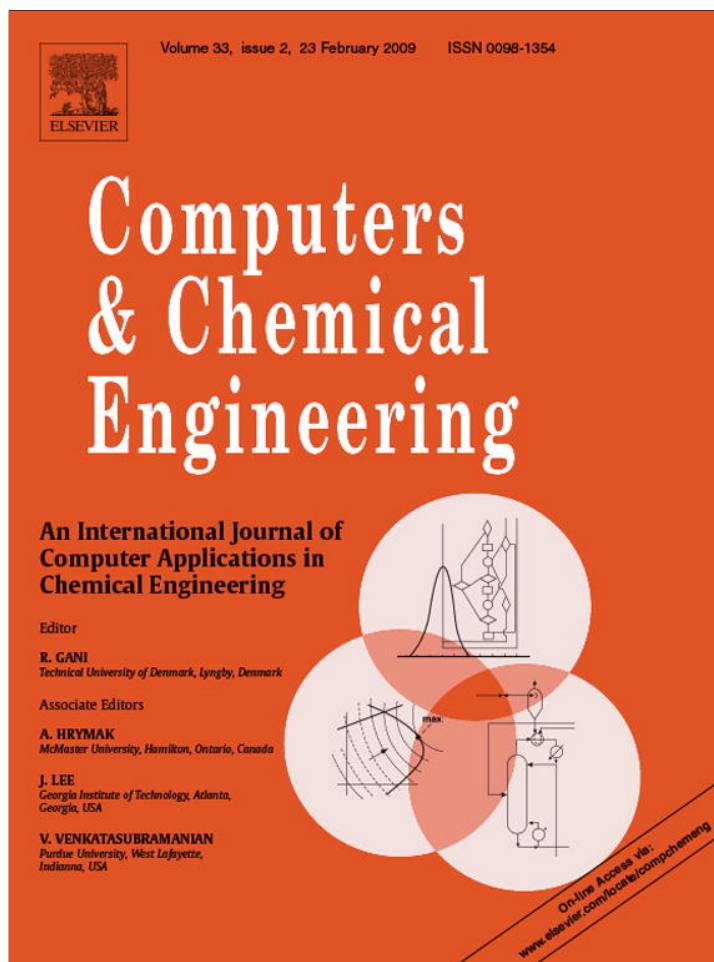


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A new algorithm for estimating association parameters in molecular-based equations of state by quantum chemistry

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ABSTRACT

This note presents a new algorithm for estimating association parameters within molecular-based equations of state that allows the user to incorporate results from quantum chemistry. Using the simplified SAFT equation as an example, we show that the traditional parameter estimation approach (i.e., fitting parameters to vapor pressure and liquid density data) provides results that run counter to quantum chemistry findings on association strengths. Numerical results show that the parameter estimation approach proposed in this work provides a much more appropriate match to quantum chemistry results and gives markedly different amounts of site–site bonding.

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1. Introduction

Fileti, Chaudhuri, & Canuto (2004) have recently used *ab initio* quantum chemistry calculations (specifically Moller–Plesset and Coupled Cluster methods in Gaussian 98) to show that hydrogen bonding strengths in alcohol–water mixtures depend on which molecule serves as the proton donor and which molecule serves as the proton acceptor. Fig. 1 gives a summary of the work of Fileti et al., where the symbols E, W, and M in Fig. 1 denote ethanol, water, and methanol, respectively, and the binding energies shown are for the highest level of correlation CCSD(T) – Coupled Cluster with full Single and full Double excitations and Triple excitations by perturbation. Note that the binding energy for the EW hetero-dimer, in which ethanol is the proton donor, is roughly 21% weaker than the binding energy for WE, in which water is the proton donor. For methanol and water, the effect is slightly weaker, where the MW bond is 12% weaker than the WM bond.

In modern molecular-based equations of state, simplifying assumptions result in hydrogen-bonding strengths that often do not agree with *ab initio* findings. Accordingly, this note introduces a simple parameter estimation algorithm that incorporates *ab initio* information and results in more reasonable relative association

strengths. In the material that follows, we provide some of the background information on molecular-based equations of state and then present a computational algorithm to determine association strengths.

2. Individual site contributions to the mole fractions of un-bonded sites

Modern molecular-based equations of state are based on residual Helmholtz free energy contributions from the various system interactions. Here we focus on the interactions due to association, which are modeled by placing bonding sites on molecules to mimic areas where electron density is enhanced or depleted in the molecule. The sites interact and the fractional contributions of site–site association interactions take the form of a matrix, β_{ij} , whose elements are given by

$$\beta_{ij} = \frac{N_{Av} \rho x_i X^i X^j \Delta^{ij}}{N_{Av} \sum_{k=1}^M (x_k \rho X^k X^i \Delta^{ik})}, \quad i = 1, \dots, M; \quad j = 1, \dots, M \quad (1)$$

where N_{Av} is Avogadro's number, ρ is the system density, M is the number of total sites on all unique molecules and x_i (or x_k) is the mole fraction of that molecule in the mixture. X^i is the mole-fraction of sites i which are un-bonded while Δ^{ij} is the association strength between sites i and j . Eq. (1) can be simplified to

$$\beta_{ij} = \frac{x_i X^i X^j \Delta^{ij}}{\sum_{k=1}^M (x_k X^k X^i \Delta^{ik})}, \quad i = 1, \dots, M; \quad j = 1, \dots, M \quad (2)$$

