Big Electronic Structure Computations for Small Hydrated Anions

ScotCHEM 2018
Computational Chemistry Symposium

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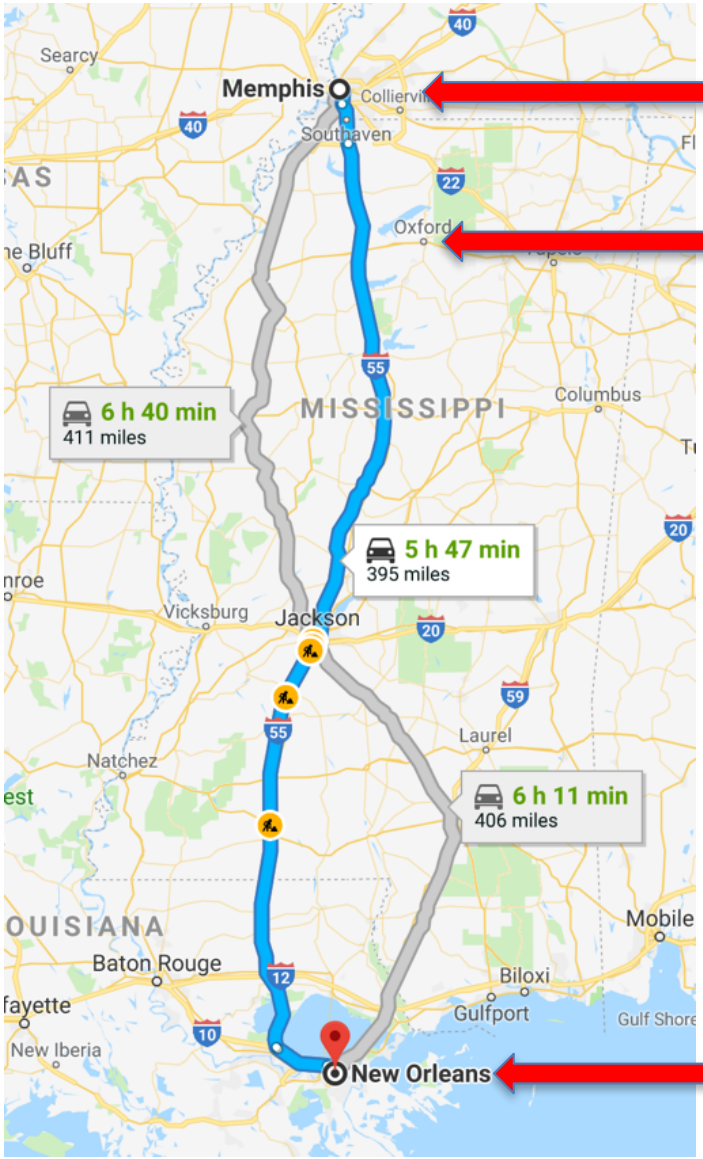
Chemistry and Biochemistry

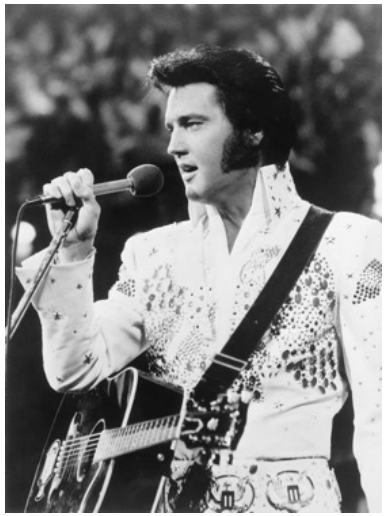
University of Mississippi

The "Other" Oxford



Memphis, TN

Oxford, MS



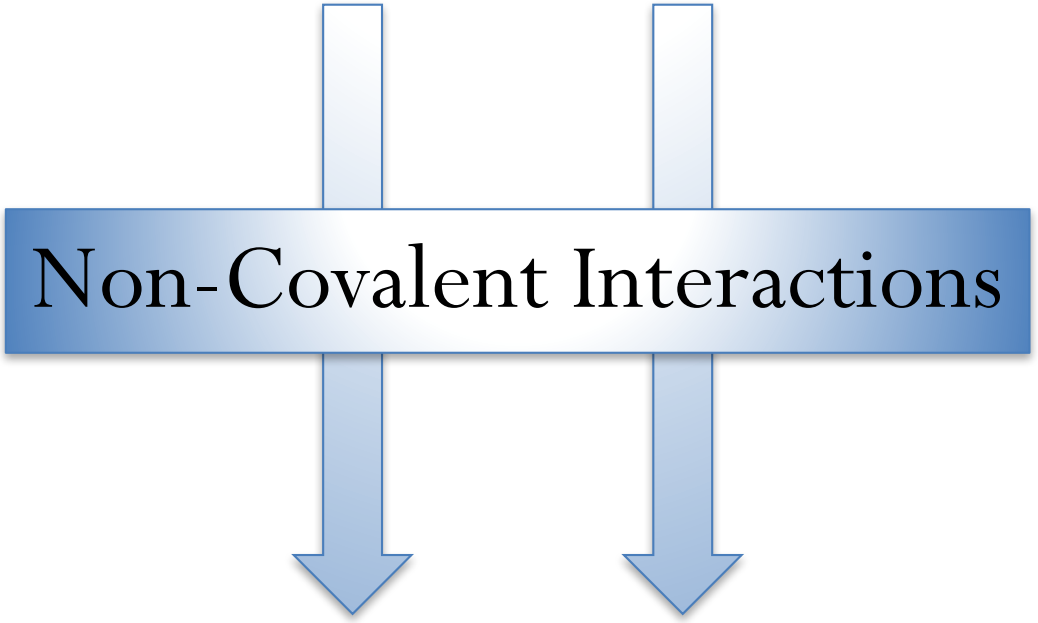
New Orleans, LA

Outline

- Motivation and Background
- 2-body:Many-body QM:QM Frequencies
- A Closer Look at $F^-(H_2O)_n$
- Conclusions
- Acknowledgements

