

## FCI quality energy for H<sub>2</sub>O with a frozen core in cc-pV9Z: 8 electrons in 957 orbitals with micro-hartree precision

The total electronic energy for the ground electronic state of a water molecule, using the standard molecular Hamiltonian and a Dunning basis set with 957 spatial orbitals (1914 spin orbitals), is calculated with the two deepest core electrons frozen and the 8 remaining electrons fully correlated. The 8-electron energy is estimated to be accurate to within  $\pm 2$  micro-hartree of the true energy for this Hamiltonian and basis set. The calculations were done using a fully deterministic, composite coupled cluster approach.

### I. INTRODUCTION

Empirical ionization energies of the water molecule have been determined to a precision of at best  $\pm 0.003$  kcal/mol (about  $4.8 \mu E_h$ ) in 2015 [1, 2], and empirical atomization energies of the water molecule have been determined to a precision of at best . Recently, computer spectroscopy has been able to determine energy differences with accuracies of around  $\pm 1 \text{ cm}^{-1}$  ( $2.2 \mu E_h$ ) or better, for atoms and small molecules with a small number of electrons: If total energies can be calculated to with a precision of  $\pm \sigma$  then energy differences involving them can be determined with a precision  $\pm \sqrt{2}\sigma$  assuming gaussian?. Therefore calculating total (electronic?) energies of the water molecule to a precision of around  $\pm 3 \mu E_h$  or better can be seen as a first step towards determining properties of the water molecule with unprecedented precision. The total electronic energy of a molecule can have many calculations contributing to it, and none of them can be calculated with a precision worse than about  $\pm 3 \mu E_h$  if we wish to determine the total (electronic?) energy to no worse than  $\pm 3 \mu E_h$ .

In this paper I calculate one contribution (the standard Hamiltonian...) to within  $\pm 2$  uH which is likely the best precision ever achieved for 8e- in 957 orbitals. Determining properties to this accuracy would require basis set extrapolations, which typically (in the most standard way) involve CBS for HF, which itself will need some work, but at least this paper eliminates the FCI portion of things as the bottleneck in this journey.

### II. METHODOLOGY

#### A. Hamiltonian

Standard Hamiltonian definition.

#### B. Basis sets

The electronic wavefunction was modeled using a linear combination of atomic orbitals (LCAO) in which Gaussian-type basis sets were used for the atomic orbitals. A series of these basis sets was used, from the cc-pVXZ family, which was first proposed by Dunning [3]. For  $X = 2$  to 6, the basis sets were obtained from

the EMSL basis set exchange, and for  $X = 7$  to 9 the basis sets were obtained privately by David Feller. The exponents and contraction coefficients for all basis sets used in this work, are available on GitHub.

The total number of spatial orbitals for each basis set

#### C. 1- and 2-electron integral calculations

#### D. Hartree-Fock calculations

#### E. Electron correlation calculations

#### F. Software

Where I got the basis sets. What I did with CC, what program I used for integrals, SCF, integral transformation, and CC.

#### G. Estimation of $\pm 2 \mu E_h$ uncertainty for FCI energy with cc-pV9Z

### III. RESULTS

summary of results, maybe this table and a table showing the differences in CC values

### IV. DISCUSSION

#### A. Bottlenecks:

Bottlenecks:

- lack of method to get CBS limit of HF for triatomics.
- speed of CCSDTQ for 7Z (cfour will take 150 days? with 768G or would require 1.5T which doesn't allow more than 30 days, and NCC doesn't allow restarts ... not sure about MRCC... Hanrath program unavailable.)
- speed of CCSDTQP for 5Z (lack of hand-coded CCSDTQP, lack of parallel I/O in MRCC, lack of Hanrath code, speed of CC-QMC to get error down).
- ability to do CCSDTQ(P) for 5Z/6Z, or CCSDT(Q) for 7Z, 8Z, 9Z (MRCC can't restart perturbative calculations).

