Exploiting regularity in systematic sequences of wavefunctions which approach the full CI limit*

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Summary. The ground state total energy and related 1-electron properties are computed for three small molecules (N_2, H_2O, and H_2CN) using several systematic sequences of wavefunctions which approach the full CI. These sequences include multireference CI, averaged coupled pair functional and quasidegenerate variational perturbation theory wavefunctions. It is demonstrated that sufficient regularity exists in the sequence of variationally computed energies to permit extrapolation to the full CI limit using simple analytic expressions. It is furthermore demonstrated that a subset of the original list of configurations employed in the normal singles and doubles CI procedure can be selected using second order perturbation theory without adversely affecting the extrapolation to the full CI limit. This significantly broadens the range of applicability of the method. Along these lines, a scheme is proposed for the extrapolation of the selected CI results to the zero threshold (i.e. unselected) values in cases where the numbers of configurations associated with the latter would render the calculations intractable. Due to the vast reduction in the number of configurations which are handled variationally, the proposed scheme makes it possible to derive estimates of the full CI limit in cases where explicit full CI is either very difficult or currently impossible.

Key words: CI limit – Systematic sequences of wavefunctions – Wavefunctions, full CI limit

1 Introduction

The use of *ab initio* methods to address questions of chemical importance has increased dramatically over the past four decades. This growth has been fueled by (1) the widespread availability of computer programs which permit even nonspecialists to access sophisticated computational models and (2) the

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continuous improvement in high speed computer hardware which makes the implementation of these models practical. Paralleling the increased use of *ab initio* methods among chemists in general has been a trend among theoreticians to push for significantly higher levels of agreement with experiment, especially for small molecules. For the sake of the present discussion we can define "small" as those systems having 50 electrons or less. Among the developments which have proven helpful in this drive for increased accuracy are a series of dramatic improvements in our ability to perform full configuration interaction (FCI) calculations [1]. Such wavefunctions represent the exact solution of the molecular Schrödinger equation within a fixed 1-particle basis set.

Unfortunately the factorial growth in the number of configurations with both basis set and number of electrons renders FCI intractable for all but very small systems. The necessity of having to deal with enormous numbers of configurations often forces researchers to use basis sets of limited flexibility which offer little hope of reproducing experiment. In cases of high symmetry some of these limitations may be relaxed. Even so, FCI calculations require enormous quantities of computer time and memory on some of the fastest machines presently available. For example, a recent 10-electron FCI on the Mg atom carried out in a $[4s, 3p, 2d, 1f]$ basis generated over a billion determinants and required approximately three weeks of supercomputer "wall clock" time to achieve better than milihartree convergence in the total energy [2].

FCI results are increasingly referenced in order to benchmark the accuracy of more approximate methods. As mentioned above, this benchmarking is done, of necessity, with somewhat limited basis sets. If favorable agreement is found with small basis sets it is often argued by inference that similar behavior should be expected as the basis set is enlarged. Recent calculations of the dissociation energy of N_2 serve to illustrate this approach. Bauschlicher and Langhoff [3] performed a FCI calculation in the nitrogen $2p$ space with a double *zeta* + polarization (DZP) basis in order to evaluate the performance of the multireference singles and doubles CI method based on complete active space self-consistent-field orbitals (CAS-SCF/MR SD-CI) and the coupled pair functional (CPF) method. Aside from comparing the two approximate methods to the exact result, few conclusions could be drawn regarding theory's ability to reproduce experiment since the DZP basis was inherently capable of no better than 1 eV accuracy. This represented an error of 10% relative to the experimental D_e (9.9 eV [4]). After its reliability was established at the DZP level, the MR SD-CI method was employed by Bauschlicher and Langhoff with greater confidence using more elaborate basis sets. The same approach was taken by Almlöf et al. [5] in an attempt to compute D_e to within so-called "chemical accuracy", i.e. to within 0.043 eV or 1 kcal/mol. More recently, even larger 10-electron FCI calculations were used by Werner and Knowles [6] to calibrate the "internally contracted" CI method for N_2.

To the best of our knowledge the DZP basis set work of Bauschlicher and Taylor [7] on HF, CH_2, and SiH_2 is the only report in the literature of 1-electron properties evaluated at the FCI level with a nontrivial basis set. As an adjunct to their extensive FCI studies focusing on energy differences, they analyzed the dipole moment and polarizability properties. The former was the only first-order property studied. For the purposes of the present work the reported dipole moments were judged to converge so rapidly with respect to even modest levels of correlation recovery as to provide poor choices for study. For example, at the SD-CI level (or 2-configuration reference space CI level for $^1A_1$ CH_2) the computed properties were already in excellent agreement with the FCI values.

We have chosen instead to examine the N_2, H_2O and H_2CN systems in hopes that they might better illustrate certain features of the convergence of energy and properties to the full CI.

Studies, such as the ones just mentioned of N_2, fall into the category of "methods calibration" since the quantity being computed, i.e. the dissociation energy, was never in question. The goal of these studies was to learn something about the ability of various computational models to reproduce experiment. The importance of "methods calibration" stems from our inability to assign useful *a priori* error bars in *ab initio* methods. At present the only way to establish confidence in a computational method is to document its ability to reproduce experiment or more accurate calculations over a broad range of problems. Since FCI results represent the exact values of whatever property is being sought, it is desirable to be able to estimate full CI energies and 1-electron properties for as wide a range of systems as possible, including systems which cannot currently be treated by explicit FCI with basis sets that systematically approach a complete basis set.

The present methods evolved from the pioneering work of Buenker and Peyerimhoff [8] who have long advocated the combined use of configuration selection and energy extrapolation techniques. However, Buenker and Peyerimhoff have traditionally used much smaller reference spaces and smaller CI spaces. The present work also differs in that it suggests an explicit functional form with which the sequence of energies (or properties) can be fit.

A related method is the CIPSI technique of Malrieu and coworkers [9] which is based on a division of the configurations into three sets, related to their importance in the wavefunction. The numerous small contributions to the total energy are estimated via second order perturbation theory. Illas et al. [10] have recently compared the CIPSI method against full CI results for first row atoms (B–F) and the BH and FH hydrides. With relatively small basis sets containing a single shell of polarization functions, the agreement was within 1 millihartree. The present work, by emphasizing the sequence of wavefunctions and their corresponding energies (and properties), seeks to avoid questions of how accurate any one specific calculation might be. If more accuracy is required then another point along the sequence, i.e. a larger calculation, may be required as input to the proposed extrapolation procedure.

In the approach recently suggested by Harrison [11] the full CI energy is estimated by combining very large reference spaces and second order perturbation theory. In comparison with the present methods, the reference spaces used by Harrison are more than an order of magnitude larger. This, in turn, requires that he must consider much larger configuration spaces in the perturbation theory part of the calculation and, to the extent that properties are desired, the wavefunction which is obtained by diagonalizing the reference space may not be sufficiently accurate. His approach does offer the advantage that in its current implementation it runs in parallel.

In this work calculations were performed on three small molecules (N_2, H_2O, and H_2CN) with a variety of basis sets ranging from a simple "split valence" set on up to a "quadruple *zeta*" level with multiple polarization functions. While all three molecules are well described by a single configuration, as judged by the size of the leading coefficient in the CI expansion, this should not be construed as implying rapid, monotonic convergence for every property. The goal we are seeking, the FCI energy and properties, could only be explicitly computed for N_2 with the smallest basis. However, the split valence + polarization (SVP) and DZP basis set FCI *energies* were available in the literature for N_2 and H_2O and

may serve as a guide in measuring the degree of convergence for our sequence of wavefunctions. Because of its importance in so many aspects of chemical research we shall first focus on the total energy. Then we will proceed to examine various charge and spin density 1-electron properties.

We will examine the convergence characteristics of several systematic sequences of wavefunctions in order to determine if sufficient regularity exists to permit useful extrapolation to the full CI limit. This implies the ability to perform calculations which are computationally tractable yet provide estimates of the full CI limit within acceptable limits. What is judged "acceptable" will obviously depend upon one's perspective. In one context "acceptable" might imply the ability to predict energies and properties with relatively high precision for use in benchmarking other methods. In another context less precision might be acceptable, in light of far larger effects due to basis set truncation errors. For example, an error in the extrapolated full CI dipole moment of ± 0.02 a.u. might be more than "acceptable" when it is known that basis set improvements would change the value by, say, 0.2 a.u. Highly precise but inaccurate values are seldom of importance. Ultimately, the values which quantum chemists would most like to be able to compute are those associated with a complete basis set full CI.

2 Choosing a systematic sequence of wavefunctions

It is not difficult to construct sequences of wavefunctions which asymptotically approach a full CI. Some obvious examples include:

(i) *CI truncated at progressively higher excitation levels*. This approach suffers from the rapid increase in the number of excitations, which go as:

$$\binom{N}{n}\binom{2K-N}{n}$$

where n is the excitation level, $2K$ is the number of spin orbitals and N is the number of electrons. This number becomes extremely large for even small molecules with moderate sized basis sets and high excitation levels. If this sequence is truncated too quickly the size consistency error may be unacceptably large.

(ii) *CAS-SCF with ever larger active orbital spaces*. Although in common practice CAS-SCF avoids dealing with the enormous numbers of configurations normally associated with full CI, by limiting the range of orbitals into which electrons will be excited, it too quickly suffers from the same disastrous growth in the size of the problem as a function of K and N. Furthermore, by including *all* possible excitations consistent with a given number of electrons and orbitals the CAS-SCF method may be forced to include large numbers of configurations which have no significant effect on the energy or properties.

(iii) *Perturbation theory (PT) carried out to increasingly higher order*. While this approach has the advantage of size consistency a potential disadvantage lies with the slowness in convergence of the perturbation theory expansion or potential for it to fail to converge at all.

Although each of these methods can in principle approximate the full CI, an important aspect which must be considered is the efficiency with which they converge. If a given sequence fails to significantly reduce the amount of computer time relative to the actual FCI calculation, it will be of little use.