Motivation

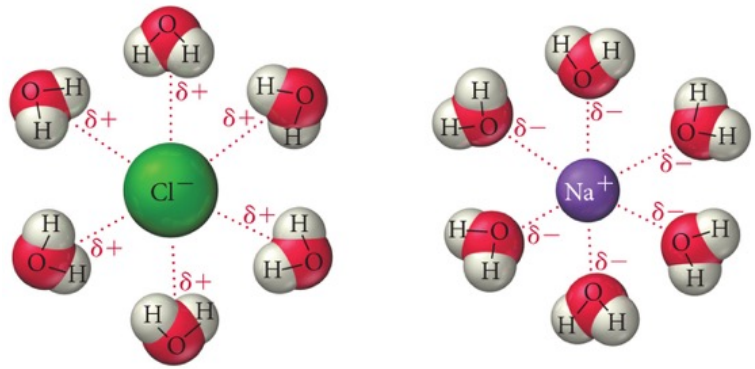
Molecules



Properties/Functionality of Materials

Motivation

- Non-covalent interactions
  - Dipole/dipole interactions — Hydrogen bonding
  - London dispersion forces — π-stacking
  - σ-hole interactions — Halogen bonding
- Integral role in chemistry, physics and biology
  - Structure and function of biomolecules and polymers
  - Solvation
  - Condensed phase properties
  - Crystal engineering
  - Directed self-assembly
  - Molecular recognition
  - Hydrophobic (and hydrophilic) effects



Hydrogen Bonding: A Familiar Example

- Strong and highly directional non-covalent interaction
  - X = N, O, F, etc.

$$\overset{\delta-}{\text{X}}\text{–}\overset{\delta+}{\text{H}} \cdots \overset{\delta-}{\text{X}}\text{–}\overset{\delta+}{\text{H}}$$

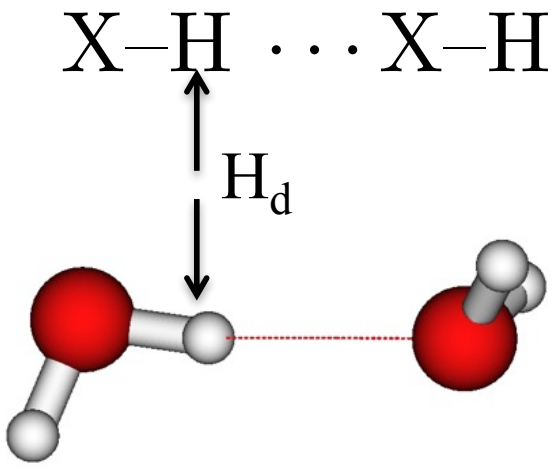
- Much stronger than dipole/dipole interactions
  - Propane — b.p. = –42 °C
    - $CH_3CH_2CH_3$ — 44 g mol^{-1} — 0.08 Debye
  - Dimethyl ether — b.p. = –22 °C
    - CH_3OCH_3 — 46 g mol^{-1} — 1.3 Debye
  - Ethanol — b.p. = +78 °C
    - CH_3CH_2OH — 46 g mol^{-1} — 1.7 Debye

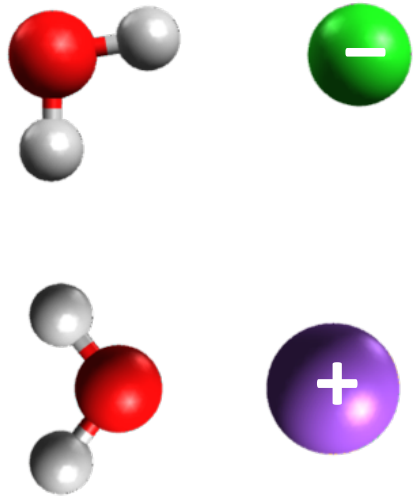
ΔT_{bp} = +20 °C

ΔT_{bp} = +100 °C

Spectroscopic Signatures of H-bonding

- Characteristic spectral signature
  - Donor stretching frequency shifts to lower energy





OH stretch	ν_3 asymm	ν_1 symm
monomer	3756 cm^{-1}	3657 cm^{-1}
dimer	3602 cm^{-1}	
$\Delta\nu$ (OH_d):	–154 cm^{-1}	–55 cm^{-1}

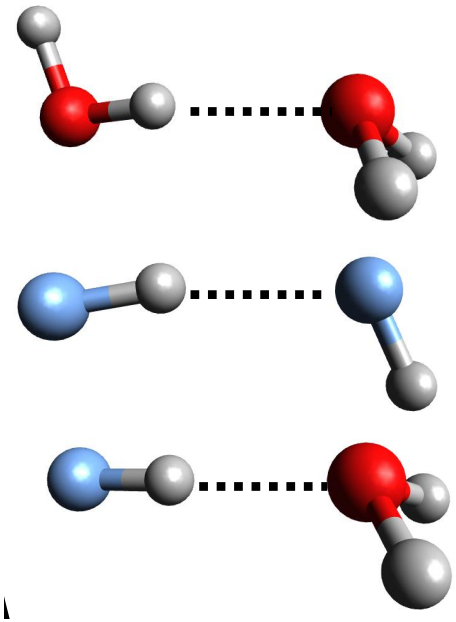
a.k.a. "red shift"

The Goal

	Donor Stretch (cm^{-1})		Shift (cm^{-1})		D_0 (kcal mol^{-1})	
	Expt	Theory	Expt	Theory	Expt	Theory
$(H_2O)_2$ *	3602	3605	–55	–49	3.1	3.0
$(HF)_2$ *	3868	3869	–93	–93	3.0	3.0
HF/H_2O †	3634	3636	–332	–333	**8.2**	6.3

*J.C. Howard, J.L. Gray, A.J. Hardwick, L.T. Nguyen and GST, *J. Chem. Theory Comput.*, **10**, 5426 (2014).

†T.M. Sexton, J.C. Howard and GST, *J. Chem. Phys. A,* **122**, 4902, (2018).



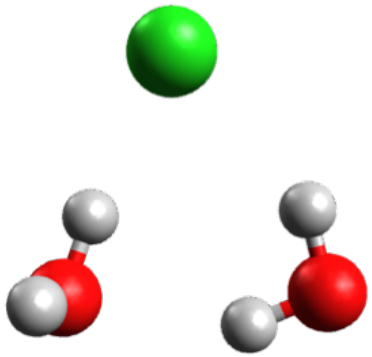
- CCSD(T)/haQZ + VPT2
- CCSD(T)/haQZ + VPT2
- CCSD(T)/ha5Z harmonic

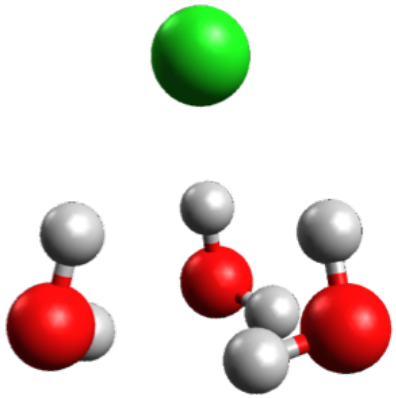
  + MP2/ha5Z VPT2 correction

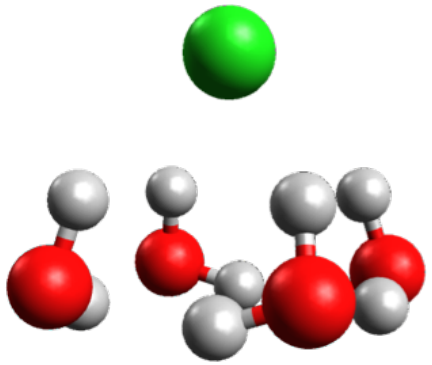
CCSD(T) Analytic Hessian Timing

Cluster	Symmetry	haTZ	haQZ
$F^-(H_2O)_1$	C_s	~1 hour	< 1 day
$F^-(H_2O)_2$	C_1	several days	<1 month
$F^-(H_2O)_3$	C_3 (C_1)	several weeks	?
$F^-(H_2O)_4$	C_4 (C_2)	?	?

