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The recently implemented second-order perturbation theory based on a complete active space self-consistent field reference function has been extended by allowing the Fock-type one-electron operator, which defines the zeroth-order Hamiltonian to have nonzero elements also in nondiagonal matrix blocks. The computer implementation is now less straightforward and more computer time will be needed in obtaining the second-order energy. The method is illustrated in a series of calculations on N_2, NO, O_2, CH_3, CH_2, and F^-.

I. INTRODUCTION

Since the late introduction of perturbation theory in quantum chemical applications by Kelly[1] in the early 1960s, perturbation theory has today gained widespread use through program systems such as GAUSSIAN[2] and is probably the only correlation method used routinely by nonspecialists. This development can be explained by the fact that for a long time it was considered a weakness that no upper bound to the energy is provided by perturbation methods. The collected experience of correlation methods has shown, however, that the property of size extensivity, which is easy to achieve with perturbation methods is more important than the upper bound property.[3]

Most applications using perturbation theory have been based on nondegenerate many-body perturbation theory (MBPT). This is a reasonable method for atomic and molecular systems whose zeroth-order electronic description may be represented by a single nondegenerate Slater determinant. The restriction excludes atomic and molecular states, in particular excited ones, which cannot be represented in zeroth order as single Slater determinants. Furthermore, if the state under consideration is degenerate or near degenerate, which is often the case for atomic and molecular valence states, the perturbation expansion converges only slowly or not at all and low-order approximations become rather unreliable. This explains the need for a quasidegenerate perturbation theory. An extension of the nondegenerate MBPT to include the quasidegenerate valence states in the zeroth-order description was first made by Bloch and Horowitz.[4] Their formulation of the theory was not size extensive but a satisfactory solution to this problem was given by Brandow[5] in 1967. The theory of quasidegenerate perturbation theory has been treated in many articles, but its applications in chemistry are developing only slowly because of the difficulty in devising a practical implementation of the theory.[6] It is therefore natural to investigate the possibility of extending low-order perturbation schemes to the case of a multiconfigurational zeroth-order wave function. An attempt was made some years ago to implement second-order perturbation theory in conjunction with complete active space self-consistent field (CASSCF) wave functions.[7] At the time, it was not possible to include the full interacting space in the first-order wave function because of the difficulty in computing the three- and four-particle density matrices, which occur for matrix elements involving internal and semiinternal excitations. The results obtained in these earlier test applications were also rather disappointing with only minor or no improvement compared to CASSCF results in computed properties such as dissociation energies, geometry parameters, and spectroscopic constants. Later Wolinski et al. derived a full second- and third-order treatment for open-shell SCF and small multiconfigurational SCF (MCSCF) reference functions and gave some illustrative results for several small molecules.[8] The results show, however, that the third-order contribution can be sizable when the reference function is of the generalized valence bond (GVB) type. Another CASSCF second-order perturbation theory has been presented by McDouall et al.[9] Their method lies between multiconfigurational perturbation theory and the original quasidegenerate MBPT formulation of Brandow.

In 1990, another attempt was made to implement second-order perturbation theory with a CASSCF wave function as the zeroth-order wave function.[10] In that work, the full interacting space was included in the first-order wave function and the zeroth-order Hamiltonian was constructed from a Fock-type one-electron operator that reduces to the Møller–Plesset Hartree–Fock (HF) operator for a case with no active orbitals. In order to make a computer implementation simple and effective, a diagonal Fock operator was used. For many applications, this choice of zeroth-order Hamiltonian is good enough, but there are also applications where a full one-electron operator is needed in order to obtain a continuous change of calculated properties with respect to changes in some parameters (for instance, geometry, electric field strength, etc.). The consequences of using an extended one-particle operator—e.g., a somewhat more complicated computer implementation, where the first-order equation has to be solved iteratively—will be discussed in the present work.

The general approach of the method has been presented in detail in Ref. 10 and only a shortened version will be given in the next section together with some extensions. Several test calculations have been performed and compared with either full configuration interactions (FCI) results or multireference CI (MRCI) results with the same basis sets.

II. THEORY

A. The first-order interacting space

In the present study, a multiconfigurational wave function $|0\rangle$ generated from a CASSCF calculation is used as the zeroth-order wave function in a perturbation approach to the correlation problem. As the theory is formulated, it is valid for *any reference state* constructed as a full CI wave function in some orbital subspace. However, the fact that the orbitals are optimized makes some simplifications in the computational procedure possible.