We choose a sequence of wavefunctions to approach the full CI as follows: a minimal list of configurations (known as the "reference space") capable of providing a qualitatively correct zeroth order description of the system is identified and a CI wavefunction consisting of all single and double excitations from each configuration in this list is then generated. For cases where the HF configuration dominates the wavefunction, as it does for all three molecules included in the work, this translates into the normal HF SD-CI. The CI wavefunction is ordered on the magnitude of the expansion coefficients and the first few (say 5–15) most important configurations serve as the new reference space out of which all single and double excitations are taken in order to form a new CI wavefunction. This new wavefunction, in turn, serves as a pool out of which the reference space is again augmented (say by doubling its size) and all single and double excitations are again generated. The whole process is repeated until effective convergence is achieved or computational resources are exhausted. For processes involving more than one state of the same the symmetry, selection of the reference space configurations can be made on the basis of more than one root.

Eventually, as the reference space grows in size there will come a point at which it is no longer possible to variationally handle all the single and double excitations. With the present hardware and software that point was reached at approximately one million configurations. In order to proceed, a technique is used to select the energetically most important double excitations. Several kinds of *a priori* selection have already been implied, but these correspond to selections of certain whole classes of excitations from the full CI list. For example, in any multireference CI calculation configurations are "selected" on the basis of what configurations are in the reference space and the fact that we limit excitations to no more than doubles. However, in this paper we shall use the term "selected CI" to refer to calculations in which we explicitly select a subset of the double excitations using a technique like second order perturbation theory.

All single excitations are automatically kept. While their effect on the energy of closed shell systems is not large, they have a significant impact on many 1-electron properties. It might be assumed that by selecting a subset of the double excitations we would necessarily suffer a marked deterioration in the computed results relative to the unselected calculation. Such is not the case. As will be discussed later, the errors introduced by configuration selection, when performed with sufficiently small selection thresholds, will often be no larger than the errors resulting from other approximations, such as the use of finite basis sets or the truncation of the CI expansion. Methods for partially compensating for the "selection error" will also be described.

In order to efficiently select the most important configurations from a list which can easily number into the tens of millions the selection is made on the basis of second order perturbation theory, where the estimated importance of configuration "i" is given by $|\langle \phi_i | H | \Psi_0 \rangle|^2/(E_i - E_0)$, for a zeroth order wavefunction, Ψ_0, taken as the lowest root of the reference space. For each choice of reference space up to five individual calculations were performed with successively smaller thresholds ($T_E = 10^{-5}$, 10^{-6}, 10^{-7}, 10^{-8}, and 0.0).

In fact, in the present work it became impossible to perform the zero threshold calculations with some of the largest basis sets and reference spaces. However, most calculations were in the 10,000–300,000 configuration range, with the largest variational calculation including about 970,000 configurations. The lists of configurations to be scanned by perturbation theory varied widely depending upon the size of the reference space and the basis set. Typically they

were several hundred thousand to one million in length, with the largest being on the order of 35 million configuration state functions (CSF's).

In our procedure each of the sequences of wavefunctions generated by increasing the reference space size for a fixed selection threshold must converge to the full CI since the reference space eventually includes all possible configurations. Of course this can only occur if the choice of reference space is based on a procedure which simultaneously reduces the selection threshold as the reference space increases. Otherwise it is conceivable that all configurations which contribute more than some threshold, say 10^{-5} hartree, are already included in the reference space and the process of generating the next larger list of configurations could not proceed. In practice even with the largest of the thresholds used in this study we were far removed from a situation where this failure might happen.

It is of interest to investigate the manner in which the variationally computed energies and properties of these systematic sequences of wavefunctions approach the full CI limit for cases where the latter is known. If simple expressions can be found to fit the behavior of the energy and properties as they approach the FCI values and these expressions are capable of predicting the limiting values within "chemical accuracy" ($\leqslant 1$ kcal/mole for the energy) then reasonable *estimates* may be possible for much larger basis sets where explicit FCI is impossible.

CI convergence was accelerated through the use of frozen natural orbitals (FNO's), i.e. natural orbitals which preserve the HF occupied space [12]. Alternatively one could have employed orbitals generated by an MCSCF procedure or a transformation of the virtual space known as K-orbitals [13]. The use of FNO's has both positive and negative effects. On the one hand, the number of configurations required to recover a certain fraction of the correlation energy is often reduced by a factor of 2 or more. But, on the other hand, the number of CI iterations required to reach convergence is often increased by 30–50%.

The choice of which orbitals to use becomes irrelevant as the wavefunction closes in on the FCI wavefunction since the FCI is invariant to orthonormal transformations among the molecular orbitals. However, for some of the more severely truncated CI's in a sequence of wavefunctions certain types of orbitals may produce irregularities in a property's convergence pattern, making extrapolation difficult. An examination of these effects was considered outside the scope of the present work.

All wavefunctions and properties were computed with the MELDF-X suite of programs [14]. All runs were performed on local workstations rated at $\leqslant 4$ MFlops with approximately 1 Gbyte of scratch disk space. Unless otherwise noted, the properties were computed as expectation values since a large number of them were desired for each wavefunction. Past experience [7] has shown there to be little difference between the use of a finite field approach for evaluating properties and the expectation value approach with wavefunctions of the type used here. In the full CI limit the two sets are identical. Total energies were converged to 10^{-7} hartree to insure adequate convergence in the properties. Only the 5 spherical components of the 6 Cartesian d's (or 7 components of the 10 cartesian f's, etc.) were used in the basis sets. Calculation on N_2 utilized D_{2h} symmetry, while calculations on H_2O and H_2CN were carried out in C_{2v} symmetry.

No claim is made that any of the proposed sequences of wavefunctions or choice of selection criterion represents the optimal choice for any particular property. Given the desire to examine the simultaneous convergence behavior of many properties associated with each wavefunction in this sequence, the use of an *energy* selection criterion was judged, on the basis of previous experience with

selected CI, to be about as effective as other choices which have been tried over the years.

In terms of the total energy, it is possible to roughly gauge the efficiency of our procedure by comparing it to the popular CAS-SCF/MR SD-CI technique. The most extensive internally contracted CI reported by Werner and Knowles [6] in their study of the dissociation energy of N_2 involved a 175 configuration reference space that generated 87,152 singles and doubles. This reference space and the CAS-SCF configuration space used to optimize the orbitals were produced by considering all possible excitations of 10 electrons among 8 orbitals. The authors made no mention of how many configurations were actually handled in the variational part of the contracted CI, but the energy was reported as −109.2565 hartree. Using the same basis set and geometry (to be described below) it was possible to obtain a slightly lower energy (−109.2580) using just 35 reference configurations and 39,353 singles and doubles. If configuration selection is performed on the 35-configuration reference space list of singles and doubles the number of configurations can be cut to only 22,500 with the loss of less than a millihartree in energy. It should be noted that the internally contracted CI method is only an approximation to MR SD-CI and the basis set used here was relatively small. Nonetheless, the preceding comparison demonstrates that our choice of wavefunctions is on par with or somewhat better than other choices found in the current literature.

3 N_2

N_2 has a long tradition of serving as a test bed for new theoretical methods. Although its wavefunction is dominated at R_e by the HF configuration, the presence of a triple bond makes for a difficult correlation problem. The molecule possesses an extra 0.04 hartree of correlation energy compared to other first row diatomics, such as the isoelectronic carbon monoxide molecule. We chose N_2 because it presented a difficult challenge for the CI method and because of the availability of a very large full CI calculation with which we could compare our results.

3.1 Energy

In Fig. 1 the energies resulting from four sequences of CI wavefunctions, corresponding to selection thresholds of 10^{-5}–10^{-7} and 0.0, are plotted against the sum of the squares of the reference configuration CI coefficients, Σc_i^2. All calculations used the Dunning–Hay [15] SV basis set. This parameter serves as a crude indicator of the quality of the reference space, with typical values lying in the range of 0.91–0.93 for HF SD-CI's. For MR SD-CI's with very large reference spaces Σc_i^2 can approach values as large as 0.95–0.98. Eventually, as the reference space continues to enlarge, all possible configurations are contained in it and $\Sigma c_i^2 = 1.0$. Unless otherwise noted, all N_2 calculations were done at a bond distance of 2.1 bohr, which is close to the experimental value of 2.074 bohr [16] and was used in previous studies of this diatomic.

Several features of Fig. 1 deserve comment. As will become more apparent in subsequent figures for larger basis sets, configuration selection has the smallest impact for the smallest reference space. The four points at $\Sigma c_i^2 = 0.92$, based on
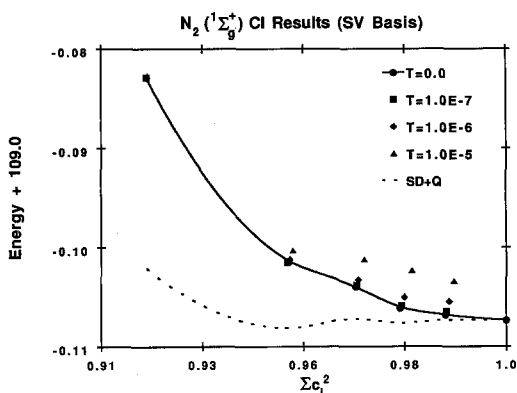
N$_2$ ($^1\Sigma_g^+$) CI Results (SV Basis)

Fig. 1. Convergence of the N$_2$ ($^1\Sigma_g^+$) valence CI energy ($R = 2.10a_0$) with respect to the sum of the squares of the reference configurations' CI coefficients using a $[3s, 2p]$ basis. Second order perturbation theory selection of configurations was performed with thresholds of $T = 10^{-5}$, 10^{-6}, 10^{-7}, and 0.0. The SD + Q curve is based on the Davidson corrected CI energies

a single (HF) configuration reference space, are nearly indistinguishable. However, as the reference space expands and Σc_i^2 increases the four sequences begin to diverge, with the largest $T = 0 \rightarrow T = 10^{-5}$ difference (0.0034 hartree) occurring with the largest reference space. The largest reference space contained 62 spin-adapted configurations and generated 12,320 single and double excitations. By way of contrast, the full CI wavefunction contained over 500,000 configurations, but its energy was only 0.0005 hartrees lower than the MR SD-CI energy associated with the largest reference space.

