

Multireference Møller–Plesset Perturbation Treatment of Potential Energy Curve of N₂

K. HIRAO

Department of Chemistry, College of General Education, Nagoya University, Nagoya, Japan

Abstract

A multireference Møller–Plesset (MR–MP) perturbation method, at the second-order level, is applied to the potential energy curve of the ground state of N₂, for comparison with a variety of standard *ab initio* methods. In spite of the drastic simplification, the MR–MP results are very reliable. The energy errors are almost independent of geometry, allowing unbiased treatment of potential energy curves. The potential efficiency and accuracy of the MR–MP approach are emphasized. © 1992 John Wiley & Sons, Inc.

Introduction

During recent years the *ab initio* molecular orbital theory has moved from a qualitative theory to a quantitative one and being available to experimentalists. The conventional correlated theories are generally effective, at least, for medium-sized molecules in their ground state, near equilibrium geometry. Typically more than 98% of the full CI correlation energy is accounted for in a given basis set. However, the difficulty with these theories is that, as the number of electrons increases and the molecular bonds are stretched, the percentage of correlation energy recovered can decrease substantially. We are now seeing a similar evolution of techniques that are accurate for any large molecule in all nuclear configurations. At the present time reasonable accuracy can be obtained, but this is not obtained cheaply. In calculations of potential energy surfaces, it is particularly important to use an approach which provides a balanced description of the various regions of surface. In addition, the explicit determination of a wavefunction requires the calculation of the variables. Unfortunately, the number of variables is normally much too large for optimization, even though significant progress has been made in the solution of large-scale secular equations. For these reasons there has been a growing interest in multireference based perturbation methods [1–4].

In the previous article [4], we have developed a multireference Møller–Plesset (MR–MP) method. The essential feature of the theory is that the multireference technique is used as a means of recognizing nondynamical, near degeneracy, correlation effects and, as a consequence, of ensuring that a molecule correctly dissociates into its fragments. Once these state-specific correlation effects are included in a reference function, the remaining are composed mainly of dynamical, transferable pair correlations. It is really caused not by the full Coulomb repulsions but by the sum of fluctuation potentials, as discussed by Sinanoğlu [5]. As a result of

TABLE I. Selected N_2 energies as a function of internuclear separation with Dzp+ basis. Energies ($-E$) are in hartree.

$r (a_0)$	SCF	MP2	MP4	CISD ^a	CCSD ^a
1.5	108.43726	108.70086	108.72011	108.70005	108.71269
1.8	108.90455	109.19682	109.21676	109.18794	109.20472
1.9	108.95142	109.25562	109.27558	109.24260	109.26115
2.0	108.96801	109.28553	109.30543	109.26741	109.28797
2.068	108.96662	109.29403	109.31385	109.27182	109.29388
2.5	108.83561	109.24415	109.26594	109.18054	109.21504
2.75	108.72623	109.19773	109.23075	109.09500	109.13919
3.0	108.61885	109.16547	109.23317	109.01092	109.06702
4.0	108.28943	109.24161	110.00465	108.76169	108.92926
5.0	108.10000	109.57697	115.94364	108.63123	—
6.0	107.99052	110.06605	131.76845	108.56262	—
100.	107.69824	—	—	108.42118	—
$r (a_0)$	MCSCF-52	MCSCF-176 ^a	MR-CISD ^a	MR-LCCM ^a	MR-MP2 ^b
1.5	108.51797	108.52680	108.71080	108.71854	108.69087
1.8	109.01134	109.02217	109.20805	109.21663	109.18706
1.9	109.06853	109.07999	109.26634	109.27517	109.24528
2.0	109.09626	109.10832	109.29516	109.30422	109.27416
2.068	109.10290	109.11534	109.30254	109.31176	109.28163
2.5	109.03128	109.04536	109.23566	109.24590	109.21659
2.75	108.96255	108.97652	109.16931	109.18019	109.15223
3.0	108.90040	108.91310	109.10861	109.12020	109.09418
3.5	108.82035	108.82749	109.02613	109.03901	109.01648
4.0	108.79409	108.79695	108.98477	109.00561	108.98290
5.0	108.78887	108.78943	108.98040	108.99285	108.96693
6.0	108.78889	108.78903	108.97879	108.99110	108.96457
100.	108.78880	108.78880	108.97786	108.99004	108.96374

