Core-core and core-valence correlation

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Abstract

The effect of $1s$ core correlation on properties and energy separations has been analyzed using full configuration-interaction (FCI) calculations. The Be $^1S - ^1P$, the C $^3P - ^5S$ and CH$^+$ $^1\Sigma^+ - ^1\Pi$ separations, and CH$^+$ spectroscopic constants, dipole moment and $^1\Sigma^+ - ^1\Pi$ transition dipole moment have been studied. The results of the FCI calculations are compared to those obtained using approximate methods. In addition, the generation of atomic natural orbital (ANO) basis sets, as a method for contracting a primitive basis set for both valence and core correlation, is discussed. When both core-core and core-valence correlation are included in the calculation, no suitable truncated CI approach consistently reproduces the FCI, and contraction of the basis set is very difficult. If the (nearly constant) core-core correlation is eliminated, and only the core-valence correlation is included, CASSCF/MRCI approaches reproduce the FCI results and basis set contraction is significantly easier.

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I. Introduction

In *ab initio* calculations on systems containing first-row atoms it is commonly assumed that the $1s$-$1s$ ("core-core" or CC) and $1s$-valence ("core-valence" or CV) correlation energy does not change, regardless of environment, and so the $1s$ electrons are not correlated in most calculations. The error associated with this approximation is quite small: generally of the same order as errors arising in the treatment of the valence electrons as a result of basis set incompleteness or truncation of the CI expansion. As correlating the core electrons substantially increases the basis set requirements, the length of the CI expansion, and problems with size-consistency, it seems unreasonable to include core correlation effects unless the error in the treatment of the valence electrons has been reduced to the point where it is smaller than the error associated with the core.

Given recent advances in methods of contracting basis sets and the improved understanding of the $n-$particle space requirements of the correlation problem, it has become possible to reduce the error in the treatment of the valence correlation to such a degree that neglect of core-core and core-valence correlation may be the largest remaining error in some calculations. Consider, for example, the $^3B_1 - {}^1A_1$ separation in CH_2. It has been shown that a six electron second-order CI (SOCI) treatment gives a separation in excellent agreement with the FCI value, that is, there is no differential error in the SOCI treatment of the valence correlation. Relativistic effects are expected to be small (an assumption supported by first-order perturbation theory) so any error in a valence treatment of the separation in CH_2 must arise from limitations in the 1-particle basis set. Using the method of atomic natural orbital (ANO) general contractions developed recently, it is possible to contract very large primitive sets to a manageable size, thereby reducing significantly the errors in the 1-particle basis set relative to older segmented basis sets. The separation computed using $(13s\ 8p\ 6d\ 4f\ 2g)/[5s\ 4p\ 3d\ 2f\ 1g]$ carbon and $(8s\ 6p\ 4d)/[4s\ 3p\ 2d]$ hydrogen ANO basis sets is expected to have a differential error in the treatment of the valence electrons of at most 0.2 kcal/mole. This is of the same size as the core (that is, CC and CV) correlation effect computed by Werner and Reinsch. It would therefore appear that further improvement of the computed CH_2 separation would require correlating the core electrons. This is by no means

straightforward, however. For example, Sasaki and Yoshimine investigated the role of core correlation on the C $^3P - {}^5S$ separation and found it very difficult to establish a reliable result. The effect of core correlation on the computed separation was actually reduced by a factor of two when a single and double excitation CI (SDCI) was augmented with selected triple and quadruple excitations. This suggests that the effect of CC and CV correlation can be very sensitive to the level of correlation treatment employed. In analogy, we expect that it will be difficult to accurately compute the core correlation contribution to the CH_2 $^3B_1 - {}^1A_1$ separation.

In order to analyze the ability of different levels of correlation treatment to account for the effects of CC and CV correlation, we compare FCI calculations to various approximate methods for some small systems. As noted above, the 1-particle basis set has proved to be one of the limiting factors in treating valence correlation, and we may expect this to be true also for CC and CV correlation. Hence, in addition to considering the level of correlation treatment, we also consider the question of determining appropriate 1-particle basis sets. While the systems investigated contain eight or fewer electrons, we expect the results to provide a guide to larger systems — the $1s^2$ pair correlation energy is essentially constant for the first row and the CV correlation energy scales accurately with the number of KL intershell electron pairs, at least at the level of the independent electron pair approximation.

