QMC dissociation energies of three-electron hemibonded radical cation dimers ... and water clusters

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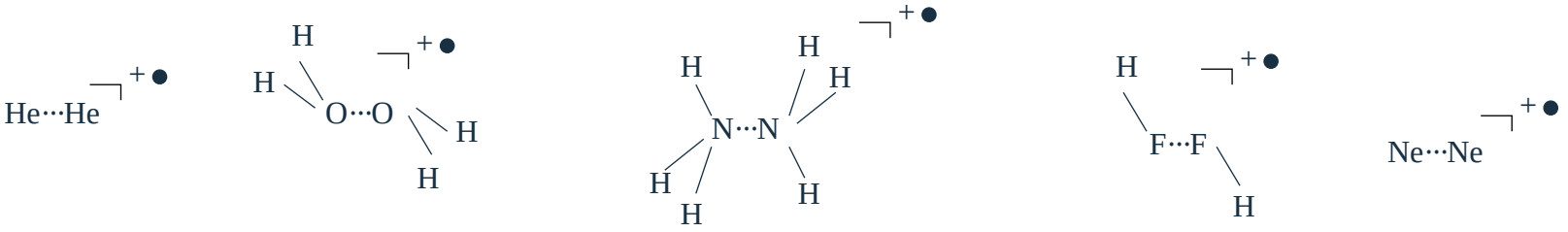
Outline

1. Two-center three-electron-bond radical cations
   - He, H_2O, NH_3, HF, Ne
   - Hemibonded



   - $A_2^{+\bullet} \rightarrow A + A^{+\bullet}$

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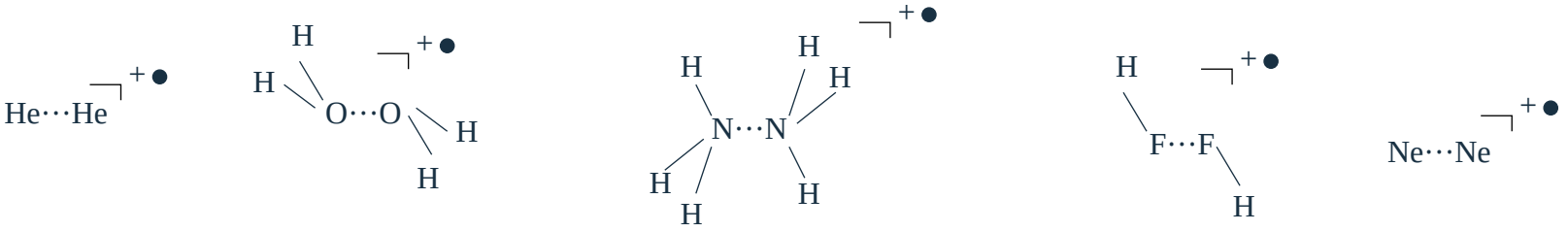
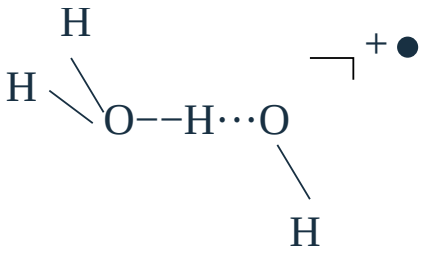


