### Quantum Monte Carlo studies of water clusters and water-acene complexes



Michael Deible 2 August 2013







# Graphene, graphite, CNT, etc. etc. etc.

- Calculating the water-graphene interaction can be done with two methods:
  - Interaction of a water on a graphene sheet in a periodic box.
  - Extrapolation of cluster results to a graphene limit.
- Gradually increasing acenes are an excellent test system because of the major role of weak interactions, and the ability to extrapolate to a graphene limit.
- These interactions are also applicable to other conjugated carbon systems of chemical and biological significance



### Under the hood - water-acenes

- O-H =0.9572 Å, H-O-H = 104.5°, C-C = 1.42 Å, C-H = 1.09 Å, C-C-C = 120°, R = 3.36 Å
- HF trial wave function, generated in Gaussian 09.
- VMC and DMC done with CASINO
- Variance minimization used to optimize 101 parameters.
  - 16 u (uu=dd/ud plus cutoff)
  - 10 chi per atom type, plus cutoffs
  - 16 f per atom type, plus cutoffs
- DMC times steps of 0.005, 0.007, 0.01 a.u.
- T-move, 30,000 80,0000 walkers.
- Trail-Needs pseudopotentials and basis sets of Xu. et al<sup>a</sup> used for H, O, and C.
  - 5*z sp* functions, DZ *p* for H, *d* for O, with 1.5*x* most diffuse p or d function.
- MP2, SAPT, and CASPT2 done in MOLPRO
- RPA calculations performed with FHI AIMS.

a. Xu, J.; Deible, M. J.; Peterson, K. A.; Jordan, K. D. Correlation Consisten Gaussian Basis Sets for H, B-Ne with Dirac-Fock AREP Pseudopotentials: Applications in Quantum Monte Carlo Calculations *J. Chem. Theory Comp.* **2013**, *9*, 2170-2178

### Comparison to other ab initio methods

	DMC, Dt=0 ("scaled")	DF-MP2 (AVTZ)	DF-DFT- SAPT (AVTZ)	CCSD(T)
Benzene water	-3.35(20)	-3.22	-3.20	-3.17 <sup>a</sup>
Anthracene water	-3.06(30)	-3.64	-3.34	-3.33 <sup>a</sup>
Triphenylene water	-2.4(4)	-3.60	-3.15	-
Corronene water	-2.3(6)	-3.64	-3.05	-3.30 <sup>b</sup>

## QMC approximations: Basis set, orbitals, pseudopotentials, time step

	GTO, HF, T-move Dt=0	GTO, LDA, T-move Dt=0	Blip, LDA, T-move Dt=0	Blip, LDA, LA Dt=0.0125
Benzene water	-3.35(20)	-3.03(26)	-2.81(27)	-2.86(7) <sup>a</sup>
Anthracene water	-3.06(30)	-3.19(44)	-	-
Triphenylene water	-2.4(4)	-2.28(53)	-	-
Corronene water	-2.3(6)	-	-	-2.23(17)

Note: All GTO basis sets use the basis sets of Xu et al. All b-splines use a plane wave basis cut off of 300 Ry. and a natural grid spacing of  $\pi/G_{max}$ 

# Effect of Locality approximation

To test the effect of the error caused by the LA on the coronene-water system, three different Jastrow factors were used:

- 1. JF optimized at the binding energy minimum, and used for the long distance configuration: -3.42(19)
- 2. JF optimized at the binding energy minimum, and at the long distance configuration: -2.23(17)
- 3. Improved JF for the binding energy minimum, where the 6 carbons around the water were treated differently than the other carbons, and fully optimized the JF at each configuration: -2.94(28)







# Effect of a multiconfigurational ground state?

- The HOMO-LUMO gap decreases as a linear acene chain grows<sup>a</sup>.
- Theoretical studies have argued for<sup>b</sup> and against<sup>c</sup> a multiconfigurational ground state for linear acenes longer than six rings.
- It's not entirely clear what this effect on weak interactions COULD be.