^a Reference [9].^b The minimum energy is -109.28251 au at $r = 2.1035$.

the short-range nature of the fluctuation potential, pair correlations are nearly independent. Thus, the pair correlations can be estimated, to a good approximation, by the second-order Møller-Plesset (MP) perturbation method [6] when near degeneracy is removed. To the second-order energy, the electron pairs decouple. The concept underlying our MR-MP approach is simple. That is, the independent electron pair model is effective if no near degeneracy is present. In the previous article [4], the MR-MP method was successfully applied to potential energy surface studies of chemical processes involving single bond breaking. In spite of the drastic simplification the MR-MP results were very reliable.

This study has as its main objective the testing of the effectiveness of the MR-MP approach for the description of a potential energy surface of the ground state N_2 . After a brief discussion of the MR-MP theory in the next section, computational results are presented in the final section.

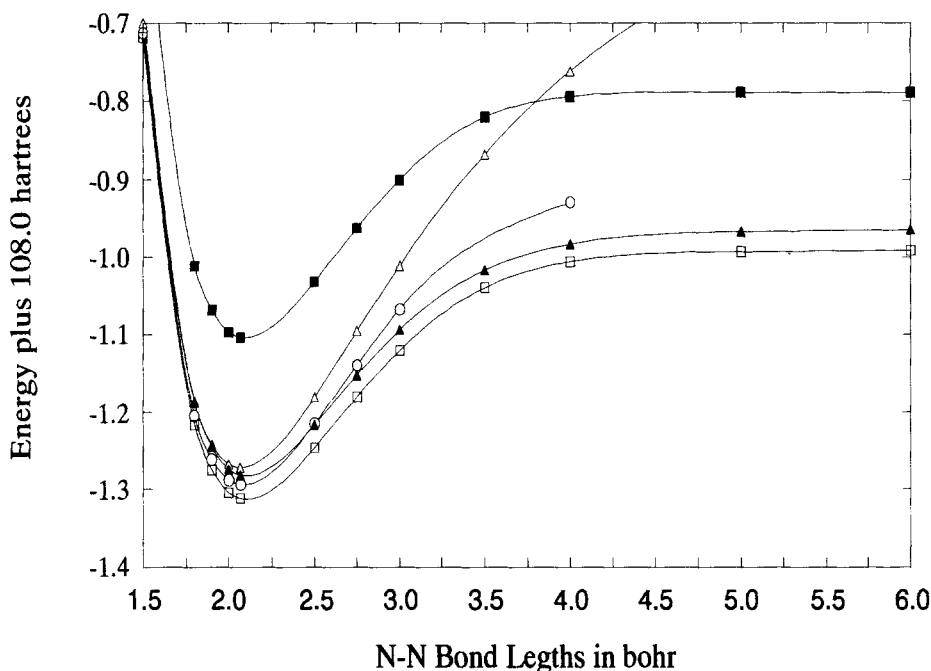


Figure 1. MCSCF-52, CISD, CCSD, MR-LCCM, and MR-MP potential curves for N_2 . The various curves are identified as follows: (—■—) MCSCF-52; (—△—) CISD; (—○—) CCSD; (—□—) MR-LCCM; and (—▲—) MR-MP.

