

**Erratum: “A solvation-free-energy functional: A  
reference-modified density functional formulation”  
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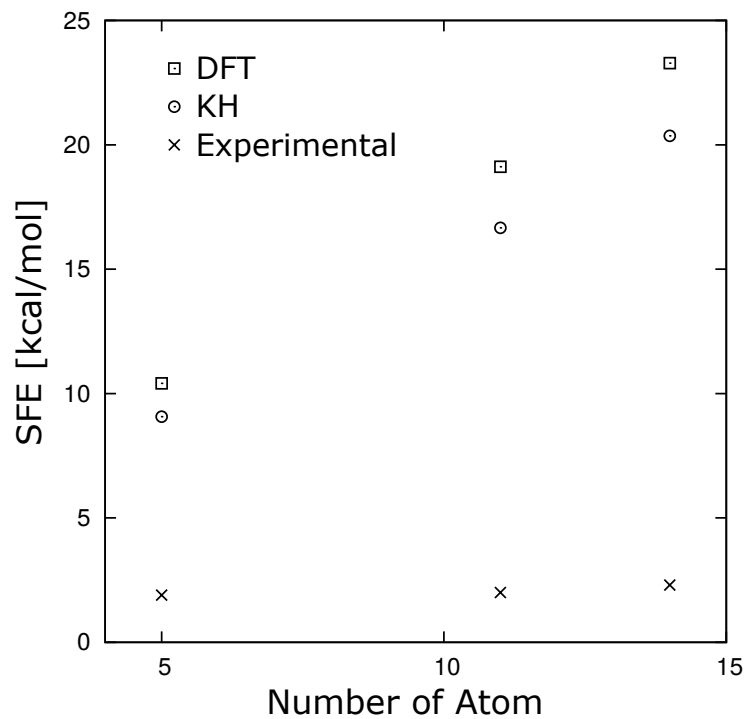
The authors found an error in the program for the calculation of the solvation free energy (SFE). We apologize for this inconvenience. First of all, we would like to revise a misprint at the second line of Eq. (40) where the square bracket “]” at the end of this line should be removed. As a result, Eq. (40) is rewritten as

$$\begin{aligned}
\Delta G_{\text{solv}} = & -\frac{1}{\beta} \sum_{a=1}^P \int d\mathbf{r}_1^a \left[ n_a(\mathbf{r}_1^a | \{U_\lambda^{PR}\}) - n_0 \right] \\
& - \int d\mathbf{r}_1^O \left[ n_O(\mathbf{r}_1^O | \{U_\lambda^{PR}\}) \right] \int d\mathbf{r}_2 W_{OO}(|\mathbf{r}_1^O - \mathbf{r}_2|) \\
& \times \left[ n_O(\mathbf{r}_2 | \{U_\lambda^{PR}\}) f'_{HS}(n_O^{\text{eff}}(\mathbf{r}_2 | n_O)) - n_0 f'_{HS}(n_0) \right] \\
& + \int d\mathbf{r}_1 W_{OO}(|\mathbf{r}_1|) n_0 f'_{HS}(n_0) \left] - n_0 f'_{HS}(n_0) \int d\mathbf{r}_1 W_{OO}(|\mathbf{r}_1|) n_0 \right] \\
& + \frac{n_0}{\beta} \sum_{a=1}^P \sum_{b=1}^P \int d\mathbf{r}_1^a d\mathbf{r}_1^b C_{ab}^{\text{ex}}(|\mathbf{r}_1^a - \mathbf{r}_1^b|) \left[ n_b(\mathbf{r}_1^b | \{U_\lambda^{PR}\}) - n_0 \right] \\
& + \frac{1}{2\beta} \sum_{a=1}^P \sum_{b=1}^P \int d\mathbf{r}_1^a d\mathbf{r}_1^b C_{ab}^{\text{ex}}(|\mathbf{r}_1^a - \mathbf{r}_1^b|) \left[ n_a(\mathbf{r}_1^a | \{U_\lambda^{PR}\}) - n_0 \right] \left[ n_b(\mathbf{r}_1^b | \{U_\lambda^{PR}\}) - n_0 \right]
\end{aligned} \tag{40}$$

