High Accuracy Fragment Methodologies

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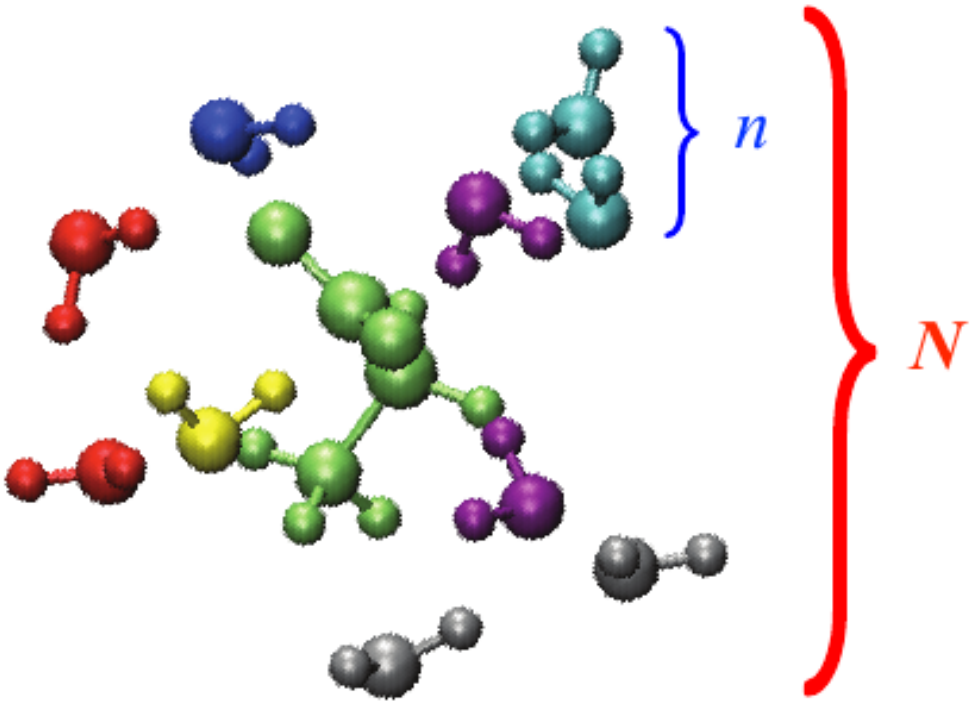
Fragment Methodologies

- ***Ab initio* methods scale non-linearly with system size**
- **Electronic matter is "near-sighted"**
  - **W. Kohn Phys. Rev. Lett. 1996**
- **Exploit this to reduce *N* to *n***



$$\mathcal{O}(N^p) \rightarrow N_{\text{frag}} \times \mathcal{O}(n^p)$$

History

- **Reviews and classifications:**
  - **Gordon et al., Chem. Rev. 112, 632 (2011)**
  - **Richard & Herbert, J. Chem. Phys. 137, 064113 (2012)**
- **There are a lot of fragment-based methods in the literature. An incomplete list:**
  - **Many-body expansion of the correlation energy (Stoll & Preuß, 1977)**
  - **Fragment Molecular Orbital (FMO) method (Kitaura, Fedorov et al., 1999)**
  - **Molecular Fractionation with Conjugated Caps (MFCC) (Zhang et al., 2003)**
  - **Multicentered QM:QM Method (Tschumper et al., 2003)**
  - **Kernel Energy Method (KEM) (Huang, Massa et al., 2004)**
  - **Systematic Molecular Fragmentation (SMF) method (Collins et al., 2005)**
  - **Binary and Ternary Interaction Method (Hirata et al., 2005)**
  - **Cardinality-Guided Molecular Tailoring Approach (CG-MTA) (Gadre et al., 2006)**
  - **SCF for Molecular Interactions (SCF-MI) (Head-Gordon et al., 2006)**
  - **Electrostatically-Embedded Many-Body (EE-MB) expansion (Truhlar et al., 2007)**
  - **Generalized Energy-Based Fragmentation (GEBF) method (Li et al., 2007)**
  - **Hybrid Many-Body Interaction (HMBI) method (Beran et al., 2009)**
  - **Molecules-in-Molecules (MIM) method (Raghavachari et al., 2011)**
  - **Variational Many-Body Expansion (Gao et al., 2012)**