Multireference Møller-Plesset Method

We start with the MCSCF wavefunctions with energies that can be expressed as

$$E = 2 \sum_i f_i h_{ii} + \sum_{ij} (a_{ij} J_{ij} - b_{ij} K_{ij}) \quad (1)$$

where the summation runs over orbital basis functions $\{\varphi_i\}$ in terms of which the wavefunction is described. Here the f_i are given by

$$2f_i = D_i^i \quad (2)$$

where D_i^i are diagonal elements of the one-electron density matrix. The a_{ij} and b_{ij} are energy coefficients and J_{ij} and K_{ij} indicate the usual Coulomb and exchange integrals, respectively. Requiring that the energy be stationary with respect to all orbital variations leads to the general variational condition

$$\sum_i \langle \delta\varphi_i | F_i^{\text{MCSCF}} | \varphi_i \rangle = 0 \quad (3)$$

where F_i^{MCSCF} is the generalized Fock operator

TABLE II. Equilibrium bond length and dissociation energy for N₂.

Method	r_e (Å)	D_e (eV)
SCF	1.0703	34.57
CSID ^a	1.0958	23.15
CCSD ^a	1.1037	9.93 ^b
MCSCF-52	1.1087	8.560
MCSCF-176 ^a	1.1098	8.903
MR-SDCI ^a	1.1120	8.857
MR-LCCM ^a	1.1128	8.778
MR-MP	1.1131	8.674
Experiment	1.0977	9.91

^a Reference [9].^b The dissociation energy is computed as the difference between the minimum and 4.0 bohr energy.

$$F_i^{\text{MCSCF}} = f_i h + \sum_j (a_{ij} J_j - b_{ij} K_j) \quad (4)$$

Now let us consider the perturbation theory based on the MCSCF function. Many-body perturbation theory is useful only if the zeroth-order Hamiltonian H_0 is a one-electron operator. Experience shows that, for closed-shell systems, the best results are obtained with the MP partitioning, that is, with the sum of one-electron Fock operator as H_0 . The possible choice of the one-electron operator for the MR case is the generalized Fock operator given by Eq. (4). However, one disadvantage of the choice is lack of the physical meaning of the operator unlike the closed-shell case. A one-electron operator which is closely analogous to the closed-shell Fock operator can be defined for MCSCF wavefunctions as

$$F = h + \sum_j f_j (2J_j - K_j) \quad (5)$$

In order to remove the arbitrariness of the density weighting, we use the *natural orbitals*. That is, canonical MCSCF orbitals are transformed to the natural orbitals before perturbing. The complete active space (CAS) SCF wavefunction [7] is invariant to unitary transformations among the active orbitals, provided the CI coefficients are reoptimized. This definition is unique and can be extended to the virtual space. The orbital energies for the doubly occupied orbitals correspond to the Koopmans' ionization potentials and those for virtual orbitals to the Koopmans' electron affinities. The orbital energies for active orbitals are the average of ionization potentials and electron affinities. The F is not diagonal in a basis of orbitals. The one-electron operator in the sense of diagonal form can be redefined in terms of natural orbitals $\{\lambda_i\}$ as

$$\hat{F} = \sum_\nu |\lambda_\nu\rangle \langle \lambda_\nu | F | \lambda_\nu \rangle \langle \lambda_\nu | \quad (6)$$

TABLE III. Energy errors ($E - E_{\text{MR-LCCM}}$, in millihartree) for N_2 .

$r (a_0)$	SCF	MP2	CISD ^a	CCSD ^a
1.5	281.28	17.68	18.49	5.85
1.8	312.08	19.81	28.69	11.92
1.9	323.75	19.55	32.57	14.02
2.0	336.21	18.69	36.81	16.25
2.068	345.14	17.73	39.94	17.88
2.5	410.29	1.75	65.36	30.86
2.75	453.96	-17.54	85.19	41.00
3.0	501.35	-45.27	109.28	53.18
4.0	716.18	-236.00	243.92	76.35
5.0	892.85	-584.12	361.62	—
6.0	1000.58	-1074.95	425.48	—
100.	1291.80	—	568.86	—

