Benchmark full configuration-interaction calculations on HF and NH$_2$

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Abstract

Full configuration-interaction (FCI) calculations are performed at selected geometries for the $^1\Sigma^+$ state of HF and the $^2B_1$ and $^2A_1$ states of NH$_2$ using both DZ and DZP gaussian basis sets. Higher excitations become more important when the bonds are stretched and the SCF reference becomes a poorer zeroth-order description of the wave function. The CASSCF-MRCI procedure gives excellent agreement with the FCI potentials, especially when corrected with a multi-reference analog of the Davidson correction.

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I. Introduction

Recent improvements in methods for full configuration-interaction (FCI) calculations [1-2] combined with the extensive memory (>256 million words) and excellent vector capabilites of the CRAY 2, permit FCI calculation with larger basis sets than used in previous benchmark calculations [3-4]. Recently, we presented FCI calculations for the ^1S state of Ne atom [5] to assess the reliability of methods such as the Davidson correction [6] and the coupled pair functional (CPF) [7] for estimating the energy contribution of higher excitations. An important observation was that the accuracy of both the Davidson correction and the CPF approximation depended on basis set quality. For example, the CPF accounted for only 40% of the quadruples contribution for a DZ basis set, but 60% of the quadruples contribution for a DZP basis set. However, the total contribution of higher excitations was relatively small in Ne, which is well described by an SCF reference. To investigate further the accuracy of approximate methods of including higher excitations, we consider herein the $^1\Sigma^+$ state of the isoelectronic HF molecule and the $^2B_1$ and $^2A_1$ states of NH_2 using both DZ and DZP gaussian basis sets. To investigate structures where the SCF is not a good zeroth-order description we consider geometries away from equilibrium.

II. Methods

For the nitrogen and fluorine atoms we used the Dunning 4s2p contraction [8] of the Huzinaga 9s5p primitive basis sets [9]. For hydrogen we used the 2s contraction [8] of the Huzinaga 4s primitive set scaled by a factor of 1.2. When polarization functions are included, the exponents are: F(3d=1.6), N(3d=0.9), and H(2p=0.8). The 3s component of the 3d functions is deleted in all calculations.

For HF the geometries considered are r_e (1.733 bohr), 1.5 times r_e (2.5995 bohr), and twice r_e (3.466 bohr). For NH_2 we consider r_e, 1.5 times r_e and twice r_e, as well as a fourth point with the H-H bond distance at the H_2 equilibrium value and the N-H distance at about twice the r_e for NH_2. The NH_2 molecule is placed in the xz plane, with the N at the origin. The coordinates actually used for NH_2 are given explicitly in Table I.

In this study we have used both an SCF and a complete-active-space self-

consistent field (CASSCF) wave function [10] as the zeroth-order reference. The SCF reference is used for the single-reference singles plus doubles configuration-interaction calculation, SDCI, SDCI + triples (SDT), SDT + quadruples (SDTQ), the coupled pair functional (CPF) wave function and the Chong-Langhoff modification [11] of CPF (MCPF). The SCF reference is also used for the FCI calculations, which are found to be invariant to the orbital basis to within a few microhartrees. The slight differences arise because the two core electrons on nitrogen and fluorine are not correlated in any calculations since this restriction dramatically reduces the length of the FCI expansion. For the $^1\Sigma^+$ state of HF the SCF reference configuration is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$, and for the $^2B_1$ state of NH_2 it is $1a_1^2 2a_1^2 3a_1^2 1b_1^1 1b_2^2$ at all geometries. For the $^2A_1$ state of NH_2 the three geometries stretching the two N-H bonds correspond to the $3a_1 \rightarrow 1b_1$ excitation relative to the $^2B_1$ configuration whereas the fourth point denoted N$\cdots$H-H corresponds to the $1b_1 \rightarrow 4a_1$ excitation.