A simple estimate of the contribution from higher order excitations not explicitly included in perturbation theory or the variational CI leads to the curve labeled "SD + Q" in Fig. 1. It was obtained by augmenting the CI energies with an additional term based on one form of the "Davidson quadruples correction" [17]:

$$\Delta E_Q = \Delta E_{SD}(1 - \Sigma c_i^2)/(2\Sigma c_i^2 - 1)$$

where ΔE_{SD} is the energy lowering for the unselected CI relative to the zeroth order energy, E_0, the eigenvalue associated with Ψ_0. A slightly simpler expression,

$$\Delta E_Q = \Delta E_{SD}(1 - \Sigma c_i^2)$$

produces somewhat better agreement with the N$_2$ full CI energy when the values of Σc_i^2 are greater than 0.94, but gives worse results for smaller values. Given the qualitative spirit of this correction it often performs better than expected, especially in the vicinity of the equilibrium geometry [18]. The accuracy of the $\Delta E_{SD}(1 - \Sigma c_i^2)$ estimate has been observed to sometimes vary considerably with bond length [1]. Nonetheless, the $E_{SD + Q}$ energies provide another sequence which may potentially yield information about the degree of convergence of the calculations.

The smooth behavior of the $T = 0$ energies in Fig. 1 suggests the possibility of using the truncated CI energies associated with the MR SD-CI wavefunctions in order to extrapolate to the FCI energy. Several simple functional forms were considered for fitting the data. On the basis of the appearance of Fig. 1 we initially tried functions of the form:

$$f(\Sigma c_i^2) = a + b* \exp[c*(1 - \Sigma c_i^2)]$$
$$g(\Sigma c_i^2) = a + b* \exp[c*(1 - \Sigma c_i^2)^2].$$

It is readily seen that with these functions the extrapolated FCI energy is simply given by $(a + b)$. Furthermore, the slope of the exponential at $\Sigma c_i^2 = 1.0$ is $-b^*c$ whereas the gaussian approaches 1.0 with zero slope.

In Table 1 the results of the fit of the CI energies with the exponential and gaussian functions are compared with E_{SD+Q} as well as the full CI energies (where available). For each of these fits there are three entries corresponding to different weights used. The first entry was obtained with no weighting, while the second and the third correspond to weighting factors of $1/(1 - \Sigma c_i^2)$ and $1/(1 - \Sigma c_i^2)^2$ respectively. It should be noted that higher powers of the quotient $1/(1 - \Sigma c_i^2)$ can in principle be used to weigh the points near to 1 more severely. However, this is not recommended when all available points are in the range 0.90–0.95. In almost every instance the use of a weighting factor has little effect on the extrapolated FCI energy.

The degree to which the two functional forms mimic the behavior of the computed energies is demonstrated by the fact that if all 6 N_2 SV basis set data points, including the full CI, are included in the fitting procedure the value of both functions at $\Sigma c_i^2 = 1.0$ differs by approximately 0.0002 hartree. The RMS standard deviations are on the order of 0.0001. As can be seen from Fig. 2, both fits are nearly indistinguishable for the SV basis set. However, when fewer data points are available for the fit, the exponential function has been generally found to perform the best for the cases examined here. The overall quality of the fit is sometimes improved if the first data point, corresponding to a simple SD-CI energy for N_2, is dropped. Nevertheless, for this small basis set the two E_{SD+Q} energies obtained from the 15- and 34-configuration reference spaces are both several tenths of a millihartree closer to the full CI energy than our extrapolated values.

As it was mentioned earlier the extrapolated FCI value for the exponential and gaussian functions is $(a + b)$. It is reasonable to assume that "a" represents a "ballpark" value of the energy while "b" represents a refinement to accommodate the exponential behavior. Therefore the value of "a" is close to the computed energies while "b" is of the order of 0.01 to 0.001. These estimates correspond to good guesses for the initial values of the parameters for all 3 systems reported here.

Larger basis sets produce qualitatively similar results, as seen in Figs. 3–5. The first of these figures shows the results of calculations done with the $(10s, 4p, 1d) \rightarrow [3s, 2p, 1d]$ SVP basis set used by Werner and Knowles [6] in their study of the N_2 dissociation energy. These authors report a full CI energy of -109.2640 ± 0.0002 hartree (at $R_e = 2.12$ bohr). The uncertainty results from their exploitation of sparsity in the matrix. That calculation involved a massive 541 million determinants (>110 million configurations). In order to compare our results with their FCI energy we performed a series of MR SD-CI's at the same 2.12 bohr bond length. The largest MR SD-CI calculation in Fig. 3, $T = 0.0/137$-reference, yielded an energy of -109.2623 and involved some 109,000 configurations. By employing a configuration selection threshold of 10^{-7} it is possible to obtain an energy only 1 millihartree higher but which contains only 40,000 configurations. This latter wavefunction possesses an energy within 2 millihartrees of E_{FCI}. It recovered $99+\%$ of the SVP valence correlation energy, but employs 2000 times fewer configurations!

Results from the new Dunning [19] correlation-consistent, polarized valence triple and quadruple zeta (cc-pVTZ and cc-pVQZ) sets are shown in Figs. 4 and 5. In popular notation, the former basis can be denoted $(10s, 5p, 2d, 1f) \rightarrow [4s, 3p, 2d, 1f]$ and the latter $(12s, 6p, 3d, 2f, 1g) \rightarrow [5s, 4p, 3d, 2f, 1g]$. Due to the

Table 1. Extrapolated full CI energies based on the zero threshold N_2CI energies[a]

Basis	# Pts.	Lowest E_{CI}[b]	Ψ_0[c]	E_{SD+Q}[d]	Estimated full CI energy		Calculated
					Exponential[e]	Gaussian[f]	E (full CI)
SV	3	−109.1040	15	−109.1071	−109.1057	−109.1055	−109.1073
		(4 008)[g]			−109.1057	−109.1055	(527 248)
					−109.1057	−109.1055	
	4	−109.1061	34	−109.1077	−109.1074	−109.1069	
		(8 830)			−109.1079	−109.1070	
					−109.1082	−109.1070	
	5	−109.1068	62	−109.1073	−109.1076	−109.1071	
		(12 320)			−109.1076	−109.1071	
					−109.1076	−109.1071	
SVP	3	−109.2546	15	−109.2664	−109.2616	−109.2614	−109.2640 ± 0.0002
		(15 618)			−109.2616	−109.2614	(110.7 million)
					−109.2616	−109.2614	
	4	−109.2580	35	−109.2659	−109.2637	−109.2632	
		(39 353)			−109.2638	−109.2636	
					−109.2639	−109.2639	
	5	−109.2608	64	−109.2654	−109.2646	−109.2635	
		(63 091)			−109.2647	−109.2636	
					−109.2649	−109.2636	
	6	−109.2623	137	−109.2644	−109.2644	−109.2635	
		(109 279)			−109.2644	−109.2636	
					−109.2643	−109.2636	
cc-pVTZ	3	−109.3599	15	−109.3777	−109.3743	−109.3701	
		(106 310)			−109.3743	−109.3701	
					−109.3743	−109.3701	
	4	−109.3648	33	−109.3777	−109.3753	−109.3719	
		(265 003)			−109.3753	−109.3720	
					−109.3754	−109.3720	
	5	−109.3693	67	−109.3775	−109.3765	−109.3734	
		(512 271)			−109.3766	−109.3735	
					−109.3767	−109.3735	
	6	−109.3717[h]	137	−109.3762	−109.3759	−109.3739	
		(927 606)			−109.3758	−109.3740	
					−109.3758	−109.3740	
cc-pVQZ	3	−109.3876	15	−109.4072	−109.4004	−109.3984	
		(406 734)			−109.4004	−109.3984	
					−109.4004	−109.3984	
	4	−109.3931[h]	33	−109.4075	−109.4038	−109.4006	
		(1 038 284)			−109.4040	−109.4007	
					−109.4041	−109.4007	
	5	−109.3981[h]	67	−109.4076	−109.4062	−109.4025	
		(2 049 738)			−109.4064	−109.4027	
					−109.4067	−109.4027	
	6	−109.4016[h]	136	−109.4072	−109.4069	−109.4036	
		(3 765 107)			−109.4071	−109.4039	
					−109.4072	−109.4039	

[a] Energies are given in hartrees. The full CI energy for the SVP basis is taken from the work of Werner and Knowles [6]. There are three entries for every fit, corresponding to fitting with no weighting, weighting with $1/[1 - \Sigma c_i^2]$ and $1/[1 - \Sigma c_i^2]^2$

[b] The lowest CI energy used in the fitting procedure

[c] The size of the largest reference space used int he fitting procedure (in CSF's)

[d] E_{CI} + Davidson Correction (see text)

[e] $(a + b^* \exp[c^*(1 - \Sigma c_i^2)])$

[f] $(a + b^* \exp[c^*(1 - \Sigma c_i^2)^2])$

[g] The number of CSF's in the wavefunction

[h] The zero threshold energy was estimated based on calculation at $T = 10^{-8}$ and $T = 10^{-9}$, as discussed in the text
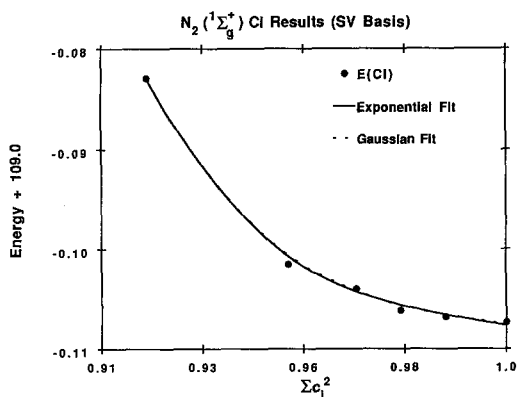
N$_2$ ($^1\Sigma_g^+$) Cl Results (SV Basis)

• E(CI)
— Exponential Fit
- - Gaussian Fit

Fig. 2. A comparison of the exponential and gaussian fits to the unselected CI energies for N$_2$ computed with a [$3s, 2p$] basis

N$_2$ ($^1\Sigma_g^+$) Cl Results (SVP Basis)