VPT2 requires $18n-5$ Hessians for $X^-(H_2O)_n$



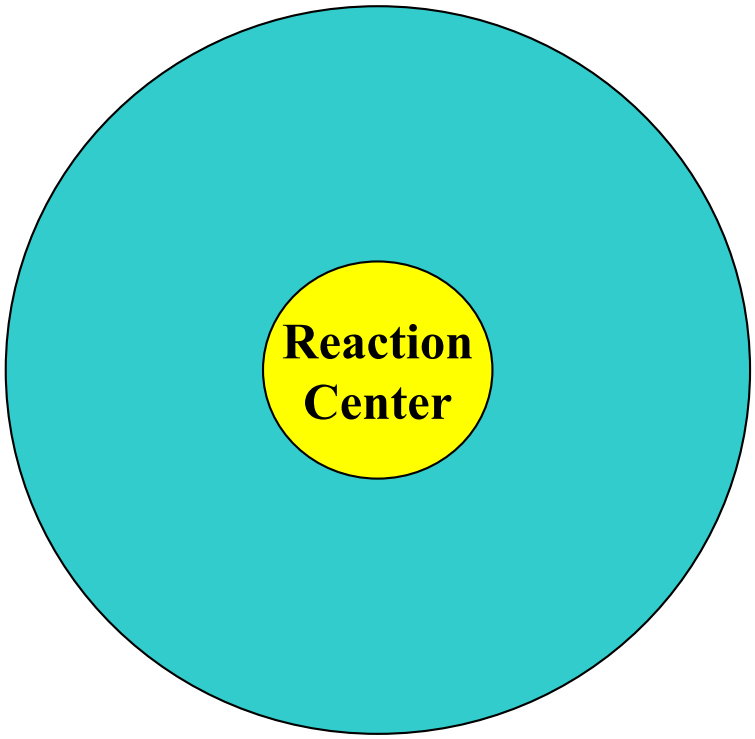




QM:QM Solution? (e.g., ONIOM)

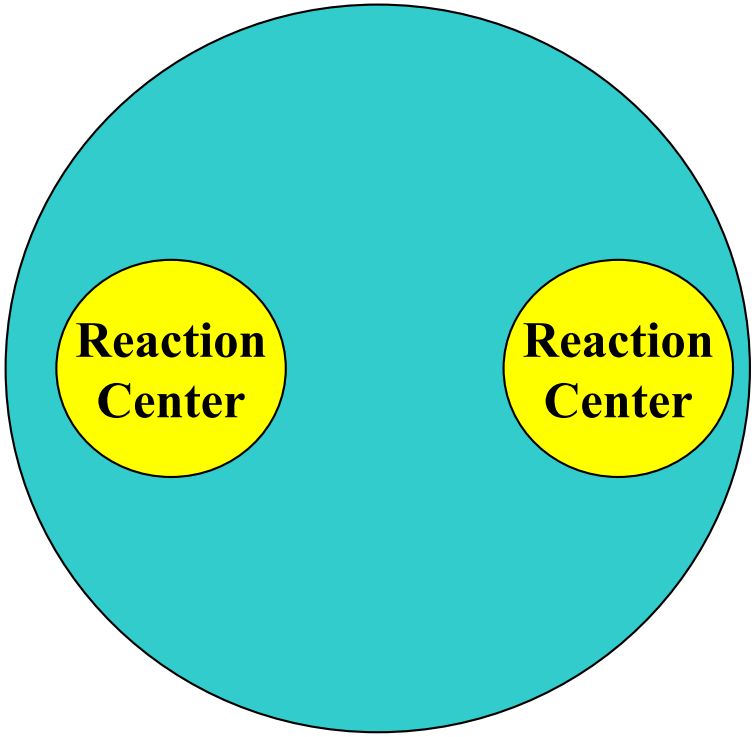
$$E_{\text{Hi:Lo}}(\text{sys}) = E_{\text{Lo}}(\text{sys}) + E_{\text{Hi}}(\text{mdl}_i) - E_{\text{Lo}}(\text{mdl}_i)$$

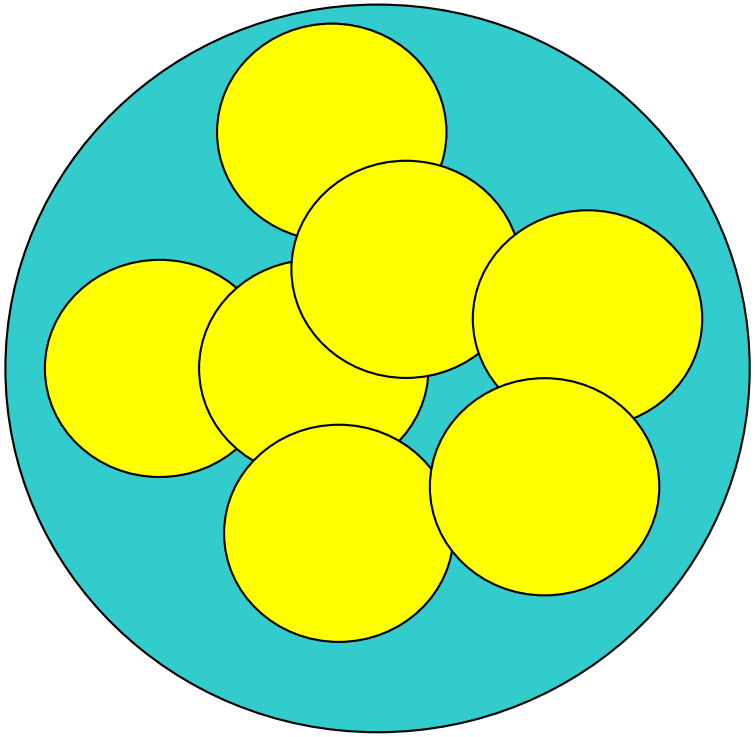
- Break large problem into tractable pieces



What about Multiple Centers?

$$E_{\text{Hi:Lo}}(\text{sys}) = E_{\text{Lo}}\ (\text{sys}) + \sum_{i=1}^{m} \{E_{\text{Hi}}(\text{mdl}_i) - E_{\text{Lo}}(\text{mdl}_i)\}$$





Hopkins and Tschumper, *J. Comput. Chem.*, **24**,1563-1568 (2003).