The multi-reference CI calculations (MRCI) are based on CASSCF wave functions. For HF, the hydrogen 1s and fluorine $2p\sigma$ orbitals and electrons are active. The MRCI calculations consist of single and doubles from the two non-vanishing configurations in the CASSCF wave function. For both states of NH_2, the nitrogen 2s and 2p orbitals and electrons are active, as well as the two hydrogen 1s orbitals and electrons. The first set of MRCI calculations using these CASSCF optimized orbitals include all references arising from all distributions of the nitrogen 2p and hydrogen 1s electrons among the active orbitals; hence the 2s electrons are correlated, but the 2s orbital is doubly occupied in all reference configurations. In the second set of MRCI calculations, denoted MRCI(BIG), all configurations in the CASSCF are included as references. For the SDCI wave functions we also include the Davidson estimate for unlinked quadruple excitations, denoted +Q. For the MRCI calculations we use a multi-reference analogue of this correction, namely $\Delta E_{SD} (1 - \sum_R C_R^2)$, where Δ_{SD} is the difference between the energy of the reference CSF's and the MRCI, and the C_R are the coefficients of the reference configurations in the MRCI wave function.

III. Results and discussion.

The total energies at the SCF and FCI level are summarized in Table I for

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both HF and NH_2. The molecular geometries used for the $^2B_1$ and $^2A_1$ states of NH_2 are given explicitly as well.

In Table II we have summarized the CI results for HF using both the DZ and DZP basis sets at three geometries (r_e,1.5*r_e,2*r_e). It is interesting that although the SDCI-SCF energy difference is considerably larger for the DZP basis, this difference increases more slowly with increasing R than for the DZ basis. The ratio of this difference at 2*r_e compared to r_e is 1.21 with the DZP basis and 1.47 with the DZ basis. Hence, the addition of the polarization function substantially improves the description of the distortions taking place as the bond is broken, and less of this effect shows up as electronic correlation. For the DZP basis the energy contribution of the triples, quadruples and higher than quadruple excitations all increase at about the same rate as the bond is broken (by about a factor of three between 2*r_e and r_e). The energy contribution of quadruple excitations at 2*r_e using the DZP basis is about 0.5 eV, which is about 40 times greater than the combined contribution of quintuple through octuple excitations.

The results in Table II show that the three configuration CASSCF calculation followed by all single and double excitations from the two configurations (σ^2 and $\sigma*^2$) that have non-vanishing coefficients in the CASSCF, provide a much more uniform description of the potential. Also, the multi-reference quadruples correction is much more uniform as a function of bond distance.

The next three rows for each basis set in Table II give a measure of the reliability of CPF methods and the Davidson correction for estimating the energy contribution of higher excitations. Note that at r_e these corrections all underestimate the quadruples correction, but as the bond length is increased the corrections become a substantial overestimate. In fact the SDCI+Q energies at 2*r_e are well below the FCI energies. Note also that this overcorrection of SDCI+Q is much less severe for the DZP basis than the DZ basis.

Since it is a rather stringent requirement of any method to reproduce the FCI total energies, a better criterion for judging a method is how well the resulting potentials parallel the FCI potential. In Table III we report for HF the energy difference between r_e and 1.5*r_e and 2*r_e at different levels of theory. That is, all potentials are normalized at r_e so that the energy differences in Table III reflect

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directly deviations with the FCI potential. The SCF description becomes quite poor as the bond is stretched, although somewhat less so for the DZP basis. The CASSCF description is better, but overcorrects because it overestimates the contribution of the dissociative configuration. The SDCI is a substantial improvement over SCF, but still retains some of the bias of the SCF. The SDCI results are improved by the Davidson correction, especially for the DZP basis, but overestimates the effect of higher excitations. The coupled pair methods are generally more reliable than SDCI+Q, and the MCPF results for the DZP basis are in particularly good agreement with the FCI results. Note that the results at the SDT level are still inadequate since the energy contribution of quadruple excitations is both large and rapidly increasing as the bond is broken. At the SDTQ level the error at $2*r_e$ in the DZP basis is less than 0.02 eV. However, the SDTQ configuration expansions are quite lengthy (48,963 CSFs for the DZP basis), and hence do not represent an optimal approach of including higher excitations. This is illustrated by the results of the much smaller MRCI expansions (1015 CSFs), which are of comparable quality. Most impressive, however, are the MRCI+Q results which agree with the FCI potential to well within chemical accuracy in every case. The comparison of the MRCI and MRCI+Q results in Table III provide strong support for the validity of the multi-reference analog of the Davidson correction.