II. The $^1S - {}^1P$ Separation in Beryllium Atom

In our study of the Be $^1S - {}^1P$ separation, we have used the $(15s\ 9p\ 5d)/[9s\ 9p\ 5d]$ Be gaussian basis set given by Graham et al. The $3s$ component of the $3d$ functions is deleted in all calculations. Note, however, that unlike the work of ref ? no other functions are deleted.

We construct zeroth-order wave functions, with symmetry and equivalence restrictions imposed, for each atomic state including only valence correlation. CC+CV correlation is then added by including all single and double excitations from all CSFs in the zeroth-order wave function. We denote both the CASSCF and multireference configuration interaction (MRCI) wave functions by their reference spaces. For example, CASSCF($2s2p$)/MRCI denotes a CASSCF calculation

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in which the $2s$ and $2p$ orbitals and electrons are active, followed by a four-electron MRCI calculation from all CSFs in the CASSCF wave function. In addition to the MRCI calculations, we also perform core-valence configuration interaction (CVCI) calculations based upon the reference wave functions. The CVCI wave functions have the restriction that all CSFs generated from double excitations out of the $1s$ core orbitals are deleted. We also consider the single-reference modified coupled pair functional (MCPF) approach based on SCF orbitals. The results obtained using these approximate methods are compared to a four-electron FCI calculation. We have also computed the separation at the two-electron FCI level, to assess the ability of approximate levels of treatment in accounting for the CC and CV correlation. The FCI calculations have been performed using a modified version of the Knowles and Handy FCI program [15] which has been interfaced to the MOLECULE-SWEDEN [16,17] codes. The MCPF calculations were performed using the integral driven vectorized codes written by Blomberg and Siegbahn. All FCI calculations were performed on the NAS CRAY 2. The CASSCF/MRCI calculations were performed on the NASA Ames CRAY X-MP/48 using the MOLECULE-SWEDEN codes.

Our study of the $^1S - {}^1P$ separation in Be atom is summarized in Table I. The separation is decreased by only 0.018 eV, or 0.3%, by $1s$ correlation, based on the difference between the FCI(4) and FCI(2) results in the [9s9p5d] contracted Gaussian basis using SCF orbitals. If we use an MCSCF core, the effect of $1s$ correlation is 0.003 eV larger. The SDCI(4) treatment recovers 61% of the $1s$ contribution, but the core contribution is found to increase the separation when quadruple excitations are accounted for using the Davidson correction (+Q). This may indicate the inadequacy of this correction when only four electrons are correlated. The CASSCF($2s2p$) calculation favors the ^1S state, but the inclusion of more extensive correlation significantly reduces the bias. However, the CASSCF($2s2p$)/MRCI calculation with or without a +Q correction does not yield an accurate estimate of the core effect. Expanding the active space results in an equivalent treatment of both states at the CASSCF level. Both the CASSCF($2s3s2p3p3d$)/MRCI and CASSCF($2s3s2p3p3d$)/MRCI+Q treatments accurately reproduce the differential core effect, as a consequence of the fact that the CASSCF($2s3s2p3p3d$) wave function recovers nearly all of the valence correlation energy in this basis. The effect of

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$1s$ correlation is significantly underestimated at the MCPF level. In this case the MCPF result is inferior to SDCI, but superior to SDCI+Q. Overall, therefore, the only calculation to correctly estimate the effect of core correlation on the $^1S - {}^1P$ separation is one that already recovers virtually all of the valence correlation at the reference space level. Unfortunately, MRCI reference spaces of this dimension are generally impossible to use in molecular calculations.

III. The $^3P - {}^5S$ Separation in Carbon Atom

The STO carbon basis set used in the calculation of the $^3P - {}^5S$ atomic separation consists of the DZ set of Clementi and Roetti, augmented with two tight $2p$ and three even-tempered $3d$ functions optimized at the six electron SDCI level for the ^3P state. This basis is explicitly given in Table II.