   - $A_2^{+\bullet} \rightarrow A + A^{+\bullet}$

2. Water radical
   - Hemibonded and proton transferred structures



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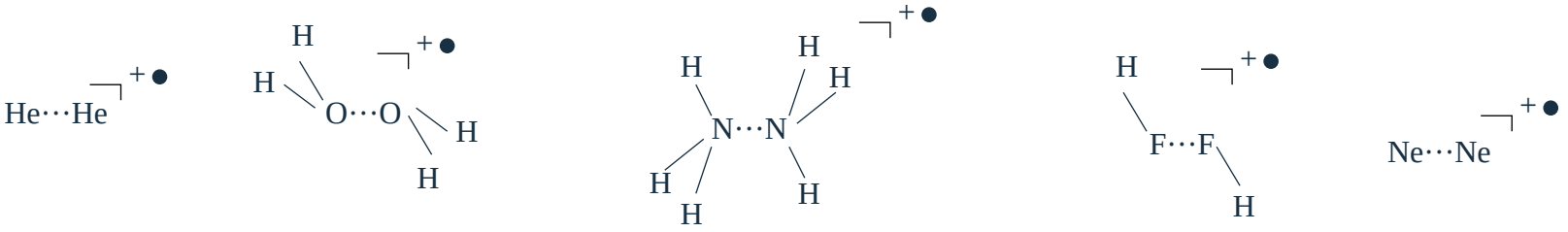

   - $A_2^{+\bullet} \rightarrow A + A^{+\bullet}$

2. Water radical
   - Hemibonded and proton transferred structures

3. Water clusters
   - Dimer: $(H_2O)_2 \rightarrow 2H_2O$
   - Trimer: $(H_2O)_3 \rightarrow 3H_2O$

Why the 3 electron hemibonded systems?

- $A \cdots A^{+\bullet}$
  - 2 electrons in a bonding state
  - 1 electron in an antibonding state

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- Failure of standard DFT: overstimation of the stability of $A_2^{+\bullet}$
  - Self-interaction error (inaccurate XC functionals)

    1 e^- system: XC functionals do not obey

    $$E_C=0;\ E_X= -E_H$$
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  - Self-interaction corrections

- MP2, MP4, CI, CCSD(T)
  - Basis set limit problem
  - Accurate dissociation energies for small systems

QMC calculations for $A_2^{+\bullet}$

- How good is QMC?
  - Benchmark: experiment and CCSD(T)
  - Good test for pseudopotentials

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- Slater-Jastrow trial wave function
  - Hartree-Fock single-particle orbitals using Gaussian basis sets (CCSD(T) geometries)
  - Jastrow factor
- All electron
- Pseudopotential

Helium: $He_2^{+\bullet} \rightarrow He + He^{+\bullet}$

Total energies (Ha)

		He	$He^{+\bullet}$	$He_2^{+\bullet}$
AE	HF	-2.86165	-1.99997	-4.93281
	VMC	-2.90360(6)	-1.99997(4)	-4.9899(4)
	DMC	-2.903724(8)	-2.00000(1)	-4.99416(6)
Psp	HF	-2.86017	-1.99785	-4.92923
	VMC	-2.90189(6)	-1.99814(7)	-4.98968(7)
	DMC	-2.90229(1)	-1.99827(1)	-4.99046(4)

% correlation energy

	He	$He_2^{+\bullet}$
AE	99.7	93.1
pseudo	99.1	98.7

Helium: $He_2^{+\bullet} \rightarrow He + He^{+\bullet}$

Total energies (Ha)

		He	$He^{+\bullet}$	$He_2^{+\bullet}$	D_e (kcal/mol)
AE	HF	-2.86165	-1.99997	-4.93281	44.67
	VMC	-2.90360(6)	-1.99997(4)	-4.9899(4)	54.1(3)
	DMC	-2.903724(8)	-2.00000(1)	-4.99416(6)	56.75(4)
Psp	HF	-2.86017	-1.99785	-4.92923	44.68
	VMC	-2.90189(6)	-1.99814(7)	-4.98968(7)	56.26(7)
	DMC	-2.90229(1)	-1.99827(1)	-4.99046(4)	56.41(3)

	D_e (kcal/mol)
BLYP	83.30
B3LYP	77.38
CCSD(T)	56.04
SS(a=0.2)	54.94
Exp	56.94

Water. $(H_2O)_2^{+\bullet} \rightarrow H_2O + H_2O^{+\bullet}$

Total energies (Ha)

		H_2O	$H_2O^{+\bullet}$	$(H_2O)_2^{+\bullet}$
AE	HF	-76.0587	-75.6580	-151.7430
	VMC	-76.324(5)	-75.905(2)	-152.257(7)
	DMC	-76.42102(4)	-75.9538(2)	-152.4341(3)
Psp	HF	-16.8947	-16.4954	-33.4202
	VMC	-17.182(2)	-16.723(2)	-33.947(3)
	DMC	-17.20634(2)	-16.7389(2)	-34.00614(8)