In addition to the dissociation of HF, where one chemical bond is being broken, we consider for the $^2B_1$ and $^2A_1$ states of NH_2 the simultaneous extension of both N-H bonds. The energy difference between the FCI and various levels of theory using both the DZ and DZP gaussian basis sets are summarized for the $^2B_1$ and $^2A_1$ states in Tables IV and V, respectively. Four geometries are considered – equilibrium, both bonds stretched to 1.5 and 2.0 times r_e, and an N···H-H structure with the H-H bond length that of the ground state of H_2 and the N-H bond at about $2*r_e$. Explicit coordinates are given in Table I. As for the HF molecule, the SCF reference becomes an increasingly poorer zeroth-order description of the system as the bond length is increased, particularly for the $^2B_1$ ground state. Although the SDCI accounts for a substantial portion of this difference, the difference with the FCI and hence the contribution of higher excitations increases rapidly as the bonds are stretched. In contrast, the difference between the FCI and CASSCF is more

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constant and actually decreases slightly with increasing r; hence the errors in the MRCI treatment are generally less at $2*r_e$ than at r_e. In general, the differences with the FCI are further reduced when the multi-reference quadruples correction is added, although in every case MRCI+Q is below the FCI energy. The coupled pair functional methods and the SDCI+Q, which are based on the SCF reference, have larger differences with the FCI, and these differences increase as the SCF reference becomes a poorer representation of the wave function. These approximate methods for incorporating higher excitations are substantially closer to the FCI energies than are the SDCI energies. Generally they give energies that lie above the FCI for the r_e and $1.5*r_e$ geometries, but often overshoot (particularly CPF) the energy at $2*r_e$. The MCPF method, which uses somewhat more complex but more realistic renormalization denominators, tends to overshoot less and thus has a larger domain of applicability.

The theoretical potentials at various levels of theory are compared to the FCI potentials for the $^2B_1$ and $^2A_1$ states in Tables VI and VII, respectively. These results again illustrate how poor the SCF potential becomes as r increases. The CASSCF overestimates the importance of the dissociative configurations and errs in the opposite direction, although it is better than the SDCI potential, which retains much of the bias of the SCF. However, the Davidson correction helps substantially and the SDCI+Q potential is approaching chemical accuracy. The MRCI potentials are substantially better. Again, the multi-reference Davidson correction generally gives further improvements in the potentials.

The energy between the minimum in the $^2B_1$ and $^2A_1$ potentials of NH_2 (T_e) is given with respect to the FCI result at each level of correlation treatment for the DZ and DZP basis sets in Table VIII. Since the SCF reference provides nearly equivalent descriptions of both states, the differences with the FCI results are not very large. Apart from the SCF and CASSCF results, the T_e are within 0.05 eV of the FCI result. Interestingly the multi-reference Davidson correction actually makes the agreement worse, although the errors are in every case small.

IV. Conclusions

The CASSCF MRCI calculations are in excellent agreement with the FCI cal-

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culations, especially after including a correction for quadruple excitations. This is not surprising considering that the CASSCF potential parallels the FCI potential better than does the SDCI potential. The inclusion of an estimate of higher excitations, either by the Davidson correction or by CPF works reasonably well, except for NH_2 at $2*r_e$, where the SCF reference is much poorer. The MCPF method gives an improved description of the $2*r_e$ point, but does not significantly alter the results at the other points, where the SCF is a better reference.

The accuracy of the different approximations are found to vary somewhat with the quality of the basis set used. These results should supply a better test of methods than the previous FCI calculations, most of which were restricted to a DZ basis set.

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Table I. Total energies (a.u.) for the full CI(SCF) calculations.