The calculations of the C $^3P - {}^5S$ separation and the comparisons of different levels of correlation treatment using the STO basis are performed (and labelled) in a similar manner to those of the Be $^1S - {}^1P$ separation study. The results for C $^3P - {}^5S$ separation as a function of correlation level in the STO basis set are summarized in Table III. The effect on the $^3P - {}^5S$ separation of correlating the C $1s$ electrons is of the same magnitude as on the $^1S - {}^1P$ separation in Be. At the single reference SDCI level, the effect of $1s$ correlation is 4.4 times too large, since the error in the 6 electron treatment is much larger than the error in the 4 electron treatment. The +Q correction gives a more balanced treatment at the two correlation levels, but the $1s$ contribution to the splitting is still in error by almost a factor of two. The MCPF and CPF approaches both give a reliable estimate of the core correlation contribution. This is opposite to the Be results where SDCI gave (perhaps fortuitously) a better result for the $1s$ contribution. Still the overall success of the MCPF method (see later discussion) indicates that size consistent methods have advantages for estimating core contributions. Including the important $2s^2 \rightarrow 2p^2$ excitations in the reference space reduces the errors at both levels of correlation treatment, but the $1s$ contribution is still overestimated by a factor of three. Again adding a +Q correction gives a more balanced treatment; the $1s$ contribution is now small by a factor of about two. Adding the $3d$ orbital to the active space further improves the results, but the CASSCF($2s2p3d$)/MRCI

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calculation still overestimates the differential effect of the $1s$ correlation by almost a factor of two. If the active space were further expanded to include the $3s$ and $3p$ orbitals, the CASSCF alone would recover almost all the valence correlation in this basis. Thus an MRCI using this reference space would probably yield even better results. However, such an active space could not currently be used in molecular calculations.

We have also considered the possibility that the CC contribution to the separation is nearly constant by considering correlation treatments that include only CV and valence correlation. Even at the single reference level, the CV treatment predicts a $1s$ correlation contribution to the splitting that is in error by only 0.07 kcal/mole, compared to 1.12 kcal/mole at the SDCI(6) level where both CC and CV effects are included. Expanding the reference space to include all CSFs in the $2s2p$ CASSCF slightly (0.06 kcal/mole) overestimates the $1s$ contribution to the splitting at the CVCI level. Further expansion of the reference space has little additional effect. Therefore, either there is a -0.06 kcal/mole differential effect of CC correlation, or excluding CC correlation increases the computed CV correlation effect, because the exclusion effect of the CC double excitations is eliminated. It may therefore be preferable to include CV correlation, but neglect CC correlation. This not only reduces the computational requirements and size of the calculation, but also eliminates the possibility of substantially overestimating the total core effect when CC correlation is included.

Another aspect of our study of the $^3P - {}^5S$ atomic separation in carbon atom is the question of how to construct a contracted Gaussian basis capable of describing CC and CV as well as valence correlation. The primitive Gaussian basis set used in this study was based on the van Duijneveldt ($11s$ $8p$) primitive set: the innermost p function (exponent 83.33316) was replaced by three functions with exponents 650.84, 202.343, and 62.9074 giving a p set with sufficiently compact functions to allow correlation of the $1s$ electrons. Eight even-tempered $3d$ functions, with exponents of the form $\alpha = 2.5^n \alpha_0$, with n=0,7, are added. With $\alpha_0(3d)$ equal to 0.060724, the most compact $3d$ function has an exponent of 37.063, which gives a d set appropriate for correlating the $1s$.

The orbitals are obtained from SCF calculations (which include symmetry and

equivalence restrictions) on the $2s^2 2p^2$ (^3P) and the $2s^1 2p^3$ (^5S) states. For both states we obtain SDCI wave functions in which all six electrons are correlated, denoted SDCI(6). SDCI treatments correlating either four or six electrons are then performed using subsets of the SDCI(6) natural orbitals (NOs), and compared to using the full set of NOs. NOs are also determined for a wave function in which the CC correlation has been eliminated: only the valence and CV correlation is included. Subsets of these CV NOs are then used in CI(4) and further CV calculations to study the error associated with truncation of the basis set. This truncation study follows the spirit of the ANO contraction procedure, although the SCF wave functions are not reoptimized in the truncated basis sets.

