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Benchmark full configuration-interaction calculations on H_2O, F and F^-

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Abstract

Full configuration-interaction calculations are reported, and compared to other methods, for H_2O at its equilibrium geometry and at two geometries with the H-O bonds stretched. Since the percentage of the SCF reference in the FCI wave function decreases greatly with the bond elongation, the accuracy of techniques based on a single reference do not compare well with the FCI results. However, the results from a CASSCF/MRCI treatment are in good agreement with the FCI. Correlation effects in F compared to Ne are far more similar than for F^- compared to Ne, despite F^- and Ne being isoelectronic. Since the importance of higher than double excitations is more important for F^- than F, a very high percentage of the correlation must be obtained to accurately compute the electron affinity. In a CASSCF/MRCI treatment the higher than quadruple excitations contribute 0.02 eV to the EA, even for modest basis sets.

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I. Introduction

We have recently compared several different computational procedures to full configuration-interaction (FCI) calculations for Ne atom [1], O atom and its negative ion O^- [2], HF and NH_2 [3]. Unlike previous FCI calculations [4-5] and subsequent tests of methods [6-8], double zeta plus polarization (DZP) or larger basis sets were used. Our recent calculations were made possible by recent theoretical [9-10] and technological advances [11]. The benchmark calculations [1-3] showed that the quality of such approximations as the Davidson correction [12] or the coupled-pair functional (CPF) method [13] varied with the basis set and with the weight of the SCF reference in the CI expansion. While the dependence of the accuracy of such approximations on the weight of the SCF reference is not unexpected, the dependence upon the basis set was a surprise. For example, in Ne atom the Davidson correction underestimates the importance of quadruples for basis sets without polarization functions, but overestimates their importance by 20% for a basis set with two sets of polarization functions. The CPF approach shows the opposite effect, improving as the basis set is expanded.

Normally, it is not the absolute accuracy of the methods, but the relative accuracy across a potential surface, that is more important. The HF and NH_2 calculations show that for large geometrical distortions, the SCF reference becomes sufficiently poor that the above approximations are in general unreliable. Multi-reference singles and doubles CI (MRSDCI) calculations based upon a complete active space SCF (CASSCF) [14] wave function give potentials that far better parallel the FCI results. The inclusion of the multi-reference analog of the Davidson correction is found to either improve or leave unchanged the accuracy of the CASSCF/MRCI treatment. While the calculations on HF and NH_2 lead to considerable optimism as to the accuracy of the CASSCF/MRCI approach, calculations on the electron affinity (EA) of O atom show that even this method has its limitations; a very large CASSCF/MRCI treatment (308 reference configuration state functions (CSF's) in D_{2h}) is not able to account for all of the differential higher excitation contributions to the EA.

The previous results have led us to consider H_2O, F and F^-. H_2O has one more electron than NH_2, thus we are able to see if the accuracy of the different approximations depends upon the number of electrons. The decomposition of the correlation by excitation level shows F to be more similar to Ne, while F^- is different from either F or Ne. It is this different character of the correlation which leads to the problems associated with computing the EA.

II. Method of calculation

The O basis set is the Dunning [15] [4s2p] contraction of the Huzinaga [16] (9s5p) primitive set augmented with a d polarization function with an exponent of 1.2. The H basis set is the [2s] contraction of the (4s) primitive set scaled by 1.2 [15] and augmented with a set of p (α=0.8) polarization functions. For the F and F^- calculations the (9s5p) primitive set is contracted to either [4s2p] following Dunning [15], or to [5s3p] by freeing the outermost primitive in the contraction. To adequately describe F^-, the diffuse p set optimized by Dunning and Hay [17] is added, yielding a final valence basis sets of the form (9s6p)/[4s3p] and (9s6p)/[5s4p]. Since the bases sets are given to a different number of significant figures in references 15 and 17, to avoid confusion we tabulate the basis sets in Table I. A 3d polarization function is optimized at the FCI level for F^-. The optimal value was found to be 1.60, the same as that found by Ahlrichs et al. [18] in the optimization for HF at the independent electron pair approximation (IEPA). Therefore, when two d functions are added, the exponents are taken from Ahlrichs [18], α=4.5 and 1.3. In all calculations the 3s components of the 3d orbitals are deleted.

