})) \\ + \int_{\Omega_B} d\mathbf{r} n(\mathbf{r}) \bar{\epsilon}_{\text{c,md}}^{\text{sr,PBE}}(n(\mathbf{r}), \zeta(\mathbf{r}), s(\mathbf{r}), n_2(\mathbf{r}), \mu(\mathbf{r})). \end{aligned} \quad (2)$$

Therefore, a sufficient condition to obtain size consistency is that all the local quantities  $n(\mathbf{r}), \zeta(\mathbf{r}), s(\mathbf{r}), n_2(\mathbf{r}), \mu(\mathbf{r})$  are *intensive*, i.e. that they *locally* coincide in the supersystem  $A + B$  and in each isolated fragment  $X = A$  or  $B$ . Hence, for  $\mathbf{r} \in \Omega_X$ , we should have

$$n_{A+B}(\mathbf{r}) = n_X(\mathbf{r}), \quad (3a)$$

$$\zeta_{A+B}(\mathbf{r}) = \zeta_X(\mathbf{r}), \quad (3b)$$

$$s_{A+B}(\mathbf{r}) = s_X(\mathbf{r}), \quad (3c)$$

$$n_{2,A+B}(\mathbf{r}) = n_{2,X}(\mathbf{r}), \quad (3d)$$

$$\mu_{A+B}(\mathbf{r}) = \mu_X(\mathbf{r}), \quad (3e)$$

where the left-hand-side quantities are for the supersystem and the right-hand-side quantities are for an isolated fragment. Such conditions can be difficult to fulfil in the presence of degeneracies since the system  $X$  can be in a different mixed state (i.e. ensemble) in the supersystem  $A + B$  and in the isolated fragment<sup>1</sup>. Here, we will consider the simple case where the wave function of the supersystem is multiplicatively separable, i.e.

$$|\Psi_{A+B}\rangle = |\Psi_A\rangle \otimes |\Psi_B\rangle, \quad (4)$$

where  $\otimes$  is the antisymmetric tensor product. In this case, it is easy to shown that Eqs. (3a)-(3c) are valid, as well known, and it remains to show that Eqs. (3d) and (3e) are also valid. Before

showing this, we note that even though we do not explicitly consider the case of degeneracies, the lack of size consistency which could arise from spin-multiplet degeneracies can be avoided by the same strategy used for imposing the energy independence on  $S_z$ , i.e. by using the effective spin polarization  $\tilde{\zeta}(n(\mathbf{r}), n_2(\mathbf{r}))$  or a zero spin polarization  $\tilde{\zeta}(\mathbf{r}) = 0$ . Moreover, the lack of size consistency which could arise from spatial degeneracies (e.g., coming from atomic p states) can also be avoided by selecting the same member of the ensemble in the supersystem and in the isolated fragment. This applies to the systems treated in this work.

### B. Intensity of the on-top pair density

A crucial ingredient in the type of functionals used in the present paper together with the definition of the local-range separation parameter is the on-top pair density defined as

$$n_2(\mathbf{r}) = \sum_{pqrs} \phi_p(\mathbf{r}) \phi_q(\mathbf{r}) \Gamma_{pq}^{rs} \phi_r(\mathbf{r}) \phi_s(\mathbf{r}), \quad (5)$$

with  $\Gamma_{pq}^{rs} = 2 \langle \Psi | \hat{a}_{r\downarrow}^\dagger \hat{a}_{s\uparrow}^\dagger \hat{a}_{q\uparrow} \hat{a}_{p\downarrow} | \Psi \rangle$ . Assume now that the wave function  $\Psi_{A+B}$  of the super system  $A + B$  can be written as a product of two wave functions defined on two non-overlapping and non-interacting fragments  $A$  and  $B$

$$|\Psi_{A+B}\rangle = |\Psi_A\rangle \times |\Psi_B\rangle. \quad (6)$$

Labelling the orbitals of fragment  $A$  as  $p_A, q_A, r_A, s_A$  and of fragment  $B$  as  $p_B, q_B, r_B, s_B$  and assuming that they don't overlap, one can split the two-body density operator as

$$\hat{\Gamma}(\mathbf{r}_1, \mathbf{r}_2) = \hat{\Gamma}_{AA}(\mathbf{r}_1, \mathbf{r}_2) + \hat{\Gamma}_{BB}(\mathbf{r}_1, \mathbf{r}_2) + \hat{\Gamma}_{AB}(\mathbf{r}_1, \mathbf{r}_2) \quad (7)$$

with

$$\begin{aligned} \hat{\Gamma}_{AA}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{p_A, q_A, r_A, s_A} \phi_{r_A}(\mathbf{r}_1) \phi_{s_A}(\mathbf{r}_2) \phi_{p_A}(\mathbf{r}_1) \phi_{q_A}(\mathbf{r}_2) \\ \hat{a}_{r_A, \downarrow}^\dagger \hat{a}_{s_A, \uparrow}^\dagger \hat{a}_{q_A, \uparrow} \hat{a}_{p_A, \downarrow}, \end{aligned} \quad (8)$$