We now consider the difficulties of contracting the (13s 10p 8d) primitive carbon Gaussian basis set using the ANO procedure to give contracted sets capable of describing valence, CV and CC correlation. In the uncontracted basis set, the SDCI(4) and SDCI(6) $^3P - {}^5S$ separations differ by 1.66 kcal/mole (see Table IV). If the NOs of the SDCI(6) wave function are used (without truncation) as the basis set, the core effect on the separation is increased to 1.78 kcal/mole. The next five entries in Table IV depict how the $^3P - {}^5S$ separation varies as different subsets of the natural orbitals are employed to define the ANO contractions. For all contracted basis sets considered, the error at the SDCI(6) level is much greater than at the SDCI(4) level. Further, the errors at the SDCI(4) and SDCI(6) level as well as the CC+CV contribution to the separation all decrease monotonically with expansion of the ANO set. Clearly, the smaller contracted sets are biased towards the calculation of valence correlation, even though the NOs are obtained from the SDCI(6) treatment. In the [5s 4p 3d] basis set, the error in the valence treatment has become quite small, but the CC+CV contribution is still nearly 100% in error. Although further expansion of the basis continues to reduce the error in the CC+CV contribution to the separation, the error is still 13% for an [8s 7p 6d] contracted set. As the [5s 4p 3d] basis yields essentially the same valence contribution as the full set of ANOs, it is clear that the convergence of the combined CC and CV correlation effects as a function of basis set truncation is much slower than for the valence contribution. This may be due to the different relationship between correlation energy and the natural orbital occupations for the core and valence:

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it can be demonstrated using perturbation theory that the occupation numbers of NOs correlating the $1s$ electrons are smaller, for a given energy lowering, than for the valence shell. It is thus difficult to define criteria for selecting NOs to treat core and valence contributions equally.

We also considered an alternative approach of obtaining an ANO contracted basis that involved separate CI expansions in which the CC, CV and valence correlation effects were separated. The orbitals were merged from the following three CI calculations: single and double excitations from the $1s$ orbital, single-reference CVCI, and SDCI(4). The goal was to obtain a basis set that could describe valence, CC and CV correlation equally well by merging orbitals from the NOs of these three expansions. For small contracted basis sets this procedure is, in fact, far superior to using SDCI(6) NOs. For example, a $[5s\ 4p\ 3d]$ set, with the two most important s, p and d correlating orbitals taken from SDCI(4), and one of each type from the CI correlating only the $1s$ electrons, has an error of only 0.55 kcal/mole in the separation at the four electron level and of only 0.84 kcal/mole when six electrons are correlated. This is evidently a more balanced treatment than that obtained using SDCI(6) NOs. However, attempts to further expand the basis set encounter linear dependence problems, because of the large overlap of the more weakly occupied natural orbitals in the three CI wave functions. Thus even if the $n-$particle space requirements for describing core correlation could be identified, no method for designing compact, accurate basis sets for valence, CV, and CC correlation, analogous to ANO sets for valence correlation, currently presents itself.

When the NOs are taken from the CVCI wave function, the valence correlation again converges quickly, much more so than the CV correlation. However, basis set convergence to the uncontracted CV result is more rapid than to the combined CC+CV result. It should, therefore, be easier to develop a contracted basis set for valence and CV correlation. Unfortunately, rather large basis sets are required to compute both the valence and CV effects accurately, and it should be noted that a larger range of exponents is required in the primitive basis. As a corollary, it will be even more difficult to design adequate segmented basis sets of tolerable size.

IV. Core Correlation Contribution to Molecular Properties

For the CH^+ calculations, we use the same Slater basis as in our study of the $^3P - {}^5S$ separation in carbon atom, except that the three 3d functions are reduced to two. For hydrogen, the $\{2s\ 1p\}$ Slater functions of Moore $et\ al.$ are used. These STO basis sets are given in Table II.

