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Commentationes

A Comparison of One-Electron Properties Calculated from Gaussian SCF and CI Wavefunctions

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Ground state LCAO–MO–SCF single- and multiconfiguration wavefunctions of NH_3 and CH_3^-, constructed from a large contracted Gaussian basis set, have been analyzed in terms of one-electron expectation values.

Both sets of values agree fairly well with the experimental data in the case of NH_3. It is expected therefore that the results obtained for CH_3^- are also reliable.

Einfach- und Mehrfachdeterminanten-LCAO–MO–SCF-Funktionen für NH_3 und CH_3^- wurden zur Berechnung von Einelektroneneigenschaften herangezogen. Die Übereinstimmung ist in beiden Fällen bei NH_3 gut, man darf daher für CH_3^- dasselbe erwarten.

Introduction

The ultimate goal of any computed wavefunction must be the accurate prediction of an experimentally measurable value. To date, the most often calculated expectation value of an observable has been the total energy. But, as a criterion of the quality of an approximate wavefunction, the calculated energy may be only a crude measure. It is quite conceivable, and often true in practice, that for certain critical values of the electron co-ordinates, the error in the wavefunction is considerably larger than the error in total energy.

Thus, in order to gain some insight into the quality of a wavefunction, one must calculate many different expectation values and compare these with both calculated and experimentally measured values. Because the wavefunctions used here do not describe vibrational and rotational motion, relativistic corrections or coupling with nuclear moments, etc., the calculated expectation values should not be expected to be identical to the corresponding experimental values. How-

Table 1. *Details of the* NH_3 *and* CH_3^- *wavefunctions*

Molecule	R_{X-H}	Out-of-plane	No. Gaussian functions		Energy (No. configurations)	
XH_3		angle	primitive	constructed	SCF	CI
NH_3	1.913	22.14°	73	36	−56.21171(1)	−56.37470(918)
CH_3^-	2.090	23.5°	67	36	−39.51292(1)	−39.66450(911)

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ever, by assuming that these corrections to the electronic wavefunction are minimal, these comparison can be made.

The SCF and CI wavefunctions for NH_3 and CH_3^- have been described previously [1], but for convenience some characteristic data are summarized in Table 1.

Occupational Numbers

The natural orbitals and one-electron density matrices were computed for NH_3 and CH_3^- in their minimum energy conformations. The occupation numbers of the principal natural orbitals are listed in Table 2. The traces of the density matrix, for both molecules, agreed with the number of electrons to six significant figures.

Table 2. *Occupation numbers of the principal natural orbitals of* NH_3 *and* CH_3^-

Orbital	Occupation number NH_3	 CH_3^-
$1a_1$	0.99998	0.99999
$2a_1$	0.99246	0.98954
$3a_1$	0.98722	0.98144
$1e$	0.98528	0.98434

As may be seen from the occupation numbers in Table 2, the occupation numbers of CH_3^- have decreased more than those of NH_3. So, if the CI energy is expressed as a percentage of the total correlation energy, it might be expected that this percentage would be greater for CH_3^- than for NH_3. Such is not the case in the present calculations, where the percentage for CH_3^- is 48.7% and the percentage for NH_3 is 49.5%. However, it is probable that the estimated correlation energy of CH_3^- (-0.310 hartree) is too large, due to the lack of both an experimental zero point energy and an accurate Hartree-Fock limit.

Multipole Moments

The dipole moment is the only multipole moment of NH_3 which has been experimentally measured. Many SCF calculations have been used to calculate the dipole moment also; but, only a few of these calculations have been sufficiently extensive to include the other moments. The dipole (μ), second ($Q_{\alpha\alpha}$), and related quadrupole (θ_{zz}), as well as the third ($R_{\alpha\beta\gamma}$) and the related octopole ($\Omega_{\alpha\alpha\alpha}$) moments, as calculated from the present SCF and CI wavefunctions for NH_3 and CH_3^- are tabulated in Table 3.