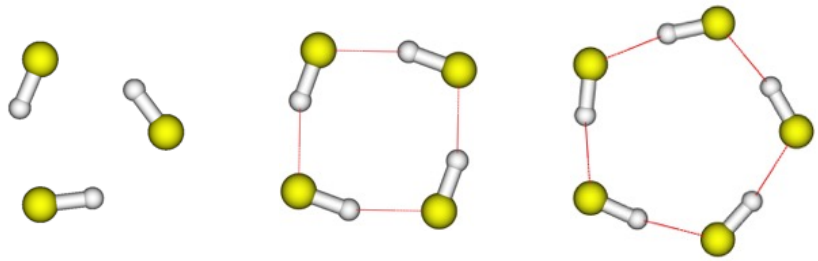
Multicentered QM:QM (ONIOM)

$$
\begin{aligned}
E_{\text{Hi:Lo}}(\text{sys}) &= E_{\text{Lo}}\ (\text{sys}) \\
&+ \sum_{i=1}^{m} \{E_{\text{Hi}}(\text{mdl}_i) - E_{\text{Lo}}(\text{mdl}_i)\} \\
&- \sum_{i=1}^{m-1} \sum_{j>i}^{m} \{E_{\text{Hi}}(\text{mdl}_i \cap \text{mdl}_j) - E_{\text{Lo}}(\text{mdl}_i \cap \text{mdl}_j)\} \\
&+ \sum_{i=1}^{m-2} \sum_{j>i}^{m-1} \sum_{k>j}^{m} \{E_{\text{Hi}}(\text{mdl}_i \cap \text{mdl}_j \cap \text{mdl}_k) - E_{\text{Lo}}(\text{mdl}_i \cap \text{mdl}_j \cap \text{mdl}_k)\} \\
&+ \cdots \\
&+ (-1)^{n-1} \sum_{i=1}^{m-n+1} \sum_{j>i}^{m-n+2} \cdots \sum_{l>k}^{m} \{E_{\text{Hi}}(\text{mdl}_i \cap \cdots \cap \text{mdl}_l) - E_{\text{Lo}}(\text{mdl}_i \cap \cdots \cap \text{mdl}_l)\}
\end{aligned}
$$

Hopkins and Tschumper, *Mol. Phys.*, **103**, 309 (2005).

N-Body:Many-Body QM:QM

- Many-body expansion (MBE) dominated by low-order terms
- D_e in kJ mol^{-1}
  - $(HF)_3$: 64 ± 2
  - $(HF)_4$: 116 ± 3
  - $(HF)_5$: 158 ± 4



  - 2-body: CCSD(T)-R12 aug-cc-pV(Q/5)Z
  - 3-body: CCSD(T) aug-cc-pV(T/Q)Z
  - 4,5-body: MP2-R12 aug-cc-pV(T/Q)Z
- QM:QM for n=3 and QM:QM:QM for n=4,5
- Proposed extension to gradients and Hessians

Klopper, Quack and Suhm, Mol. Phys., **94**, 105 (1998).

2-body:Many-body QM:QM

- Multi-centered ONIOM + Many-body expansion

$$E = E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 + \ldots + \Delta E_N$$

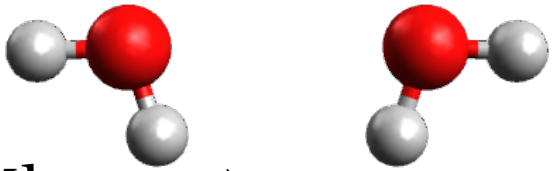
  - Hi level: Up through 2-body interactions
  - Lo level: 3-body and higher-order contributions

$$E_{\text{int}}^{\text{2bHi:Lo}} = E_{\text{2b int}}^{\text{Hi}} + \delta E_{\geq \text{3b}}^{\text{Lo}}$$

$$= E_{\text{2b int}}^{\text{Hi}} + \delta E_{\text{non-add}}^{\text{Lo}}$$

CPL, **407**, 362-267 (2005) and *CPL*, **427**, 185-191 (2006).

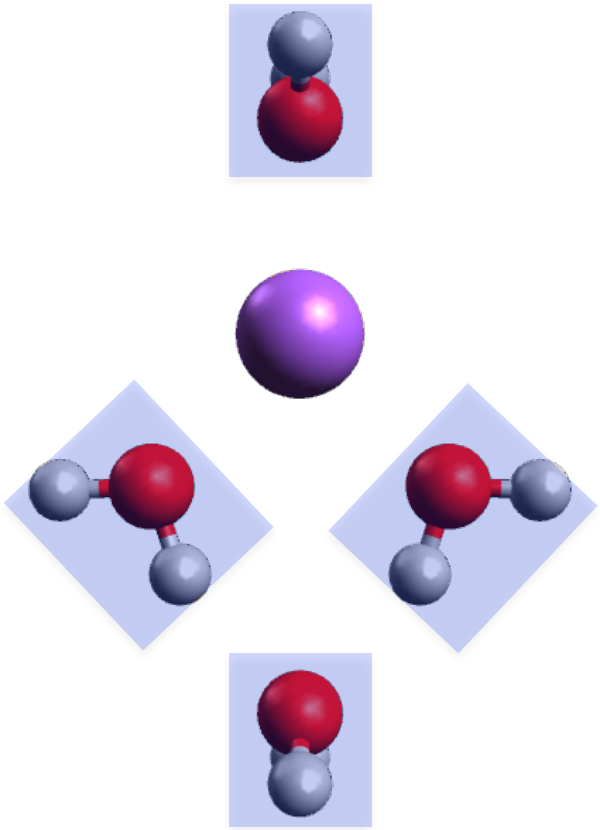
- Analytic gradients and Hessians



- Systematic convergence (3b:Mb, 4b:Mb, etc.)