For CH^+ we consider the spectroscopic constants (r_e, ω_e, D_e) of the $^1\Sigma^+$ state, the dipole moment of the $^1\Sigma^+$ and $^1\Pi$ states (with respect to an origin at C), and the energy separation and transition dipole moment between the $^1\Sigma^+$ and $^1\Pi$ states. For the calculation of D_e, we use both SCF and CASSCF reference wave functions. The SCF occupation used is

$$^1\Sigma^+ \qquad 1\sigma^2 2\sigma^2 3\sigma^2. \tag{1}$$

In the CASSCF calculations, there are four electrons active in the MOs derived from the carbon 2s and 2p and hydrogen 1s orbitals. We also consider CVCI wave functions, just as for the C $^5S - {}^3P$ separation. The FCI and SDCI calculations are based upon SCF orbitals. The MRCI calculations are based on the CASSCF orbitals and include all CSFs in the CASSCF as references. The energy of the separated atom limit for the FCI calculations is given by the sum of the FCI result for C^+ and the H atom energy, while for all other calculations it is computed as the CH^+ energy at a bond length of $40a_0$. Since the SCF does not dissociate correctly, for the SCF and SDCI treatments we use the configuration

$$^3\Sigma^+ \qquad 1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1. \tag{2}$$

for this limit.

For the calculation of the $^1\Sigma^+ - {}^1\Pi$ transition moment we optimize the orbitals using a state-averaged CASSCF approach. This calculation has the same CASSCF active space as that used to compute the D_e. The MRCI calculations include all CSFs in the respective CASSCF wave functions as reference configurations. In addition to these calculations, we consider expanding the CASSCF and MRCI reference spaces to include the 1δ orbital. The individual state dipole moments are computed as expectation values.

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The results of calculations on CH^+ are summarized in Table V. The inclusion of $1s$ correlation increases D_e by 0.01 eV (0.24 kcal/mole) at the FCI level. At the SDCI(4) level the error in D_e is 2.25 kcal/mole, and $1s$ correlation further decreases D_e: this is probably a manifestation of lack of size consistency. The Davidson correction reduces the error in D_e, but $1s$ correlation still reduces D_e slightly. At the MRCI or MRCI+Q level, D_e is significantly improved and the core contribution is quantitatively accounted for. The SCF/CVCI treatment underestimates the magnitude of the $1s$ contribution to D_e, but, unlike the single-reference SDCI treatments, does indicate that $1s$ correlation should increase D_e. The multireference CVCI calculations yield a CV contribution to the bond energy in excellent agreement with that deduced from the FCI calculations. Hence when only CV correlation is included, D_e converges more quickly to the FCI results. All methods correctly predict a shortening of the CH bond length when core correlation is included, and all methods except SDCI predict the magnitude of this bond contraction rather accurately. The core correlation contribution to ω_e is small and is again predicted accurately by all methods except SDCI. It is encouraging that obtaining the core correlation contribution to spectroscopic constants for a given state is rather easier than obtaining the contribution to differences between states, at least for the cases studied here.

The effect of core correlation on the dipole moments of the $^1\Sigma^+$ and $^1\Pi$ states and the $^1\Sigma^+ - ^1\Pi$ separation and transition moment is very small, and not consistently well described by approximate levels of correlation treatment. For example, at the MRCI level the core contribution to the dipole moment is accurate for the $^1\Sigma^+$ state, but overestimated for the $^1\Pi$ state. Similar conclusions can be drawn concerning the core contribution to the electronic transition moment. Hence, although the approximate correlation methods do very well in terms of the absolute magnitude of these moments, they do very poorly on accounting for the small $1s$ core correlation contribution to these properties. Note also that most of the differential error is in the 6 electron treatments. We have also considered adding the 1δ orbital to the active space, since Werner found it to have an important effect on the lifetime of the $^2\Delta$ state in CH. However, in CH^+, this has only a small effect on both the absolute value of the moments as well as the core contribution to the properties.

Note also that the core contributions to the moments are not significantly better at the CVCI level. Hence it would appear that very high levels of correlation treatment are required to accurately predict the small $1s$ core contribution to molecular properties.