% correlation energy

	H_2O	$H_2O^{+\bullet}$	$(H_2O)_2^{+\bullet}$
AE	73.2	83.5	74.4
pseudo	92.1	93.4	89.9

Water. $(H_2O)_2^{+\bullet} \rightarrow H_2O + H_2O^{+\bullet}$

Total energies (Ha)

		H_2O	$H_2O^{+\bullet}$	$(H_2O)_2^{+\bullet}$	D_e (kcal/mol)
AE	HF	-76.0587	-75.6580	-151.7430	45.24
	VMC	-76.324(5)	-75.905(2)	-152.257(7)	29.5
	DMC	-76.42102(4)	-75.9538(2)	-152.4341(3)	37.2(2)
Psp	HF	-16.8947	-16.4954	-33.4202	46.74
	VMC	-17.182(2)	-16.723(2)	-33.947(3)	26.4
	DMC	-17.20634(2)	-16.7389(2)	-34.00614(8)	38.2(1)

	H_2O
CCSD(T)-R12	-76.437333
CCSD(T) CBS limit	-76.439(2)
DMC	-76.4207(2)
Experiment	-76.438

	D_e (kcal/mol)
BLYP	52.43
B3LYP	59.69
MP2/QZ	38.05
CCSD(T)	39.2;40.75
SS(a=0.2)	41.43

Ammonia. $(NH_3)_2^{+\bullet} \rightarrow NH_3 + NH_3^{+\bullet}$

Total energies (Ha)

		NH_3	$NH_3^{+\bullet}$	$(NH_3)_2^{+\bullet}$
AE	HF	-56.2188	-55.9028	-112.1517
	VMC	-56.474(4)	-56.109(3)	-112.636(5)
	DMC	-56.55028(7)	-56.17563(6)	-112.78082(3)
Psp	HF	-11.4581	-11.1434	-22.6327
	VMC	-11.711(2)	-11.340(1)	-23.097(2)
	DMC	-11.730147(3)	-11.35668(2)	-23.14230(8)

% correlation energy

	NH_3	$NH_3^{+\bullet}$	$(NH_3)_2^{+\bullet}$
AE	77.0	75.6	77.0
pseudo	93.0	92.2	91.1

Ammonia. $(NH_3)_2^{+\bullet} \rightarrow NH_3 + NH_3^{+\bullet}$

Total energies (Ha)

		NH_3	$NH_3^{+\bullet}$	$(NH_3)_2^{+\bullet}$	D_e (kcal/mol)
AE	HF	-56.2188	-55.9028	-112.1517	18.89
	VMC	-56.474(4)	-56.109(3)	-112.636(5)	33(3)
	DMC	-56.55028(7)	-56.17563(6)	-112.78082(3)	34.46(5)
Psp	HF	-11.4581	-11.1434	-22.6327	19.58
	VMC	-11.711(2)	-11.340(1)	-23.097(2)	29(2)
	DMC	-11.730147(3)	-11.35668(2)	-23.14230(8)	34.81(5)

	D_e (kcal/mol)
BLYP	48.55
B3LYP	44.21
MP2/6-311G**	38.05
CCSD(T)	36.34
SS(a=0.2)	34.61

Hydrogen Fluoride. $(HF)_2^{+\bullet} \rightarrow HF + HF^{+\bullet}$

Total energies (Ha)

		HF	$HF^{+\bullet}$	$(HF)_2^{+\bullet}$
AE	HF	-100.06079	-99.53669	-199.61933
	VMC	-100.335(6)	-99.787(6)	-200.182(9)
	DMC	-100.44162(7)	-99.84915(7)	-200.3506(1)
Psp	HF	-24.51781	-23.99394	-48.53175
	VMC	-24.805(3)	-24.216(3)	-49.050(4)
	DMC	-24.82861(2)	-24.23526(2)	-49.11834(6)