—•—T=0.0
■ T=1.0E-7
♦ T=1.0E-6
▲ T=1.0E-5
- - SD+Q

Fig. 3. Convergence of the N$_2$ ($^1\Sigma_g^+$) valence CI energy ($R = 2.12a_0$) with respect to the sum of the squares of the reference configurations' CI coefficients with a [$3s, 2p, 1d$] basis. Second order perturbation theory energy selection was performed with thresholds of $T = 10^{-5}$, 10^{-6}, 10^{-7}, and 0.0. The SD + Q curve is based on the Davidson corrected CI energies
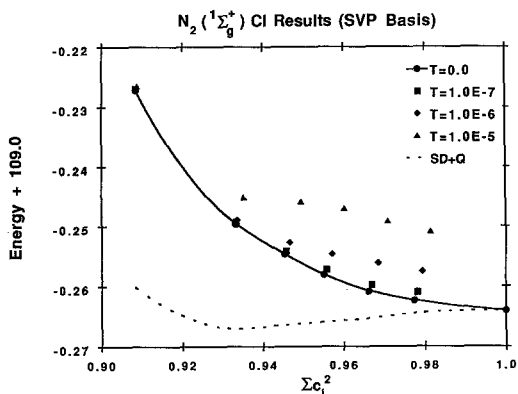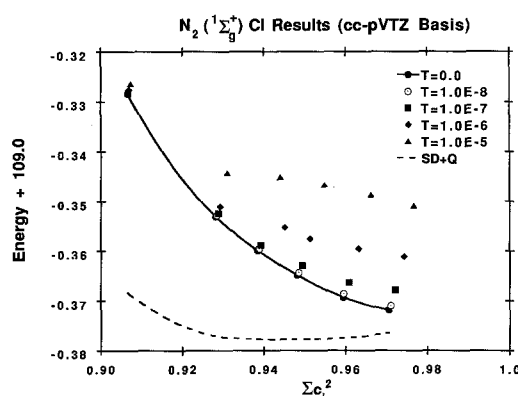
Fig. 4. Convergence of the N$_2$ ($^1\Sigma_g^+$) valence CI energy ($R = 2.10a_0$) with respect to the sum of the squares of the reference configurations' CI coefficients with the correlation consistent [$4s, 3p, 2d, 1f$] basis. Second order perturbation theory energy selection was performed with thresholds of $T = 10^{-5}$, 10^{-6}, 10^{-7}, 10^{-8}, and 0.0. The SD + Q curve is based on the Davidson corrected CI energies. The $T = 0.0$ energy at ∼0.97 was estimated by the procedure described in the text using calculations up to and including $T = 10^{-9}$

N$_2$ ($^1\Sigma_g^+$) Cl Results (cc-pVTZ Basis)

—•—T=0.0
○ T=1.0E-8
■ T=1.0E-7
♦ T=1.0E-6
▲ T=1.0E-5
- - SD+Q

large number of configurations, the lowest $T = 0$ point for the cc-pVTZ figure was extrapolated from a $T = 10^{-9}$ calculation using a procedure to be described. Similarly, the energies for some of the $T = 0$ wavefunctions with the cc-pVQZ basis set were estimated by the same procedure. These energies are believed accurate to ± 0.0001 hartree.
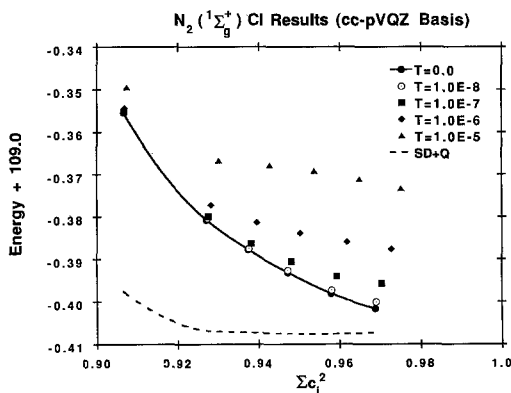
Fig. 5. Convergence of the N_2 ($^1\Sigma_g^+$) valence CI energy ($R = 2.10a_0$) with respect to the sum of the squares of the reference configurations' CI coefficients with the correlation consistent [5s, 4p, 3d, 2f, 1g] basis. Second order perturbation theory energy selection was performed with thresholds of $T = 10^{-5}$, 10^{-6}, 10^{-7}, 10^{-8}, and 0.0. The SD + Q curve is based on the Davidson corrected CI energies. The $T = 0.0$ energies beyond 0.93 were estimated by the procedure described in the text using calculations up to and including $T = 10^{-9}$

Although the data plotted in Figs. 3–5 are qualitatively the same as those obtained with the smaller SV basis, for large Σc_i^2 the effects of performing configuration selection are seen to be even more pronounced. Thus, if one wishes to obtain variational energies within some ε of the unselected values over a range of basis sets, it would be necessary to resort to progressively smaller selection thresholds as $\Sigma c_i^2 \rightarrow 1.0$ and the size of the basis set increases. Fortunately, even with the largest basis set considered for N_2 it is possible to approach within a millihartree of the $T = 0$ energies by employing selection thresholds which still left the calculations tractable on our workstations.

While the unselected (i.e. $T = 0$) energies have been shown to smoothly approach the E_{FCI} asymptote, curves derived from selection thresholds of 10^{-5} or 10^{-6} exhibit two features which make them less useful for any extrapolation procedure: (1) a curve passing through these energies shows an inflection point and (2) there is a substantial difference in energy relative to the unselected curve. As indicated above, the magnitude of the energy penalty for a fixed threshold increases with the size of the reference space and the size of the basis set. The smallest threshold used in generating a complete sequence of wavefunctions was 10^{-8}. To give an indication of the size of the error produced this threshold, the largest $E_{T=0} - E_{T=1.0E-8}$ difference we encountered was on the order of 0.002 hartree. As can be seen in Figs. 3–5, in most cases a threshold of 10^{-8} produced errors of less than a millihartree.

If necessary, thresholds as small as 10^{-9} can be employed. Such a value may still result in substantial reductions in the numbers of configurations which must be treated variationally. However, it is not always possible to perform calculations with such small thresholds. The reason for our interest in calculations with selection thresholds as large as 10^{-6} lies in the extent to which the numbers of configurations are reduced compared to the unselected case. In many cases the reduction can amount to several orders of magnitude or more.

One way of minimizing the energy penalty associated with performing selected CI calculations would be to approximate the discarded energy with its second order perturbation theory counterpart, $\Delta E_{\text{PT-discarded}}$, which was previously computed in the selection procedure. In practice a straightforward appending of $\Delta E_{\text{PT-discarded}}$ to the variational energy proved to be too inaccurate since perturbation theory typically overestimates ΔE_{SD} by 20–30%. Alternatively, one might simply scale $\Delta E_{\text{PT-discarded}}$ by the ratio of the variational energy

2nd Order Pert. Theory Performance for N_2

- 137-ref. space (SVP Basis)
——0.620 + 0.005*exp(0.8*|log(T)|)
♦ 15-ref. space (SVP Basis)
▲ 136-ref. space (TZP Basis)
– – Fit to 136-ref. Data
— Fit to 15-ref. Data

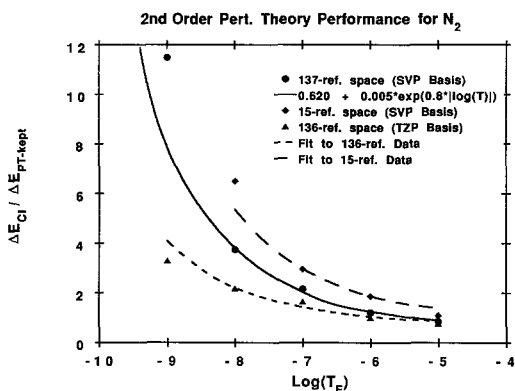$\Delta E_{CI} / \Delta E_{PT\text{-kept}}$

$Log(T_E)$

Fig. 6. The variation in the accuracy of the second order energy as a function of the size of the energy contributions for two different basis sets. The accuracy is measured by the ratio of the variational energy lowering divided by the predicted lowering corresponding to the configurations kept at a certain selection threshold $T(E)$, $\Delta E_{CI}/\Delta E_{PT\text{-kept}}$. Results are given for the SVP and cc-pVTZ basis sets with several reference spaces. The *solid curve* was obtained by performing a least squares fit to the $\log(T) = -8, -7, -6$ and -5 SVP 137-configuration reference space points

lowering divided by the PT estimate of the same quantity, $\Delta E_{SD}/\Delta E_{PT\text{-kept}}$, as has been done for many years by Davidson and coworkers [20]. However, as we will see, an improved estimate can be obtained by recognizing that this ratio is a function of the size of the energy contributions. We have found that for a certain range of energies the application of a fixed ratio scaling may be worse than simply using the raw $\Delta E_{PT\text{-discarded}}$.

As seen in Fig. 6, where the ratio $S_{PT} = \Delta E_{SD}/\Delta E_{PT\text{-kept}}$ for the configurations in the energy range $T_N \to T_{N+1}$ is plotted against the log of the selection threshold for two different reference spaces, the dependence on $\log(T)$ is approximately exponential. S_{PT} begins with values of 0.7–0.9 for large thresholds and increases by almost an order of magnitude as you go to very small thresholds. Similar trends were obtained for H_2O and H_2CN.

Since the bulk of the correlation energy is *overestimated* by perturbation theory, whereas the contributions lying beyond $T = 10^{-6}$ are *underestimated*, it is difficult to avoid either overestimating or underestimating $E_{CI}(T = 0)$ when using a simple scaling factor based on a single $\Delta E_{SD}/\Delta E_{PT\text{-kept}}$ ratio determined with respect to the total correlation energy recovered. The last 10–15% of the correlation energy contained in the samller threshold ranges represents a nonnegligible quantity. A slightly more sophisticated approach is needed if greater accuracy is sought in the estimated $E_{CI}(T = 0)$.

Results shown in Fig. 6 were computed with different reference spaces and basis sets. The $\Delta E_{SD}/\Delta E_{PT\text{-kept}}$ ratio is plotted against the log of the selection threshold. The solid line, corresponding to a least squares exponential fit to the $\log(T) = -8, -7, -6$ and -5 points using a function of the form $c_1 + c_2 \exp(0.8*N)$, where N is taken as the absolute value of $\log(T)$, is seen to closely approximate the 137-ref. data. Restricting the fit to fewer points produces similar results in the large threshold region, i.e. $\log(T) = -7$ to -6, where most of the energy is contained. Table 2 shows the improvement in the estimated $T = 0$ energies over the simpler scaling procedure. By combining $T = 10^{-6}$ variational energies with the scaled second order perturbation theory energies it was possible to estimate the unselected energies to within 1 millihartree. For example, the estimated $T = 0$ energies appearing under the "$T = 10^{-6}$ Results" column of Table 2 were obtained by adding the scaled PT estimates of the energy lowering in the 10^{-6}–10^{-7}, 10^{-7}–10^{-8} and 10^{-8}–10^{-9} energy ranges to $E_{CI}(T = 10^{-6})$.