The total dipole moment is invariant to the choice of the origin relative to which the dipole is calculated. None of the other moments are invariant to the choice of the origin; hence, by convention, the origin was chosen as the centre of mass (-0.12804 bohr along the z axis for NH_3 and -0.167614 bohr along the z axis for CH_3^-). The calculated dipole moments of both NH_3 and CH_3^- increased when electron correlation was included in the wave function (cf. Table 3) and this increase, at least for NH_3, was a convergence to the experimental value. Apparently,

Table 3. *Moments of the charge distribution of* NH_3 *as calculated from the* SCF *and* CI *wavefunctions*[a]

Moment	NH_3			CH_3^-	
	SCF	CI	Expt	SCF	CI
μ[c]	-1.9463	-1.9187[b]	-1.4820[d]	-1.4710	-1.4570
Q_{xx}[e]	-6.2229	-6.3428	—	-11.8878	-11.9782
Q_{zz}	-8.8036	-8.8329	—	-16.0433	-16.1372
$\langle r^2\rangle$[f]	7.3899	7.4459[b]	7.1406[b]	11.7960	-11.8537
Θ_{zz}[e]	-2.5807	-2.4901[b]	-1.0[g]	-4.1554	-4.1577
R_{yyy}[h]	0.9175	0.8514	—	-0.2739	-0.3108
R_{zzz}	-0.5820	-0.5560	—	-2.7776	-2.8300
R_{xxz}	-0.6237	-0.5694	—	-0.5062	-0.4976
R_z[h]	-1.8296	-1.6949	—	-3.7901	-3.8252
Ω_{yyy}[h]	2.2936	2.1326	—	-0.6849	-0.7643
Ω_{zzz}	1.2893	1.1524	—	-1.2588	-1.3371

[a] Second and third moments are relative to the centre of mass.

[b] These values reported by Harrison [5] to be -2.11, $+7.577$ and -3.14 respectively.

[c] Dipole moment in Debye, 1 au = 2.54154 Debye.

[d] Ref. [20].

[e] Second moments and quadrupole moment in units of 10^{-26} esu-cm^2, 1 au = 1.344911×10^{-26} esu/cm^2.

[f] In units of 10^{-16} cm^2, 1 au = 0.280016×10^{-16} cm^2, $\langle r^2\rangle CH_3^-$ nuclear = 3.5055.

[g] Ref. [7].

[h] Third moment and octopole moment in units of 10^{-34} esu-cm^3, 1 au = 0.711688×10^{-34} esu/cm^3.

the dipole moment does approach the exact value as the wavefunction is improved with respect to total energy.

The second moment ($Q_{\alpha\alpha}$) is a measure of the absolute size of the charge distribution in each direction; whereas, the quadrupole moment is both a measure of size and shape (deviation from spherical symmetry). For the particular case where a molecule possesses C_{3v} symmetry, $\theta_{xx} = \theta_{yy} = -1/2\theta_{zz}$, where $\theta_{\alpha\beta}$ is as defined by Buckingham [2]

$$\theta_{\alpha\beta} = 1/2(3Q_{\alpha\beta} - Q_{\gamma\gamma}\delta_{\alpha\beta}).$$

Physical intuition might suggest that the calculated SCF charge distribution would expand when the wavefunction accounts for the correlation effect. Table 3 shows that this hypothesis is true for the CI wavefunctions for NH_3 and CH_3^-. Also, when Franchine and Vergani [3] computed second moments for NH_3 from an SCF wavefunction with a minimum STO basis set ($Q_{xx} = -4.2777$, $Q_{zz} = -5.3994$) and from the resulting group functions ($Q_{xx} = 4.3267$, $Q_{zz} = -5.3994$), they found that the inclusion of a correlation factor increased the size of the charge distribution. Recent group function (i.e. geminal) calculations [4], with the same GTF basis as used here, also showed an increase in the second moments. Thus, for inexact wavefunctions, the change in the size of the charge distribution appears to be independent of the method of introducing correlation and does confirm the intuitive expansion of the charge distribution. But, judging from the quadrupole moments, this expansion in charge distribution occurs with a concomittant increase in its spherical symmetry.

Previous SCF calculations [5, 6] have shown that the calculated quadrupole moment was strongly influenced by the choice of the gaussian basis set. In one of these calculations [5], the smallest basis set gave poorer approximations of both the experimental dipole moment and the total energy; yet, it gave the best approximation of the recommended value [7] of the quadrupole moment. However, considering the relative accuracies of the present calculations, the recommended value of -1.0 for the quadrupole moment does appear to be too high.