% correlation energy

	HF	$HF^{+\bullet}$	$(HF)_2^{+\bullet}$
AE	72.0	80.1	76.9
pseudo	92.4	92.0	88.3

Hydrogen Fluoride. $(HF)_2^{+\bullet} \rightarrow HF + HF^{+\bullet}$

Total energies (Ha)

		HF	$HF^{+\bullet}$	$(HF)_2^{+\bullet}$	D_e (kcal/mol)
AE	HF	-100.06079	-99.53669	-199.61933	13.71
	VMC	-100.335(6)	-99.787(6)	-200.182(9)	37.65060
	DMC	-100.44162(7)	-99.84915(7)	-200.3506(1)	37.5(1)
Psp	HF	-24.51781	-23.99394	-48.53175	12.55
	VMC	-24.805(3)	-24.216(3)	-49.050(4)	18.19779
	DMC	-24.82861(2)	-24.23526(2)	-49.11834(6)	34.18(4)

	D_e (kcal/mol)
BLYP	68.80
B3LYP	58.50
MP2/6-311G**	43.05
CCSD(T)	40.22
SS(a=0.2)	46.33

Neon. $Ne_2^{+\bullet} \rightarrow Ne + Ne^{+\bullet}$

Total energies (Ha)

		Ne	$Ne^{+\bullet}$	$Ne_2^{+\bullet}$
AE	HF	-128.539306	-127.816842	-256.358275
	VMC	-128.895(7)	-128.089(7)	-257.00(1)
	DMC	-128.92554(7)	-128.12954(6)	-257.0946(2)
Psp	HF	-34.610135	-33.887225	-68.500548
	VMC	-34.883(3)	-34.094(3)	-68.995(5)
	DMC	-34.9066(3)	-34.11083(3)	-69.05587(7)

% correlation energy

	Ne	$Ne^{+\bullet}$	$Ne_2^{+\bullet}$
AE	92.1	87.0	87.0
pseudo	92.0	92.4	89.0

Neon. $Ne_2^{+\bullet} \rightarrow Ne + Ne^{+\bullet}$

Total energies (Ha)

		Ne	$Ne^{+\bullet}$	$Ne_2^{+\bullet}$	D_e (kcal/mol)
AE	HF	-128.539306	-127.816842	-256.358275	1.33
	VMC	-128.895(7)	-128.089(7)	-257.00(1)	10
	DMC	-128.92554(7)	-128.12954(6)	-257.0946(2)	24.8(1)
Psp	HF	-34.610135	-33.887225	-68.500548	2.00
	VMC	-34.883(3)	-34.094(3)	-68.995(5)	11(4)
	DMC	-34.90660(3)	-34.11083(3)	-69.05587(7)	24.12(5)

	D_e (kcal/mol)
BLYP	75.41
B3LYP	60.54
MP2/6-311G**	31.72
CCSD(T)	30.87
SS(a=0.2)	47.95

Summary for hemibonded systems

- QMC works well for the D_e of 3-electron hemibonded systems
  - Consistent values between QMC and existing CCSD(T) calculations
  - AE and pseudopotential calculations are in good agreement

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Very good quality of the pseudopotentials used

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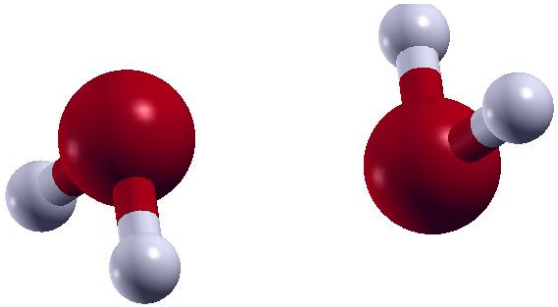
Useful for larger systems