$r (a_0)$	MCSCF-52	MCSCF-176 ^a	MR-CISD ^a	MR-MP
1.5	200.57	191.74	7.74	27.67
1.8	205.29	194.46	8.58	29.57
1.9	206.64	195.18	8.83	29.89
2.0	207.96	195.90	9.06	30.06
2.068	208.86	196.42	9.22	30.13
2.5	214.62	200.54	10.20	29.31
2.75	217.64	203.67	10.88	27.96
3.0	219.80	207.10	11.59	26.15
3.5	218.66	211.52	12.88	22.53
4.0	211.52	208.66	20.84	22.71
5.0	203.98	203.42	12.45	25.92
6.0	202.21	202.07	12.31	26.53
100.	201.24	201.24	12.18	26.30

^a Reference [9].

We then have eigenfunctions Φ_I and eigenvalues W_I of the zeroth-order Hamiltonian H_0

$$H_0 \Phi_I = W_I \Phi_I \quad (7)$$

with

$$H_0 = \sum_I |\Phi_I\rangle \langle \Phi_I| \sum_i \hat{F}(i) |\Phi_I\rangle \langle \Phi_I| \quad (8)$$

The Φ_0 is the MCSCF wavefunction with the eigenvalue

$$W_0 = 2 \sum_i f_i \langle \lambda_i | F | \lambda_i \rangle \quad (9)$$

The sum in Eq. (8) goes over all possible orthonormal configurations $\{\Phi_I\}$ which may be constructed from the occupied and virtual orbitals. The functions $\{\Phi_I^{(1)}\}$

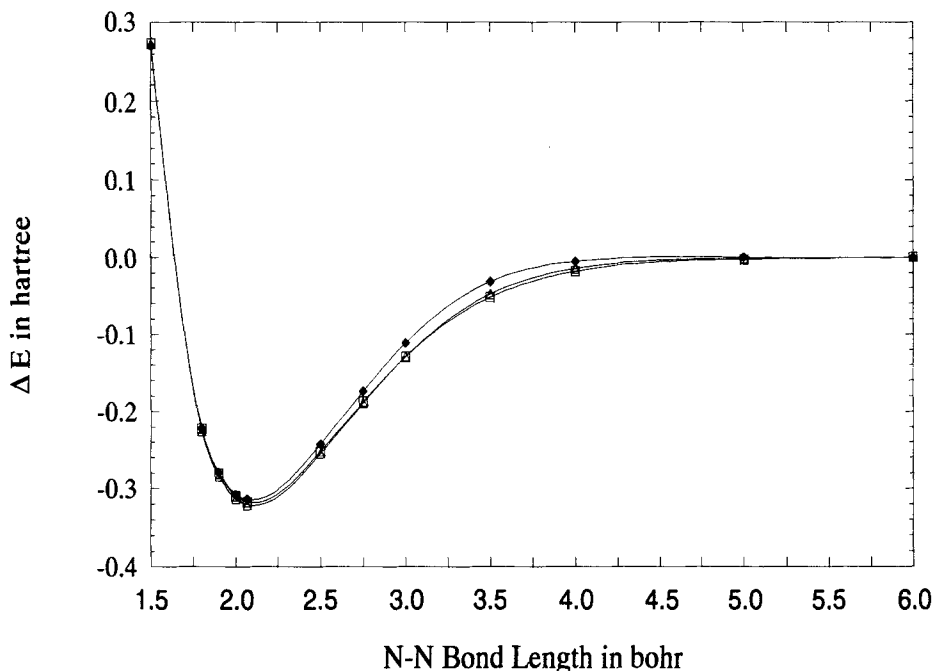


Figure 2. MCSCF-52, MR-MP, and MR-LCCM potential curves for N_2 shifted such that their respective dissociated energies are zero. The various curves are identified as follows: (—◆—) MCSCF-52; (—□—) MR-MP; and (—△—) MR-LCCM.