	DZ	DZP	geometry[a]
r_e	-100.147204(-100.021973)	-100.250969(-100.047087)	1.733
$1.5*r_e$	-100.079441(-99.924625)	-100.160393(-99.933229)	2.5995
$2*r_e$	-100.008676(-99.815206)	-100.081108(-99.817572)	3.466

$NH_2\ {}^2B_1$

	DZ	DZP	geometry[b](x,z)
r_e	-55.646028(-55.543825)	-55.742620(-55.573008)	1.5186,1.1993
$1.5*r_e$	-55.534809(-55.373780)	-55.605209(-55.387413)	2.2779,1.79895
$2*r_e$	-55.449427(-55.185112)	-55.505524(-55.188719)	3.0372,2.3986
$N+H_2$	-55.472746(-55.383141)	-55.544560(-55.388944)	0.7006,3.8062

$NH_2\ {}^2A_1$

	DZ	DZP	geo(x,z)
r_e	-55.603404(-55.505424)	-55.688762(-55.523192)	1.7972,0.5840
$1.5*r_e$	-55.449846(-55.311550)	-55.517614(-55.32145)	2.6958,0.8760
$2*r_e$	-55.355766(-55.155112)	-55.415133(-55.157046)	3.5944,1.1680
$N+H_2$	-55.462119(-55.364954)	-55.536081(-55.370425)	0.7006,3.8062

[a] The H-F bond length in bohr.
[b] The x,z corridinates, where the molecule is placed in the xz plane with the N at 0,0,0, and the H atoms at x,0,z, and -x,0,z.

Table II. Energy differences (au) between different levels of correlation treatment for the $^1\Sigma^+$ state of HF.

A. DZ BASIS	r_e	$1.5 * r_e$	$2 * r_e$
SDCI-SCF	-0.11951300	-0.14499600	-0.17531200
SDT-SDCI	-0.00106500	-0.00189500	-0.00491100
SDTQ-SDT	-0.00444400	-0.00756900	-0.01261700
FCI-SDTQ	-0.00020900	-0.00035600	-0.00063000
MRCI-CASSCF	-0.09672100	-0.09518000	-0.08502900
MRCI+Q-MRCI	-0.00251900	-0.00273100	-0.00228300
CPF-SDCI	-0.00302000	-0.00637900	-0.01430100
SDCI+Q-SDCI	-0.00391000	-0.00914200	-0.02510300
MCPF-SCCI	-0.00320500	-0.00712900	-0.01713700

B. DZP BASIS			
SDCI-SCF	-0.19450300	-0.21229400	-0.23596100
SDT-SDCI	-0.00236800	-0.00375300	-0.00842200
SDTQ-SDT	-0.00672900	-0.01062300	-0.01823500
FCI-SDTQ	-0.00028200	-0.00049400	-0.00091800
MRCI-CASSCF	-0.17409400	-0.16719100	-0.15418300
MRCI+Q-MRCI	-0.00607600	-0.00615600	-0.00528000
CPF-SDCI	-0.00613000	-0.01063900	-0.02227100
SDCI+Q-SDCI	-0.00778300	-0.01345900	-0.02886600
MCPF-SDCI	-0.00640100	-0.01139400	-0.02466700

Table III. Energy differences (au) between the FCI and different levels of correlation treatment for the $^1\Sigma^+$ state of HF.

DZ Basis

Method	$1.5*r_e$-r_e	$2*r_e$-r_e
SCF	0.029585	0.068239
SDCI	0.004102	0.012440
SDCI+Q	-0.001130	-0.008753
CPF	0.000743	0.001159
MCPF	0.000178	-0.001492
SDT	0.003272	0.008594
SDTQ	0.000147	0.000421
CASSCF	-0.001289	-0.011865
MRCI	0.000252	-0.000173
MRCI+Q	0.000040	0.000063

DZP basis set

SCF	0.023282	0.059654
SDCI	0.005491	0.018196
SDCI+Q	-0.000185	-0.002887
CPF	0.000982	0.002055
MCPF	0.000498	-0.000070
SDT	0.004106	0.012142
SDTQ	0.000212	0.000636
CASSCF	-0.006811	-0.020667
MRCI	0.000092	-0.000756
MRCI+Q	0.000012	0.000040

Table IV. Energy differences (au) between the FCI and other levels of correlation treatment for the $^2B_1$ state of NH_2.[a]