Water radical: $(H_2O)_2^{+\bullet}$

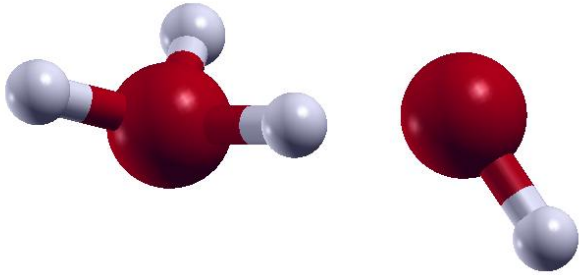
Hemibonded structure

$(H_2O\cdots OH_2)^{+\bullet}$



Proton transferred structure

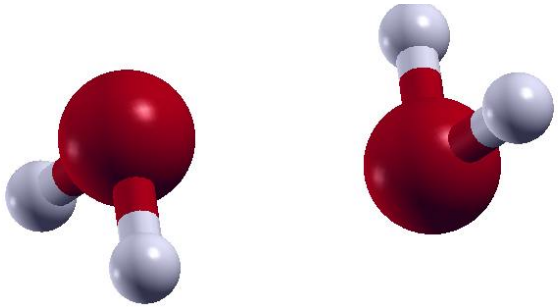
$(H_3O\cdots OH)^{+\bullet}$



Water radical: $(H_2O)_2^{+\bullet}$

Hemibonded structure

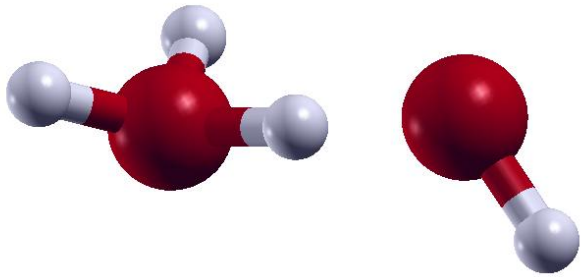
$(H_2O\cdots OH_2)^{+\bullet}$



E_{DMC}	=-152.4341(3)	Ha
$E_{CCSD(T)}$	=-152.2847	Ha

Proton transferred structure

$(H_3O\cdots OH)^{+\bullet}$



E_{DMC}	=-152.4496(2)	Ha
$E_{CCSD(T)}$	=-152.2967	Ha

	Δ (kcal/mol)
DFT	-5.1
MP4	8.9
CCSD(T) extr	7.7
DMC (AE)	9.7(2)
DMC (Psp)	10.13(8)

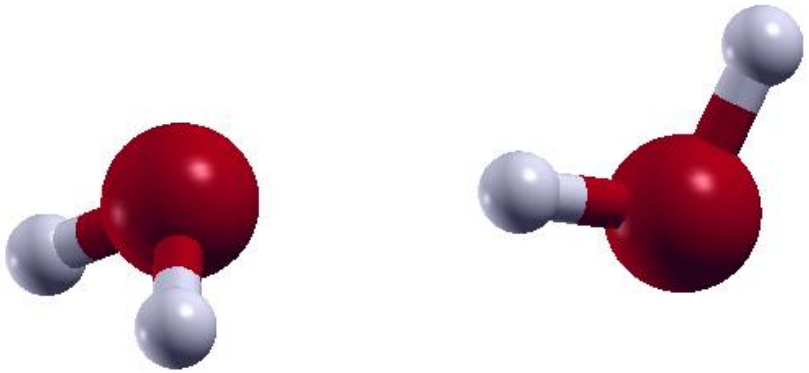
Slightly different geometry:

	Δ (kcal/mol)
DMC (AE)	14.8 (5)
DMC (Psp)	14.6 (2)

Water clusters

- A lot of literature
  - HF: with increasing basis sets
  - DFT: several XC functionals
  - MP2: extrapolating to the Complete Basis Set (CBS) limit
  - CCSD(T)
- Basis Set Superposition Error: artificially lowers the energy of the monomer
- CP correction (undercorrection)
- Open to experimental verification (except for the dimer)

