Supporting Information for "Explicit Consideration of Spatial Hydrogen Bonding Direction for Activity Coefficient Prediction based on Implicit Solvation Calculations"

Wei-Lin Chen[a] and Shiang-Tai Lin[a*]

[a]Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Corresponding author. Tel.:+886 2 3366 1369; fax: +886 2 2362 3040. E-mail address:stlin@ntu.edu.tw (S.-T. Lin).

1. The determination of vector from atom *i* toward hydrogen bonding center ($\hat{D}^{j-th}_{i}$)

The general approach in determining the hydrogen bonding center is illustrated as below. $\hat{AB}$ represents the unit vector from point A toward point B.

(a) AX_2E_2

Example: oxygen on water

$$\hat{AB} = \frac{\vec{AB}}{|\vec{AB}|} \text{ and } \hat{AC} = \frac{\vec{AC}}{|\vec{AC}|}$$

$$\hat{N} = \frac{\hat{AB} \times \hat{AC}}{|\hat{AB} \times \hat{AC}|} \text{ and } \hat{P} = -\frac{\hat{AB} + \hat{AC}}{|\hat{AB} + \hat{AC}|}$$

then

$$\hat{D}^{1-th}_{i} = \hat{AD} = \frac{\hat{N} \times \tan\left(\frac{109.5}{2}\right) + \hat{P}}{\left|\hat{N} \times \tan\left(\frac{109.5}{2}\right) + \hat{P}\right|}$$

$$\hat{D}^{2-th}_{i} = \hat{AE} = \frac{-\hat{N} \times \tan\left(\frac{109.5}{2}\right) + \hat{P}}{\left|-\hat{N} \times \tan\left(\frac{109.5}{2}\right) + \hat{P}\right|}$$

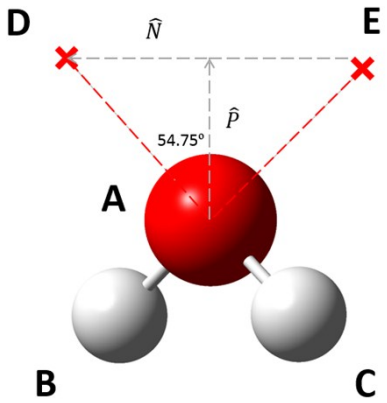


Fig. S1. The geometry of water and its hydrogen bonding center (red cross).

(b) AX_3E_1

Example: nitrogen on n-butyl amine

$$\hat{AB} = \frac{\vec{AB}}{|\vec{AB}|}, \quad \hat{AC} = \frac{\vec{AC}}{|\vec{AC}|} \text{ and } \quad \hat{AD} = \frac{\vec{AD}}{|\vec{AD}|}$$

then

$$\hat{D}^{1\text{-th}}_{i} = \hat{AE} = -\frac{\hat{AB} + \hat{AC} + \hat{AD}}{|\hat{AB} + \hat{AC} + \hat{AD}|}$$

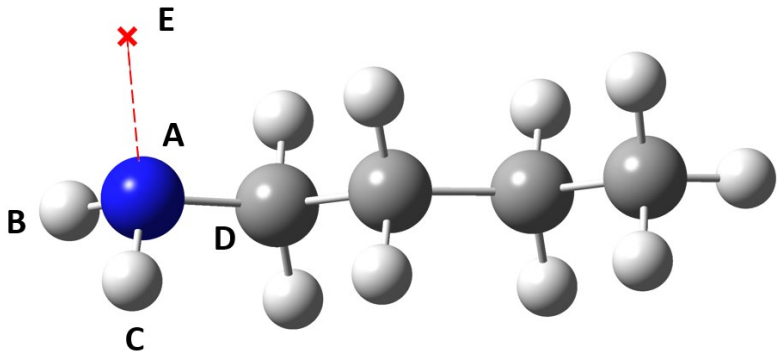


Fig. S2. The geometry of n-butyl amine and its hydrogen bonding center (red cross).