(and equivalently for  $B$ ), and

$$\begin{aligned} \hat{\Gamma}_{AB} = \sum_{p_A, q_B, r_A, s_B} \phi_{r_A}(\mathbf{r}_1) \phi_{s_B}(\mathbf{r}_2) \phi_{p_A}(\mathbf{r}_1) \phi_{q_B}(\mathbf{r}_2) \\ \left( \hat{a}_{r_A, \downarrow}^\dagger \hat{a}_{p_A, \downarrow} \hat{a}_{s_B, \uparrow}^\dagger \hat{a}_{q_B, \uparrow} + \hat{a}_{s_B, \uparrow}^\dagger \hat{a}_{q_B, \uparrow} \hat{a}_{r_A, \downarrow}^\dagger \hat{a}_{p_A, \downarrow} \right). \end{aligned} \quad (9)$$

Therefore, one can express the two-body density as

$$n_{2, \Psi_{A+B}}(\mathbf{r}_1, \mathbf{r}_2) = n_{2, \Psi_{AA}}(\mathbf{r}_1, \mathbf{r}_2) + n_{2, \Psi_{BB}}(\mathbf{r}_1, \mathbf{r}_2) + n_{2, \Psi_{AB}}(\mathbf{r}_1, \mathbf{r}_2) \quad (10)$$

where  $n_{2, \Psi_{AA}}(\mathbf{r}_1, \mathbf{r}_2)$  and  $n_{2, \Psi_{BB}}(\mathbf{r}_1, \mathbf{r}_2)$  are the two-body densities of the isolated fragments

$$n_{2, \Psi_{AA}}(\mathbf{r}_1, \mathbf{r}_2) = \langle \Psi_A | \hat{\Gamma}_{AA}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_A \rangle \quad (11)$$

(and equivalently for  $B$ ), and  $n_{2\Psi^{AB}}(\mathbf{r}_1, \mathbf{r}_2)$  is simply the product of the one body densities of the sub systems

$$n_{2\Psi^{AB}}(\mathbf{r}_1, \mathbf{r}_2) = n_A(\mathbf{r}_1)n_B(\mathbf{r}_2) + n_B(\mathbf{r}_1)n_A(\mathbf{r}_2), \quad (12)$$

$$n_A(\mathbf{r}) = \sum_{p_A r_A} \phi_{p_A}(\mathbf{r}) \langle \Psi_A | \hat{a}_{s_A, \uparrow}^\dagger \hat{a}_{q_A, \uparrow} | \Psi_A \rangle \phi_{r_A}(\mathbf{r}), \quad (13)$$

(and equivalently for  $B$ ). As the densities of  $A$  and  $B$  are by definition non overlapping, one can express the on-top pair density as the sum of the on-top pair densities of the isolated systems

$$n_{2, \Psi_{A+B}}(\mathbf{r}) = n_{2, \Psi^{AA}}(\mathbf{r}, \mathbf{r}) + n_{2, \Psi^{BB}}(\mathbf{r}, \mathbf{r}) \quad (14)$$

As  $n_{2, \Psi^{A/A}}(\mathbf{r}) = 0$  if  $\mathbf{r} \in B$  (and equivalently for  $n_{2, \Psi^{B/B}}(\mathbf{r})$  on  $A$ ), one can conclude that provided that the wave function is multiplicative, the on-top pair density is a local intensive quantity.