Table 2. Extrapolation to the unselected N_2 CI energies using second order perturbation theory to estimε the energy contribution from the unselected configurations

SVP Basis

	$T = 10^{-6}$ results			$T = 10^{-7}$ results			
$\Psi_0{}^a$	E_{CI}	# CSF's	Est. $E_{CI}(T=0)^b$	E_{CI}	# CSF's	Est. $E_{CI}(T=0)$	$E_{CI}(T=0$
15	−109.2527	6 450	−0.2531/−0.2546	−109.2541	11 383	−0.2541/−0.2543	−109.254
35	−109.2546	9 129	−0.2555/−0.2589	−109.2572	22 511	−0.2573/−0.2577	−109.257
64	−109.2561	10 498	−0.2575/−0.2613	−109.2598	39 093	−0.2599/−0.2608	−109.260
137	−109.2575	14 698	−0.2593/−0.2620	−109.2610	40 637	−0.2615/−0.2625	−109.262

cc-pVTZ Basis

	$T = 10^{-6}$ results			$T = 10^{-7}$ results			
$\Psi_0{}^a$	E_{CI}	# CSF's	Est. $E_{CI}(T=0)^b$	E_{CI}	# CSF's	Est. $E_{CI}(T=0)$	$E_{CI}(T=0$
15	−109.3552	14 245	−0.3572/−0.3613	−109.3590	44 541	−0.3590/−0.3596	−109.3599
33	−109.3575	17 982	−0.3605/−0.3681	−109.3629	69 803	−0.3634/−0.3646	−109.3648
67	−109.3595	21 951	−0.3636/−0.3722	−109.3663	89 335	−0.3672/−0.3700	−109.369
136	−109.3612	29 225	−0.3662/−0.3721	−109.3678	102 814	−0.3693/−0.3733	−109.3716

[a] The number of configurations in the reference space

[b] The estimated zero threshold energy + 109.0. The value estimated by scaling $\Delta E_{PT\text{-thrown away}}$ by ΔE_C $\Delta E_{PT\text{-kept}}$ is given in front of the slash. The second value is based on the "exponential" scaling described i the text

[c] The number of configurations in the SVP zero threshold calculations are: 15 618, 39 353, 63 091, an 109 279 for the 15 CSF, 35 CSF, 64 CSF, and 137 CSF reference spaces, respectively

[d] The number of configurations in the cc-pVTZ zero threshold calculations are: 106 310, 265 003, 512 27 and 927 606 for the 15 CSF, 33 CSF, 67 CSF, and 136 CSF reference spaces, respectively

Thus, with an additional loss of 0.0005 hartree beyond that which accompanied the truncation of the full 110 million CI space to the 100,000 configuration ($T = 0/137$-ref.) space, we can achieve a further reduction in the number of configurations which must be handled variationally by another factor of 8. In terms of the energy, the vast majority of the FCI configurations are of trivial importance.

It is also apparent from Fig. 6 that, as expected, second order perturbation theory based on the smaller 15 configuration reference space does a poorer job than the larger reference space, since the $\Delta E_{SD}/\Delta E_{PT\text{-kept}}$ ratios deviate more from 1.0. If the basis set is increased to the triple zeta + polarization (TZP) level the ratios seem to rise even less steeply as $T \to 0$. Therefore, at least for the N_2 molecule, second order perturbation theory's ability to predict the effect of the large number of small energy contributions to the variational energy is improved by using larger reference spaces and larger basis sets. The improvement found for the larger basis set is somewhat subtle in that perturbation theory actually does a slightly worse job on the first 90% of the correlation energy. Improvement is found only for that last 10% comprised of a large number of small contributions.
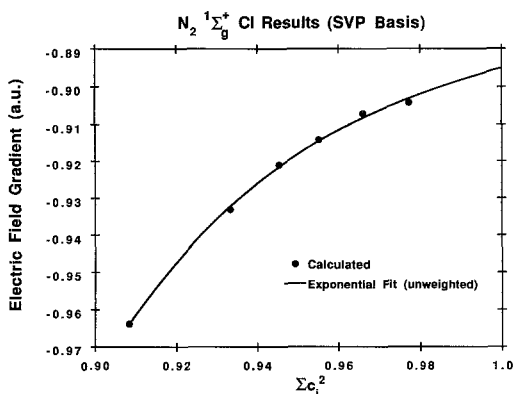
N$_2$ $^1\Sigma_g^+$ CI Results (SVP Basis)

Fig. 7. Convergence of the electric field gradient at the nitrogen nucleus in N$_2$ with respect to the sum of the squares of the reference configurations' CI coefficients

3.2 Properties

In general, extrapolating the 1-electron properties to the full CI limit presents more of a challenge than extrapolating the total energy due to the fact that there is no variational principle at work. They may not approach the asymptotic limit monotonically. Furthermore, the selection of configurations on the basis of their energy contribution to the wavefunction may be far less efficient for properties. Despite these difficulties, in practice we find that most properties converge even *more rapidly* than the energy and in many cases convergence is smooth enough to permit the use of a fitting/extrapolation procedure similar to what was proposed for the energy. As will be seen there are exceptions to each of these statements. For example, the hyperfine spin properties, to be discussed in regard to H$_2$CN, appear to converge more slowly than the energy.

In Fig. 7 the electric field gradient at the nitrogen atom in N$_2$ is plotted against Σc_i^2, the same independent variable used to plot the energy convergence. An exponential expression of the form $a + b * \exp[c*(1 - \Sigma c_i^2)]$ is seen to accurately fit all available data. The use of a gaussian expression produces nearly identical results. On the other hand, the zz component of the electric quadrupole moment, Θ_{zz} shown in Fig. 8, comes within 0.01 a.u. of the apparent full CI limit with even a small reference space. As Σc_i^2 increases beyond 0.93 the computed
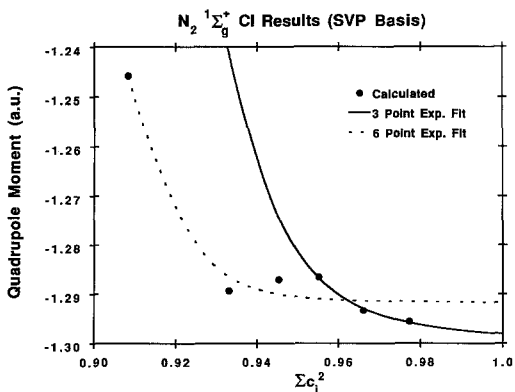
N$_2$ $^1\Sigma_g^+$ CI Results (SVP Basis)

Fig. 8. Convergence of the zz component of the quadrupole moment in N$_2$ with respect to the sum of the squares of the reference configurations' CI coefficients
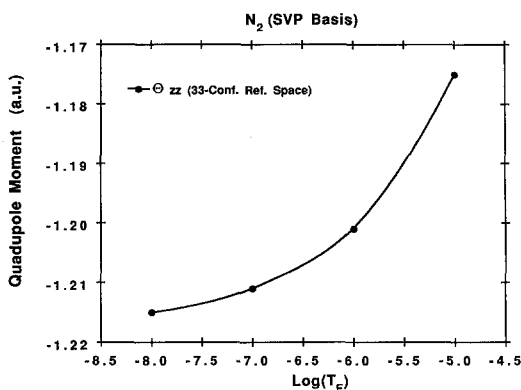
N₂ (SVP Basis)

Fig. 9. Convergence of the zz component of the quadrupole moment in N_2 with respect to the log of the perturbation theory energy selection threshold

Θ_{zz} values seem to wander somewhat and then exponentially approach the limiting value as Σc_i^2 approaches 1.0. In such a case it is possible to extrapolate using all existing data points without obtaining a ridiculous estimate, but whenever the quantity in question is oscillating the use of a fitting prodecure procedure should be used with care. Indeed, to the extent these two examples are indicative of other properties it would appear that each property must be considered individually before a determination can be made about the suitability of the data for extrapolation.

With the total energy is proved possible to estimate the unselected, i.e. $T = 0.0$, result in cases where it was impossible to explicitly perform the calculation from a combination of the selected CI energies and a scaled PT estimate of the energy thrown away. For the properties there is no counterpart because they are evaluated as expectation values using the first order density matrix. However, the convergence of the properties is usually quite smooth, as seen in Fig. 9, where the quadrupole moment is plotted as a function of the log of the selection threshold. Whenever this type of behavior is observed it should be possible to extrapolate to the zero threshold limit using one of the functional forms discussed for the energy.

It should also be noted that the error introduced by employing even quite large selection thresholds ($\sim 10^{-6}$) is often less than the basis set truncation error. For example, the estimated full CI quadrupole moment obtained with the cc-pVTZ basis is on the order of 0.09 a.u.'s smaller than the full CI value obtained with the SVP basis. Further enlarging the basis set, we find an additional -0.06 lowering associated with the cc-pVQZ set. Thus, each of these changes resulting from basis set enlargement exceeds the 0.02–0.04 a.u. error resulting from configuration selection.

Table 3 summarizes our computed and extrapolated findings on N_2. For this molecule the SD-CI properties are all quite close to the estimated full CI values, even with the largest basis. For example, the cc-pVQZ basis set SD-CI quadrupole moment includes more than 70% of the effects of full correlation recovery. This is not always the case, as will be seen in the discussion of H_2CN.