Magnetic Susceptibility

Van Vleck has shown [8] that the average molar susceptibility of a molecule with no resultant angular momentum is proportional to the sum of a diamagnetic term (depending only on the ground state wavefunction) and a second-order or paramagnetic term (depending on all the excited electronic states). Quantum mechanically, the average diamagnetic susceptibility is directly proportional to the value of $\langle r^2 \rangle$

$$\begin{aligned}\chi^d_{\mathrm{Av}} &= (-e^2 N/6\,mc^2)\,\langle [r(cm)]^2 \rangle \\ &= 0.7922765 \times 10^{-6}\,\langle [r(\mathrm{bohr})]^2 \rangle .\end{aligned}$$

The calculated molar diamagnetic susceptibility (in units of ppm) for NH_3 was -21.07 from the CI wavefunction and -20.91 from the SCF wavefunction. The experimentally determined [9] total susceptibility of gaseous ammonia is $\chi = -16.3$ ppm. From spectroscopic data the paramagnetic susceptibility has been calculated as $\chi^p = +4.3$ ppm [10]. Using the additivity formula, $\chi^d = \chi - \chi^p = -20.6$ ppm, which compared favourably with the above calculated values. This result also compared favourably with $\chi^d = -21.6$, which was calculated by Moccia [11], and $\chi^d = -20.95$, calculated by Harrison [15]. However, the excellent agreement of the magnetic susceptibility (which is represented by a "r^2" operator) with experiment does not concur with the poor agreement of the quadrupole moment. The quadrupole moment is presumably a more sensitive quantity since it depends on the sum of both electronic and nuclear contributions. But, the accuracy of the present calculations with respect to the magnetic susceptibility, does again suggest that the recommended value [7] of the quadrupole moment is incorrect.

Potential and Magnetic Shielding

Along with the one-electron energy, the potentials ($\langle 1/r \rangle$) at the proton F[H], and at the heavy atom F[N] and F[C], as determined from the SCF and CI wavefunctions, are tabulated in Table 4. The only experimental quantity to which any of these values could be compared was the average diamagnetic shielding at the proton. The computed average diamagnetic shielding at the proton for NH_3 was:

$$\begin{aligned}\sigma^p_{\mathrm{Av}}[\mathrm{H}]_{\mathrm{NH_3}} &= (e^2/3mc^2)\langle 1/r \rangle \\ &= 17.74959 \times 10^{-6}\langle 1/r \rangle \\ &= 95.50 \text{ ppm for the SCF wavefunction and} \\ &= 95.45 \text{ ppm for the CI wavefunction.}\end{aligned}$$

Table 4. *Potentials*[a] *at the proton* (F[H]) *and the heavy atom* (F[X])

Component	F[H]				F[X]			
	SCF		CI		SCF		CI	
	NH_3	CH_3^-	NH_3	CH_3^-	NH_3	CH_3^-	NH_3	CH_3^-
Nuclear	4.3104	3.4733	4.3104	3.4733	1.5680	1.4354	1.5680	1.4354
Electronic	−5.3804	−4.8845	−5.3774	−4.8812	−19.9573	−16.4786	−19.9610	−16.4905
Total	−1.0701	−1.4112	−1.0670	−1.4080	−18.3892	−15.0432	−18.3930	−15.0551
$V[1]$[b]	−155.8432	−113.5251	−155.8592	−113.5867				

[a] In au = 9.07618×10^{-2} esu/cm.

[b] One-electron potential energy, $V[1] = Z_X F[X] + 3F[H]$.

The experimentally measured total proton magnetic shielding in NH_3 [12] is 30.5 ppm. If it is assumed that calculated diamagnetic shielding constant is accurate, then the paramagnetic contribution would be −65.0 ppm. A relationship between the proton spin rotation coupling constants and the paramagnetic shielding has been given by Flygare [13]. According to Flygare we may write:

$$\sigma^p_{\mathrm{Av}}[k] = \frac{e^2}{6mc^2} \frac{hc}{2e\mu_n g_k} \cdot \frac{2M^{(k)}_{xx}}{G_x} \cdot \frac{M^{(k)}_{zz}}{G_z} - 2 \sum_l{}' z_l (r_k)^{-1}$$

where μ_n is the nuclear magneton, z_l is the charge on the lth nucleus and the summation is over all nuclei l but not including k. Using the above relationship and the coupling constants