which span the first-order space used here are mutually orthogonal, orthogonal to all configurations in the reference. However, the first-order basis generated by double excitations of the reference wavefunction [1,3] is not orthogonal and orthogonalization step is necessary to avoid the complications of perturbation calculations in a nonorthogonal basis. The perturbation is $V = H - H_0$. This choice of H_0 in the Rayleigh-Schrödinger perturbation series guarantees size consistency if the reference function is size consistent. There is a very close parallel between the standard single reference MP theory and its MR version. The first-order wavefunction, for instance, contains only double substitutions. Singles cannot contribute due to the generalized Brillouin theorem [8]. Triples and higher substitutions are also excluded because any configurations having a nonzero matrix element with the reference function do not enter into the first-order correction to the wavefunction.

The present MR-MP method is very efficient and cost effective. Neither iteration nor diagonalization is necessary in the calculation of the first-order corrections. The importance of efficiency cannot be overestimated.

Potential Curve of N_2

The ground-state potential energy surface for N_2 has been well studied [9] by a variety of standard *ab initio* techniques such as single reference CI singles and doubles

TABLE IV. External, semi-internal, and internal contributions to the correlation energy for the ground state of N_2 . Energies ($-E$) are in hartree.

$r(a_0)$	Contributions			Total
	External	Semi-internal	Internal	$E_{MR-MP2} - E_{MCSCF}$
1.5	0.11363	0.05322	0.00605	0.17290
1.8	0.10875	0.05951	0.00745	0.17572
1.9	0.10723	0.06164	0.00788	0.17675
2.0	0.10578	0.06382	0.00829	0.17789
2.068	0.10484	0.06534	0.00855	0.17873
2.5	0.09981	0.07575	0.00974	0.18530
2.75	0.09796	0.08192	0.00981	0.18969
3.0	0.09711	0.08750	0.00917	0.19378
3.5	0.09790	0.09242	0.00581	0.19612
4.0	0.09913	0.08697	0.00272	0.18881
5.0	0.10094	0.07655	0.00057	0.17806
6.0	0.10172	0.07383	0.00013	0.17568
100.	0.10176	0.07318	0.00000	0.17494

(CISD), finite-order MP perturbation theory, coupled cluster singles and doubles (CCSD) [10], multireference CISD (MR-CISD) and linearized MR coupled cluster method (MR-LCCM) [11]. We also apply our MR-MP approach, at the second-order level (MR-MP2), to the bond-breaking process of N_2 . The basis set (DZ p+) and geometries used in the present calculations were identical to those used by Laidig, Saxe, and Bartlett [9]. The reference space for the MR-MP method was of the CAS SCF type. The CAS SCF wavefunctions were obtained by distributing six electrons among the six 2p active orbitals, corresponding to 52 reference configurations. This is the smallest active space which leads to the qualitatively correct description of the triple bond dissociation process. On the other hand, MR-CISD and MR-LCCM results by Bartlett et al. [9] were obtained based on the CAS SCF function with 176 reference functions. The MCSCF calculations will be distinguished via either a -52 or a -176 suffix. The two 1s-core orbitals were frozen.

Results obtained for the potential curves of N_2 with the DZ p+ basis set are given in Table I and Figure 1. The dissociation energies (D_e) and equilibrium distances (r_e) are listed in Table II.