The configuration space, in which the wave function is expanded, can be decomposed in four subspaces V_0, V_K, V_{SD} and $V_{TQ...}$, where (1) V_0 is the one-dimensional space spanned by the CAS reference function $|0\rangle$; (2) V_K is the space spanned by the orthogonal complement to $|0\rangle$ in the restricted full CI subspace used to generate the CAS wave function; (3) V_{SD} is the space spanned by all single and double replacement states generated from V_0 and not included in (1) and (2); and (4) $V_{TQ...}$ is the space which contains all higher-order excitations not included in (1)–(3). Since the functions in the subspaces (2) and (4) do not interact with the reference function via the total Hamiltonian, the zeroth-order Hamiltonian will be formulated in such a way that the first-order wave function is in V_{SD} (*vide infra*). The functions needed in the expansion of the first-order wave function will then be[10]

internal	$\widehat{E}_{ti}\widehat{E}_{uv}|0\rangle,$	(1a)
	$\widehat{E}_{ti}\widehat{E}_{uj}|0\rangle,$	(1b)
semiinternal	$\widehat{E}_{at}\widehat{E}_{uv}|0\rangle,$	(1c)
	$\widehat{E}_{ai}\widehat{E}_{tu}|0\rangle,\widehat{E}_{ti}\widehat{E}_{au}|0\rangle,$	(1d)
	$\widehat{E}_{ti}\widehat{E}_{aj}|0\rangle,$	(1e)
external	$\widehat{E}_{at}\widehat{E}_{bu}|0\rangle,$	(1f)
	$\widehat{E}_{ai}\widehat{E}_{bt}|0\rangle,$	(1g)
	$\widehat{E}_{ai}\widehat{E}_{bj}|0\rangle,$	(1h)

where $\widehat{E}_{pq}$ are the spin-averaged excitation operators and (i,j) are inactive, (t,u,v) active, and (a,b) secondary orbital indices. The functions in Eqs. (1) are referred to as internal, semiinternal, and external when none, one, or two orbitals belong to the secondary subspace, respectively. The functions (1a)–(1h) span different subspaces of V_{SD} and we will label them as $V_A,...,V_H$, respectively. The sum of these eight subspaces comprises V_{SD}.

The first-order wave function is now expanded in the functions in Eqs. (1)

$$|\Psi_1\rangle = \sum_{j=1}^{M} C_j|j\rangle, \quad |j\rangle\in V_{SD}, \quad (2)$$

where $M\!\geqslant\!\dim V_{SD}$ is the number of functions in Eqs. (1) and $\{C_j, j=1,...,M\}$ is a solution of the system of linear equations

$$\sum_{j=1}^{M} C_j\langle i|\widehat{H}_0 - E_0|j\rangle = -\langle i|\widehat{H}|0\rangle, \quad i=1,...,M, \quad (3)$$

where $E_0 = \langle 0|\widehat{H}_0|0\rangle$ is the zeroth-order energy. The expansion functions $|j\rangle$ in Eq. (2) are not necessarily orthogonal and may also be linearly dependent.

B. The zeroth-order Hamiltonian

In defining the zeroth-order Hamiltonian, we want three conditions to be fulfilled. The first and most important condition is that the perturbation expansion converges rapidly. However, this can only be tested by performing actual calculations and comparing the results with the corresponding full CI results. Second, the zeroth-order Hamiltonian should preferably be equivalent to the Møller–Plesset Hamiltonian in the limiting case of a closed-shell reference function. Third, it should be possible to make an efficient computer implementation of the method. These conditions can be fulfilled for a zeroth-order Hamiltonian of the following form:

$$\widehat{H}_0 = \widehat{P}_0\widetilde{\widehat{F}P}_0 + \widehat{P}_K\widetilde{\widehat{F}P}_K + \widehat{P}_{SD}\widetilde{\widehat{F}P}_{SD} + \widehat{P}_{TQ...}\widetilde{\widehat{F}P}_{TQ...}, \quad (4)$$

where $\widehat{P}_0 = |0\rangle\langle 0|$ is the projector onto V_0, $\widehat{P}_K$ is the projector onto V_K, $\widehat{P}_{SD}$ is the projector onto V_{SD}, $\widehat{P}_{TQ...}$ is the projector onto $V_{TQ...}$, and $\widehat{F}$ is a one-particle operator. With this choice of $\widehat{H}_0$, we also achieve that only vectors belonging to V_{SD} will contribute to the first-order wave function and the second-order energy. The remaining operator to be defined is the one-particle operator $\widehat{F}$. The freedom in choosing this operator is reduced since we want it to reproduce the results from closed-shell Møller–Plesset second-order perturbation theory. As was discussed in Ref. 10, the operator

$$\widehat{F} = \sum_{pq} f_{pq}\widehat{E}_{pq}, \quad (5)$$

where f_{pq} are the spin-averaged expectation values of the operators

$$\widehat{F}_{pq\sigma} = \hat{a}_{p\sigma}[\widehat{H},\hat{a}_{q\sigma}^{\dagger}] - \hat{a}_{p\sigma}^{\dagger}[\widehat{H},\hat{a}_{q\sigma}] \quad (6)$$