$$M^{\mathrm{H}}_{xx} = 17.98191, \qquad M^{\mathrm{H}}_{zz} = 17.0277 \; Kc/sec$$

of Kukolich [14], and the rotational constants

$$G_x = 28.31333, \qquad G_z = 18.57516 \text{ Mc/sec}$$

of Benedict and Pyler [15], the experimental value for the paramagnetic shielding at the proton in NH_3 was calculated as −64.5 ppm. This results in a diamagnetic shielding of 95.0 ppm, and compares very favourably with the calculated diamagnetic shielding. This agreement is not surprising in the light of the accuracy of other SCF calculations [5, 6] with even smaller and less complete basis sets. Also, because the $1/r_H$ operator is part of the Hamiltonian, it could be assumed that the potential is well represented by an SCF wavefunction. This assumption was confirmed by the negligible change in potential when correlation was included in the wavefunction.

Electric Field

The electric fields of both NH_3 and CH_3^-, as calculated from the SCF and CI wavefunctions, are shown in Table 5. Although the calculated electric field cannot be related to experimentally measurable quantitites, the accuracy of the computed field can be ascertained by computing the force F_N on a nucleus N of a molecule in a stationary state

$$\begin{aligned} F_N &= -[f_N + \langle \psi | \mathscr{H} | V_N \psi \rangle + \langle V_N \psi | \mathscr{H} | \psi \rangle] \\ &= -[f_N + \delta_N] \end{aligned}$$

Table 5. *Components of the electric field*[a] *on a nucleus,* $E[X]$, *for* NH_3 *and* CH_3^- *as calculated from the SCF and CI wavefunctions*

Molecule XH$_3$		$E[X]_z$ Nuclear	Electronic	Total	$E[H]_z$ Nuclear	Electronic	Total
NH_3	SCF	0.3089	−0.2500	0.0589	−0.7207	0.7223	0.0016
	CI	0.3089	−0.2495	0.0594	−0.7207	0.7183	−0.0024
CH_3^-	SCF	0.2739	−0.2382	0.0357	−0.5477	0.5465	−0.0012
	CI	0.2739	−0.2352	0.0386	−0.5477	0.5409	−0.0068

[a] In au, 1 au = 0.823770 × 10^{-2} dynes.

where f_N is the Hellmann-Feynmann force [16] and the residual (δ) is zero for both a Hartree-Fock and an exact wavefunction.

For an XH$_3$ molecule at equilibrium geometry, $F_X + \sum_i F_{H_i}$ equals zero by definition. Thus

$$f_X + \sum_{i=1}^{3} f_{H_i} = -[\delta_X + \sum_{i=1}^{3} \delta H_i]$$

$$f_{XH_3} = -\delta_{XH_3}$$

and the sum of the Hellmann-Feynmann forces on all the nuclei is a direct measure of the sum of all of the residuals and thus of the accuracy of the wavefunction. These Hellmann-Feynmann sums, as computed from the respective SCF and CI electric field values, were 3.43×10^{-3} and 3.36×10^{-3} dynes for NH_3 and 1.73×10^{-3} and 1.50×10^{-3} dynes for CH_3^-. All the above sums appear to be small, however, since few previous calculations have computed these forces, no absolute comparisons can be made. It is hoped that in the future these results might be useful as a standard of comparison.

Quadrupole Coupling Constants

The computed elements of the electric field gradient tensor (q) are given in Table 6 for the heavy atoms, and in Table 7 for the deuterons. The field gradients for the deuterons are given in the principal axis system which diagonalizes the field gradient tensor (X, Y', Z' for D in NH_2D and CH_2D^-, and X, Y, Z for N

Table 6. *Field gradient*[a] *at nitrogen in* NH_3 *and at carbon in* CH_3^-

	q_{XX}			q_{YY}			q_{ZZ}		
	Nuclear	Electronic	Total	Nuclear	Electronic	Total	Nuclear	Electronic	Total
NH_3(SCF)	−0.1229	−0.4267	−0.5496	−0.1229	−0.4267	−0.5496	0.2459	0.8535	1.0994
NH_3(CI)	−0.1229	−0.4603	−0.5832	−0.1229	−0.4603	−0.4603	0.2458	0.9206	1.1664
CH_3^-(SCF)	−0.0859	−0.0989	−0.1843	−0.0859	−0.0989	−0.1843	0.1719	0.1698	0.3687
CH_3^-(CI)	−0.0859	−0.1040	−0.1899	−0.0859	−0.1040	−0.1899	0.1719	0.2081	0.3800

[a] In au, 1 au = 0.324123 × 10^{16} esu/cm^3.