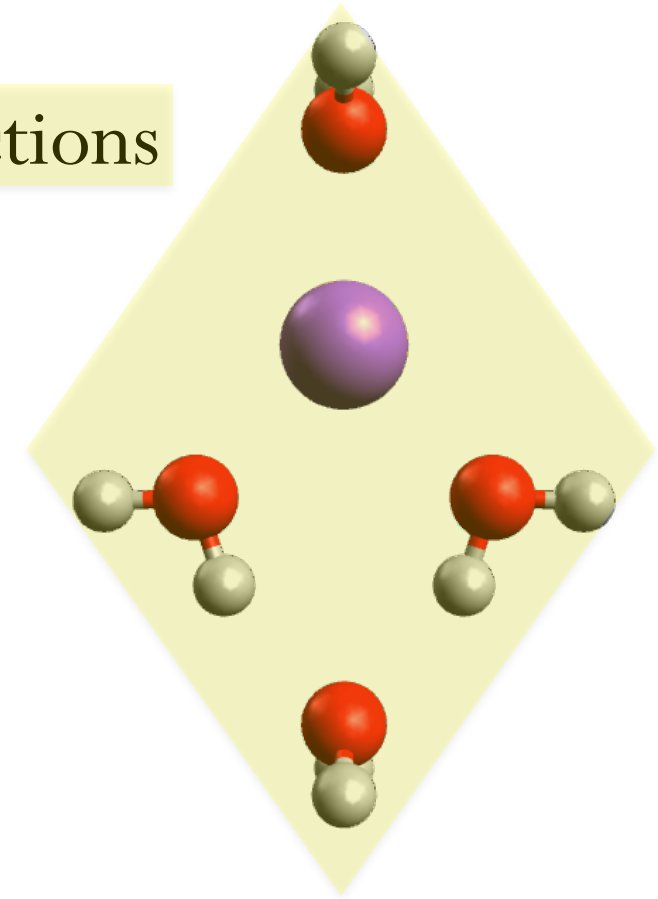
2-Body:Many-Body QM:QM

- "Hi" level method: Up to 2-body interactions
  - CCSD(T) for N fragments and $\binom{N}{2}$ dimers
  - Up to 10 unique "pairs" for N=5



2-Body:Many-Body QM:QM

- "Hi" level method: Up to 2-body interactions
  - CCSD(T) for N fragments and $\binom{N}{2}$ dimers
  - Up to 10 unique "pairs" for N=5
- "Lo" level method: ≥3-body interactions
  - MP2 for entire cluster



Similar Approaches

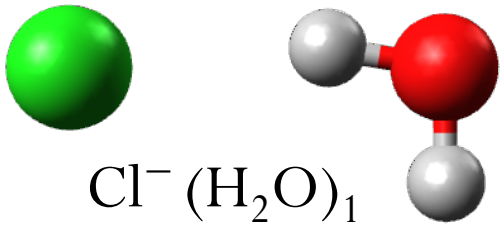
- Molecules-in-molecules (MIM)
  - Mayhall and Raghavachari, *JCTC*, **7**, 1336-1343 (2011)
- Stratified Approximation Many-Body Approach (SAMBA)
  - Góra, Podeszwa, Cenek and Szalewicz, *JCP*, **135**, 224102 (2011)
- Many related methods targeting large systems
- Very good reviews of fragmentation and MBE methods
  - *"Fragmentation Methods: A Route to Accurate Calculations on Large Systems"*, Gordon, Fedorov, Pruitt and Slipchenko, *Chem. Rev*. **112**, 632-672 (2012)
  - *"A generalized many-body expansion and a unified view of fragment-based methods in electronic structure theory"*, Richard and Herbert, *JCP*, **137**, 064113 (2012)
  - Special issue of *Acc. Chem. Res*. **47**, no. 9 (2014).
  - Special issue of *Chem. Rev.*, **115**, no. 12 (2015).

Properties for 2b:Mb, 3b:Mb, etc.

- Energies
  - *Mol. Phys.*, **103**, 309 (2005)
  - *Chem. Phys. Lett.*, **427**, 185 (2006)
  - *J. Chem. Phys.*, **135**, 044123 (2011)
- Analytic Gradients (geometry optimizations)
  - *Mol. Phys.*, **105**, 2777 (2008)
  - *JCTC*, **7**, 2753 (2011)
- Analytic Hessians (vibrational frequencies)
  - *J. Chem. Phys.*, **139**, 184113 (2013)

MP2 Deviations from CCSD(T)

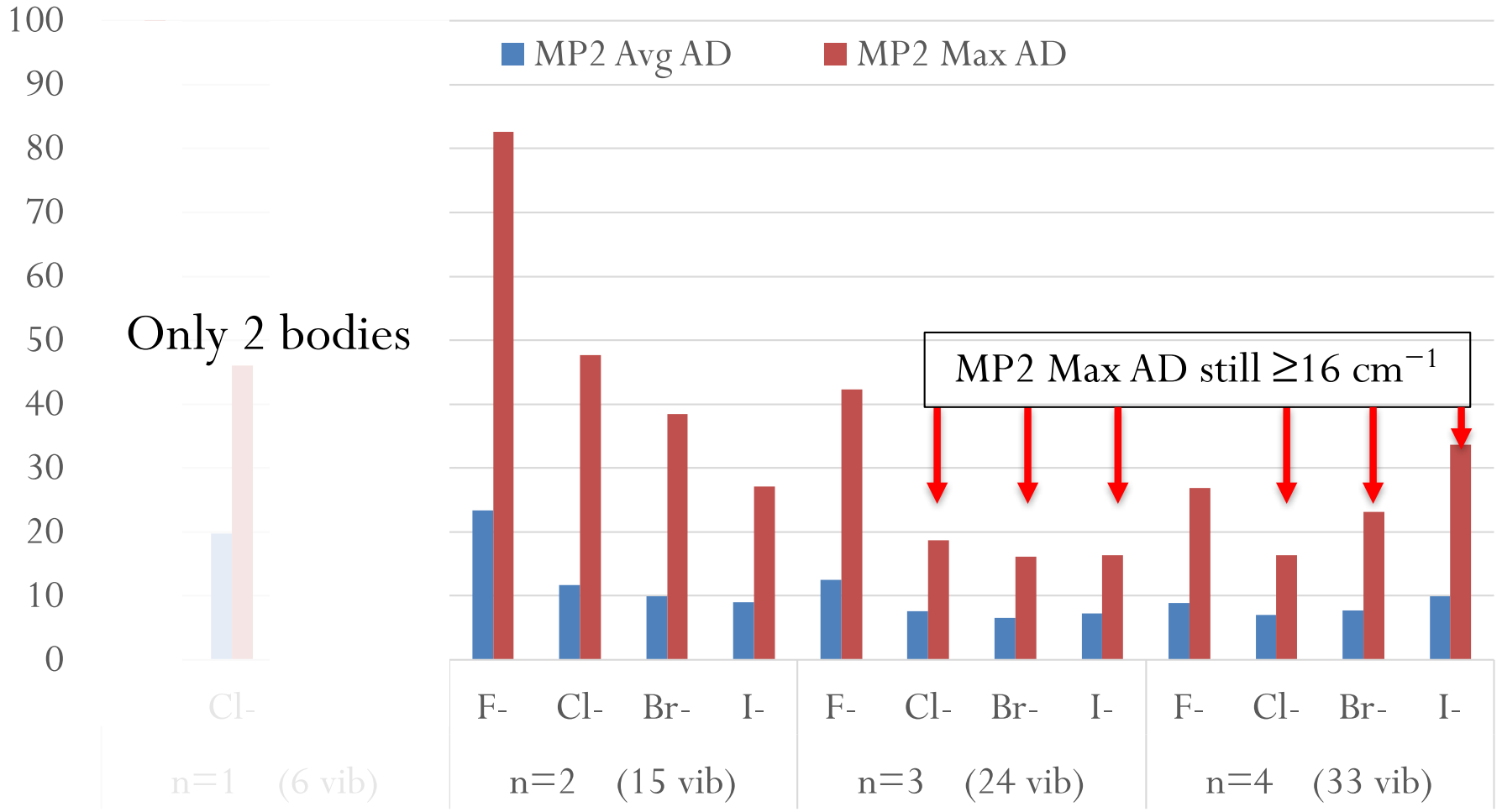
CCSD(T)	MP2	Deviation
176.9	180.9	−4.1
326.8	336.2	−9.4
720.3	734.2	−13.9
1692.1	1675.4	+16.7
3446.7	3400.8	+46.0
3866.6	3895.1	−28.5