Table I.

	cc-pV2Z	cc-pV3Z	cc-pV4Z	cc-pV5Z	cc-pV6Z	cc-pV7Z	cc-pV8Z	cc-pV9Z
RHF	-76.026 778 80	-76.057 139 16	-76.064 804	-76.067 060	-76.067 376	-76.067 426	-76.067 449	-76.067 455
CCSD	-76.237 998 10	-76.324 545 75	-76.350 801	-76.359 519	-76.362 323	-76.363 594	-76.364 296	-76.364 659
CCSD(T)	-76.241 033 59	-76.332 192 23	-76.359 794	-76.369 041	-76.372 019	-76.373 362	-76.374 100	-76.374 481
CCSDT	-76.241 195 72	-76.332 268 49	-76.359 807	-76.368 997	-76.371 941	-76.373 264	-76.373 990	-76.374 364
CCSDT(Q)	-76.241 679 91	-76.332 623 49	-76.360 217	-76.369 431	-76.372 384	-76.373 706	-76.374 432	-76.374 806
CCSDTQ	-76.241 650 58	-76.332 587 70	-76.360 183	-76.369 394	-76.372 345	-76.373 667	-76.374 393	-76.374 768
CCSDTQ(P)	-76.241 665 00	-76.332 602 77	-76.360 189	-76.369 401	-76.372 352	-76.373 674	-76.374 400	-76.374 774
CCSDTQP	-76.241 665 92	-76.332 606 22	-76.360 198	-76.369 410	-76.372 361	-76.373 683	-76.374 409	-76.374 783
CCSDTQP(H)	-76.241 667 98	-76.332 606 77	-76.360 199	-76.369 410	-76.372 361	-76.373 683	-76.374 410	-76.374 784
CCSDTQPH	-76.241 668 32	-76.332 606 94	-76.360 199	-76.369 410	-76.372 361	-76.373 683	-76.374 410	-76.374 784
CCSDTQPH(S)	-76.241 668 38	-76.332 606 99	-76.360 199	-76.369 410	-76.372 361	-76.373 683	-76.374 410	-76.374 784
CCSDTQPHS	-76.241 668 43	-76.332 607 05	-76.360 199	-76.369 410	-76.372 362	-76.373 684	-76.374 410	-76.374 784
CCSDTQPHS(O)	-76.241 668 43	-76.332 607 05	-76.360 199	-76.369 410	-76.372 362	-76.373 684	-76.374 410	-76.374 784
FCI = CCSDTQPHSO	-76.241 668 45	-76.332 607 07	-76.360 199	-76.369 410	-76.372 362	-76.373 684	-76.374 410	-76.374 784

Table II.

	cc-pV2Z	cc-pV3Z	cc-pV4Z	cc-pV5Z	cc-pV6Z	cc-pV7Z	cc-pV8Z	cc-pV9Z
CCSD(T)-CCSD	-3035.	-7646.	-8993.	-9522.	-9696.	-9768.	-9805	-9822
CCSDT-CCSD(T)	-162.	-76.	-13.	44.	77.	98.	110	117
CCSDT(Q)-CCSDT	-484.	-355.	-410.	-434.	-442.			
CCSDTQ-CCSDT(Q)	29.3	35.8	34.4	36.7	38.4	<b>38.9(0.5)</b>		
CCSDTQ(P)-CCSDTQ	-14.4	-15.1	-6.5					
CCSDTQP-CCSDTQ(P)	-0.9	-3.5	-9.0					
CCSDTQP-CCSDTQ	-15.3	-18.5	<b>-15.5(3.0)</b>					
CCSDTQP(H)-CCSDTQP	-2.1	-0.5						
CCSDTQPH-CCSDTQP(H)	-0.3	-0.2						
CCSDTQPH-CCSDTQP	-2.4	<b>-0.7(1.7)</b>						
CCSDTQPH(S)-CCSDTQPH	-0.053							
CCSDTQPHS-CCSDTQPH(S)	-0.053							
CCSDTQPHS(O)-CCSDTQPHS	-0.003							
CCSDTQPHSO-CCSDTQPHS(O)	-0.019							
CCSDTQPHSO-CCSDTQP	<b>-0.128</b>							

Table III.

	cc-pV9Z
RHF	-76.067 455 2
CCSDT	-76.374 364 2
CCSDTQ	-76.373 961
CCSDTQP	-76.373 976
CCSDTQPH	-76.373 977
FCI = CCSDTQPHO	-76.373 977

- getting higher than CCSDTQP is not necessary for any basis sets that it's not already possible for, and getting higher than CCSDTQ does not seem necessary for anything beyond 7Z?

- [1] C. Lauzin, U. Jacovella, and F. Merkt, [Molecular Physics](#) **113**, 3918 (2015).
- [2] D. Feller and E. R. Davidson, [Journal of Chemical Physics](#) **148**, 234308 (2018).
- [3] T. H. Dunning, Jr, J. Chem. Phys. **90**, 1007 (1989).