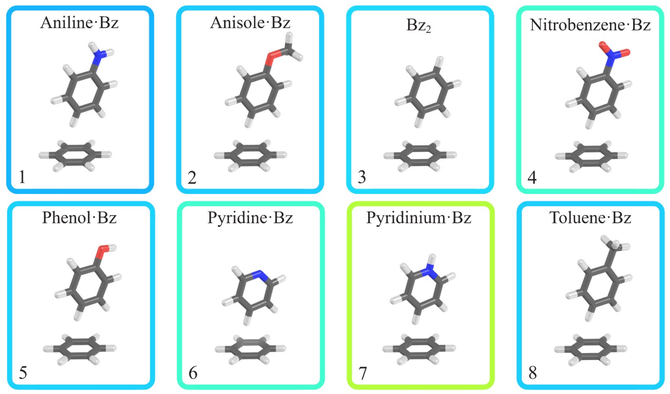
Effect of Implicit Solvation on Solute-Solute Interaction Strengths

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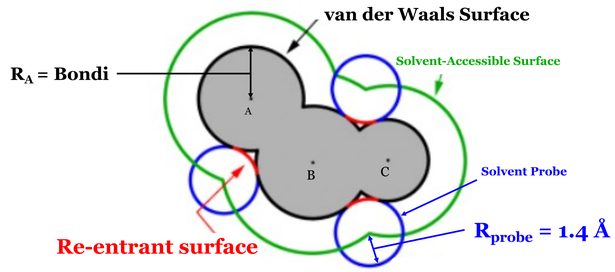
Test Set



Structure Preparation[1] in Psi4	
Optimization	Enforced C_s symmetry @ T-shaped Bz_2 Geometry
Method[2-4]	B3LYP-D3M(BJ)/aug-cc-pVDZ

Solvent Method

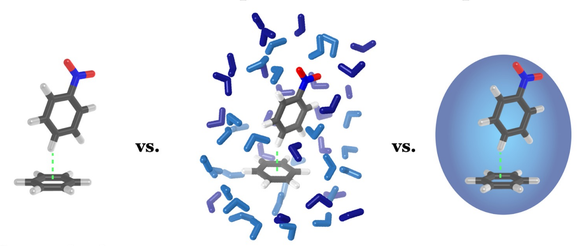
Conductor-like Polarizable Continuum Model (C-PCM)	
Solute Cavity Surface	Unionized, atom-centered van der Waals spheres
Solute Cavity Radii	$\alpha_{vdW} R_{vdW,A} + R_{probe}$ (α_{vdW} = 1.0 if R_{probe} parameter is used) + ... + ...
Surface Discretization Grid	SG-1
Boundary	Switching/Gaussian (SWIG)
Dielectric Water Constant	80.1



Adapted from Fig. 1.a of Ref. 5

Project Focus

Gas Phase vs. **Explicit Solvent** vs. **Implicit Solvent**



Supramolecular Approach:

$IE_{gas} = E_{AB} - E_A - E_B$

Embedded Dimer w/ ISAPT:

$IE_{explicit} = E_{elst} + E_{exch} + E_{ind} + E_{disp}$

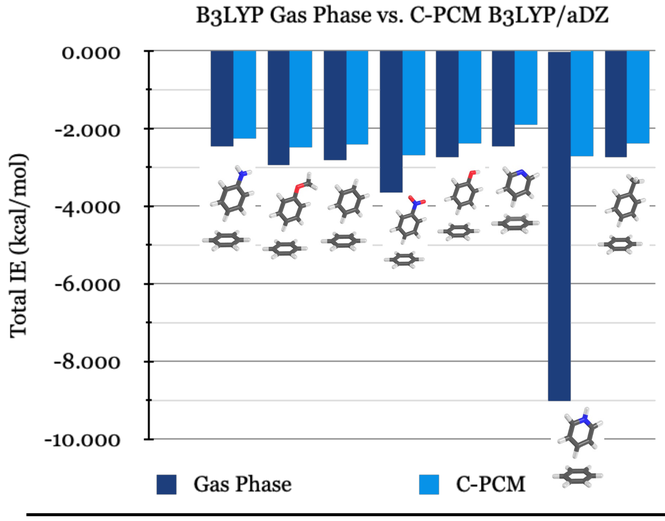
What's the "right" approach?