For H_2O we consider the equilibrium geometry (r_e), as defined in Table II, and two configurations where the H-O-H angle is unchanged and the O-H bonds are stretched to 1.5*r_e and 2*r_e. At these three geometries we consider several different levels of treatment. Many correlation treatments are based on a single reference, and for these the SCF orbitals are used. In order to reduce the dimension of the FCI expansion, the 1s electrons are not correlated in any of the calculations. The first level of correlation includes single and double excitations from the SCF reference (SDCI). We use both the Davidson correction [12] (denoted +Q) and the CPF [13] (an essentially size-consistent reformulation of SDCI) to estimate the importance of higher excitations. The importance of higher excitations is also treated via a multi-reference SDCI calculation. These MRCI calculations are based upon a CASSCF optimization of the orbitals and include all of the CSF's in the CASSCF as references. Two different CASSCF calculations are performed. The first correlates the two O-H bonds; the four bonding electrons are distributed within the two active a_1 and two active b_2 orbitals. Although this CASSCF gives proper dissociation, the MRCI calculation shows important configurations (coefficient greater than 0.05 in the MRCI wave function) not included in the reference space. These additional CSF's involve excitations out of the b_1 lone pair of oxygen. To account for this additional important correlation effect, the two b_1 electrons and two b_1 orbitals are added to the CASSCF active space. The MRCI(BIG) calculation based upon the CASSCF(BIG) orbitals does not show any additional important CSF's. The importance of the additional CSF's associated with the b_1 lone pair decreases as the bond length is increased. As the H atoms donate charge to the oxygen, this additional correlation reflects some O^- character near r_e which vanishes as H_2O dissociates. The MRCI(BIG) calculations contain only 31096 CSF's, as compared to the FCI calculations which contain 6 740 280 CSF's, expanded into 28 233 466 determinants and 113 million intermediate states [9,10] in the Knowles and Handy FCI procedure.

The calculations for F and F^- proceed along the same lines as for H_2O. The 1s electrons are not correlated in any of the calculations. The CASSCF wave functions have the 2p electrons and the 2p and 2p′ orbitals as active. In addition to the calculations performed for H_2O, two additional single-reference procedures are used. The first includes all single, double and triple excitations (SDT), while the second includes in addition the quadruple excitations (SDTQ). For the largest basis set, the SDTQ calculation leads to a CI expansion of 110679 CSF's, which is at about the limit of our conventional CI program. This is far larger than the 19996 CSF's in the MRCI expansion, but far smaller than the 6 574 356 CSF's (27 944 852 determinants and 224 million intermediate states) in the FCI wave function.

III. Results and discussion

The total energies of the H_2O calculations are summarized in Table II, while the correlation contributions are decomposed in Table III. The correlation energy, relative to SCF, varies rapidly with R(O-H), increasing by a factor of 1.71 between r_e

and $2*r_e$. The single and doubles correlation energy shows a much smaller change, increasing by a factor of only 1.45. Thus the error in the SDCI calculation is quite large. (The difference between the FCI potential and those at other levels is illustrated by shifting the potential curves to bring them into agreement with the FCI potential at r_e, see Table IV). The smaller increase in the correlation energy with r for the SDCI relative to the FCI shows the differential importance of the higher than double excitations with increasing r. The Davidson correction applied to the SDCI and the CPF method both show the correct trend of increasing rapidly with distance. However, the Davidson correction is too small everywhere, with the error increasing with increasing r. The CPF estimate is also too small at r_e, but becomes too large at $2*r_e$. Thus, at each point, the CPF has about the same error as the Davidson correction, but since the error changes sign, the error in the CPF between $1.5*r_e$ and $2*r_e$ is larger.