Linear acene HOMO-LUMO gap

a. Jenness, G; Karalti, O; Al-Saidi, W.A.; Jordan, K. *J. Phys Chem A*, **115**, 5955 (2011)
b. Hachmann, J.; Dorando, J. J.; Avil, M.; Chan, G. K. *J. Chem. Phys.* **2008** *12*7 134309.
c. Hajgató, B.; Szieberth, D.; Geerlings, P.; De Proft, F.; Deleuze, M. S. *J. Chem. Phys.* **2009** *131* 224321

### Effect of a multiconfigurational ground state?





	DMC, Dt=0 ("scaled")	RPA/PBE (tier 3)	RPA-s/PBE (tier 3)	CASPT2 (AVTZ)
Benzene water	-3.35(20)	-2.50 <sup>a</sup>	-2.90	-3.24
Anthracene water	-3.06(30)	-2.70 <sup>a</sup>	-	-3.71
Triphenylene water	-2.4(4)	-	-	-3.35
Corronene water	-2.3(6)	-2.50	-3.00	-

### Conclusions

- Many of the approximations in DMC can still give reproducible binding energies for water acene systems
- The exact reason for DMC tends to under bind larger acenes compared to other *ab initio* methods remains unclear.

### Water clusters: past and present

- The dissociation energy of water clusters offers a unique benchmark for comparing ab inito, DFT, and empirical force field results.
- Dissociation energies of clusters of various sizes have been found using a wide range of methods:
  - Wave function methods: MP2, CCSD(T)
  - DFT methods: various functionals, dispersion corrections
  - Quantum Monte Carlo methods: DMC
  - Many body decomposition methods



### 4444-a

- This cluster does not exist in any of the ices, but can exist inside of a (14,0) carbon nanotube.
- Several recent studies have calculated the binding energy of this water-16 cluster.
- CCSD(T) / aug-cc-pVTZ calculations were performed<sup>a</sup>.
- N-body decomposition procedures have also been used<sup>b</sup>.
- DMC can be used to compare these methods and along with CBS limit MP2 calculations.



### 4444-a – Something interesting



c. Leverentz, H. R.; Qi, H. W.; Truhlar, D. G. J. Chem. Theory Comp. 2013, 9, 995-1007.

### Many-Body Interaction Energies (kcal/mol)

Current Study			/	et al.	
Contribution	HF	MP2	CCSD(T)	MP2	CCSD(T)
one-body	17.56	7.12	7.10	7.53	7.42
two-body	-74.66	-133.95	-134.67	-134.37	-136.93
three-body	-34.41	-34.12	-32.17	-33.89	-32.42
four-body	-0.73	-0.89		-0.92	(-0.92)
five-body	0.38	0.38?			
N ≥ 6	-1.08	-2.7			
net	-92.94	-161.84		-161.65	-162.85

# Many-Body Interaction Energies (kcal/mol)



· A test of the extrapolation procedure:

- Extrapolate the MP2 and CCSD(T) dimer binding energies with two points (ATZ,AQZ) and with three points (ATZ, AQZ, A5Z)
- Three point extrapolated energies are very close to the VQZ-F12 results
- For MP2, the dimer binding energy is the same for the two and three point extrapolation.
- For CCSD(T), the dimer binding energy is about 0.05 kcal/mol larger when a two point extrapolation is used then when a three point extrapolation is used.

	Under	<sup>r</sup> estimate			
Contrib	ution	CCSD(T)	AMOEBAª	TTM3-F <sup>♭</sup>	<b>WHBB</b> <sup>c</sup>
one-bod	у	7.10	8.85	7.52	7.50
two-body	У	-134.67	-130.20	-147.83	-134.00
three-bo	dy	-32.17	<b>,</b> -36.63	-20.48	-32.65
four-bod	У		, -2.72	-0.83	-0.83
five-body	у		0.87	0.28	0.28
N ≥ 6			-0.17	-0.02	-0.02
net			-159.99	-161.36	-159.74
	Ove	r estimate			