$Cl^-(H_2O)_1$

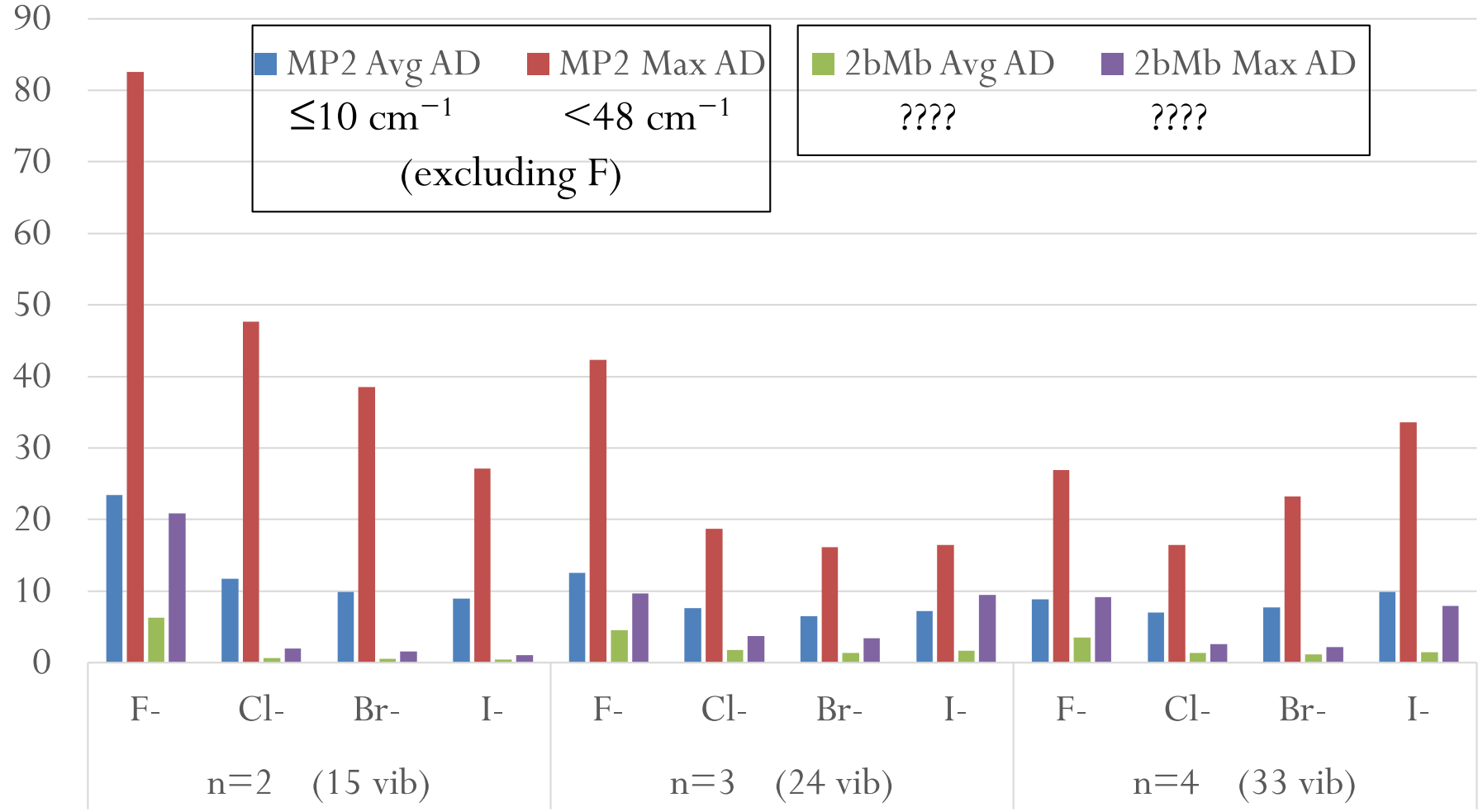
All values computed with haDZ basis set and reported in cm^{-1}
(cc-pVDZ for H and aug-cc-pVTZ for all other atoms)

MP2 Deviations from CCSD(T)