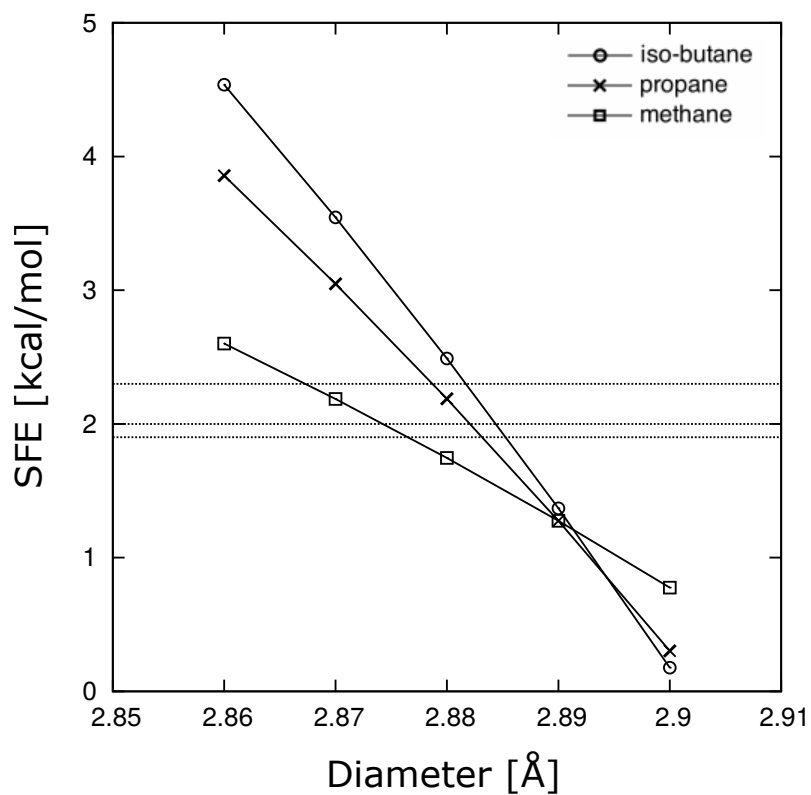
The first term on the right hand side of Eq. (40) is given by the sum of all components with respect to the density distribution functions. In the case that TIP3P model of water [References 54 and 55 in the article] is used as the solvent, the oxygen site and two hydrogen sites should be included in the calculation on the first term. However, we took into account only the oxygen component in the calculation of the results shown in Figs. 2, 3, 4, and 6, and Tables 1 and 2. In the same way, only the oxygen component in the first term of Eq. (37) was taken into account in the second-order DFT calculation shown in Fig. 1. In this erratum, we revise all the results that have been calculated using Eqs. (37) and (40). All the reference numbers that are referred to in this erratum accord to the ones in the article.

In the SFE calculation based on the reference-modified density functional theory (RMDFT), we have to determine a hard sphere (HS) diameter for the reference system. Hard-sphere-diameter dependence of the SFE value for small hydrophobic solutes that is calculated