Table 7. *Field gradient*[a, b] *at hydrogen (deuteron) in* $NH_3(NH_2D)$ *and* $CH_3^-(CH_2D^-)$

Molecule		q_{XX}	$q_{Y'Y'}$	$q_{Z'Z'}$	η[c]	α[d]
	Nuclear	1.0169	−2.0643	1.0474	0.1328	0.61°
NH_3 (SCF)	Electronic	−0.8291	1.6312	−0.8022		
	Total	0.1878	−0.4331	0.2453		
	Nuclear	1.0169	−2.0643	1.0475	0.1281	0.64°
NH_3 (CI)	Electronic	−0.8264	1.6275	−0.8010		
	Total	0.1904	−0.4368	0.2464		
	Nuclear	0.6709	−1.3641	0.6931	0.1519	1.73°
CH_3^- (SCF)	Electronic	−0.5346	1.0428	−0.5081		
	Total	0.1362	−0.3219	0.1850		
	Nuclear	0.6709	−1.3641	0.6932	0.1482	1.75°
CH_3^- (CI)	Electronic	−0.5351	1.0452	−0.5101		
	Total	0.1350	−1.3189	0.1831		

[a] In au, 1 au $= 0.324123 \times 10^{16}$ esu/cm^3.

[b] In principal axis system $[X, Y', Z']$.

[c] $\eta = (q_{XX} - q_{Y'Y'})/q_{Z'Z'}$.

[d] α is the angle between the NH(CH) bond and the A axis (see Fig. 1).

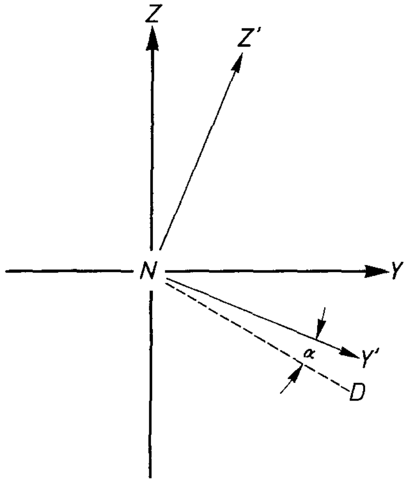

Fig. 1. Principal axes (X, Y and Z) of the ^{14}N field gradient tensor (the X axis, not shown, forms a dextral system with Y and Z); the X, Y' and Z' axes are the principal axes of the deuteron field gradient tensor. The Y–N–D angle is 22.14° and the values of α are given in Table 7

and C in these molecules). These co-ordinate systems are shown in Fig. 1. The asymmetry parameter, η, was defined as:

$$\eta = (q_{\alpha\alpha} - q_{\beta\beta})/q_{\gamma\gamma}.$$

The labels of the principal axes (α, β and γ) have been chosen such that $|q_{\gamma\gamma}| \geqq |q_{\beta\beta} - q_{\alpha\alpha}|$. For the present cases $\alpha = X$, $\beta = Y'$ and $\gamma = Z'$.

The calculated field gradients can be utilized in two manners. First, if the exact nuclear quadrupole moment of a nucleus is known, the accuracy of the theoretically calculated field gradient can be determined by comparing the calculated nuclear quadrupole coupling constant (eQq/h) to the experimentally measured value. The presently calculated ^{14}N and deuteron (D) coupling constants for NH_3 are tabulated in Table 8. In this table, the quadrupole moment of the deuteron was taken as 0.2796 [17], and the quadrupole moment of the ^{14}N nucleus was taken as 1.47 [18] and 1.56 [19] where all were in units of 10^{-26} e.cm^2. The second manner of utilizing the computed field gradient is to combine this calculated field gradient with the experimentally determined quadrupole coupling constants in order to arrive at a value for the nuclear quadrupole moment (Q). The nuclear quadrupole moments calculated for and prior to this research are shown in Table 9.