4 H₂O

Calculations analogous to the ones already described for N_2 were performed on the water molecule with a DZP basis. Figure 10 shows the convergence

Table 3. Calculated and extrapolated properties for $N_2(^1\Sigma_g^+)$[a]

	SV Basis Set Results			SVP Basis Set Results		
	SCF	SD-CI	Full CI	SCF	SD-CI	Est. Full CI
Energy	−108.8778	−109.0829	−109.1073	−108.9330	−109.2271	−109.2640 ± 0.0002[b]
Θ_{zz}	−1.785	−1.980	−2.053	−1.059	−1.246	−1.296
$\langle r**2 \rangle$	40.074	39.917	40.051	39.653	39.474	39.513
$\langle \delta \rangle$	−195.514	−195.457	−195.425	−193.512	−193.532	−193.509
$\langle 1/r \rangle$	21.569	21.579	21.593	21.579	21.613	21.515
HF Force	−0.240	−0.240	−0.242	−0.077	−0.077	−0.079
EFG	−0.890	−0.744	−0.708	−1.129	−0.964	−0.905

	cc-pVTZ Basis Set Results			cc-pVQZ Basis Set Results		
	SCF	SD-CI	Est. Full CI	SCF	SD-CI	Est. Full CI
Energy	−108.9803	−109.3283	−109.3758	−108.9878	−109.3554	−109.4072
Θ_{zz}	−0.985	−1.146	−1.209	−0.936	−1.086	−1.146
$\langle r**2 \rangle$	39.449	39.256	39.291	39.524	39.313	39.342
$\langle \delta \rangle$	−197.871	−197.953	−197.926	−201.597	−201.649	−201.622
$\langle 1/r \rangle$	21.600	21.646	21.648	21.600	21.643	21.649
HF Force	−0.014	−0.028	−0.032	0.011	−0.002	−0.005
EFG	−1.335	−1.185	−1.113	−1.349	−1.204	−1.130

[a] $R = 2.10$ bohr except for the SVP basis, where $R = 2.12$ bohr was used for the sake of comparison with Werner and Knowles in [6]. Ten valence electron were correlated. The SV basis set results are from an explicit full CI. All other results are extrapolated as described in the text. The total energy is given in hartrees. Other properties are in atomic units. "HF Force" is the Hellman–Feyman force. EFG = electric field gradient
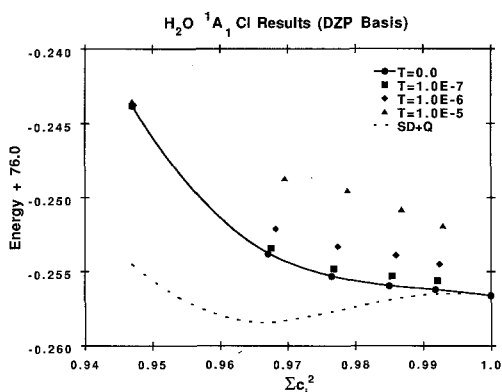[b] From Werner and Knowles [6]

Fig. 10. Convergence of the H_2O $^1A_1$ valence CI energy ($R = 1.88973a_0$, HOH = 104.5°) with respect to the sum of the squares of the reference configurations' CI coefficients with a [4s, 2p, 1d/2s, 1p] basis. Second order perturbation theory energy selection was performed with thresholds of $T = 10^{-5}$, 10^{-6}, 10^{-7}, and 0.0. The SD + Q curve is based on the Davidson corrected CI energies

behavior in the total energy to be similar to what was observed for N_2. The computed full CI energy was taken from the work of Bauschlicher and Taylor [21]. Table 4 lists the results of fitting the computed energies to the exponential and gaussian functions discussed above. Agreement between the computed energies and the fits is even better than for N_2, with standard deviations less than

0.0001 hartree. The extrapolated full CI energies are seen to be in good agreement with the computed E_{FCI}. The E_{SD+Q} estimates, while in generally good agreement, are somewhat less accurate than the extrapolations based on the exponential, gaussian functional forms.

A comparison of the results in Table 4 with the related findings reported in Harrison's [11] recent work, shows that equally low variational energies can be achieved by the present methods with much smaller reference spaces. For example, the lowest variational energy reported by Harrison at the equilibrium geometry was -76.2553 and used 24,337 reference configurations. While the reference space is the only space which is diagonalized in Harrison's approach, the more than 2 million singles and doubles which were generated represents a sizable fraction of the 6.7 million configurations in the full CI. The first entry in Table 4 shows the same variational energy generated from only 32 configurations. The size of the matrix which was diagonalized was on the order of 29,000.

Estimated full CI properties for water, obtained with the same procedure used for N_2, are as follows: $\mu_z = -0.835$ a.u., $\Theta_{yy} = 1.847$ a.u., $\langle r^2 \rangle = 19.862$ a.u., $\langle \delta(O) \rangle = -295.166$ a.u., $\langle \delta(H) \rangle = -0.386$ a.u., HF Force(O) $= -0.090$ a.u., HF Force(H) $= -0.005$ a.u., EFG(O) $= -1.883$ a.u., EFG(H) $= 0.397$ a.u.

5 H$_2$CN

Up to this point we have considered the 8-valence electron H_2O and 10-valence electron N_2 closed shell systems. Next we consider the 15-electron H_2CN ($^2B_2$) radical, whose isotropic hyperfine spin properties, a_{iso}, were the subject of a recent *ab initio* study by Chipman et al. [22]. In that study the use of large basis sets and extensive MCSCF/CI and quadratic CI [23] calculations failed to yield

Table 4. Extrapolated full CI energies based on the unselected H_2O CI energies obtained with a DZP basis[a]

# Pts.	Lowest E_{CI}[b]	Ψ_0[c]	E_{SD+Q}[d]	Estimated full CI energy Exponential[e]	Gaussian[f]	Calculated E (full CI)
3	-76.2553	32	-76.2577	-76.2564	-76.2563	-76.2566
				-76.2564	-76.2563	
				-76.2564	-76.2563	
4	-76.2560	65	-76.2569	-76.2565	-76.2564	
				-76.2565	-76.2564	
				-76.2565	-76.2564	
5	-76.2562	123	-76.2565	-76.2564	-76.2563	
				-76.2564	-76.2563	
				-76.2564	-76.2563	

[a] Energies are given in hartrees. The calculated full CI energy is taken from Bauschlicher and Taylor [17]. There are three entries for every fit, corresponding to fitting with no weighting, weighting with $1/[1 - \Sigma c_i^2]$ and $1/[1 - \Sigma c_i^2]^2$
[b] The lowest CI energy used in the fitting procedure
[c] The size of the largest reference space used in the fitting procedure (in CSF's)
[d] E_{CI} + Davidson Correction (see text)
[e] $(a + b^* \exp[c^*(1 - \Sigma c_i^2)])$
[f] $(a + b^* \exp[c^*(1 - \Sigma c_i^2)^2])$

quantitative agreement with experiment. For example, the isotropic hyperfine constant for hydrogen, $a(H)$, was computed to lie in the range of 50–70 G, compared to an experimental value of 87.4 G measured in an Ar matrix at 4 K [24]. The primary reason for the remaining error was thought to be the slow convergence of the correlation contribution to the properties. A_{iso} is proportional to the unpaired spin density, $\langle \delta(O) \rangle_{spin}$, at the various magnetic nuclei in a molecule. With hyperfine spin calculations it is necessary to correlate both core and valence sets of electrons, as both contribute about equally to the properties and are of opposite sign. Moreover, the core and valence contributions are each many times larger than the final answer.

In the present work we have chosen to extend some of the calculations reported by Chipman et al. [22]. Thus, the same two basis sets which were used in the MR SD-CI calculations from that study were used here. For the smaller of the two sets, which was of DZP quality, we were able to supplement the previous findings with new results obtained with larger reference spaces and smaller thresholds. For the larger set the reference spaces were taken from the previous work, but a slightly different frozen natural orbital basis was used.

A DZP basis set is probably the minimal level necessary to achieve qualitative agreement with experiment. Even so, an explicit full CI in this basis would involve approximately 10^{13} configurations. These calculations were performed at the optimal restricted HF geometry. Subsequent calculations were carried out in a larger 148 function, modified cc-pVTZ set, including extra diffuse functions and increased flexibility in the core region [25]. This basis, which can be denoted as $(11s, 6p, 3d, 2f) \rightarrow [7s, 5p, 3d, 2f]$ on C and N and $(8s, 3p, 2d) \rightarrow [4s, 3p, 2d]$ on H, should be capable of at least semi-quantitative results. The modified cc-pVTZ calculations were performed at the optimal cc-pVTZ SD-CI geometry.

In Fig. 11 the convergence of the CI energy for the DZP basis is plotted as a function of Σc_i^2 for a variety of selection thresholds in a manner similar to the plots for N_2 and H_2O. In addition, energies obtained from the nonvariational averaged coupled pair functional [26] (ACPF) and quasidegenerate variational perturbation theory [27] (QDVPT) methods are also plotted. Werner and Knowles [28] have recently compared the ACPF and QDVPT methods with their contracted CI technique for the calculation of spectroscopic constants in first row diatomics. For the sake of comparison in our study, the same CI-coefficient based reference spaces were used for all three sequences of calculations. Some experimentation was done with an ACPF-coefficient based reference spaces, but
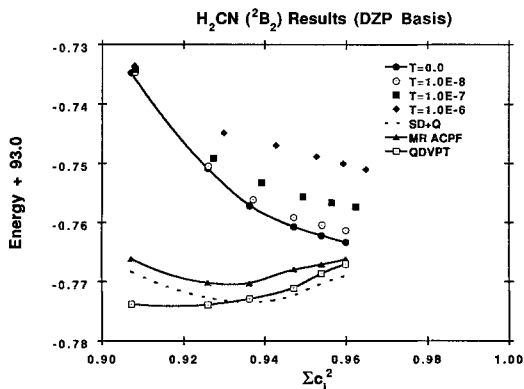

Fig. 11. Convergence of the H_2CN $^2B_2$ 15-electron CI energy ($R_{CN} = 2.530a_0$, $R_{CH} = 2.048a_0$, HCH = 118.7°) with respect to the sum of the squares of the reference configurations' CI coefficients with a $[4s, 2p, 1d]$ basis. Second order perturbation theory energy selection was performed with thresholds of $T = 10^{-6}$, 10^{-7}, and 0.0. The SD + Q curve is based on the Davidson corrected CI energies

Table 5. Extrapolated full CI energies based on the H_2CN energies obtained with a DZP basis[a]

# Pts.	Lowest E_{CI}[b]	Ψ_0[c]	E_{SD+Q}[d]	Estimated full CI energy Exponential[e]	Gaussian[f]
3	−93.7571	76	−93.7735	−93.7733	−93.7666
				−93.7733	−93.7666
				−93.7733	−93.7666
4	−93.7601	175	−93.7724	−93.7690	−93.7674
				−93.7688	−93.7674
				−93.7686	−93.7674
5	−93.7620	278	−93.7701	−93.7675	−93.7673
				−93.7670	−93.7668
				−93.7666	−93.7664
6	−93.7633	375	−93.7690	−93.7671	−93.7667
				−93.7669	−93.7666
				−93.7668	−93.7666

[a] Energies are given in hartrees. There are three entries for every fit, corresponding to fitting with no weighting, weighting with $1/[1 - \Sigma c_i^2]$ and $1/[1 - \Sigma c_i^2]^2$
[b] The lowest CI energy used in the fitting procedure
[c] The size of the largest reference space used in the fitting procedure (in CSF's)
[d] E_{CI} + Davidson Correction (see text)
[e] $(a + b* \exp[c*\Sigma c_i^2])$
[f] $(a + b* \exp[c*(\Sigma c_i^2)^2])$

it was found that this approach lead to essentially the same reference spaces as the CI-based approach when the reference space included more than 10 configurations.