$IE_{PCM} = ?$

Objectives
Quantify the B3LYP gas phase interaction energy between two molecules
Quantify the C-PCM B3LYP/aDZ interaction energy between two molecules
Analyze the influence of an implicit aqueous environment on interaction energy between two molecules
Determine the utility of C-PCM as a solvent environment

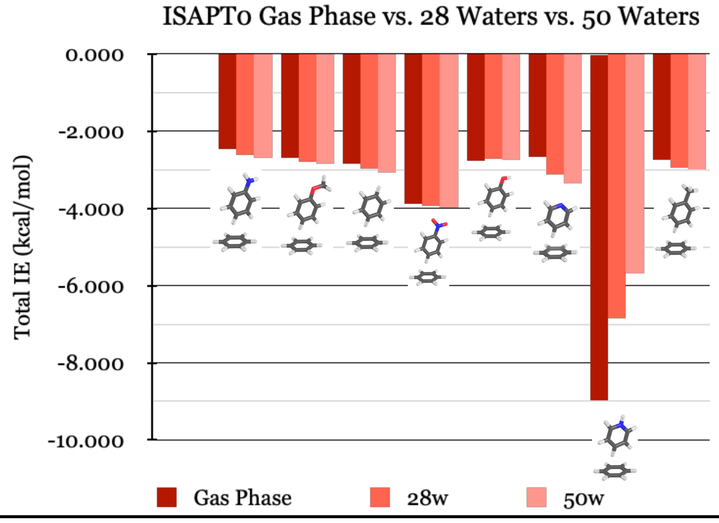
Implicit Aqueous Environment

B3LYP-D3M(BJ)/aug-cc-pVDZ Interaction Energies (kcal/mol) w/ Counterpoise Correction			
	Gas	C-PCM Water	W - G
Aniline-Bz	-2.465	-2.26	0.20
Anisole-Bz	-2.940	-2.49	0.45
Benzene-Bz	-2.821	-2.42	0.40
Nitrobenzene-Bz	-3.639	-2.69	0.95
Phenol-Bz	-2.738	-2.39	0.35
Pyridine-Bz	-2.469	-1.91	0.56
Pyridinium-Bz	-9.010	-2.70	6.31
Toluene-Bz	-2.734	-2.39	0.34



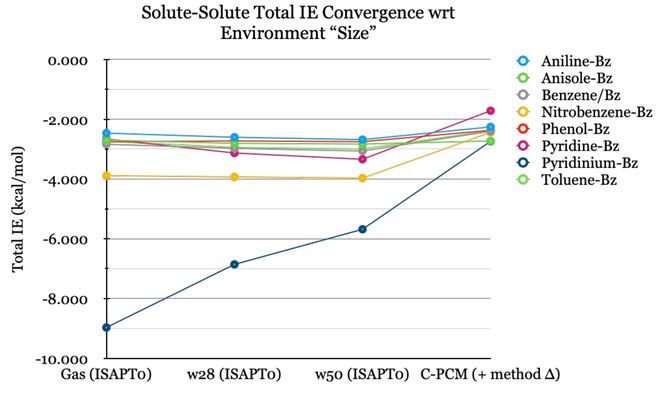
Explicit Aqueous Environment

(F-I)SAPTo/jun-cc-pVDZ Interaction Energies (kcal/mol)					
	Gas	(H2O)28	28W - G	(H2O)50	50W - G
Aniline-Bz	-2.466	-2.604	-0.138	-2.683	-0.217
Anisole-Bz	-2.701	-2.805	-0.104	-2.833	-0.132
Benzene-Bz	-2.838	-2.976	-0.138	-3.064	-0.226
Nitrobenzene-Bz	-3.888	-3.933	-0.045	-3.972	-0.084
Phenol-Bz	-2.756	-2.726	-0.030	-2.752	-0.004
Pyridine-Bz	-2.662	-3.131	-0.469	-3.341	-0.679
Pyridinium-Bz	-8.972	-6.859	2.113	-5.684	3.288
Toluene-Bz	-2.739	-2.944	-0.205	-2.998	-0.259



Conclusions

Solute-Solute IE (kcal/mol) Convergence wrt Environment "Size"			
Gas (SAPTo)	$(H_2O)_{28}$ (ISAPTo)	$(H_2O)_{50}$ (ISAPTo)	C-PCM (+ method Δ)
-2.466	-2.604	-2.683	-2.259
-2.701	-2.805	-2.833	-2.729
-2.838	-2.976	-3.064	-2.403
-3.888	-3.933	-3.972	-2.441
-2.756	-2.726	-2.752	-2.372
-2.662	-3.131	-3.341	-1.717
-8.972	-6.859	-5.684	-2.740
-2.739	-2.944	-2.998	-2.385



References:

1. D. Sirianni, X. Zhu, D. Sitkoff, et al., *J. Chem, Phys.* 156, 194306 (2020).
2. S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* 132, 154104 (2010).
3. S. Grimme, S. Ehrlich, and L Goerigk, *J. Comput. Chem.* 3≠2, 1456 (2011).
4. E. R. Johnson and A. D. Becke, *J. Chem. Phys.* 123, 024101 (2005).
5. A. W. Lange, J. M. Herbert, B. J. Albrecht, and Z.-Q. You, *Mol. Phys.* 118, e1644384 (2020)

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