Many-Body Expansion (MBE)

- **Possible to exactly expand the supersystem energy in terms of:**
  - **Fragment energies**
  - **Fragment interactions**

$$E_0 = \sum_{I=1}^{N} E_I + \sum_{I<J}^{{}_N C_2} \Delta E_{IJ} + \sum_{I<J<K}^{{}_N C_3} \Delta E_{IJK} + \cdots + \Delta E_{IJK\cdots N}$$

$$\Delta E_{IJ} \equiv E_{IJ} - E_I - E_J$$

$$\Delta E_{IJK} \equiv E_{IJK} - \Delta E_{IJ} - \Delta E_{IK} - \Delta E_{JK} - E_I - E_J - E_K$$

MBE Cont.

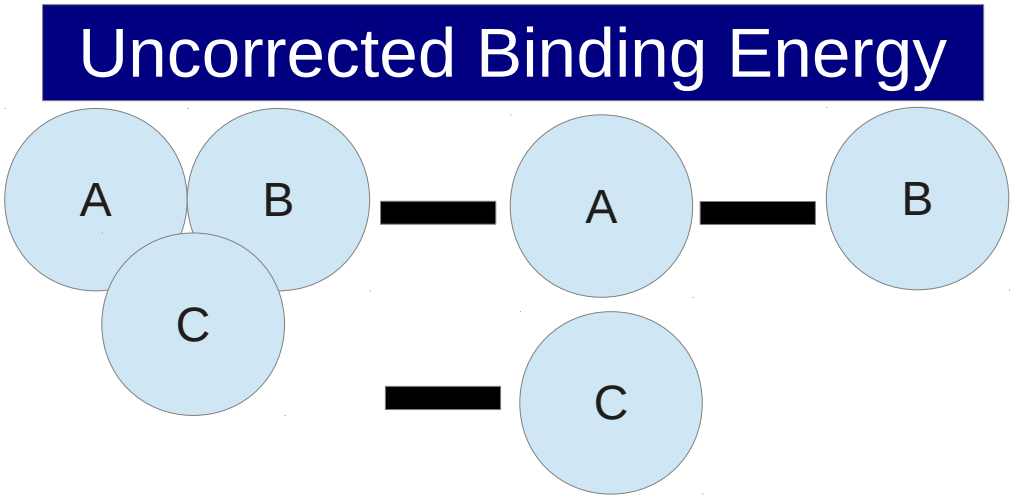
- **The MBE is:**
  - **Capable of chemical accuracy**
  - **Systematically improvable**
  - **“Embarrassingly parallel”**
- **Faster convergence if we include intersections**
  - **Adds (n+1)-body terms at n-body level**
    - Richard & Herbert, JCP 137, 064113 (2012)
    - Richard & Herbert, JCTC 9, 1408 (2013)

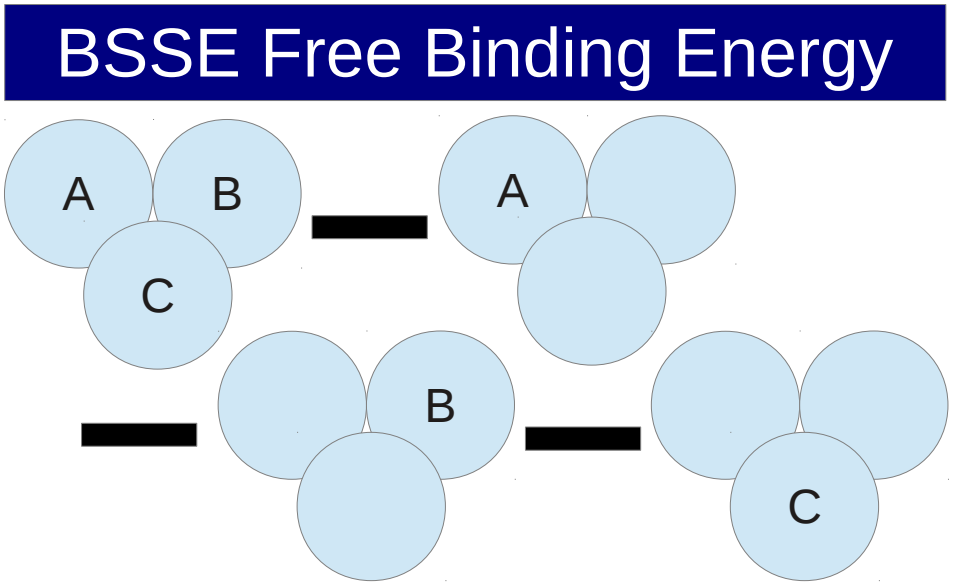
MBE cont.