The CASSCF treatments, when compared to the SCF, show an even larger change in correlation energy with R(O-H) than does the FCI. This is to be expected, since the CASSCF correctly dissociates to ground state atoms while the SCF does not. Since there is more correlation in the molecule than in the atoms, when compared to the FCI, the CASSCF's show a difference with the FCI with R(O-H) which in the opposite direction from the SCF. However, the shape of the potential in the CASSCF calculations is in better agreement with the FCI than either the SCF or SDCI calculations. The inclusion of more extensive correlation reduces the error further, but the differential correlation effect is much smaller than that at other levels (for example E(MRCI)-E(CASSCF) changes by only a factor 1.26, which reduces to 1.12 with the larger CASSCF reference). The inclusion of the multi-reference analog of the Davidson correction leads to an energy lower than that at the FCI level. This overshoot for the MRCI+Q calculations was also found for NH_2 [3]. The inclusion of this correction reduces the error in the calculation, but the error is actually reduced further for the smaller reference space. Thus the increase in the number of references improves the MRCI results, but the MRCI+Q results do not show the same monotonic improvements with the number of references; this is also true for NH_2 [3]. However, the errors in either of the MRCI+Q calculations are acceptable, and much smaller than the single reference based approaches.

The ratio of the total correlation energy for the $^1A_1$ state of H_2O to the $^2B_1$ state of NH_2 decreases from 1.27 at r_e to 1.17 at $2*r_e$. This is to be expected considering that H_2O has one more electron than NH_2. However, in spite of the increase in the total correlation energy, the accuracy of the MRCI and MRCI+Q potentials is very similar for H_2O and NH_2, that is, errors of no more than 1.2 kcal/mole in the potentials relative to r_e; in fact H_2O has a slightly smaller relative error. Thus the accuracy of the MRCI approach does not appear to depend on the number of electrons correlated for systems of this size.

The correlation contributions for F and F^- are decomposed in Table V, and the results for the EA is summarized in Table VI. The previous Ne atom results are also summarized in Table V for comparison. The total correlation energy of F^- is 1.09 times larger than for Ne, even though they have the same number of electrons. For comparison F has only 83% of the correlation energy of Ne. The difference in correlation energy between Ne and F^- arises from the increased (by about a factor of two) importance of the triple (measured as E(SDT)-E(SD)), quadruple, and higher than quadruple excitations. This is quite different from F, for which the higher than double excitations contribution is 85% of that for Ne, that is, the relative importance of the single and doubles and the higher excitations is about the same for F and Ne. The greater importance of the higher excitations for F^- than F makes the determination of the EA, which depends on obtaining all the differential correlation energy, a difficult task, as compared, say to a potential curve where only relative accuracy is needed. The importance of higher than double excitations is illustrated in Table VI: for the smallest basis set used ([4s3p1d]) the SCF EA is in error by 2 eV, which is reduced by 1.37 eV with the inclusion of SD correlation, but the FCI EA is still larger by 0.21 eV. Higher excitations comprise about 13% of the correlation contribution to the EA. If the basis set is improved to [5s4p2d], the contribution of the higher than double excitation increases to 15% of the total correlation. If the Davidson correction or CPF approach is used to account for the higher excitations the EA is improved over the SDCI, but is still not equal to the FCI result. These corrections underestimate the importance of higher excitations for both systems. It is well known [19] that the most important correlation effect for F and F^- is the 2p to 2p′ excitation. When this is included in the CASSCF calculation, the EA is considerably improved over the SCF result, giving about 80% of the difference between SCF and SDCI. Using this CASSCF reference leads to a MRCI EA which is better than either the CPF or SDCI+Q treatments, and in good agreement with the FCI, being only 0.02eV smaller. If the estimate of higher excitations is included, an energy lower than the FCI result is obtained for both F and F^-. However, this correction may overestimate the higher excitations in an equivalent manner for both systems, since the results at this level are equal to those at the FCI level.

At the FCI level, the 2s correlation was found to contribute significantly to the EA of oxygen [2]. In Table VI, we also report the EA when only the 2p electrons are correlated. While correlating only the 2p electrons increases the SDCI EA by 0.13 to 0.18 eV relative to correlating both the 2s and 2p electrons, at the FCI level the EA is increased by only 0.08 to 0.12 eV. The negative contribution to the EA of the 2s-2s and 2s-2p correlation decreases with the inclusion of higher excitations. For O/O^-, with a very large basis set the 2s contribution actually increases the EA, but only when higher excitations are included. This is understandable in light of the factor of two larger contribution from higher excitations in the negative ions.