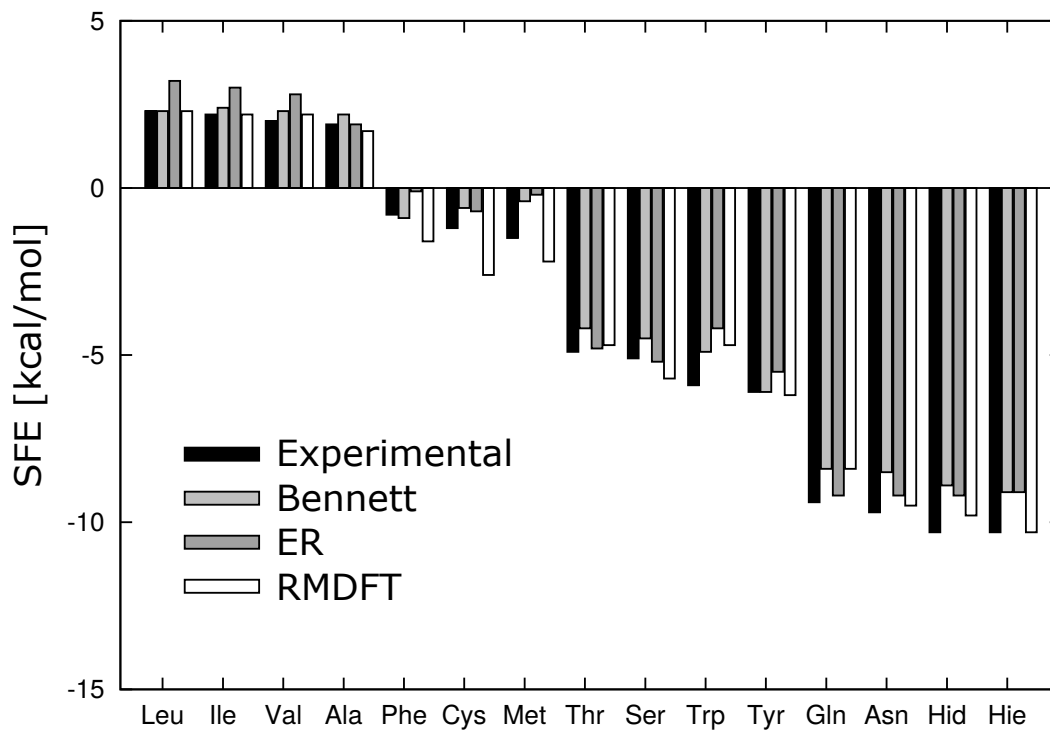
using the RMDFT functional of Eq. (40) is shown in Fig. 2. According to the revised results, we determined an optimal HS diameter as 2.88 Å, which is slightly larger than 2.83 Å that had been determined using Eq. (40) with only the oxygen component for the first term. In Figs. 3, 4, and 6, and Tables 1 and 2, the revised results that are calculated using Eq. (40) with the HS diameter value of 2.88 Å are shown. With respect to Fig. 3 and Table 1, the mean absolute error (MAD) and root mean square deviation (RMSD) between the RMDFT results and the experimental data for the neutral amino acid side-chain analogues <sup>[43]</sup> are 0.48 and 0.64 kcal/mol, respectively, while the MAD and RMSD between the RMDFT results and the molecular simulation results provided by the Bennett acceptance ratio method <sup>[9]</sup> are 0.71 and 0.91 kcal/mol, respectively. As for Fig. 4, the MAD and RMSD values between the RMDFT results and the experimental data for 504 small organic molecules <sup>[52,57]</sup> are 1.08 and 1.44 kcal/mol, respectively, while the MAD and RMSD values between the RMDFT results and molecular dynamics simulations <sup>[52]</sup> are 0.95 and 1.25 kcal/mol, respectively. It should be noted that the revised results are almost same as the previous results. The first term on the right hand side of Eq. (40) basically gives a positive contribution to the SFE because it is in proportion to the excess partial molar volume of the solute. Therefore, the expected underestimation of the SFE values caused by the lack of two hydrogen components in Eq. (40) had been canceled out by the optimization of the reference HS diameter.



**Figure 1.** Comparison of the experimental and theoretical SFE values for methane, propane, and isobutane. The circles and squares indicate the results obtained using the two HNC-type approximations of the SFE, namely, the Singer-Chandler-like 3D-RISM-KH function<sup>[2,33]</sup> and the DFT with the second-order expansion approximation, respectively. The experimental data are represented by the crosses.<sup>[43]</sup>



**Figure 2.** Hard-sphere-diameter dependence of the SFE values obtained using the RMDFT functional of eq. (40). The open circles, crosses, and open squares indicate the RMDFT results for isobutane, propane, and methane, respectively. The dotted lines indicate the experimental SFE values for isobutane, propane, and methane, <sup>[43]</sup> respectively, in the given order from the top.



