Supplementary Material for: The non-negativity condition of the target density in Frozen-Density Embedding Theory based simulations

Niccolò Ricardi,[1, a)] Cristina E. González-Espinoza,[1, b)] and Tomasz Adam Wesołowski[1, c)]

Department of Physical Chemistry, University of Geneva, Geneva (Switzerland)

(Dated: 10 April 2022)

[a)]Electronic mail: Niccolo.Ricardi@unige.ch

[b)]Electronic mail: Cristina.GonzalezEspinoza@unige.ch

[c)]Electronic mail: Tomasz.Wesolowski@unige.ch

S1. PROOF THAT $M[\rho_B - \rho_{AB}^o] \leq P[\rho_A^o + \rho_B - \rho_{AB}^o]$

We start with the obvious equality,

$$\int \rho_A^o + \rho_B - \rho_{AB}^o = 0, \tag{S1}$$

from which it follows that:

$$\int\limits_{\rho_{AB}^o < \rho_A^o + \rho_B} \rho_A^o + \rho_B - \rho_{AB}^o = \int\limits_{\rho_{AB}^o > \rho_A^o + \rho_B} \rho_{AB}^o - \rho_A^o - \rho_B. \tag{S2}$$

The above relation used in the definition of P leads to:

$$\begin{aligned} P[\rho_A^o + \rho_B - \rho_{AB}^o] =& \frac{1}{2} \cdot \int |\rho_A^o + \rho_B - \rho_{AB}^o| \\ =& \frac{1}{2} \cdot \int\limits_{\rho_{AB}^o < \rho_A^o + \rho_B} \rho_A^o + \rho_B - \rho_{AB}^o + \\ & \frac{1}{2} \cdot \int\limits_{\rho_{AB}^o > \rho_A^o + \rho_B} \rho_A^o + \rho_B - \rho_{AB}^o \\ =& \int\limits_{\rho_{AB}^o < \rho_A^o + \rho_B} \rho_A^o + \rho_B - \rho_{AB}^o. \end{aligned} \tag{S3}$$

Splitting the domain of integration of the final integral above leads to:

$$\begin{aligned} P[\rho_A^o + \rho_B - \rho_{AB}^o] =& \int\limits_{\rho_{AB}^o < \rho_B} \rho_A^o + \rho_B - \rho_{AB}^o + \\ & \int\limits_{\rho_B \leq \rho_{AB}^o < \rho_B + \rho_A^o} \rho_A^o + \rho_B - \rho_{AB}^o \end{aligned} \tag{S4}$$

$$\begin{aligned} =& \int\limits_{\rho_{AB}^o < \rho_B} \rho_B - \rho_{AB}^o + \\ +& \int\limits_{\rho_{AB}^o < \rho_B} \rho_A^o + \int\limits_{\rho_B \leq \rho_{AB}^o < \rho_B + \rho_A^o} \rho_A^o + \rho_B - \rho_{AB}^o \end{aligned} \tag{S5}$$

The first integral in the right-hand-side of the equation above is equal to $M[\rho_{AB}^o - \rho_B]$ whereas the second and third are non-negative. As a result:

$$P[\rho_A^o + \rho_B - \rho_{AB}^o] \geq M[\rho_{AB}^o - \rho_B], \tag{S6}$$

which ends the proof.