IV. Conclusions

The MRCI potentials (and MRCI with the multi-reference analog of the Davidson correction) are found to be in excellent agreement with FCI calculations. The error in the H_2O calculations are very similar to that found for NH_2, even though the total correlation energy of H_2O is about 1.2 times larger. The contribution of higher than double and of higher than quadruple excitations is found to be a factor of two larger for F^- than Ne, whereas the single and doubles correlation energy differs by only 10%. For F, the single and doubles, and higher than doubles, are the same percentage of the correlation as in Ne. Since the distribution of the correlation energy by excitation level is different between F and F^-, all of the correlation must be computed to account for the difference in order to obtain accurate EA.

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Table I. The valence basis sets.

s		p	
		O (9s5p)/[4s2p]	
exponent	coefficient	exponent	coefficient
7817.0	0.002031	35.18	0.019580
1176.0	0.015436	7.904	0.124200
273.2	0.073771	2.305	0.394714
81.17	0.247606	0.7171	0.627375
27.18	0.611832	0.2137	1.000000
3.414	0.241205		
9.532	1.000000		
0.9398	1.000000		
0.2846	1.000000		
H (4s)/[2s]			
exponent	coefficient		
19.2384	0.032828		
2.89872	0.231204		
0.653472	0.817226		
0.177552	1.000000		
		F (9s5p)/[4s2p]	
exponent	coefficient	exponent	coefficient
9994.79	0.002017	44.3555	0.020868
1506.03	0.015295	10.0820	0.130092
350.269	0.073110	2.9959	0.396219
104.053	0.246420	0.9383	0.620368
34.8432	0.612593	0.2733	1.000000
4.3688	0.242489		
12.2164	1.000000		
1.2078	1.000000		
0.3634	1.000000		

Table II. Total energies (a.u.) for the H_2O calculations.

Calculation		geometry[a]	
	r_e	$1.5*r_e$	$2*r_e$
SCF	-76.040542	-75.800494	-75.582286
SDCI	-76.243772	-76.040984	-75.876606
FCI	-76.256624	-76.071405	-75.952269
CPF	-76.252504	-76.064365	-75.956222
SDCI+Q	-76.254549	-76.067003	-75.942257
CAS	-76.094713	-75.924781	-75.823721
MRCI	-76.251643	-76.066885	-75.948557
MRCI+Q	-76.257983	-76.072741	-75.952973
CAS(BIG)	-76.129876	-75.953141	-75.839916
MRCI(BIG)	-76.254108	-76.069363	-75.950517
MRCI(BIG)+Q	-76.257805	-76.072943	-75.953731

[a] The O is located at (0,0,0) and the H nuclear coordinates are: r_e (±1.494187, 0, 1.156923), $1.5*r_e$ (±2.241281, 0, 1.735385), and $2*r_e$ (±2.988374, 0, 2.313846).

Table III. A decomposition of the correlation contributions for water, in a.u.

Calculation		geometry	
	r_e	$1.5*r_e$	$2*r_e$
E(SDCI)-E(SCF)	0.203230	0.240490	0.294320
E(FCI)-E(SCF)	0.216082	0.270911	0.369983
E(FCI)-E(SDCI)	0.012852	0.030421	0.075663
E(CPF)-E(SDCI)	0.008732	0.023381	0.079616
E(SDCI+Q)-E(SDCI)	0.010777	0.026019	0.065651
E(CAS)-E(SCF)	0.054171	0.124287	0.241435
E(MRCI)-E(CAS)	0.156930	0.142104	0.124836
E(MRCI)-E(SDCI)	0.007871	0.025901	0.071951
E(FCI)-E(MRCI)	0.004981	0.004520	0.003712
E(MRCI+Q)-E(MRCI)	0.006340	0.005856	0.004416
E(FCI)-E(MRCI+Q)	-0.001359	-0.001336	-0.000704
E(CAS(BIG))-E(SCF)	0.089334	0.152647	0.257630
E(MRCI(BIG))-E(CAS(BIG))	0.124232	0.116222	0.110601
E(MRCI(BIG))-E(SDCI)	0.010336	0.028379	0.073911
E(FCI)-E(MRCI(BIG))	0.002516	0.002042	0.001752
E(MRCI(BIG)+Q)-E(MRCI(BIG))	0.003697	0.003580	0.003214
E(FCI)-E(MRCI(BIG)+Q)	-0.001181	-0.001538	-0.001462