DZ Basis

Method	r_e	$1.5*r_e$	$2*r_e$	$N \cdots H_2$
SCF	0.102203	0.161029	0.264315	0.08960518
SDCI	0.004609	0.016439	0.055109	0.00621524
MCPF	0.001403	0.002836	0.009711	0.00032756
CPF'[b]	0.001489	0.002595	-0.005823	0.00082237
CPF	0.001460	0.001868	-0.023677	0.00078711
SDCI+Q	0.000447	-0.000890	-0.004487	0.00075817
CASSCF	0.051976	0.045721	0.039039	0.04644218
MRCI	0.001172	0.000714	0.000542	0.00114810
MRCI(BIG)	0.001116	0.000644	0.000509	0.00098085
MRCI+Q	-0.000154	-0.000492	-0.000264	-0.00029528
MRCI(BIG)+Q	-0.000055	-0.000355	-0.000219	-0.00007293

DZP Basis

Method	r_e	$1.5*r_e$	$2*r_e$	$N \cdots H_2$
SCF	0.169612	0.217796	0.316805	0.15561649
SDCI	0.009003	0.023472	0.069157	0.01329291
MCPF	0.002365	0.004967	0.015670	0.00200373
CPF'[b]	0.002509	0.004707	0.003116	0.00178015
CPF	0.002480	0.004190	-0.009212	0.00169289
SDCI+Q	0.000572	0.001584	0.009026	0.00244093
CASSCF	0.121869	0.107084	0.094456	0.11400831
MRCI	0.003446	0.002279	0.001501	0.00337559
MRCI(BIG)	0.003202	0.001940	0.001338	0.00292420
MRCI+Q	-0.001271	-0.002047	-0.001735	-0.00162566
MRCI(BIG)+Q	-0.001239	-0.001980	-0.001741	-0.00146699

[a] Negative entry indicates the energy is lower than the FCI.

[b] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

Table V. Energy differences (au) between the FCI and other levels of correlation treatment for the $^2A_1$ state of NH_2.[a]

	DZ Basis			
Method	r_e	$1.5*r_e$	$2*r_e$	$N \cdots H_2$
SCF	0.097980	0.138296	0.200654	0.09716511
SDCI	0.004336	0.012032	0.032600	0.01312506
MCPF	0.001456	0.003365	-0.000088	0.00118610
CPF'[b]	0.001532	0.003347	-0.018390	0.00297603
CPF	0.001519	0.003375	-0.014174	0.00289667
SDCI+Q	0.000616	0.000893	-0.004761	0.00542632
CASSCF	0.058332	0.058208	0.043838	0.04449573
MRCI	0.001251	0.001572	0.000811	0.00090852
MRCI(BIG)	0.001009	0.001114	0.000735	0.00087816
MRCI+Q	-0.001631	-0.002968	-0.000326	-0.00005773
MRCI(BIG)+Q	-0.000516	-0.000610	-0.000238	-0.00007346

	DZP Basis			
SCF	0.165570	0.196167	0.258087	0.16565612
SDCI	0.008482	0.018097	0.048673	0.02229559
MCPF	0.002290	0.004900	0.005865	0.00550461
CPF'[b]	0.002431	0.004970	-0.015832	0.00424528
CPF	0.002413	0.005022	-0.016182	0.00412679
SDCI+Q	0.000618	0.002403	0.006886	0.00922251
CASSCF	0.127696	0.118050	0.102355	0.11461881
MRCI	0.003929	0.003935	0.002267	0.00316584
MRCI(BIG)	0.003228	0.002836	0.001803	0.00278544
MRCI+Q	-0.003106	-0.005010	-0.001670	-0.00117540
MRCI(BIG)+Q	-0.001809	-0.002219	-0.001918	-0.00157857

[a] Negative entry indicates the energy is lower than the FCI.

[b] The Chong-Langhoff implementation of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

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Table VI. Energy differences (au) between the FCI and different levels of correlation treatment for the $^2B_1$ state of NH_2.