The SCF potential well is over three times as deep as the experimental values of 9.91 eV and the equilibrium distance is nearly 0.03 Å shorter. The single reference based finite-order perturbation series was found to diverge beyond approximately 3.0 bohr. Even in the minimum region the series is oscillatory. The single reference CISD dissociation energy is still too high by over a factor of 2 compared to experiment. The CISD and experimental r_e values differ by only 0.002 Å. The full CI r_e in this basis is estimated around 1.113 Å [9]. If this is the case, the CISD r_e is nearly 0.02 Å too short. The CCSD, which is equivalent to our symmetry adapted cluster (SAC) theory [12], appears to give a much better estimate of r_e . Also the CCSD curve is accurate out to 4.0 bohr. However, it was reported that CCSD curve beyond 4.5

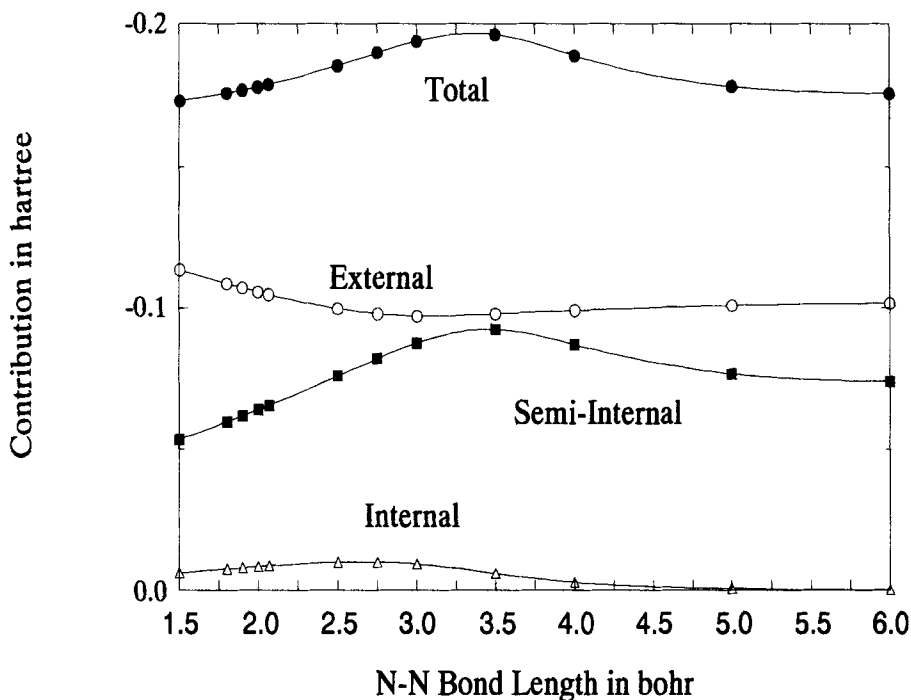


Figure 3. External, semi-internal, and internal contributions to the total correlation energy ($E_{\text{MR-MP2}} - E_{\text{MCSCF}}$), in hartree, as a function of the internuclear separation.

bohr cannot be obtained due to the convergence difficulties of the CCSD equations [9]. Thus, none of these single reference based methods can describe all regions of the N_2 potential curve to high accuracy.

Now let us examine the energy errors along the bond lengths. Since the full CI calculations are not available in this basis set, we defined the energy error as the difference between the computed energy and the MR-LCCM energy. These energy errors are displayed in Table III. In the calculation of potential energy surfaces, it is important to keep this error as constant as possible, in order to obtain an accurate surface. It is obvious from Table III that the single reference based methods cannot be expected, in general, to satisfy this requirement. Appropriate multireference based methods, on the other hand, can give a more balanced treatment and nearly constant errors.

The dissociation energies and equilibrium geometries have been improved in the MR based methods. The MCSCF-52 surface itself contains no substantial qualitative defects. Like MR-CISD and MR-LCCM, the MR-MP2 energy curve dissociates correctly and the three are nearly parallel. While the MR-MP is size consistent, the MR-CISD is not rigorously size consistent just like any truncated CI. The present MR-MP2 gives $D_e = 8.67$ eV and $r_e = 1.113$ Å. The D_e is computed only 12% in error and r_e is within 0.015 Å of experiment and nearly identical with the estimated full CI

r_e . In Figure 2 we draw potential curves for N_2 computed in MCSCF-52, MR-MP2, and MR-LCCM methods shifted such that their respective dissociated energies are zero. The MCSCF-52 dissociation energy of 8.56 eV is within 0.22 eV of the MR-LCCM result. However, the MCSCF-52 curve deviates most from MR-LCCM surface in the region surrounding 3.5 bohr. On the contrary, the MR-MP2 curve is quite close to the MR-LCCM curve for the entire bond lengths. This suggests that the higher order contributions are almost independent of the internuclear configuration and therefore cancel in a calculation of potential energy surfaces.