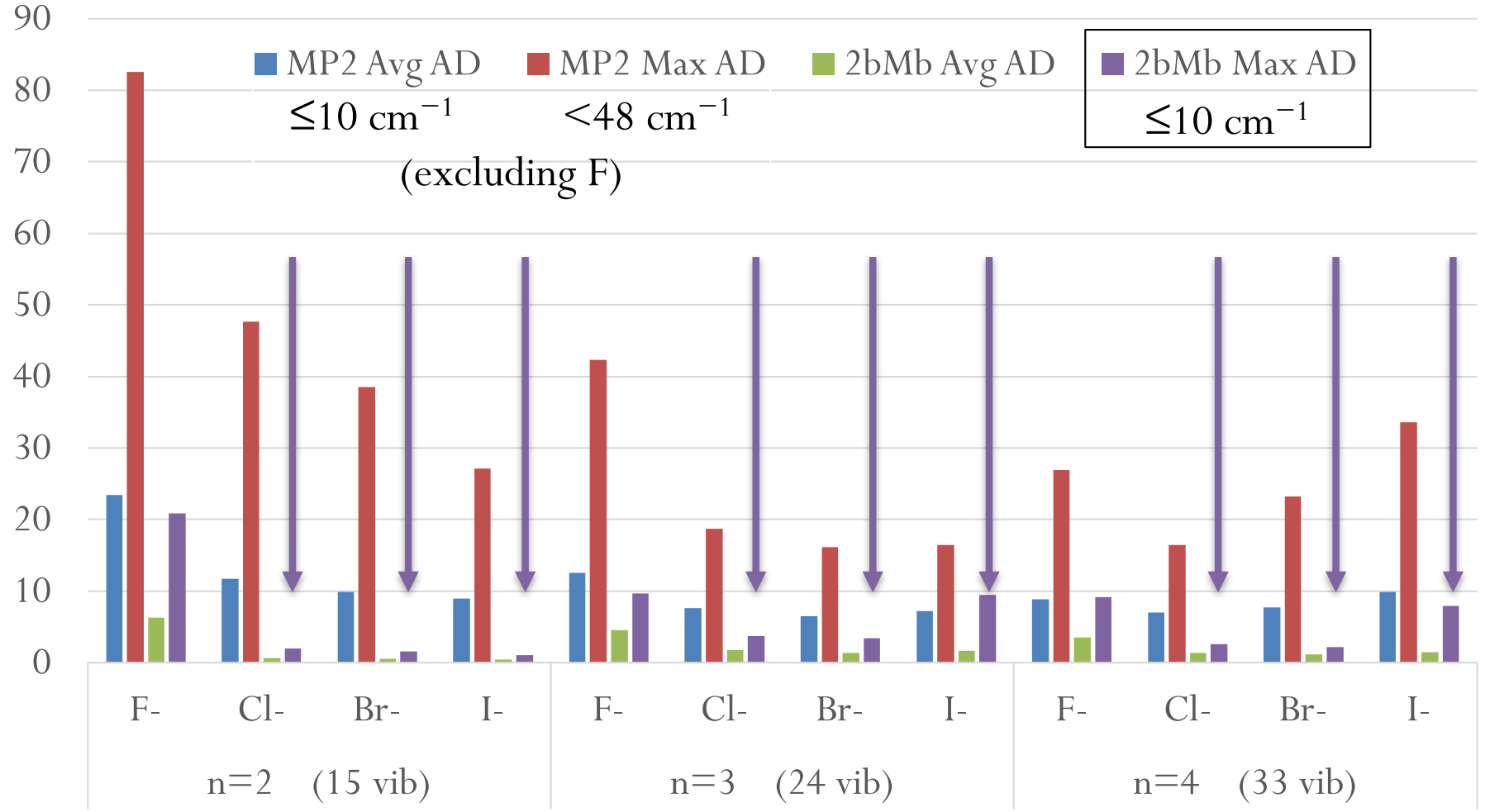
All values computed with haDZ basis set and reported in cm^{-1}

MP2 Deviations from CCSD(T)



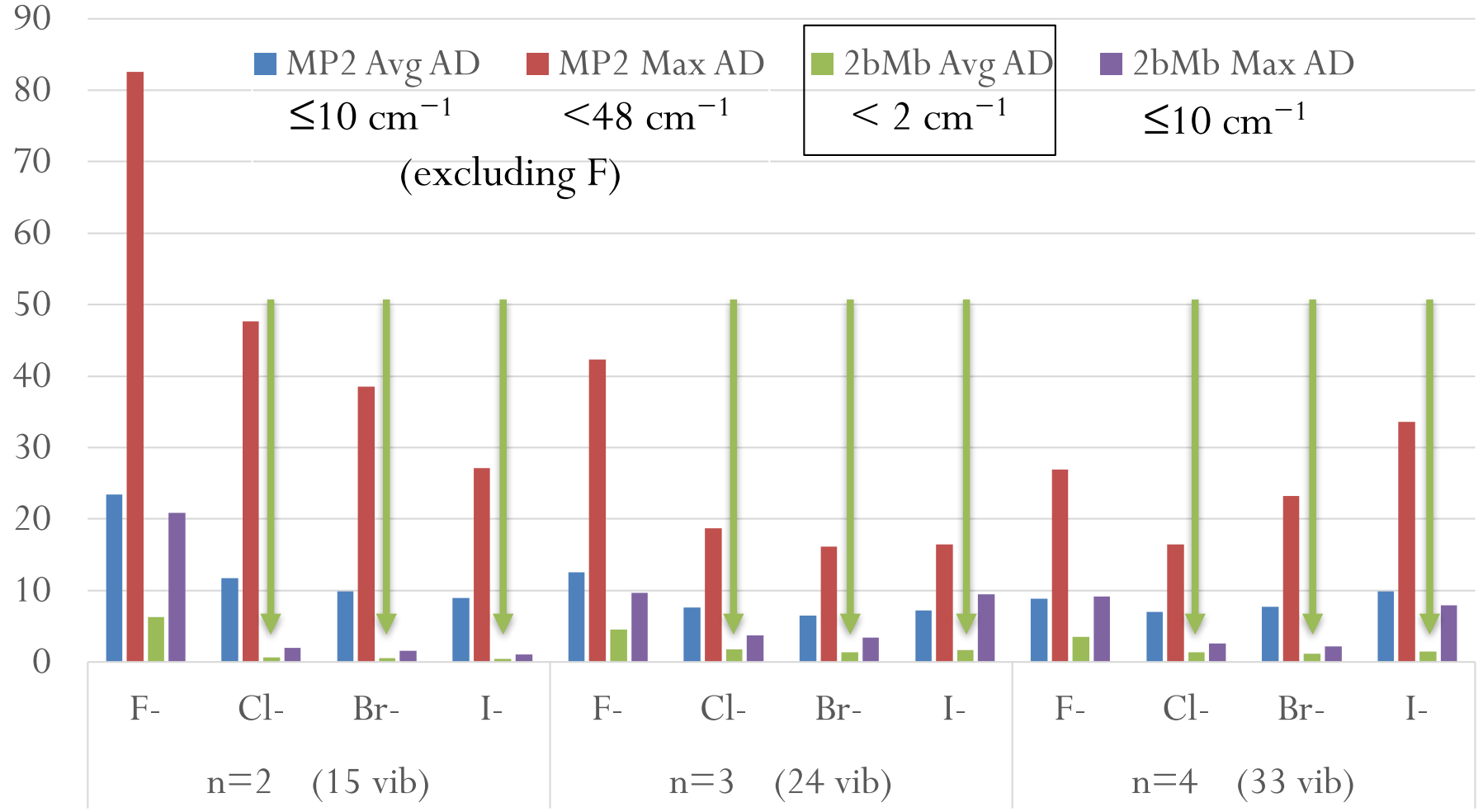
All values computed with haDZ basis set and reported in cm^{-1}

2b:Mb Deviations from CCSD(T)



All values computed with haDZ basis set and reported in cm^{-1}

2b:Mb Deviations from CCSD(T)