DZ Basis

Method	$1.5*r_e$-r_e	$2*r_e$-r_e	$N\cdots H_2$-r_e
SCF	0.05882552	0.16211179	-0.01259813
SDCI	0.01183033	0.05050009	0.00160673
MCPF	0.00143290	0.00830835	-0.00107530
CPF'[a]	0.00110573	-0.00731251	-0.00066686
CPF	0.00040776	-0.02513683	-0.00067285
SDCI+Q	-0.00133646	-0.00493371	0.00031155
CASSCF	-0.00625527	-0.01293716	-0.00553361
MRCI	-0.00045866	-0.00062996	-0.00002432
MRCI(BIG)	-0.00047153	-0.00060722	-0.00013494
MRCI+Q	-0.00033712	-0.00010991	-0.00014079
MRCI(BIG)+Q	-0.00029993	-0.00016385	-0.00001821

DZP Basis

Method	$1.5*r_e$-r_e	$2*r_e$-r_e	$N\cdots H_2$-r_e
SCF	0.04818368	0.14719287	-0.01399544
SDCI	0.01446939	0.06015405	0.00428998
MCPF	0.00260180	0.01330525	-0.00036150
CPF'[a]	0.00219774	0.00060737	-0.00072896
CPF	0.00171006	-0.01169217	-0.00078678
SDCI+Q	0.00101197	0.00845456	0.00186908
CASSCF	-0.01478520	-0.02741322	-0.00786048
MRCI	-0.00116640	-0.00194520	-0.00007021
MRCI(BIG)	-0.00126231	-0.00186384	-0.00027800
MRCI+Q	-0.00077575	-0.00046378	-0.00035453
MRCI(BIG)+Q	-0.00074106	-0.00050181	-0.00022757

[a] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

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Table VII. Energy differences (au) between the FCI and different levels of correlation treatment for the $^2A_1$ state of NH_2.

DZ Basis

Method	$1.5*r_e-r_e$	$2*r_e-r_e$	$N\cdots H_2-r_e$
SCF	0.04031524	0.10267371	-0.00081533
SDCI	0.00769570	0.02826419	0.00878918
MCPF	0.00190896	-0.00154370	-0.00026974
CPF'[a]	0.00181481	-0.01992232	0.00144354
CPF	0.00185597	-0.01569280	0.00137788
SDCI+Q	0.00027680	-0.00537750	0.00480983
CASSCF	-0.00012341	-0.01449361	-0.01383588
MRCI	0.00032109	-0.00043952	-0.00034228
MRCI(BIG)	0.00010478	-0.00027385	-0.00013077
MRCI+Q	-0.00133786	0.00130498	0.00157288
MRCI(BIG)+Q	-0.00009474	0.00027806	0.00044224

DZP Basis

Method	$1.5*r_e-r_e$	$2*r_e-r_e$	$N\cdots H_2-r_e$
SCF	0.03059766	0.09251729	0.00008646
SDCI	0.00961563	0.04019126	0.01381379
MCPF	0.00261021	0.00357473	0.00321466
CPF'[a]	0.00253934	-0.01826289	0.00181431
CPF	0.00260866	-0.01859546	0.00171334
SDCI+Q	0.00178540	0.00626841	0.00860488
CASSCF	-0.00964579	-0.02534059	-0.01307699
MRCI	0.00000590	-0.00166202	-0.00076318
MRCI(BIG)	-0.00039130	-0.00142503	-0.00044209
MRCI+Q	-0.00190407	0.00143620	0.00193059
MRCI(BIG)+Q	-0.00041014	-0.00010893	0.00023031

[a] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

Table VIII. T_e's relative to the full CI.

Method	DZ	DZP
SCF	-0.004223	-0.004042
SDCI	-0.000273	-0.000521
MCPF	0.000053	-0.000075
CPF'[a]	0.000043	-0.000078
CPF	0.000059	-0.000066
SDCI+Q	0.000170	0.000046
CASSCF	0.006356	0.005827
MRCI	0.000078	0.000483
MRCI(BIG)	-0.000107	0.000025
MRCI+Q	-0.001476	-0.001835
MRCI(BIG)+Q	-0.000461	-0.000569
FCI[b]	0.042624	0.053858

[a] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

[b] Full CI T_e.

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