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Nomenclature

A	Helmholtz free energy
M	total number of association sites on all unique molecules
N_{Av}	Avogadro's number
U	potential energy of hydrogen bonding (kcal/mol)
x_i	mole fraction of component i
X^i	mole fraction of sites i which are un-bonded

Greek symbol

Δ^{ij}	association strength (cm ³)
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and shows that the fractional contributions of site–site interactions to the mole fractions of un-bonded sites are independent of molar density.

3. Partitioning the residual Helmholtz free energy of association

We can also quantify the site–site contributions to the residual Helmholtz free energy of association by calculating a matrix of fractional site–site contributions, $[\alpha]$, using

$$\alpha_{ij} = \beta_{ij} \left(\frac{A_i^{\text{assoc}}}{A^{\text{assoc}}} \right) \quad (3)$$

where A_i^{assoc} is the residual Helmholtz free energy of association for site i , which can contain self- and cross associating effects and is given by

$$A_i^{\text{assoc}} = RT \{x_i [\ln(X^i) - 0.5X^i] + 0.5\} \quad (4)$$

4. Relative hydrogen bonding energies

We used Eqs. (1)–(4) to determine the relative hydrogen bonding energies for an equimolar liquid mixture of ethanol–water at 283.15 K and 1 atm using the Simplified Statistical Associating Fluid Theory (SSAFT) equation (Fu & Sandler, 1995). Note that the SSAFT approach, and all others within the SAFT family, assumes that cross association strength parameters are the same regardless of which

Table 1

A^{assoc} site–site contributions – equal and unequal association strengths.

Hydrogen bond type	Relative energy of association		
	SSAFT ^a	This work ^b	Quantum chemistry
EE self-association	13.4011	1.3053	1.2744
EW cross association	2.1016	0.9769	0.9705
WE cross association	1.4474	1.2281	1.2132
WW self-association	1.0000	1.0000	1.0000

^a Equal Δ^{ij}

^b Unequal Δ^{ij} .

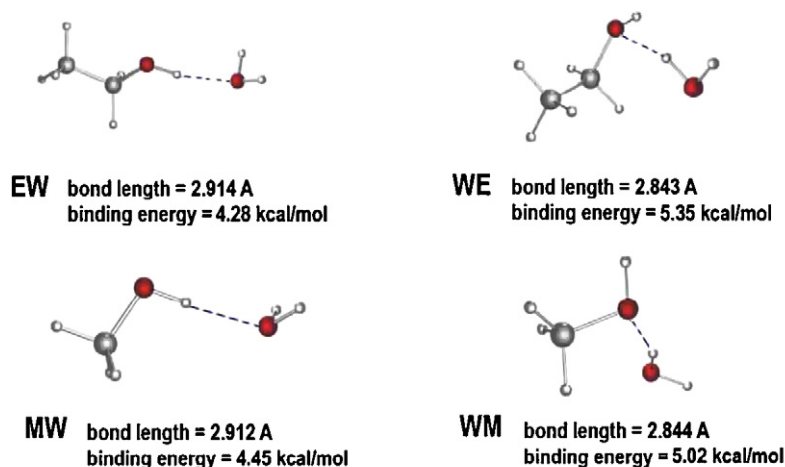
molecule acts as the proton donor and proton acceptor, which is not normally true. The resulting values for SSAFT and CCSD(T) are given in Table 1, where the results are provided relative to the WW self-association value.

It is clear that while quantum chemistry predicts the relative strengths of hydrogen bonds in the order EE, WE, WW, and EW (from strongest to weakest), the SSAFT equation predicts relative hydrogen bonding strengths in the order EE, EW, WE, and WW from strongest to weakest. SSAFT predicts a WE cross association hydrogen bond that is almost 32% weaker than EW cross association while the results in Fileti et al. (2004) show that the WE hydrogen bond is roughly 21% stronger than the EW hydrogen bond. Moreover, the hydrogen bond energy of EE self-association is too large relative to *ab initio* values.

5. A simple optimization algorithm for association strength (Δ^{ij}) parameter estimation

Given the discrepancies between *ab initio* findings and molecular-based equation of state predictions with equal association strengths, we propose a simple parameter estimation method that allows us to incorporate *ab initio* information into a molecular-based equation of state.