- **Currently limit ourselves to MBE**
- **Past MBE studies:**
  - **Replicate supersystem properties**
  - **Double ζ basis sets**
- **Current Goal:**
  - **Experimental and/or high accuracy benchmarks**
    - **Approximate CCSD(T)/CBS**
      - **Basis-set superposition error (BSSE) is a problem**
      - **Slow convergence to CBS limit**

Counterpoise (CP) Correction

- **BSSE is corrected by the CP correction**
  - **Boys & Bernardi J. Mol. Phys. 1970**
  - **Corrections use the full basis-set**
    - ***N* monomers need *N+1* full basis calculations**





Many-Body CP method [MBCPn]

- **Motivation: decrease time of a CP correction:**
  - **Fragment the CP corrections**
    - **Fragment the ghost atom + real system**
  - **Many MBE terms are 0**
    - **Consist of only ghost atoms**
  - **Embarrassingly parallel**

MBCP(n)

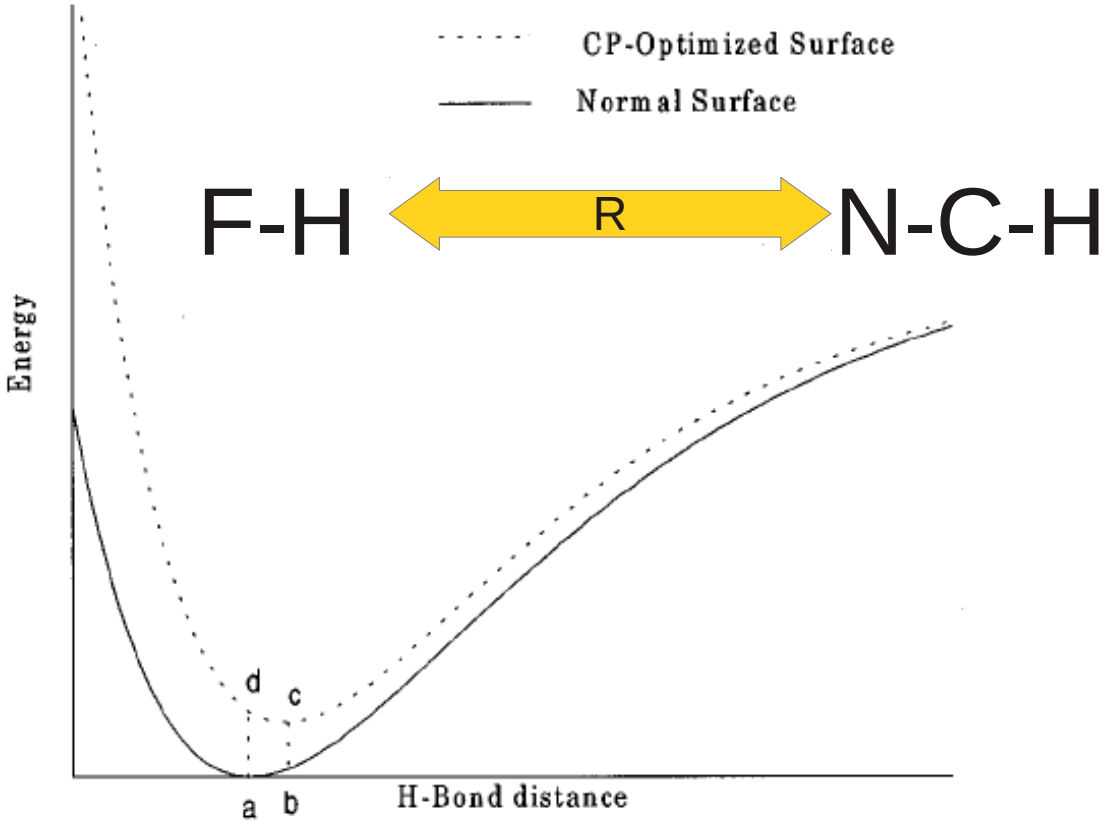
$$\Delta E_I^{(2)} = -(N-1)E_I^I + \sum_{J\neq I}^{N} E_I^{IJ}$$