As discussed in the Introduction, it is now possible to determine the valence limit for the $^3B_1 - {}^1A_1$ splitting in methylene to within a few tenths of a kcal/mole, and given that this error is of the order of the core correlation effects discussed above it is useful to try to estimate the CC and CV contribution. Our study of core correlation effects is summarized in Table VI. All calculations employed the $(13s\ 10p\ 8d)$ carbon basis set used in the ^5S-^3P study fully uncontracted. This was augmented by a single f ANO contracted from 4 primitives, based on the ^3P state of carbon atom. For the hydrogen basis set we used a $(8s\ 6p\ 4d)$ set contracted to $[3s\ 2p\ 1d]$ based on calculations for H_2,as described in ref. ??. The geometries used were: $^3B_1$, $r_{CH} = 1.079$ Å, $\angle(HCH) = 132.7°$; $^1A_1$, $r_{CH} = 1.112$ Å, $\angle(HCH) = 101.3°$. Interestingly, the valence MRCI treatment yields a smaller separation (by some 0.25 kcal/mole) than the earlier study in a $[4s\ 3p\ 2d\ 1f/3s\ 2p\ 1d]$ ANO basis, evidently as a result of uncontracting the carbon basis. The CV correlation is determined as the difference between a $2s2p$ CASSCF/MRCI treatment and a CVCI treatment (that is, including single excitations from the core) using the same active space. The $^3B_1$ CVCI comprises about 1.5 million CSFs, and requires less than 4 minutes per iteration on the CRAY X-MP. The CV contribution is found to increase the splitting by 0.35 kcal/mole at both the MRCI and MRCI+Q levels. Further, MCPF calculations were performed to obtain an estimate of the CC+CV contribution as the difference between the six and eight electron MCPF separations. The result is a contribution of 0.42 kcal/mole, which again increases the separation. Based on our analogous studies of the $^3P - {}^5S$ splitting in carbon atom discussed above, it seems likely that these estimates are upper bounds to the true core contribution to the CH_2 separation.

IV. Conclusions

The FCI calculations indicate that core correlation effects are small, and very difficult to compute accurately. When both CC and CV correlation are included,

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very large CASSCF/MRCI calculations are required to reproduce the FCI results. In general, a very high level of correlation treatment is required to accurately reproduce the relatively small core contribution to energy differences. None of the approximate methods considered here gives consistently accurate results for these contributions, not even CASSCF/MRCI (unless the CASSCF itself recovers most of the valence shell correlation energy). In addition, the basis set requirements are likely to be more than double the size of typical valence basis sets. The better agreement between the FCI calculations and those that include only CV correlation suggests that it may be best to include only singles from the core and neglect the more nearly constant CC correlation, especially for spectroscopic constants such as bond lengths and harmonic frequencies. This greatly reduces the basis set and level of correlation requirements for computing the differential effects of core correlation. Overall the MCPF method accounts for core correlation rather well, indicating that accounting for size consistency is an important consideration.

In view of the difficulties in *ab initio* approaches to computing core correlation effects, there may be advantages to semi-empirical methods for accounting for core correlation, such as effective potential schemes. While discussion of such methods is outside the scope of the present investigation, the effective potential approach of Müller and Meyer appears promising as a means of including core correlation effects while avoiding many of the difficulties discussed above. Such methods clearly deserve attention.

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Table I. The Be $^1P - {}^1S$ separation as a function of level of correlation treatment.

	E(^1S)	E(^1P)	ΔE(eV)	error[a]	percent[b]
FCI(4el)	-14.656623	-14.461356	5.314	....	
SCF	-14.572543	-14.394175	4.854	0.460	
FCI(2el)	-14.618339	-14.422397	5.332	-0.018	
SDCI	-14.653218	-14.457673	5.321	-0.007	61
SDCI+Q	-14.659658	-14.462763	5.358	-0.044	-144
SCF CV	-14.622586	-14.426904	5.325	-0.011	39
2s2pCAS	-14.616309	-14.394175	6.045	-0.731	
2s2pMRCI	-14.656516	-14.457673	5.411	-0.097	-439
2s2pMRCI+Q	-14.656672	-14.462763	5.277	0.037	306
2s3s2p3p3dCASSCF	-14.618339	-14.421100	5.367	-0.053	-194
2s3s2p3p3dMRCI	-14.656599	-14.461290	5.315	-0.001	94
2s3s2p3p3dMRCI+Q	-14.656680	-14.461418	5.313	0.001	100
2s2p CV	-14.622774	-14.426904	5.330	-0.016	11
2s3s2p3p3d CV	-14.622794	-14.427218	5.322	-0.008	56
MCPF	-14.656370	-14.460654	5.326	-0.012	33

[a] The error relative to the FCI(4) treatment.