Over estimate

Contribution	CCSD(T)	<b>AMOEBA</b> <sup>a</sup>	TTM3-F <sup>b</sup>	<b>WHBB</b> <sup>c</sup>
one-body	7.10	8.85	7.52 🗸	7.50
two-body	-134.67	-130.20	-147.83	-134.00
three-body	-32.17	-36.63	<u>,</u> 20.48	-32.65
four-body		-2.72	/ -0.83	-0.83
five-body		0.87	0.28	0.28
N ≥ 6		-0.17	-0.02	-0.02
net		-159.99	-161.36	-159.74
	Under	restimate		Sneaky!

a. Ren, P.; Ponder, J. W. *J. Phys. Chem. B* 2003, *107*, 5933-5947.
b. Fanourgakis, G. S.; Xantheas, S. S. *J. Chem. Phys.* 2008, *128*, 074506:1-11.
c. Wang, Y.; Huang, X.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. *J. Chem. Phys.* 2011, *134*, 094509:1-12

Contribution	CCSD(T)	<b>AMOEBA</b> <sup>a</sup>	TTM3-F <sup>ь</sup>	<b>WHBB</b> <sup>c</sup>	
one-body	7.10	8.85	7.52	7.50 Patridge-Schwenke	è
two-body	-134.67	-130.20	-147.83	-134.00 Fit to CCSD(T)/AVT	ΓZ
three-body	-32.17	-36.63	-20.48	-32.65number of	
four-body		-2.72	-0.83	-0.83	
five-body		0.87	0.28	0.28	
N ≥ 6		-0.17	<del>,</del> 0.02	-0.02	
net		-159.99	-161.36	-159.74	
		Negli	gible?		

a. Ren, P.; Ponder, J. W. J. Phys. Chem. B 2003, 107, 5933-5947.
b. Fanourgakis, G. S.; Xantheas, S. S. J. Chem. Phys. 2008, 128, 074506:1-11.
c. Wang, Y.; Huang, X.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. J. Chem. Phys. 2011, 134, 094509:1-12

Contribution	CCSD(T)	<b>AMOEBA</b> <sup>a</sup>	TTM3-F <sup>b</sup>	<b>WHBB</b> <sup>c</sup>	[
one-body	7.10	8.85	7.52	ך 7.50	Total= -159.15 kcal/mol_1_2
two-body	-134.67	-130.20	-147.83	-134.00	kcal/mol less
three-body	-32.71	-36.63	-20.48	-32.65	than CCSD(T)
four-body	(-0.73)	-2.72	-0.83	-0.83	contribution.
five-body		0.87	0.28	0.28	
N ≥ 6		-0.17	-0.02	-0.02	
net	160.28	-159.99	-161.36	-159.74	

A study of ten tetramers from 4444-a indicate that CCSD(T)-F12b/VTZ-F12 interaction energies are more negative than MP2-F12/VTZ-F12 interaction energies, with the largest value being 0.005 kcal/mol.

Thus, CCSD(T) four-body energies could be a few tenths of a kcal/mol larger than the corresponding MP2 results, but the five- and higher-body contributions are the major cause of deviation in the net interaction energy.

### Under the hood - 4444-a

- B3LYP trial wave function, generated in Gaussian 09.
- VMC and DMC done with CASINO
- Variance minimization used to optimize 65 parameters.
  - 16 u (uu=dd/ud plus cutoff)
  - 6 chi per atom type, plus cutoffs
  - 16 f per atom type, plus cutoffs
- DMC times steps of 0.0025, 0.005, 0.0075 a.u.
- T-move, 50,000 walkers.
- Trail-Needs pseudopotentials and basis sets of Xu. et al<sup>a</sup> used for H and O.
  - 5z sp functions, TZ p for H, d for O, with 1.5x most diffuse p or d function.
- MP2 done in MOLPRO
- Extrapolation method of Feller, used for the HF energy and Helgaker for the correlation energy.