The results of fitting the CI data to the two functional forms discussed previously is shown in Table 5. Both fits yield estimated full CI energies within 1 millihartree of each other independent of the number of points used in the fit. The E_{SD+Q} estimates generally lie below the other estimates. Since the actual full CI energy is unavailable for comparison, it is impossible to judge if the fitted extrapolations are more or less accurate than the Davidson-corrected estimates in this case.

Compared to the convergence plots for N_2 and H_2O where data points were available at values of Σc_i^2 as large as 0.97, there are no points beyond $\Sigma c_i^2 = 0.96$ in Fig. 11. This should not be interpreted as indicating that smaller reference spaces were used for H_2CN. In reality the largest reference space contained 375 spin-adapted configurations compared to a maximum of 136 for N_2 and 123 for water. In general more reference configurations are required for open shell systems and for larger numbers of electrons to achieve the same "quality" reference spaces, as measured by the Σc_i^2.

The ACPF and QDVPT are closer to being size consistent than the CI method. Since the reference space is treated variationally, in the limit that the reference space becomes very large these methods will give the same results as CI. Both methods show less variation in the energy for small values of Σc_i^2, as does the E_{SD+Q} curve. In that same region of the plot, all three approximations (ACPF, QDVPT, SD + Q) clearly do a better job of approaching the full CI limit. For larger values of Σc_i^2 things are less clear, at least with regard to the SD + Q curve which may overestimate the quadruples correction by an amount larger than the MR SD-CI energies underestimate the full CI.
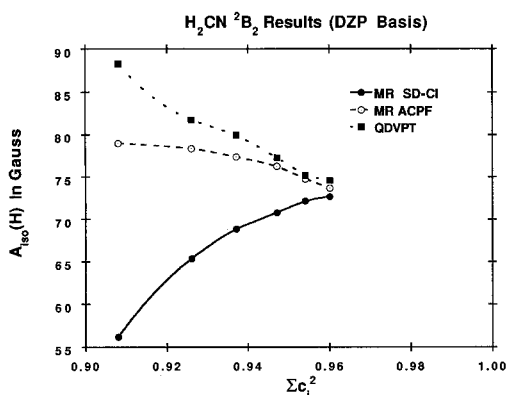
H$_2$CN ^{2}B$_2$ Results (DZP Basis)

Fig. 12. Convergence of the H$_2$CN isotropic hyperfine parameter on hydrogen with respect to Σc_i^2 for MR SD-CI, ACPF and QDVPT sequences of wavefunctions

In the H$_2$CN study of Chipman et al. the isotropic hyperfine splitting constant on hydrogen proved the most difficult for which to obtain good agreement with experiment. It was, thus, of interest to see if the ACPF or QDVPT methods were better to predict this quantity. Indeed, for small reference space, i.e. for small values of Σc_i^2, both methods appear to be in better agreement with the apparent FCI asymptotic limit in Fig. 12. However, for larger reference spaces the reverse may be true, with the MR SD-CI numbers being closer to $a(\text{H})_{\text{FCI}}$. In the absence of an unambiguous FCI value for $a(\text{H})$ it is impossible to be more definite.

Both ACPF and QDVPT values of $a(\text{H})$ approach the limiting value from above, while the MR SD-CI wavefunctions approach from below. Because isotropic hyperfine parameters are normally underestimated by restricted HF-based CI it happens that both of the nonvariational methods fortuitously are in better agreement with experiment than their CI counterpart. Nevertheless, if this cancellation of errors proved to be commonplace, the ACPF and QDVPT would hold some advantage in predicting experiment. The existence of what appears to be an inflection point in the ACPF $a(\text{H})$ curve may make it more difficult to extrapolate. Along those same lines, the QDVPT curve shows some wiggles which don't appear in the CI results, but that shouldn't preclude attempting to fit the QDVPT data. However, in this work no attempt was made to extrapolate the results from either method. With both the ACPF and QDVPT methods properties were evaluated by the finite field technique.

For properties other than a_{iso} the CI method may provide faster convergence to the full CI limit. In Fig. 13 the H$_2$CN dipole moment convergence pattern is shown for all three methods. As with the quadrupole moment in N$_2$, the CI values oscillate for small Σc_i^2. The actual DZP values of the ^{1}H, ^{14}N, and ^{13}C isotropic hyperfine coupling parameters for H$_2$CN, as well as the dipole and quadrupole moments are listed in Table 6 along with the ACPF and QDVPT values.

It was not possible to complete as thorough an analysis with the larger [7s, 5p, 3d, 2f/4s, 3p, 2d] basis. The results which we were able to obtain are listed in Table 7. No abnormalities which might prevent the application of the extrapolation techniques discussed previously are evident. Considering the large increase in the number of basis functions (40 → 148) the hydrogen isotropic hyperfine and molecular dipole moment properties are remarkably similar to the DZP findings. With small reference spaces the isotropic hyperfine for nitrogen and carbon are considerably smaller than those obtained with the DZP basis. However, the calculations with larger reference spaces are far from converged
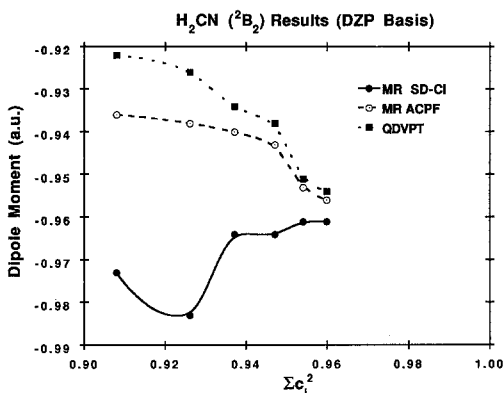
Fig. 13. Convergence of the H_2CN dipole moment with respect to Σc_i^2 for MR SD-CI, ACPF and QDVPT sequences of wavefunctions

with respect to the configuration selection threshold. It may be that the estimated full CI values turn out to be larger than their DZP counterparts, bringing the theoretical calculations more in line with experiment.

Once again the ACPF and QDVPT methods appear to approach the full CI limit from above, i.e. the absolute magnitude of the energy and hyperfine properties are larger than the full CI limit. As mentioned earlier, the ACPF and QDVPT techniques use a finite field approach to computing molecular properties, whereas the CI properties are computed as an expectation value. In order to judge the effect of this difference we normalized the 1-reference configuration ACPF and QDVPT wavefunctions and computed the properties as expectation values. These results are listed in parentheses in Table 6. For the dipole and quadrupole moments the effects are on the order of 1% or less. For the hyperfine properties the effects are much larger, in each case tending to reduce a_{iso} and bring it closer to the CI value. In spite of the substantial ($>30\%$) differences in the computed values of $a(H)$ for small reference spaces and large selection thresholds, this disparity rapidly disappears as the reference space increases.

6 Conclusion

Through the continuing efforts of many research groups around the world, much progress has been made towards the goal of computing energies and properties "as good as" those obtained with a large basis set, full CI wavefunction. However, the overwhelming numbers of configurations which must be treated in explicit full CI calculations severely limits the range of applicability of the method. Although low-level methods such as MP2 and SD-CI are often capable of recovering 80–90% of the correlation energy in well-behaved systems, there are times when this level of accuracy is insufficient. Recovery of the remaining correlation via brute force techniques quickly becomes prohibitive as the number of excitations expands enormously with each additional percent sought.

In this work we propose a MR SD-CI scheme which seeks to reproduce the results of a full CI but which avoids having to deal with most of the configurations. By emphasizing the results of a *sequence* of wavefunctions, it helps minimize the problems associated with choosing a particular set of configurations to populate the reference space. The scheme is computationally efficient enough to treat systems involving numbers of electrons and basis sets well beyond the

Table 6. H_2CN energies and properties obtained using configuration selected calculations with a DZP basis[a]

$\Psi_0{}^{b}$	T_E	# Selected	Energy	MR-SDCI results E_{SD+Q}	$a(H)$	$a(N)$	$a(C)$	μ_z	Θ_{yy}
1	0.0	19 789	−93.7347	−93.7683	56.2	4.2	−19.7	−0.973	1.471
21	0.0	297 630	−93.7508	−93.7727	65.4	6.4	−24.7	−0.983	1.460
76	0.0	968 617	−93.7571	−93.7735	69.6	7.9	−28.6	−0.963	1.437
175	0.0[c]	1 954 609	−93.7607	−93.7724	70.8	9.4	−28.7	−0.964	1.438
278	0.0[c]	2 884 248	−93.7620	−93.7701	72.2	9.4	−28.9	−0.961	1.434
375	0.0[c]	3 774 606	−93.7633	−93.7690	72.7	9.4	−28.9	−0.961	1.434

$\Psi_0{}^{b}$	T_E	# Selected	Energy	MR-ACPF results $a(H)$	$a(N)$	$a(C)$	μ_z	Θ_{yy}
1	0.0	19 789	−93.7661	79.0	10.9	−31.2	−0.936	1.424
21	0.0	297 630	−93.7702	78.4	12.3	−34.3	−0.938	1.407
76	$1.0E-8$	258 522	−93.7703	76.5	11.6	−30.6	−0.940	1.413
175	$1.0E-8$	394 671	−93.7693	75.2	8.9	−30.0	−0.943	1.412
278	$1.0E-8$	481 405	−93.7674	73.7	9.0	−29.5	−0.953	1.420
375	$1.0E-8$	553 354	−93.7661	72.6	9.1	−29.2	−0.957	1.425