(c) AX_1E_2

Example: oxygen on acetone

$$\hat{AB} = \frac{\vec{AB}}{|\vec{AB}|} \text{ and } \quad \hat{AC} = \frac{\vec{AC}}{|\vec{AC}|}$$

then

$$\hat{D}^{1\text{-th}}_{i} = \hat{DE} = -\hat{AC}$$

$$\hat{D}^{2\text{-th}}_{i} = \hat{DF} = -\hat{AB}$$

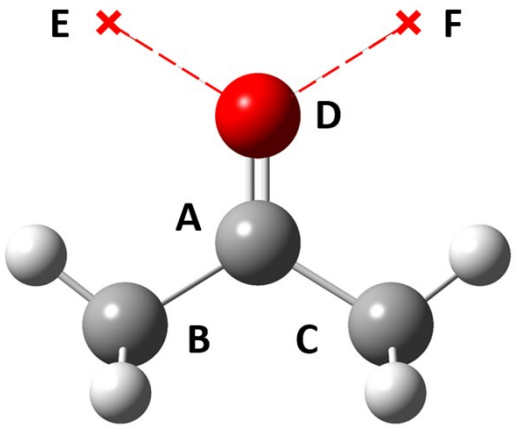


Fig. S3. The geometry of acetone and its hydrogen bonding center (red cross).

(d) AX_1E_1 and AX_1

Example: nitrogen on acetonitrile (AX_1E_1) and hydrogen on water (AX_1)

$$\hat{AB} = \frac{\vec{AB}}{|\vec{AB}|}$$

then

$$\hat{D}^{1\text{-th}}_{i} = \hat{AC} = -\hat{AB}$$

(i) (ii)

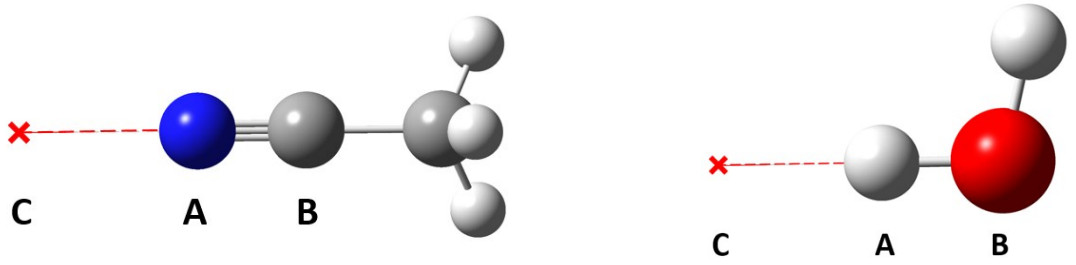


Fig. S4. The geometry including its hydrogen bonding center (red cross) of (i) acetonitrile and (ii) water.

(e) AX_3E_2

Example: nitrogen on n-methyl formamide.

This is a special case for nitrogen whose structure is different from AX_3E_1. Because the electronic orbital resembles to Π orbital, the *hb* center is assume to be vertical against its backbone as in Fig S5.

$$\hat{AB} = \frac{\vec{AB}}{|\vec{AB}|} \text{ and } \hat{AC} = \frac{\vec{AC}}{|\vec{AC}|}$$

if $\cos\theta = \frac{\hat{AB} \cdot \hat{AC}}{|\hat{AB}| \times |\hat{AC}|} < \cos(15°)$ then

