

FCI quality energy for H₂O 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 ± 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 ± 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 $\pm 2 \text{ uH}$ 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

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

III. RESULTS

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

Table I.

	cc-pV2Z	cc-pV3Z	cc-pV4Z	cc-pV5Z
RHF	-76.026 77 88	-76.057 139 16	-76.064 804 29	-76.067 059 7
CCSD	-76.237 998 10	-76.324 545 75	-76.350 800 61	-76.359 518 9
CCSD(T)	-76.241 033 59	-76.332 192 23	-76.359 793 96	-76.369 041 1
CCSDT	-76.241 195 72	-76.332 268 49	-76.359 807 24	-76.368 996 8
CCSDT(Q)	-76.241 679 91	-76.332 623 49	-76.360 217 39	-76.369 430 9
CCSDTQ	-76.241 650 58	-76.332 587 70	-76.360 183 01	-76.369 394 1
CCSDTQ(P)	-76.241 665 00	-76.332 602 77	-76.360 189 48	-76.369 400 6
CCSDTQP	-76.241 665 92	-76.332 606 22	-76.360 198 47	-76.369 409 6
CCSDTQP(H)	-76.241 667 98	-76.332 606 77	-76.360 199 02	-76.369 410 1
CCSDTQPH	-76.241 668 32	-76.332 606 94	-76.360 199 19	-76.369 410 3
CCSDTQPH(S)	-76.241 668 38	-76.332 606 99	-76.360 199 24	-76.369 410 4
CCSDTQPHS	-76.241 668 43	-76.332 607 05	-76.360 199 29	-76.369 410 4
CCSDTQPHS(O)	-76.241 668 43	-76.332 607 05	-76.360 199 30	-76.369 410 4
CCSDTQPHSO	-76.241 668 45	-76.332 607 07	-76.360 199 31	-76.369 410 4

IV. DISCUSSION

A. How uncertainty is determined

B. 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).

- 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?

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- [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).