### C. Property of the local-range separation parameter

The local range separation parameter depends on the on-top pair density at a given point  $\mathbf{r}$  and on the numerator

$$f_{\Psi}(\mathbf{r}, \mathbf{r}) = \sum_{pqrstu \in \mathcal{B}} \phi_p(\mathbf{r})\phi_q(\mathbf{r})V_{pq}^{rs}\Gamma_{rs}^{tu}\phi_t(\mathbf{r})\phi_u(\mathbf{r}). \quad (15)$$

As the summations run over all orbitals in the basis set  $\mathcal{B}$ , the quantity  $f_{\Psi}(\mathbf{r}, \mathbf{r})$  is orbital invariant and therefore can be expressed in terms of localized orbitals. In the limit of dissociated fragments, the coulomb interaction is vanishing between  $A$  and  $B$  and therefore any two-electron integral involving orbitals on both the system  $A$  and  $B$  vanishes. Therefore, one can rewrite eq. (15) as

$$f_{\Psi_{A+B}}(\mathbf{r}, \mathbf{r}) = f_{\Psi_{AA}}(\mathbf{r}, \mathbf{r}) + f_{\Psi_{BB}}(\mathbf{r}, \mathbf{r}), \quad (16)$$

with

$$f_{\Psi_{AA}}(\mathbf{r}, \mathbf{r}) = \sum_{p_A q_A r_A s_A t_A u_A} \phi_{p_A}(\mathbf{r})\phi_{q_A}(\mathbf{r})V_{p_A q_A}^{r_A s_A}\Gamma_{r_A s_A}^{t_A u_A}\phi_{t_A}(\mathbf{r})\phi_{u_A}(\mathbf{r}), \quad (17)$$

(and equivalently for  $B$ ). As a consequence, the local range-separation parameter in the super system  $A + B$

$$\mu(\mathbf{r}; \Psi^{A+B}) = \frac{\sqrt{\pi} f_{\Psi_{A+B}}(\mathbf{r}, \mathbf{r})}{2 n_{2, \Psi_{A+B}}(\mathbf{r})} \quad (18)$$

which, in the case of a multiplicative wave function is nothing but

$$\mu(\mathbf{r}; \Psi^{A+B}) = \mu(\mathbf{r}; \Psi^A) + \mu(\mathbf{r}; \Psi^B). \quad (19)$$

As  $\mu(\mathbf{r}; \Psi^A) = 0$  if  $\mathbf{r} \in B$  (and equivalently for  $\mu(\mathbf{r}; \Psi^B)$  on  $B$ ),  $\mu(\mathbf{r}; \Psi^{A+B})$  is an intensive quantity. The conclusion of this paragraph is that, provided that the wave function for the system  $A + B$  is multiplicative in the limit of the dissociated fragments, all quantities used for the basis set correction are intensive and therefore the basis set correction is size consistent.

## II. COMPUTATIONAL CONSIDERATIONS

The computational cost of the present approach is driven by two quantities: the computation of the on-top pair density and the  $\mu_{\Psi^B}(\mathbf{r})$  on the real-space grid. Within a blind approach, for each grid point the computational cost is of order  $n_B^4$  and  $n_B^6$  for the on-top pair density  $n_{2, \Psi^B}(\mathbf{r})$  and the local range separation parameter  $\mu_{\Psi^B}(\mathbf{r})$ , respectively. Nevertheless, using CASSCF wave functions to compute these quantities leads to significant simplifications which can substantially reduce the CPU time.

### A. Computation of the on-top pair density for a CASSCF wave function

Given a generic wave function developed on a basis set with  $n_B$  basis functions, the evaluation of the on-top pair density is of order  $(n_B)^4$ . Nevertheless, assuming that the wave function  $\Psi^B$  is of CASSCF type, a lot of simplifications happen. If the active space is referred as the set of spatial orbitals  $\mathcal{A}$  which are labelled by the indices  $t, u, v, w$ , and the doubly occupied orbitals are the set of spatial orbitals  $\mathcal{C}$  labeled by the indices  $i, j$ , one can write the on-top pair density of a CASSCF wave function as

$$n_{2, \Psi^B}(\mathbf{r}) = n_{2, \mathcal{A}}(\mathbf{r}) + n_{\mathcal{C}}(\mathbf{r})n_{\mathcal{A}}(\mathbf{r}) + (n_{\mathcal{C}}(\mathbf{r}))^2 \quad (20)$$

where

$$n_{2, \mathcal{A}}(\mathbf{r}) = \sum_{t, u, v, w \in \mathcal{A}} 2 \langle \Psi^B | \hat{a}_{t, \downarrow}^\dagger \hat{a}_{u, \uparrow}^\dagger \hat{a}_{v, \uparrow} \hat{a}_{w, \downarrow} | \Psi^B \rangle \phi_t(\mathbf{r})\phi_u(\mathbf{r})\phi_v(\mathbf{r})\phi_w(\mathbf{r}) \quad (21)$$