$$\hat{N} = \frac{\hat{AB} \times \hat{AC}}{|\hat{AB} \times \hat{AC}|}$$

$$\hat{D}^{1\text{-th}}_{i} = \hat{AD} = \hat{N}$$

$$\hat{D}^{2\text{-th}}_{i} = \hat{AE} = -\hat{N}$$

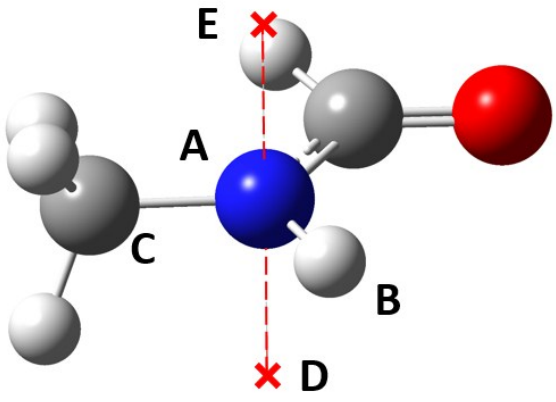


Fig. S5. The geometry of n-methyl formamide and its hydrogen bonding center (red cross).

2. Examples of the hydrogen bonding surface

The hydrogen bonding surface in COSMO-SAC(DHB) model of (1) methanol, (2) n-butyl amine, (3) n-methyl formamide and (4) acetonitrile are illustrated in Fig. S6. The *hb* σ-profile of COSMO-SAC 2002, COSMO-SAC 2010 and COSMO-SAC(DHB) are also compared in Fig. S6.

3. Detail prediction accuracy in VLE

The VLE system are categorized into three types: (a) self-association, (b) cross-association with one *hb* donor and (c) cross-association with two *hb* donor. The mean deviation and standard deviation of AARD-P and AAD-y for the three types of systems are listed in Table S1 and Table S2. The improvement on all three types of VLE validate the directional hydrogen bond approach can advance the prediction accuracy systematically.

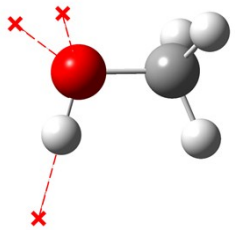
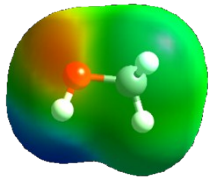
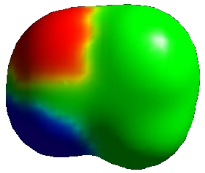
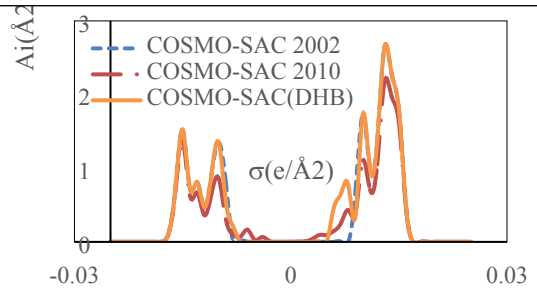
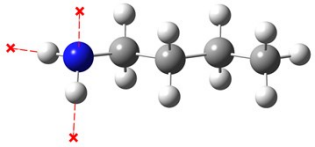
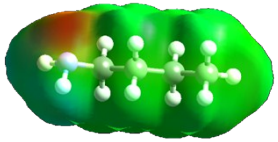
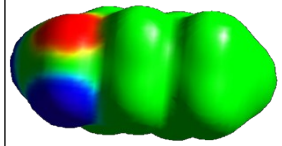
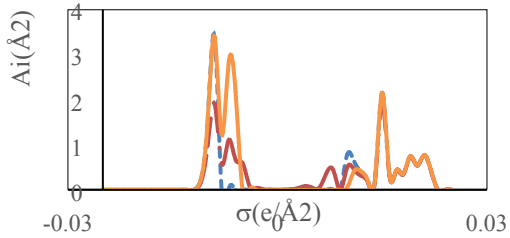
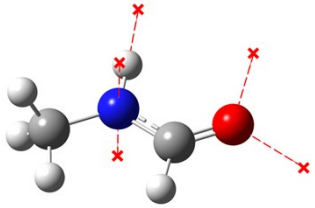
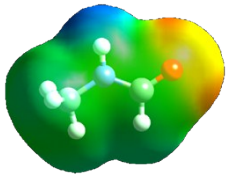
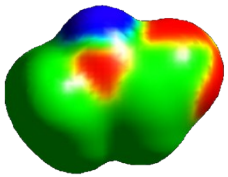
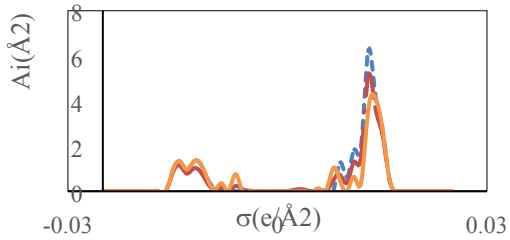
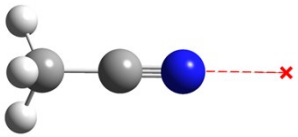
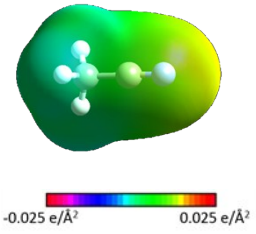
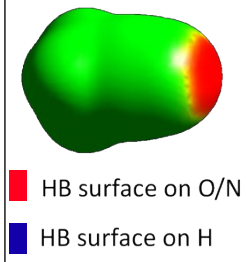
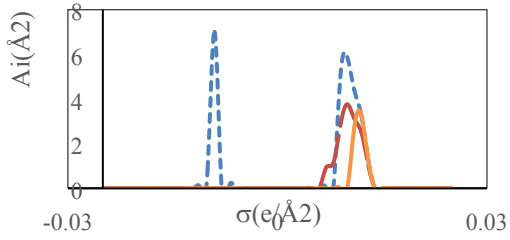
Molecule and its type	Geometry Structure	COSMO-surface	*hb* surface	The σ-profile in *hb* level
(1) Methanol AX_2E_2 (O) AX (H)				
(2) N-Butyl amine AX_3E_1 (N) AX (H)				
(3) N-Methyl formamide AX_1E_2(O) AX_3E_2 (N) AX (H)				
(4) Acetonitrile AX_1E_1 (N)				