The deuteron coupling constants of the CI wavefunction, calculated in an axis system (X, Y'', Z'') where the ND bond formed the Y'' axis, were as follows: $(eQq/h)_{Y''Y''} = 288.7$ and $(eQq/h)_{Z''Z''} = -158.6$ kc/sec. The resulting asymmetry parameter (η) was 0.117. When the ^{14}N quadrupole moment ($Q^{14}N$) was taken

Table 8. *Quadrupole coupling constants for* $^{14}NH_2D$

Calc	$(eQq/h)_D$[a]				$(eQq/h)_N$[b, c]	(eQq/h)[b, d]
	XX[e]	$Y'Y'$[f]	$Z'Z'$	η[g]	ZZ[e]	ZZ[e]
SCF	−123.4	284.5	−161.2	0.135	−3.80	−4.03
CI	−125.1	287.0	−161.9	0.128	−4.03	−4.28
Kern[h]	−151.4	339	−188	0.11	−4.20	
Harrison[i]	−134.7	304.9	−170.2	0.116	−3.49	
Expt		282[j]		0°	−4.08[k]	

[a] In kilocycles per second.

[b] In megacycles per second.

[c] $Q = 1.47 \times 10^{-26}$ e cm^2.

[d] $Q = 1.56 \times 10^{-26}$ e cm^2.

[e] X, Y and Z are the principal axes of the ^{14}N quadrupole coupling constant tensor, see figure.

[f] X, Y' and Z' are the principal axes of the deuteron quadrupole coupling constant tensor, see Fig. 1.

[g] $\eta = [(eQq/h)_{XX} - (eQq/h)_{Z'Z'}]/(eQq/h)_{Y'Y'}$.

[h] Kern, C. W.: J. chem. Physics **46**, 4543 (1967).

[i] Ref. [5].

[j] Thaddeus, P., Krishner, L. C., Cahill, P.: J. chem. Physics **41**, 1542 (1964).

[k] Ref. [14].

Table 9. *Nuclear electric quadrupole moment* (Q) *of* ^{14}N

Computed wavefunction	Total energy	$Q \times 10^{26}$ (e cm^2)
Kaldor and Shavitt[a] STO	−56.099	1.36
O'Konski and T.-K. Ha[b]	−56.169	1.51
Present SCF	−56.212	1.58
Present CI value	−56.375	1.49
Suggested value[c]		1.56

[a] Kaldor, U., Shavitt, I.: J. chem. Physics **45**, 888 (1966).

[b] Ref. [19].

[c] Ref. [7].

as 1.56×10^{-26} cm^2 (but not when taken as 1.47×10^{-26} cm^2), the SCF wavefunction produced a more exact ^{14}N coupling constant than did the CI wavefunction, even though the CI wavefunction was more accurate for all other properties. One explanation for this improbable situation is that the suggested ^{14}N quadrupole moment (1.56) is in reality too high but nevertheless suitable for SCF calculations.

Mulliken Populations

The electron population on the atoms, computed from a Mulliken population analysis of the SCF and CI wavefunctions, are shown for all molecules in Table 10. It is interesting to note that in this table, the hydrogen atoms of CH_3^- possess an excess of negative charge, and that this negative has been decreased by the CI calculation. But, an SCF calculation by Millie and Berthier [20], using a larger [6, 4, 2/3, 1] basis set, indicated an excess of positive charge on the hydrogens. It appears that like the barrier height, the electron populations are very dependent on the basis set and similarly of only qualitative accuracy.

Table 10. *Gross electron populations*

Atom	NH_3		CH_3^-	
	SCF	CI	SCF	CI
[X][a]	7.7801	7.7686	6.9470	6.9603
[H]	0.7399	0.7440	1.0177	1.0132

[a] Atom [X] is the heavy atom N or C.

Conclusions

Only the diamagnetic contributions to the one-electron properties were calculated in this research because the CI secular problem was solved only for the ground state wavefunction. Considering the small differences in the CI and SCF computed values, it appears that single configuration wavefunctions do yield accurate one-electron expectation values, and that the work necessary to improve these expectation values is not always comensurate with the results. However, considering that a single CI calculation with 1000 configurations takes less than 6 hours of 7094-II computation time, the above, does not argue with the fact that the method of configuration interaction has been a reasonably efficient and effective method of lowering the energy to within 50% of the theoretical limit. Hopefully, this energy lowering indicates a concomittant improvement in the wavefunction itself.

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