**Figure 3.** SFE values of the neutral amino acid side-chain analogues. The SFE values calculated using the RMDFT functional of eq. (40) are compared with the experimental values <sup>[43]</sup> and the computational values determined using the Bennett acceptance ratio method <sup>[9]</sup> and the energy-representation (ER) method. <sup>[13]</sup>

**Table 1.** SFE values of the amino acid side-chain analogues in water<sup>a</sup>

<b>Amino Acid</b>	<b>Analog solute</b>	<b>Experimental <sup>b</sup></b>	<b>Bennett <sup>c</sup></b>	<b>ER <sup>d</sup></b>	<b>RMDFT <sup>e</sup></b>
<b>Leu</b>	Isobutane	2.3	2.3	3.2	2.3
<b>Ile</b>	n-Butane	2.2	2.4	3.0	2.2
<b>Val</b>	Propane	2.0	2.3	2.8	2.2
<b>Ala</b>	Methane	1.9	2.2	1.9	1.7
<b>Phe</b>	Toluene	-0.8	-0.9	-0.1	-1.6
<b>Cys</b>	Methanethiol	-1.2	-0.6	-0.7	-2.6
<b>Met</b>	Methyl ethyl sulfide	-1.5	-0.4	-0.2	-2.2
<b>Thr</b>	Ethanol	-4.9	-4.2	-4.8	-4.7
<b>Ser</b>	Methanol	-5.1	-4.5	-5.2	-5.7
<b>Trp</b>	3-Methylindole	-5.9	-4.9	-4.2	-4.7
<b>Tyr</b>	p-Cresol	-6.1	-5.5	-5.2	-6.2
<b>Gln</b>	Propionamide	-9.4	-8.4	-9.2	-8.4
<b>Asn</b>	Acetamide	-9.7	-8.5	-9.2	-9.5
<b>Hid</b>	4-Methylimidazole	-10.3	-8.9	-9.2	-9.8
<b>Hie</b>	4-Methylimidazole	-10.3	-9.1	-9.1	-10.3

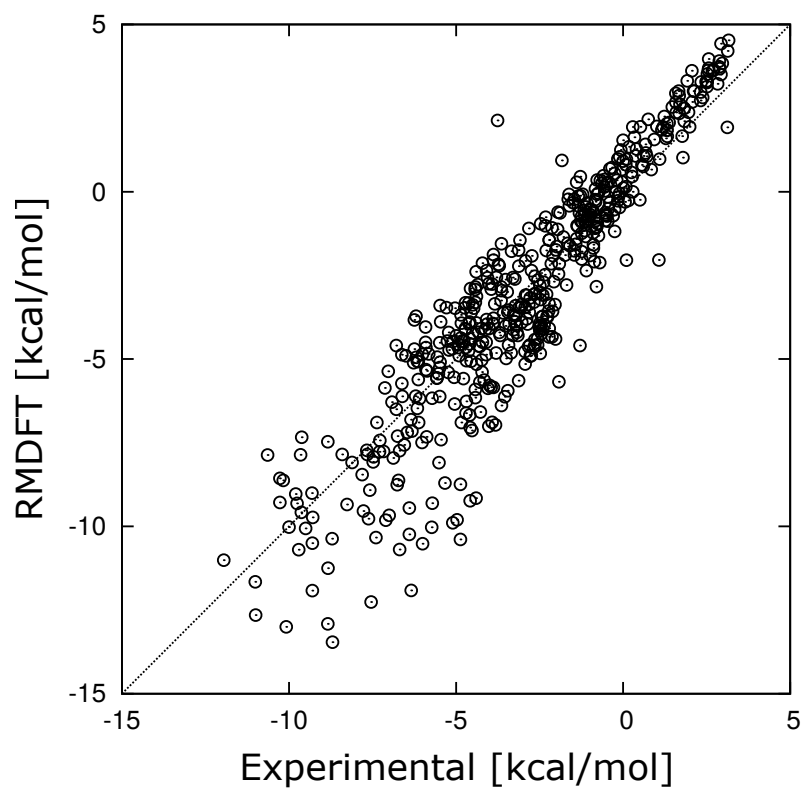
<sup>a</sup> Energy unit is kcal/mol.

<sup>b</sup> The experimental data are taken from the literature.<sup>[43]</sup>

<sup>c</sup> This column shows the values calculated using the Bennett acceptance ratio method.<sup>[9]</sup>

<sup>d</sup> This column shows the values calculated by Karino *et al.* using the energy-representation (ER) method.<sup>[13]</sup>

<sup>e</sup> This column shows the values calculated using the RMDFT functional.