In terms of the Fermi sea determined by the reference function the first-order corrections to the wavefunction may be classified in terms of the number (0, 1, or 2) of external orbitals introduced as internal, semi-internal, and external. In Table IV and Figure 3 we showed external, semi-internal, and internal contributions to the total correlation energy, $(E_{MR-MP2} - E_{MCSCF})$, as a function of the bond length. The internal correlation is found to be small within 0.01 au. The semi-internal terms include significant single excitations which arise from the failure of the reference function to satisfy the Brillouin theorem. Although the semi-internal correlation is about half of the external correlation near the equilibrium distance, it increases as the bond length and becomes maximum at about 3.5 bohr and competitive to the external correlation. The external terms resemble the pair correlations of the closed-shell theory. As expected the external terms are found to be rather insensitive to the change of the bond length. Therefore, the total correlation curve is almost parallel to the semi-internal curve. This suggests that the balanced description of the potential curves cannot be obtained before the semi-internal terms are correctly taken into account.

The MR-MP method is designed to compete directly against the traditional highly correlated methods. The theory retains the attractive features of the single reference MP theory without a consequent loss of efficiency. The MR-MP results were shown to compare favorably with those of the highly correlated methods for the description of the triple bond breaking. The present approach is very powerful as a reliable method for the computation of correlation energy where errors of the order of a few percent are acceptable.

Acknowledgments

This study has partially been supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture. Computations were carried out at the Nagoya University Computational Center. The MCSCF wavefunctions were calculated by the HONDO7 program [13].

Bibliography

- [1] K. Wolinski, H. L. Sellers, and P. Pulay, *Chem. Phys. Lett.* **140**, 225 (1987).
- [2] J. J. W. McDouall, K. Peasley, and M. A. Robb, *Chem. Phys. Lett.* **148**, 183 (1988).
- [3] K. Andersson, P. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990); K. Andersson, P. Malmqvist, and B. O. Roos, *ibid.* **96**, 1218 (1992).
- [4] K. Hirao, *Chem. Phys. Lett.* **190**, 374 (1992).

- [5] O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962); *ibid.* **36**, 3198 (1962); Adv. Chem. Phys. **6**, 315 (1964).
- [6] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
- [7] P. E. Siegbahn, A. Heiberg, B. O. Roos, and B. Levy, Physica Scripta **21**, 323 (1980); B. Roos, P. R. Taylor, and P. E. Siegbahn, Chem. Phys. **48**, 157 (1980); B. O. Roos, Int. J. Quantum Chem. **S14**, 175 (1980).
- [8] B. Levy and G. Berthier, Int. J. Quantum Chem. **2**, 307 (1968).
- [9] W. D. Laidig, P. Saxe, and R. J. Bartlett, J. Chem. Phys. **86**, 887 (1987).
- [10] R. J. Bartlett, Ann. Rev. Phys. Chem. **32**, 359 (1981).
- [11] W. D. Laidig and R. J. Bartlett, Chem. Phys. Lett. **104**, 424 (1984).
- [12] H. Nakatsuji and K. Hirao, J. Chem. Phys. **68**, 2053 (1978); K. Hirao, J. Chem. Phys. **79**, 5000 (1983).
- [13] M. Dupuis, J. D. Watts, H. O. Villar, and G. J. B. Hurst, IBM Technical Report KGN-181 (1988), QCPE Program #544, University of Indiana.

Received April 15, 1992