 $E_{\text{int}}^{HF}(X) = E_{\text{int}}^{HF}(CBS) + Ae^{-\alpha}X$ 

 $E_{\text{int}}^{corr}(X) = E_{\text{int}}^{corr}(X)(CBS) + BX^{-3}$ 

a. Xu, J.; Deible, M. J.; Peterson, K. A.; Jordan, K. D. J. Chem. Theory Comp. 2013, 9, 2170-2178

	MOD-V3 – "scaled"									
				Initial ti	me step measu	rements				
			Short			Long				
	Dt=0 (a.u.)	Chi	Slope (a.u./a.u.)			Dt=0 (a.u.)	Chi	Slope (a.u./a.u.)		E int (Kcal / mol)
Benzene water	-54.8204 <mark>(</mark> 2)	0.0472	-0.1691			-54.8151 <b>(</b> 2)	0.3328	-0.1822		-3.35(18)
Anthracene water	-102.5673(4)	0.4913	-0.3189			-102.5624(3)	0.2732	-0.3389		-3.07(31)
Triphenylene water	-126.4554(4)	1.9346	-0.3045			-126.4515(5)	0.2801	-0.3298		-2.45(40)
TPW-LDA	-126.4786(6)	0.0427	0.3335			-126.4750(6)	0.3567	0.2412		-2.26(53)
Corronene water	-160.5274(5)	1.6393	-0.3243			-160.5240(4)	10.6173	-0.2985		-2.14(40)
	SCF energy	VMC energy (w/o JF)	VMC energy (w/ JF)	variance	VMC improv	SCF energy	VMC energy (w/o JF)	VMC energy (w/ JF)	variance	VMC improv
Benzene water	-53.4464	-53.453(9)	-54.692(3)	0.90(3)	1.2456	-53.4449	-53.44(1)	-54.702(3)	0.86(1)	1.2571
Anthracene water	-99.8228	-99.814(8)	-102.323(2)	1.67(2)	2.5002	-99.8217	-99.801(8)	-102.310(2)	1.67(2)	2.4883
Triphenylene water	-123.0237	-123.023(9)	-126.126(3)	2.08(1)	3.1023	-123.0232	-123.031(9)	-126.142(3)	2.03(1)	3.1188
TPW-LDA	-126.0222	-122.907(9)	-126.139(3)	2.02(1)	0.1168	-126.0154	-122.920(9)	-126.167(3)	2.00(1)	0.1516
Corronene water	- <mark>156.131</mark> 9	-156.14(1)	-160.090(4)	2.75(3)	3.9581	-156.1317	-156.14(1)	-160.090(4)	2.69(2)	3.9583

MOD-V3 – "scaled"								
E int at each time step								
Slope (kcal/mol/a.u Dt=0 DF-DFT- Chi .) (Kcal/mol) SAPT (AVTZ								
Benzene water	0.3233	8.3647	-3.35(20)	-3.20				
Anthracene water	0.0291	10.5869	-3.06 <b>(</b> 30)	-3.34				
Triphenylene water	1.8396	14.0011	-2.4(4)	-3.15				
TPW-LDA	0.3300	60.3155	-2.3(6)	-3.15				
Corronene water	1.2642	-17.7998	-2.1(4)	-3.05*				

	Anthracene-water (C2V)		Triphenyler (C1	ne-water )	Coronene-Water (C1)	
LUMO+1	0.0850	A1	0.0661	A	0.0442	Α
LUMO	0.0310	A1	0.0653	A	0.0440	Α
HOMO	-0.2533	B2	-0.2871	А	-0.2587	Α
HOMO-1	-0.3247	B1	-0.2876	Α	-0.2587	Α

#### SAPT decomposition (Kcal/mol)

	Benzene	anthracene	triphenylene	coronene
E1pol	-2.85	-2.29	-1.86	-1.73
E1exch	3.24	2.85	2.76	2.79
E2ind	-1.28	-1.22	-1.27	-1.29
E2ind-exch	0.82	0.76	0.78	0.8
DHF	-0.26	-0.21	-0.21	-0.2
Net induction	-0.71	-0.67	-0.70	-0.69
E2disp	-3.28	-3.66	-3.77	-3.83
E2disp-exch	0.44	0.43	0.42	0.42
Net dispersion	-2.84	-3.23	-3.35	-3.42
total interaction				
energy	-3.16	-3.34	-3.15	-3.05