$$\Delta E_I^{(3)} = \tfrac{1}{2}N(N-1)E_I^I - (N-2)\sum_{J\neq I}^{N} E_I^{IJ} + \sum_{J\neq I}^{N}\sum_{\substack{K<J \\ K\neq I}}^{N} E_I^{IJK} \ .$$

- **Advantages:**
  - **No full system basis-sets**
  - **Easily extends to higher orders**

Relevance to Spectroscopy

- Accurate spectra require accurate potential energy surfaces
  - Simon et al. JCP 105(1996) 11024

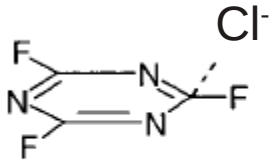


Relevance Cont.

- Zero Point Energies
  - Mascal et al. JACS 124 (2002) 6274

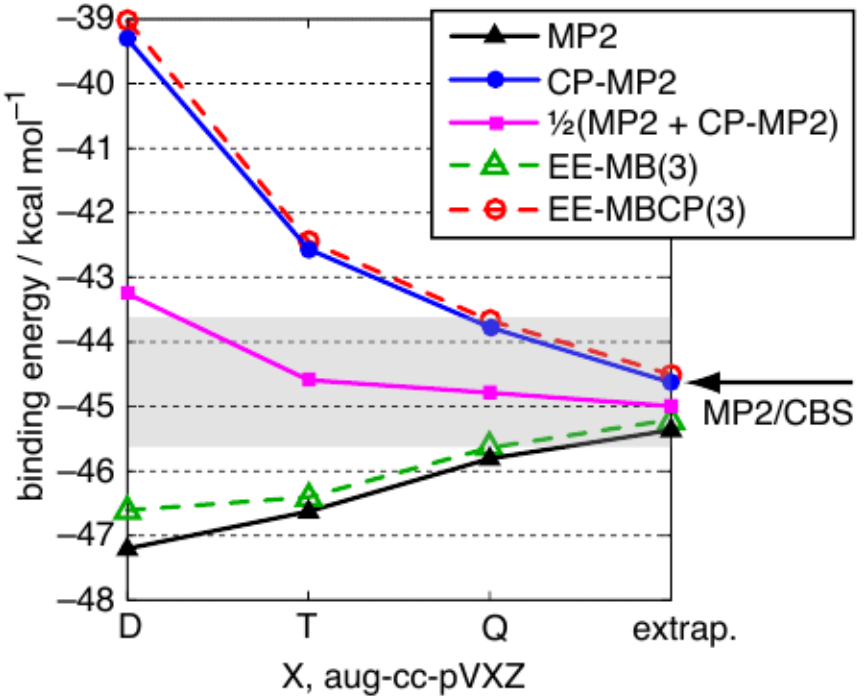
species	$E_{(MP2+ZPE)}$	$E_{(MP2+ZPE-BSSE)}$
triazine + chloride π (**3a**)	−8.3	−4.8
triazine + fluoride π (**3b**)	−12.1[b]	−9.2
triazine + azide π (**3c**)	−7.6	−4.5
triazine + fluoride "attack" (**5b**)	−25.0	−18.5
triazine + azide "attack" (**5c**)	−9.0	−5.9
triazine + chloride H-bond (**7a**)	−9.6	−7.4
triazine + fluoride H-bond (**7b**)	−18.4	−16.5
triazine + azide H-bond (**7c**)	−8.0	−6.5
triazine + azide "stack" (**8**)	−10.6	−6.4
F_3triazine + chloride π (**4a**)	−19.7	−14.8
F_3triazine + fluoride π (**4b**)	−27.7[b]	−24.0
F_3triazine + azide π (**4c**)	−17.9	−13.9
F_3triazine + chloride "attack" (**6a**)	−22.1	−11.1
F_3triazine + fluoride "attack" (**6b**)	−56.1	−48.8
F_3triazine + azide "attack" (**6c**)	−27.0	−17.5
F_3triazine + azide "stack" (**9**)	−20.0	−14.3