All values computed with haDZ basis set and reported in cm^{-1}

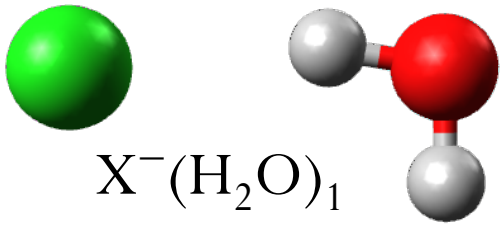
The F^- Problem: More Methods

- CFOUR and MRCC
  - CCSD(T), CCSDT, CCSDT(Q), CCSDTQ
  - Gradients and Hessians
    - Analytic when available
    - Finite difference procedures otherwise

The F^- Problem: D_e

	CCSD(T) D_e	MP2 D_e	Deviation
F^-	27.2	27.4	+0.2
Cl^-	15.0	14.7	−0.3
Br^-	13.3	13.1	−0.2
H^-	19.1	17.3	−1.8

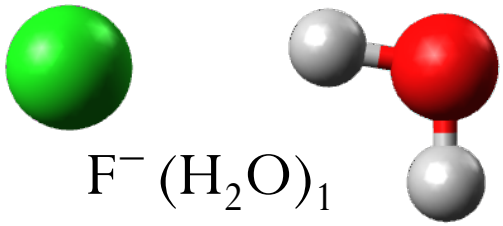
All values computed with haTZ basis set and reported in kcal mol^{-1}



$X^-(H_2O)_1$

The F^- Problem: Frequencies

CCSD(T)	MP2	Deviation
389.0	383.7	+5.3
576.9	575.2	+1.7
1171.7	1164.0	+7.7
1700.4	1723.9	−23.5
2114.0	2232.9	−118.9
3895.9	3861.1	+34.8
	Avg Abs Dev	**32.0**
	Max Abs Dev	**118.9**

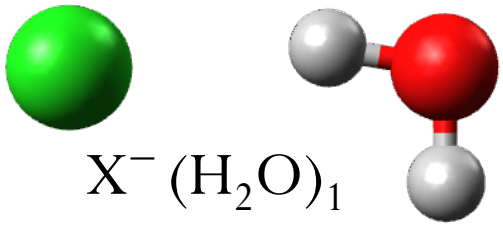


$F^-(H_2O)_1$

All values computed with haTZ basis set and reported in cm^{-1}

The F^- Problem: Frequencies

Br^-	Cl^-	F^-	
+3.4	+3.0	+5.3	
+9.3	+8.8	+1.7	
+11.7	+12.2	+7.7	
−18.6	−18.5	−23.5	
−44.2	−53.3	−118.9	
+24.4	+25.9	+34.8	
18.6	**20.3**	**32.0**	**Avg Abs Dev**
44.2	**53.3**	**118.9**	**Max Abs Dev**



$X^-(H_2O)_1$

All values computed with haTZ basis set and reported in cm^{-1}

The F^- Problem: Frequencies

Br^-	Cl^-	F^-	H^-
+3.4	+3.0	+5.3	+56.9
+9.3	+8.8	+1.7	+44.8
+11.7	+12.2	+7.7	+98.4
−18.6	−18.5	−23.5	−20.3
−44.2	−53.3	−118.9	−376.5
+24.4	+25.9	+34.8	+20.0
18.6	**20.3**	**32.0**	**102.8**
44.2	**53.3**	**118.9**	**376.5**

All values computed with haTZ basis set and reported in cm^{-1}

The H^- Problem: Frequencies

δ_{MP2}^{CCSDTQ}	$\delta_{CCSD(T)}^{CCSDTQ}$	$\delta_{MP2}^{CCSD(T)}$	$\delta_{MP2}^{CCSD(T)}$
+56.2	−1.1	+57.3	+56.9
+51.8	−2.7	+54.5	+44.8
+99.0	−1.7	+100.7	+98.4
−17.0	+2.8	−19.7	−20.3
−366.1	+23.2	−389.2	−376.5
+35.5	+9.8	+25.6	+20.0
104.3	**6.9**	**107.8**	**102.8**
366.1	**23.2**	**389.2**	**376.5**

All values computed with aug-cc-pVDZ basis set and reported in cm^{-1}

The H^- Problem: Frequencies

δ^{CCSDTQ}_{MP2}	$\delta^{CCSDTQ}_{CCSD(T)}$	δ^{CCSDTQ}_{CCSDT}	$\delta^{CCSDTQ}_{CCSDT(Q)}$
+56.2	−1.1	−0.5	+0.3
+51.8	−2.7	−0.9	+0.2
+99.0	−1.7	−1.3	+0.3
−17.0	+2.8	+1.9	−0.4
−366.1	+23.2	+14.9	−3.4
+35.5	+9.8	+7.5	+1.7
104.3	**6.9**	**4.5**	**1.1**
366.1	**23.2**	**14.9**	**3.4**

All values computed with aug-cc-pVDZ basis set and reported in cm^{-1}

The H^- Solution: Frequencies

- Appear to converge
  - CCSDT(Q)
  - CCSDTQ

- What about F^-?

The F^- Problem: Frequencies

$\delta_{MP2}^{CCSD(T)}$	$\delta_{MP2}^{CCSDT(Q)}$	$\delta_{CCSD(T)}^{CCSDT(Q)}$	$\delta_{CCSDT}^{CCSDT(Q)}$
+2.8	+3.4	+0.6	−0.1
+0.3	+1.3	+1.0	+0.2
+6.0	+8.8	+2.8	+0.6
−20.8	−17.7	+3.1	+2.6
−100.2	−90.1	+10.0	+15.1
+37.9	+47.2	+9.3	+8.3
28.0	**28.1**	**4.5**	**4.5**
100.2	**90.1**	**10.0**	**15.1**

All values computed with haDZ basis set and reported in cm^{-1}

Conclusions

- $F^-(H_2O)_2$ is likely/effectively C_2
  - Even though a TS with CCSD(T)/haTZ and haQZ
- MP2 struggles with frequencies for H^- and $F^-(H_2O)_n$
  - Largest deviations for intramolecular modes
  - Especially the donor stretch
  - Poor choice for low-level method in QM:QM
- CCSD does not appear to be much/any better

Conclusions

- 2b:Mb CCSD(T):MP2
  - Nearly identical to CCSD(T) for Cl^-, Br^- and I^-
  - Cl^- and Br^-: Max AD < 3.5 cm^{-1} for
  - I^-: Max AD ≤10 cm^{-1}
  - Largest deviations for lowest energy modes

    (need to test FD procedure)
  - haQZ benchmark harmonic frequencies underway for a much more diverse set of structures

Future Directions

- 2b:Mb QM:QM for $H^-(H_2O)_n$ and $F^-(H_2O)_n$
  - Hi level: CCSDT(Q)
  - Lo level: CCSD(T)

Thank You

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