is the purely active part of the on-top pair density,

$$n_{\mathcal{C}}(\mathbf{r}) = \sum_{i \in \mathcal{C}} (\phi_i(\mathbf{r}))^2, \quad (22)$$

and

$$n_{\mathcal{A}}(\mathbf{r}) = \sum_{t, u \in \mathcal{A}} \phi_t(\mathbf{r})\phi_u(\mathbf{r}) \langle \Psi^B | \hat{a}_{t, \downarrow}^\dagger \hat{a}_{u, \downarrow} + \hat{a}_{t, \uparrow}^\dagger \hat{a}_{u, \uparrow} | \Psi^B \rangle \quad (23)$$

is the purely active one-body density. Written as in eq. (20), the leading computational cost is the evaluation of  $n_{2, \mathcal{A}}(\mathbf{r})$  which, according to eq. (21), scales as  $(n_{\mathcal{A}})^4$  where  $n_{\mathcal{A}}$  is the number of active orbitals which is much smaller than the number of basis functions  $n_B$ . Therefore, the final computational scaling of the on-top pair density for a CASSCF wave function over the whole real-space grid is of  $(n_{\mathcal{A}})^4 n_G$ , where  $n_G$  is the number of grid points.

### B. Computation of $\mu_{\Psi^B}(\mathbf{r})$

At a given grid point, the computation of  $\mu_{\Psi^B}(\mathbf{r})$  needs the computation of  $f_{\Psi}(\mathbf{r}, \mathbf{r})$  defined in eq. (15) and the on-top pair density defined in eq. (5). In the previous paragraph we

gave an explicit form of the on-top pair density in the case of a CASSCF wave function with a computational scaling of  $(n_{\mathcal{A}})^4$ . In the present paragraph we focus on simplifications that one can obtain for the computation of  $f_{\Psi}(\mathbf{r}, \mathbf{r})$  in the case of a CASSCF wave function.

One can rewrite  $f_{\Psi}(\mathbf{r}, \mathbf{r})$  as

$$f_{\Psi}(\mathbf{r}, \mathbf{r}) = \sum_{r,s \in \mathcal{B}} \mathcal{V}_r^s(\mathbf{r}) \mathcal{N}_r^s(\mathbf{r}) \quad (24)$$

where

$$\mathcal{V}_r^s(\mathbf{r}) = \sum_{p,q \in \mathcal{B}} V_{pq}^{rs} \phi_p(\mathbf{r}) \phi_q(\mathbf{r}) \quad (25)$$

and

$$\mathcal{N}_r^s(\mathbf{r}) = \sum_{p,q \in \mathcal{B}} \Gamma_{pq}^{rs} \phi_p(\mathbf{r}) \phi_q(\mathbf{r}). \quad (26)$$

*A priori*, for a given grid point, the computational scaling of

eq. (24) is of  $(n_{\mathcal{B}})^4$  and the total computational cost over the whole grid scales therefore as  $(n_{\mathcal{B}})^4 n_G$ .

In the case of a CASSCF wave function, it is interesting to notice that  $\Gamma_{pq}^{rs}$  vanishes if one index  $p, q, r, s$  does not belong to the set of doubly occupied or active orbitals  $\mathcal{C} \cup \mathcal{A}$ . Therefore, at a given grid point, the matrix  $\mathcal{N}_r^s(\mathbf{r})$  has only at most  $(n_{\mathcal{A}} + n_{\mathcal{C}})^2$  non-zero elements, which is usually much smaller than  $(n_{\mathcal{B}})^2$ . As a consequence, in the case of a CASSCF wave function one can rewrite  $f_{\Psi}(\mathbf{r}, \mathbf{r})$  as

$$f_{\Psi}(\mathbf{r}, \mathbf{r}) = \sum_{r,s \in \mathcal{C} \cup \mathcal{A}} \mathcal{V}_r^s(\mathbf{r}) \mathcal{N}_r^s(\mathbf{r}). \quad (27)$$

Therefore the final computational cost of  $f_{\Psi}(\mathbf{r}, \mathbf{r})$  is dominated by that of  $\mathcal{V}_r^s(\mathbf{r})$ , which scales as  $(n_{\mathcal{A}} + n_{\mathcal{C}})^2 (n_{\mathcal{B}})^2 n_G$ , which is much weaker than  $(n_{\mathcal{B}})^4 n_G$ .

<sup>1</sup>A. Savin, Chem. Phys. **356**, 91 (2009).