11 kcal/mol

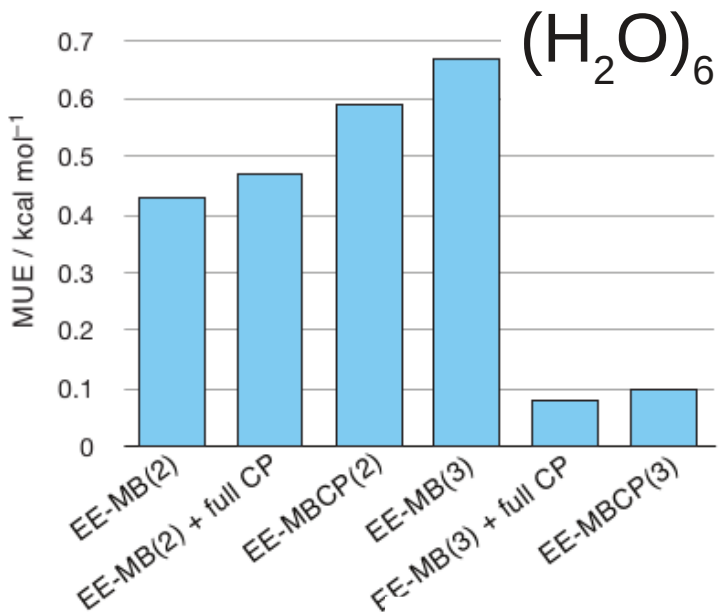


Results

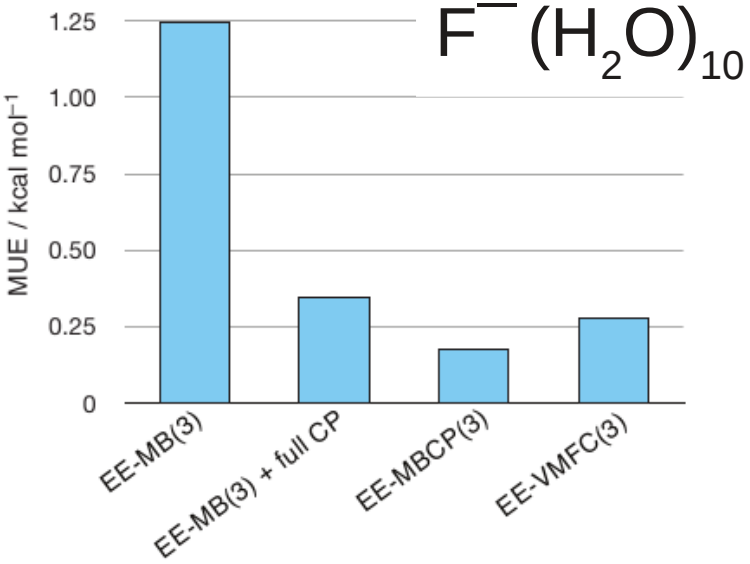
- **$(H_2O)_6$ is a well studied system**
  - **8 structures**
  - **MP2-R12/CBS & CCSD(T)/CBS**
    - **Bates & Tschumper J Phys. Chem. A (2009)**



Results Cont.