Table IV. A comparison of the potential curves for water, in a.u. All curves are shifted in energy to bring the energies at r_e into agreement with that at the full CI level. The difference energy between r_e and the other geometries is compared to the FCI potential.

Calculation	$1.5{*}r_e$-r_e	$2{*}r_e$-r_e
SCF	-0.05482900	-0.15390100
SDCI	-0.01756900	-0.06281100
CPF	-0.00292000	0.00807300
SDCI+Q	-0.00232700	-0.00793700
CAS	0.01528700	0.03336300
MRCI	0.00046100	0.00126900
MRCI+Q	-0.00002300	-0.00065500
CAS(BIG)	0.00848400	0.01439500
MRCI(BIG)	0.00047400	0.00076400
MRCI(BIG)+Q	0.00035700	0.00028100

Table V. A comparison of the correlation contributions, in a.u, for F^-, F and Ne.

F^- ion

Basis	[4s3p]	[4s3p1d]	[4s3p2d]	[5s4p2d]
E(SCF)	-99.442848	-99.442848	-99.442848	-99.443696
E(SD)-E(SCF)	0.132219	0.197820	0.220160	0.245405
E(SDT)-E(SD)	0.001913	0.003241	0.004297	0.006369
E(SDTQ)-E(SDT)	0.006558	0.008848	0.009707	0.010480
E(FCI)-E(SDTQ)	0.000486	0.000584	0.000664	0.000740
E(FCI)-E(SD)	0.008957	0.012673	0.014668	0.017589
E(SD+Q)-E(SD)	0.006106	0.009711		0.012071
E(CPF)-E(SD)	0.005043	0.008155		0.010077
E(CASSCF)-E(SCF)				0.107265
E(MRCI)-E(CASSCF)				0.152776
E(MRCI)-E(SD)				0.014636
E(MRCI+Q)-E(SD)				0.018473

F atom

Basis	[4s3p1d]	[4s3p2d]	[5s4p2d]
E(SCF)	-99.394273	-99.394273	-99.394684
E(SD)-E(SCF)	0.147416	0.165916	0.192421
E(FCI)-E(SD)	0.004931	0.006294	0.007772
E(CPF)-E(SD)			0.004741
E(SD+Q)-E(SD)			0.006344
E(FCI)-E(SCF)	0.152347	0.172210	0.200193
E(CASSCF)-E(SCF)			0.061620
E(MRCI)-E(SD)			0.005684
E(MRCI+Q)-E(SD)			0.008689

Ne atom[a]

Basis	[5s3p2d]
E(SD)-E(SCF)	0.235733
E(SDT)-E(SD)	0.003258
E(SDTQ)-E(SDT)	0.005670
E(FCI)-E(SD)	0.009131
E(FCI)-E(SDTQ)	0.000203
E(CPF)-E(SD)	0.005276
E(SD+Q)-E(SD)	0.006823

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[a] Results are taken from Reference 1.

Table VI. A comparison of the computed EA[a] for F, in eV.

		2s and 2p correlated	
Basis	[4s3p1d]	[4s3p2d]	[5s4p2d]
SCF	1.32	1.32	1.33
SDCI	2.69	2.79	2.78
FCI	2.90	3.03	3.04
DVD			2.93
CPF			2.92
CAS			2.58
MRCI			3.02
MRCI+Q			3.04
		2p correlated	
Basis	[4s3p1d]	[4s3p2d]	[5s4p2d]
SDCI	2.82	2.97	2.95
FCI	2.98	3.15	3.16

[a] For comparison the experimental value is 3.399 eV, see Reference 20.