[b] The fraction of the CC and CV correlation contribution to ΔE recovered by the level of treatment X, computed as (X-FCI(2))/(FCI(4)-FCI(2)).

Table II. The $\{4s\ 4p\ 3d\}$ carbon and $\{2s\ 1p\}$ hydrogen STO basis sets. In the $\{4s\ 4p\ 2d\}$ carbon basis set the three $3d$ functions are replaced with the two in parentheses.

	Carbon basis				
$1s$	7.52232	$2p$	8.84000	$3d$	8.8888(4.00)
$1s$	5.12306	$2p$	4.91000	$3d$	4.0000(2.00)
$2s$	1.83068	$2p$	2.73045	$3d$	1.8000
$2s$	1.15282	$2p$	1.25656		
	Hydrogen basis				
$1s$	1.1898	$2p$	1.5574		
$2s$	1.2000				

Table III. The C $^3P-\,^5S$ separation, in kcal/mole, as a function of level of correlation using the STO basis set.

A. Reference wave functions

SCF	56.71
$2s2p$CASSCF	67.53
$2s2p3d$CASSCF	86.91
$2s3s2p3p3d$CASSCF	90.22

B. Correlation treatments

	4el	Error(4el)	6el	Error(6el)	CC+CV
FCI	91.26	...	90.93	...	0.33
SDCI	89.99	-1.27	88.54	-2.39	1.45
SDCI+Q	92.41	$+1.15$	91.79	$+0.86$	0.62
MCPF	91.13	-0.13	90.72	-0.21	0.41
CPF	91.14	-0.12	90.72	-0.21	0.42
$2s2p$MRCI	90.94	-0.32	89.85	-1.08	1.09
$2s2p$MRCI+Q	92.17	$+0.91$	92.02	$+1.09$	0.15
$2s2p3d$MRCI	91.37	$+0.11$	90.79	-0.14	0.58
$2s2p3d$MRCI+Q	91.45	$+0.19$	90.98	$+0.05$	0.47

C. CV treatment

		error[a]	CV effect[b]	CV error[c]
1 ref	89.73	-1.20	0.26	-0.07
$2s2p$	90.55	-0.38	0.39	$+0.06$
$2s2p3d$	90.98	$+0.05$	0.39	$+0.06$

[a] Relative to analogous 6-electron CI treatment.
[b] Relative to analogous 4-electron CI treatment.
[a] Relative to 6-electron FCI.

Table IV. The $^3P - {}^5S$ separation in C as a function of contraction of the GTO basis set. Units are kcal/mole.

Basis	4el	Error(4el)[a]	6el	Error(6el)[a]	4el−6el	Error(4el−6el)[a]
			CC+CV treatment			
$(13s\ 10p\ 8d)$	92.28	...	90.62	...	1.66	...
$[13s\ 10p\ 8d]$	92.40	...	90.62	...	1.78	....
$[4s\ 3p\ 2d]$	91.01	−1.39	81.76	−8.86	9.25	7.47
$[5s\ 4p\ 3d]$	92.00	−0.40	88.72	−1.90	3.28	1.50
$[6s\ 5p\ 4d]$	92.26	−0.14	89.47	−1.15	2.79	1.01
$[7s\ 6p\ 5d]$	92.36	−0.04	90.22	−0.40	2.14	0.36
$[8s\ 7p\ 6d]$	92.38	−0.02	90.36	−0.26	2.02	0.24

Basis	4el	Error(4el)[a]	CV	Error(CV)[a]	4el-CV	Error(4el-CV)[a]
			CV treatment			
$(13s\ 10p\ 8d)$	92.28	...	91.96	...	0.32	...
$[13s\ 10p\ 8d]$	92.40	...	91.73	...	0.67	...
$[4s\ 3p\ 2d]$	91.76	−0.64	89.51	−2.22	2.25	1.58
$[5s\ 4p\ 3d]$	92.15	−0.25	90.86	−0.87	1.29	0.62
$[6s\ 6p\ 4d]$	92.35	−0.05	91.50	−0.23	0.85	0.18
$[7s\ 6p\ 5d]$	92.38	−0.02	91.60	−0.13	0.78	0.11

[a]Relative to the $[13s\ 10p\ 8d]$ ANO calculation.