**Figure 4.** Comparison of the SFE values of 504 small organic molecules obtained using the RMDFT functional of eq. (40) and the experimentally determined values. <sup>[52,57]</sup>



Table 2. The SFE values for the nine structures from A to I of the chignolin molecule in water.

The values within parentheses are the differences of  $\Delta G_{solv}$  from the structure A (native state),

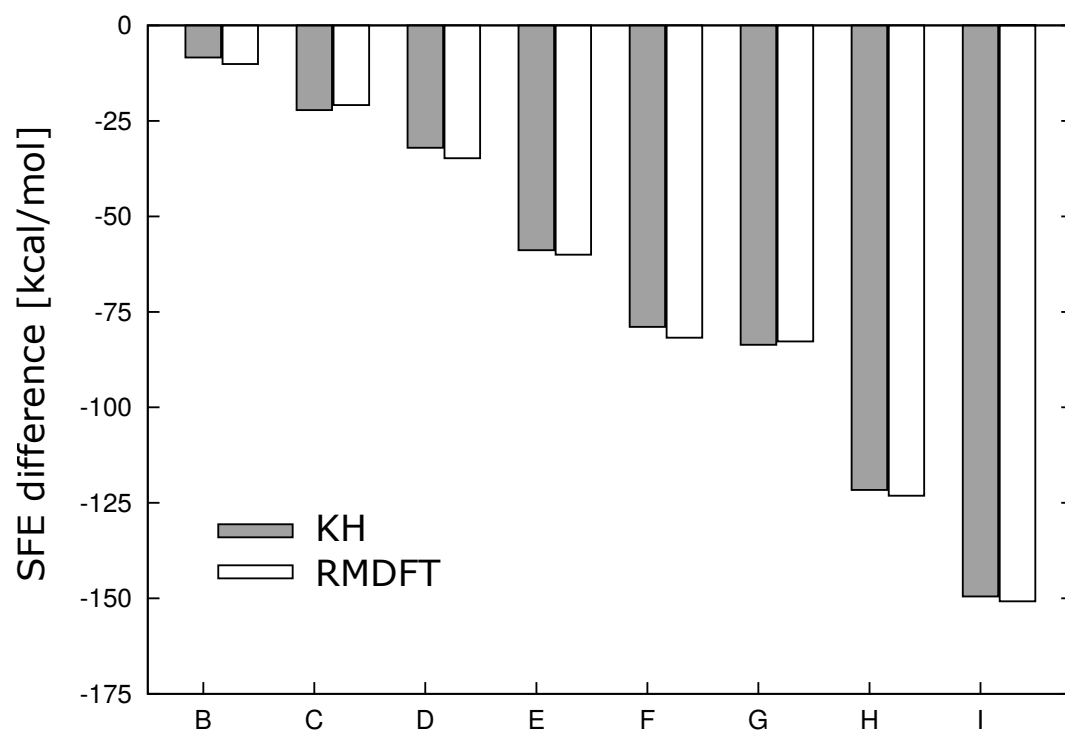
$$\Delta\Delta G_{solv}^a$$

Structures	KH <sup>b</sup>	RMDFT <sup>c</sup>
<b>A</b>	-124.7	-267.5
<b>B</b>	-133.1 (-8.4)	-277.6 (-10.1)
<b>C</b>	-146.8 (-22.1)	-288.4 (-20.9)
<b>D</b>	-156.7 (-32.0)	-302.3 (-34.8)
<b>E</b>	-183.5 (-58.8)	-327.5 (-60.0)
<b>F</b>	-203.6 (-78.9)	-349.3 (-81.8)
<b>G</b>	-208.3 (-83.6)	-350.3 (-82.8)
<b>H</b>	-246.3 (-121.6)	-390.6 (-123.1)
<b>I</b>	-274.2 (-149.5)	-418.3 (-150.8)

<sup>a</sup>Energy unit is kcal/mol.

<sup>b</sup>This column shows the values calculated using the Singer-Chandler-like 3D-RISM-KH function.<sup>[2,33]</sup>

<sup>c</sup>This column shows the values calculated using the RMDFT functional.



**Figure 6.** The differences of  $\Delta G_{solv}$  from the native structure A,  $\Delta\Delta G_{solv}$ .