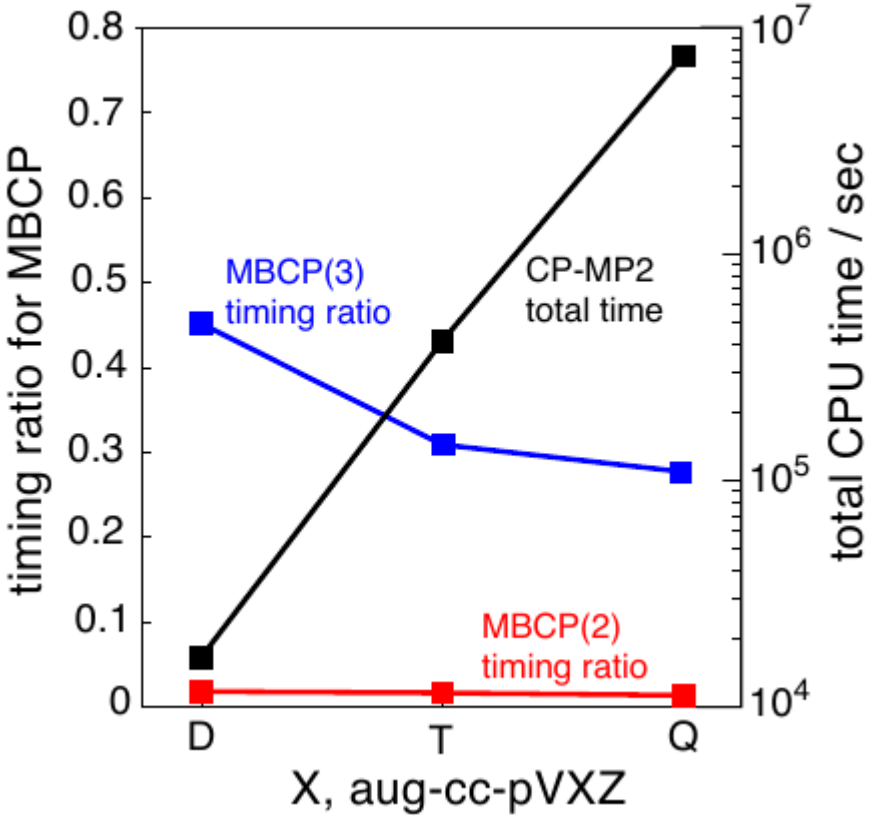
- **CP & MBCP(2) differ by ~0.1 kcal/mol**
- **CP & MBCP(3) negligibly different**



- **CP & MBCP(2) differ by ~0.6 kcal/mol**
- **CP & MBCP(3) differ by ~0.2 kcal/mol**

Results Cont.

- **Time for $F^-(H_2O)_{10}$**
- **Full CP ~100 days**
- **MBCP(3) ~1/3 time for quad ζ**
  - **0.2 kcal/mol error**
- **MBCP(2) <10%**
  - **0.6 kcal/mol error**



Triples Corrections

- **Triples correction using haTZ**
  - **aug-cc-pVTZ on O**
  - **cc-pVTZ on H**
- **2B: <0.1 kcal/mol**
- **3B: nearly exact**

Isomer	$\delta_{\mathrm{CCSD(T)}}$ [b]	error[c]	
		EE-MB(2)	EE-MB(3)
Bag	0.33	−0.08	0.00
Boat1	0.53	0.04	0.01
Boat2	0.51	0.04	0.01
Book1	0.33	−0.04	0.00
Book2	0.33	−0.04	0.01
Cage	0.13	−0.20	0.00
Cyclic	0.53	0.05	0.01
Prism	−0.06	−0.20	0.00
MUE[d]	—	0.09	0.00

Conclusions

- **Introduced an approximate CP correction**
  - **MBCP(n)**
  - **No full basis calculations required**
  - **Accuracy can be increase by increasing *n***
  - ***n*=3 truncation accuracy:**
    - **Water hexamer: almost same as full CP**
    - **Fluoride cluster: < 0.2 kcal/mol error**
- **Fragment methods are capable of chemical accuracy!!!**

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