Water dimer: $(H_2O)_2$



Water dimer: $(H_2O)_2$

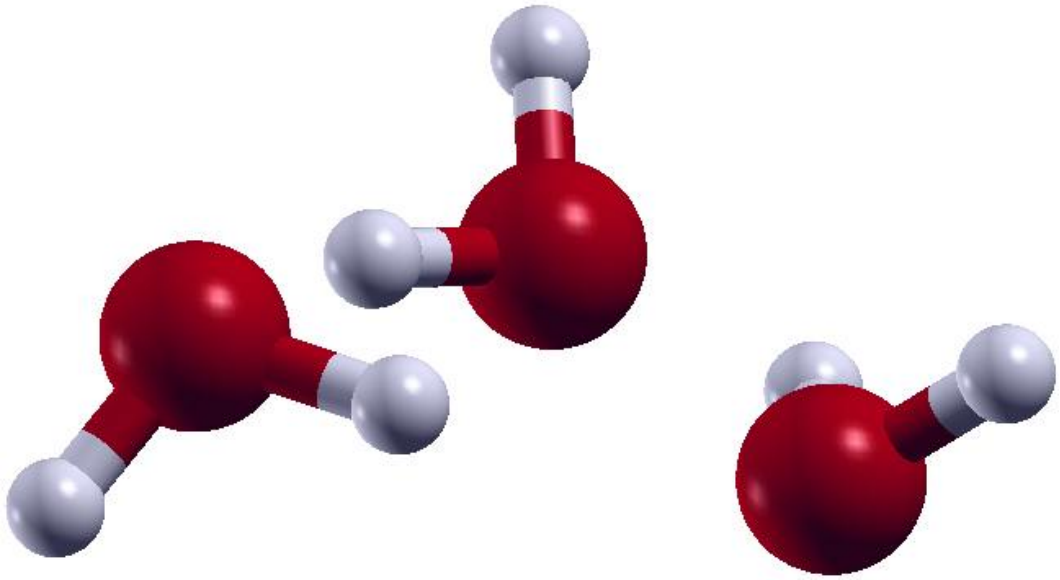
	geometry	H_2O	$(H_2O)_2$	D_e (kcal/mol)
AE	HF	-76.0587	-152.124689	4.57
	VMC	-76.324(5)	-152.699(7)	32
	DMC	-76.42102(4)	-152.85151(9)	5.94(7)
Psp	HF	-16.8947	- 33.80119	7.40
	VMC	-17.182(2)	- 34.367(3)	6
	DMC	-17.20634(2)	- 34.42132(3)	5.41(3)

% correlation energy

	H_2O	$(H_2O)_2$
AE	73.2	79.0
pseudo	92.1	91.2

	D_e (kcal/mol)
CCSD(T)	5.04(5)
MP2 CBS	5.00
DFT BLYP	4.3
DFT GGA	5.55
Experiment	5.44 ± 0.7

Water trimer: $(H_2O)_3$



Water trimer: $(H_2O)_3$

	geometry	H_2O	$(H_2O)_3$	D_e (kcal/mol)
AE	HF	-76.0587	-228.1927	10.41
	VMC	-76.324(5)	-229.032(9)	37.6
	DMC	-76.42102(4)		
Psp	HF	-16.8947	-50.7077	14.80
	VMC	-17.182(2)	-51.569(3)	14.4
	DMC	-17.20634(2)	-51.64487(6)	16.22(6)

% correlation energy

	H_2O	$(H_2O)_3$
AE	73.2	
pseudo	92.1	91.9

	D_e (kcal/mol)
MP2 6Z	15.91
MP2 est	15.9(2)
DFT BLYP	13.7

Conclusion

- QMC calculations on the dissociation energy of
  - Hemibonded He, H_2O, NH_3, HF, Ne radical dimers
  - Hemibonded and H-bonded water radicals
  - Water dimer and trimer
- Accurate results wrt experiment and quantum chemistry calculations
- Pseudopotential and AE calculations agree

$\Downarrow$ $\Downarrow$

$\Longrightarrow$ use QMC with pseudopotentials for larger systems

What next?

- Multideterminants
- Backflow
- Orbital optimization
- ...

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