- (1) Given hydrogen bonding energies, U_i , for all relevant self-association and cross association from quantum chemistry, phase composition, x , and molar density, ρ (perhaps from some previous outer loop calculations that enforces phase equilibria), select a reference energy, U_{REF} , and pick values of the Δ^{ij} parameters, ensuring that any physically meaningful symmetry is exploited.



Reference: Fileti, E.E., Chaudhuri, P., Canuto, S. Relative Strength of Hydrogen Bond Interaction in Alcohol–Water Complexes. Chem. Phys. Lett. 2004, 400, 494–499.

Fig. 1. Cross association binding energies for methanol and ethanol–water.

Table 2 X^i for equimolar liquid mixture of ethanol–water at $T=283.15\text{ K}$, $P=1\text{ atm}$.

	Ethanol		Water		
	X^1	X^2	X^3	X^4	X^5
Equal strengths	0.050588	0.017145	0.681133	0.681133	0.395709
Unequal strengths	0.352360	0.023364	0.363489	0.363489	0.055975

- (2) Solve the set of M equations for the mole fractions of un-bonded sites

$$X^i = \left[1 + N_{Av} \sum_{j=1}^M (\rho_j X^j \Delta^{ij}) \right]^{-1}, \quad i = 1, \dots, M \quad (5)$$

- (3) Calculate the individual site–site interaction contributions to the X^i and A^{assoc} (i.e., the matrices $[\beta]$ and $[\alpha]$) using Eqs. (2) and (3), respectively.
- (4) Calculate *relative* hydrogen bonding energies using the information in step 3.
- (5) Calculate the norm of the error between *relative* hydrogen bonding energies from step 4 and the *relative* hydrogen bonding energies predicted by quantum chemistry.
- (a) If the error is a minimum, stop.
- (b) Else, adjust the Δ^{ij} parameters and go to step 2.

6. Illustrative example: unequal association strengths

Here we apply the proposed parameter estimation algorithm and illustrate the impact of unequal association strengths determined from quantum chemistry on the mole fractions of un-bonded sites. The Δ^{ij} parameters for an equimolar liquid mixture of ethanol–water at 283.15 K and 1 atm were fit to match relative hydrogen bonding strengths as described in the previous section, for ethanol with two association sites and water with three association sites. All sites were identified using the following numbering convention: the –H and –O, on the hydroxyl group in ethanol were designated as sites 1 and 2, respectively, while the –H, –H, and –O on water were sites 3, 4 and 5, respectively. The resulting association strength parameter values were $\Delta^{12} = 5.0265 \times 10^{-21}$ (EE), $\Delta^{15} = 1.9099 \times 10^{-21}$ (EW), $\Delta^{23} = 4.5821 \times 10^{-21}$ (WE) and $\Delta^{35} = 1.90591 \times 10^{-21}$ (WW), and have units of cm^3 . Note that the EW and WE association strengths calculated by the proposed algorithm are significantly different, whereas they are equal using the traditional approach. Table 2 shows the resulting mole fractions of un-bonded sites, X^i , using equal and unequal association strengths for both EW- and WE-type hydrogen bonds for the SSAFT equation. Note that the mole fractions of all un-bonded sites, X^i , change quite significantly when unequal association strengths are used. Ethanol donates considerably fewer protons while water donates more pro-

tons to hydrogen bonds, so there is a marked redistribution of the proton donors and receptors between ethanol and water.

We draw the reader's attention back to Table 1, which gives site–site contributions to association for equal and unequal association strengths. Note that when the Δ^{ij} parameters are determined by fitting the relative hydrogen bonding energies to those predicted by quantum chemistry, as proposed in this note, the correct order of relative bond energies is obtained and, in particular, the EW bond is calculated to be 25% weaker than the WE bond – close to the 21% given in Fileti et al. (2004). Moreover, these calculations also show that the WW and EW relative hydrogen bonding energies are close – as given in Fileti et al. We have obtained similar results for a number of other binary mixtures including methanol–water, hydrogen fluoride–water, butanol–water, and lysophosphatidic acid–water.

7. Conclusions

A new parameter estimation approach that eliminates the need for equal association strengths in molecular-based equations of state was presented. Optimization calculations were used to directly fit the Δ^{ij} parameters so that hydrogen bonding energies more correctly reflect *relative* hydrogen bonding energies predicted by *ab initio* quantum chemistry with respect to a given reference hydrogen bonding energy. Preliminary numerical results using the SSAFT equation show that the proposed parameter estimation methodology and the resulting unequal association strengths often give a widely different distribution of the mole fractions of un-bonded association sites. Additionally, we remark that traditional parameter estimation, which fits parameters to saturated vapor pressure and liquid density data, has the unfortunate consequence of lumping physical effects. In our opinion, this note paves the way for the reliable determination of equation of state parameters from *ab initio* quantum chemistry since association parameters (i.e., the Δ^{ij} parameters) are determined directly from only hydrogen bonding effects and thus reflect only association.

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