$\Psi_0{}^{b}$	T_E	# Selected	Energy	QDVPT results $a(H)$	$a(N)$	$a(C)$	μ_z	Θ_{yy}
1	0.0	19 789	−93.7738	88.3	13.0	−36.1	−0.922	1.415
21	0.0	297 630	−93.7739	81.8	13.7	−36.8	−0.938	1.393
76	$1.0E-8$	258 522	−93.7729	78.3	12.5	−31.3	−0.934	1.406
175	$1.0E-8$	394 671	−93.7711	76.4	8.8	−30.3	−0.938	1.406
278	$1.0E-8$	481 405	−93.7686	74.3	8.9	−29.7	−0.951	1.417
375	$1.0E-8$	553 354	−93.7670	73.7	9.3	−29.2	−0.956	1.422

[a] The calculations were performed at $R_{CN} = 2.350$ bohr, $R_{CH} = 2.048$ bohr, HCH = 118.7$^\delta$. The energy is given in hartrees. The isotropic hyperfine values, $a(H)$, $a(N)$, and $a(C)$ are in Gauss and the dipole and quadrupole moments are in atomic units
[b] Size of the reference space in CSF's
[c] Estimated based on selected calculations down to $T = 10^{-8}$

current range of explicit full CI. It is also tunable in the sense that greater accuracy in the exrapolated results can be achieved with increments in computer resources which are comparatively modest.

We have demonstrated that for three small molecules (N_2, H_2O, and H_2CN) it is possible to define a systematic sequence of wavefunctions which enable us to effectively extrapolate to the full CI limit. Moreover, the derived sequence of energies and properties serve as a semiquantitative indicator of the degree of convergence in the results. The extrapolation procedure was demonstrated with a variety of basis sets ranging from a simple valence double *zeta* to an elaborate polarized quadruple *zeta* set including *g* functions on second period elements. Among the sequences which were studied were selected and unselected multireference CI, averaged coupled pair functional and quasidegenerate variational perturbation theory wavefunctions. The use of a configuration selection scheme based on second order perturbation theory was shown to permit these method to be extended to systems which were too large to otherwise handle.

Table 7. H_2CN energies and properties obtained using configuration selected calculations with a modified cc-pVTZ basis[a]

			MR-SDCI results						
Ψ_0[b]	T_E	# Selected	Energy	E_{SD+Q}	$a(H)$	$a(N)$	$a(C)$	μ_z	Θ_{yy}
1	$1.0E-4$	3 444	-93.7645		56.7	4.1	-20.9	-1.001	2.345
	$1.0E-5$	17 079	-93.8240		55.5	2.6	-19.4	-0.995	2.349
	$1.0E-6$	57 976	-93.8444		55.0	2.4	-17.9	-0.989	2.351
	$1.0E-7$	122 343	-93.8494		54.8	2.7	-17.2	-0.985	2.349
	$1.0E-8$	196 843	-93.8507	-93.8965	54.8	2.9	-17.2	-0.985	2.349
25	$1.0E-4$	22 545	-93.7693		59.9	4.8	-22.9	-0.988	2.325
	$1.0E-5$	36 123	-93.8314		58.5	4.0	-20.7	-0.985	2.328
	$1.0E-6$	91 766	-93.8582		59.1	4.1	-20.8	-0.979	2.326
	$1.0E-7$	273 072	-93.8683		60.8	4.7	-21.9	-0.969	2.315
	$1.0E-8$	792 663	-93.8721	-93.9049	62.5	4.7	-22.6	-0.969	2.311
86	$1.0E-4$	71 305	-93.7777		62.2	5.8	-24.3	-0.990	2.338
	$1.0E-5$	83 878	-93.8346		60.4	4.6	-22.0	-0.985	2.332
	$1.0E-6$	139 402	-93.8606		61.6	4.8	-22.6	-0.979	2.324
	$1.0E-7$	385 447	-93.8734		66.0	6.3	-25.4	-0.976	2.316
146	$1.0E-5$	129 797	-93.8353		61.7	4.8	-23.0		
	$1.0E-6$	183 116	-93.8605		62.3	5.1	-23.5		
	$1.0E-7$	446 932	-93.8747		66.8	6.0	-25.6		

			MR-ACPF results					
Ψ_0[b]	T_E	# Selected	Energy	$a(H)$	$a(N)$	$a(C)$	μ_z	Θ_{yy}
1	$1.0E-4$	3 444	-93.7952	78.0	11.1	-34.5	-0.987	2.288
	$1.0E-5$	17 079	-93.8625	81.1	8.9	-31.5	-0.974	2.282
	$1.0E-6$	57 976	-93.8863	82.9	9.7	-29.7	-0.960	2.281
				(76.4)[c]	(8.5)	(-26.0)	(-0.967)	(2.298)
25	$1.0E-4$	22 545	-98.7853	76.5	9.3	-31.5	-1.004	2.311
	$1.0E-5$	36 123	-93.8537	80.1	9.3	-29.9	-1.007	2.312
	$1.0E-6$	91 766	-93.8844	86.0	10.5	-32.2	-1.007	2.313
86	$1.0E-4$	71 305	-93.7886	65.8	8.3	-24.3	-0.980	2.311
	$1.0E-5$	83 870	-93.8489	64.4	7.7	-21.5	-0.970	2.295
	$1.0E-6$	139 426	-93.8786	66.6	8.5	-22.6	-0.958	2.276

			QDVPT results					
Ψ_0[b]	T_E	# Selected	Energy	$a(H)$	$a(N)$	$a(C)$	μ_z	Θ_{yy}
1	$1.0E-4$	3 444	-93.8024	86.3	13.6	-40.0	-0.979	2.270
	$1.0E-5$	17 079	-93.8721	93.4	10.8	-37.6	-0.963	2.258
	$1.0E-6$	57 976	-93.8972	97.9	12.3	-36.2	-0.946	2.256
				(86.0)	(10.0)	(-29.7)	(-0.958)	(2.286)
25	$1.0E-4$	22 545	-98.7884	81.8	10.3	-33.8	-1.012	2.310
	$1.0E-5$	36 123	-93.8582	88.4	10.6	-32.7	-1.020	2.315
	$1.0E-6$	91 766	-93.8900	98.2	12.1	-36.2	-1.028	2.322

[a] The modified cc-pVTZ basis contained extra diffuse functions and increased flexibility in the core regions. There were a total of 148 basis functions, $[7s, 5p, 3d, 2f/4s, 3p, 2d]$. The calculations were performed at $R_{CN} = 2.349$ bohr, $R_{CH} = 2.063$ bohr, HCH = 112.8°. The energy is given in hartrees, the isotropic hyperfine values, $a(H)$, $a(N)$, and $a(C)$ are in Gauss and the dipole and quadrupole moments are in atomic units

[b] Size of the reference space in CSF's

[c] Values in parentheses were computed as expectation values

References

1. For a review of recent developments in the area of full CI see: Bauschlicher CW, Langhoff SR, Taylor PR (1990) Advances in Chemical Physics 77:103
2. Olsen P, Jørgensen P, Simons J (1990) Chem Phys Lett 169:463
3. Bauschlicher CW, Langhoff SR (1987) J Chem Phys 86:5595
4. Huber KP, Herzberg G (1979) Constants of diatomic molecules. Van Nostrand Reinhold, New York
5. Almlöf J, DeLeeuw BJ, Taylor PR, Bauschlicher CW, Siegbahn P (1989) Int J Quantum Chem Symp 23:345
6. Werner H-J, Knowles P (1991) J Chem Phys 94:1264
7. Bauschlicher CW, Taylor PR (1987) Theor Chim Acta 71:263
8. Buenker RJ, Peyerimhoff S (1981) in: Csizmadia IG, Daudel R (eds) Computational theoretical organic chemistry. Reidel, Dordrecht; or Buenker RJ (1986) Int J Quantum Chem 29:435
9. Huron B, Rancurel, Malrieu JP (1973) J Chem Phys 75:5745; Evangelisti S, Daudey JP, Malrieu JP (1983) Chem Phys 75:91
10. Illas F, Rubio J, Ricart JM, Bagus PS (1991) J Chem Phys 95:1877
11. Harrison RJ (1991) J Chem Phys 94:5021
12. Barr TL, Davidson ER (1970) Phys Rev A 1:64
13. Feller D, Davidson ER (1981) J Chem Phys 74:3977
14. MELDF-X was originally written by McMurchie L, Elbert S, Langhoff S, Davidson ER. It has been substantially modified by Feller D, Cave R, Rawlings D, Frey R, Daasch R, Nitzche L, Phillips P, Iberie K, Jackels C, Davidson ER
15. Dunning TH, Hay PJ (1977) in: Schaefer HP (ed) Methods of electronic stucture theory, Vol 2. Plenum Press, New York
16. Huber KP, Herzberg G (1979) Constants of diatomic moelcules. Van Nostrand Reinhold, New York
17. Davidson ER, Silver DW (1977) Chem Phys Lett 53:403
18. Bauschlicher CW, Taylor PR, Handy NC, Knowleds PJ (1986) J Chem Phys 85:1469; or Harrison RJ, Handy NC (1983) Chem Phys Lett 95:386
19. Dunning TH (1989) J Chem Phys 90:1007
20. Nitzche LE, Davidson ER (1978) J Am Chem Soc 100:7201
21. Bauschlicher CW, Taylor PR (1986) J Chem Phys 85:2779
22. Chipman D, Carmichael I, Feller D (1991) J Phys Chem 95:4702
23. Pople JA, Head-Gordon M, Raghavachari K (1987) J Chem Phys 87:5968
24. Cochran EL, Adrian FJ, Bowers VA (1962) J Chem Phys 36:1936
25. For a discussion of the procedure used to modify the cc-pVTZ basis see: Feller D (1990) J Chem Phys 93:579
26. Gdanitz RJ, Alrichs R (1988) Chem Phys Lett 143:413
27. Cave RJ, Davidson ER (1988) J Chem Phys 89:6798
28. Werner HJ, Knowles PJ (1991) Theoret Chim Acta 78:175