Fig. S6. Illustration of the hydrogen bonding surface in COSMO-SAC(DHB) model and the comparison of *hb* σ-profile among COSMO-SAC models.

Table S1. The comparison of mean deviation and standard deviation of AARD-P in different types of vapor-liquid equilibrium.

Method		COSMO-SAC 2002		COSMO-SAC 2010		COSMO-SAC(DHB)	
Type*	Numbers of mixture	Mean Deviation	Standard Deviation	Mean Deviation	Standard Deviation	Mean Deviation	Standard Deviation
Type (a)	272	9.22	5.53	6.46	3.62	5.86	3.10
Type (b)	196	10.22	7.77	9.66	8.99	8.66	6.01
Type (c)	118	6.66	5.54	5.64	4.39	5.10	4.23

***(a) self-association, (b) cross-association with one *hb* donor and (c) cross-association with two *hb* donor in the binary VLE mixture.**

Table S2. The comparison of mean deviation and standard deviation of AAD-y in different types of vapor-liquid equilibrium.

Method		COSMO-SAC 2002		COSMO-SAC 2010		COSMO-SAC(DHB)	
Type*	Numbers of mixture	Mean Deviation	Standard Deviation	Mean Deviation	Standard Deviation	Mean Deviation	Standard Deviation
Type (a)	272	3.27	3.13	2.40	2.11	2.10	1.95
Type (b)	196	4.38	3.46	3.69	3.33	3.47	2.52
Type (c)	118	3.05	2.24	2.79	2.30	2.55	2.23

***(a) self-association, (b) cross-association with one *hb* donor and (c) cross-association with two *hb* donor in the binary VLE mixture.**