Table V. CH^+ spectroscopic constants and properties[a].

	r_e	ω_e	D_e	core correlation effect		
				r_e	ω_e	D_e
SCF	2.106	3028	3.203	—		
MCPF(4)	2.145	2811	3.992	—		
MCPF(6)	2.143	2815	4.001	-0.002	4	0.009
SDCI(4)	2.143	2826	3.924	—		
1REF-CV	2.140	2831	3.927	-0.003	5	0.003
SDCI(6)	2.139	2840	3.917	-0.005	14	-0.007
SDCI(4)+Q	2.149	2786	4.000	—		
SDCI(6)+Q	2.147	2793	3.998	-0.002	7	-0.002
CASSCF	2.154	2781	3.868	—		
MRCI(4)	2.149	2792	4.011	—		
CVCI	2.146	2796	4.022	-0.003	4	0.011
MRCI(6)	2.146	2798	4.023	-0.003	6	0.012
MRCI(4)+Q	2.149	2791	4.013	—		
MRCI(6)+Q	2.146	2796	4.026	-0.003	5	0.013
FCI(4)	2.148	2793	4.020	—		
FCI(6)	2.146	2797	4.030	-0.002	4	0.010

	Properties			
	$\mu(^1\Sigma^+)$[b]	$\mu(^1\Pi)$[b]	$\Delta E(^1\Sigma^+ - ^1\Pi)$	TM
FCI(4)	0.8589	0.7712	25209	0.2707
FCI(6)	0.8609	0.7713	25074	0.2708
FCI(6)−FCI(4)	0.0020	0.0001	-135	0.0001
CASSCF			24534	
MRCI(4)	0.8593	0.7714	25215	0.2708
Error(4)	0.0004	0.0002	4	0.0001
MRCI(6)	0.8614	0.7727	25076	0.2716
Error(6)	0.0005	0.0014	2	0.0008
MRCI(6)−MRCI(4)	0.0021	0.0013	-139	0.0008
CVCI	0.8605	0.7720	25101	0.2703
CV−MRCI(4)	0.0012	0.0006	-114	-0.0005
CASSCF(+δ)[c]			21972	
MRCI(4)	0.8593	0.7712	25186	0.2711
Error(4)	0.0004	0.0000	-23	0.0004
MRCI(6)	0.8614	0.7721	24994	0.2724
Error(6)	0.0005	0.0009	-80	0.0016

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| MRCI(6)-MRCI(4) | 0.0021 | 0.0009 | -192 | 0.0013 |

[a] Dipole moment and transition moment values in a.u., r_e in a_0, D_e in eV, ω_e and ΔE in cm^{-1}.

[b] Computed relative to origin at C.

[c] 1δ MO included in active space.

Table VI. Core-valence effects on the $^3B_1$–$^1A_1$ splitting in methylene

Level of treatment	E($^3B_1$) a.u.	E($^1A_1$) a.u.	Splitting(kcal/mole)
	6-electron treatment		
2s2p CASSCF	−38.973888	−38.957791	10.10
MRCI	−39.082203	−39.067381	9.30
MRCI+Q	−39.086480	−39.071851	9.18
+REL[a]	−0.014774	−0.014872	−0.06
MCPF	−39.082495	−39.066259	10.19
	CV treatment		
MRCI	−39.094318	−39.078935	9.65
MRCI+Q	−39.099050	−39.083854	9.53
+REL[a]	−0.014784	−0.014884	−0.06
	8-electron treatment		
MCPF	−39.135809	−39.118904	10.61

[a] Darwin and mass velocity contribution from first-order wave function at the MRCI level.