fulfills this requirement. The matrix (f_{pq}) consists of three × three blocks corresponding to the three orbital subspaces. We will now make use of the fact that the reference function is a CASSCF wave function. In this case, according to the generalized Brillouin theorem, f_{pq} is zero when one of the indices represents an inactive orbital and the other a secondary orbital. The operator $\widehat{F}$ can be simplified by defining a new set of orbitals determined by diagonalizing each of the three diagonal blocks of the matrix (f_{pq}).[11] This orbital transformation is possible only for a CASSCF reference function, since the CAS CI space is invariant to such a transformation. For a closed-shell reference state, when the number of active orbitals is zero, these orbitals correspond to the canonical Hartree–Fock orbitals. The transformed matrix (f_{pq}) is then diagonal and $\widehat{F}$ is identical to the canonical Fock operator in Hartree–Fock theory.

If f' is the transformed matrix (f_{pq}), the following equation:

$$f'_{pq} = \delta_{pq}\epsilon_p \quad (7)$$

is true if the two indices represent orbitals from the same orbital subspace. After the orbital transformation, the operator $\widehat{F}$ has the form

$$\widehat{F} = \widehat{F}_D + \widehat{F}_N, \quad (8)$$

where

$$\hat{F}_D = \sum_p \epsilon_p \hat{E}_{pp} \qquad (9)$$

and

$$\hat{F}_N = \sum_{it} (f'_{it}\hat{E}_{it} + f'_{ti}\hat{E}_{ti}) + \sum_{at} (f'_{at}\hat{E}_{at} + f'_{ta}\hat{E}_{ta}). \qquad (10)$$

The indices i, t, a, and p run over the inactive, active, secondary, and the entire orbital subspace, respectively. In the previous work[10] on this method, we put $\hat{F} = \hat{F}_D$ and then formally put the operator $\hat{F}_N$ in the perturbation operator. The major reason for this was that this would make a drastic decrease in the effort of a computer implementation possible. The solution of Eqs. (3) could then be achieved easily by a small number of diagonalizations. That this is possible is due to the fact that the matrix on the right-hand side of Eq. (3) has a very simple structure with a diagonal one-particle operator. First,

$$\langle i|\hat{H}_0 - E_0|j\rangle = 0, \quad \text{if } |i\rangle \in V_X, \quad |j\rangle \in V_Y,$$

$$X \neq Y \in \{A, ..., H\}, \qquad (11)$$

second, the matrix representation of $\hat{H}_0$ in the subspaces $V_A, ..., V_H$ have only nonzero elements in small blocks along the diagonal. Since not all the results obtained with this method were totally satisfactory, it was suspected that the reason could be that only $\hat{F}_D$ was included in $\hat{F}$. In cases where, for instance, an active orbital has an occupation number close to two, it can rotate easily with inactive orbitals in the presence of a perturbing field, or if the geometry is changed. This will lead to a discontinuous change in the zeroth-order Hamiltonian. In the present work, $\hat{F}_N$ has also been included and with this one-particle operator the zeroth-order Hamiltonian behaves continuously to orbital rotations among the three orbital subspaces. With this extended one-particle operator, Eq. (11) will no longer be true and Eq. (3) can only be solved by means of an iterative procedure.

C. The first-order wave function and the second-order energy

For simplifying the notation, we introduce the following matrices and vectors with elements:

$$(F_X)_{ij} = \langle i|\hat{F}_X|j\rangle, \quad X = D, N, \quad S_{ij} = \langle i|j\rangle,$$

$$V_i = \langle i|\hat{H}|0\rangle, \qquad (12)$$

where $i, j = 1, ..., M$ and M is the number of double replacement states in Eq. (1). Equation (3) can now be written as

$$(F_D + F_N - E_0 S)C = -V. \qquad (13)$$

Since in most cases $M > \dim V_{SD}$, the double replacement states will be linearly dependent. This linear dependence (and near linear dependence) is removed by diagonalizing the overlap matrix S and deleting the eigenvectors which correspond to zero (or close to zero) eigenvalues. After the transformation of the first-order space to an orthonormalized form, Eq. (13) can be written as

$$(\tilde{F}_D + \tilde{F}_N - E_0 1)\tilde{C} = -\tilde{V}, \qquad (14)$$

where $\tilde{F}_X = \Omega'^\dagger F_X \Omega'$, $X = D, N$, $\Omega'\tilde{C} = C$, $\tilde{V} = \Omega'^\dagger V$, $\Omega' = U\Lambda_S^{-1/2}$, and

$$\Lambda_S = U^\dagger S U. \qquad (15)$$

Λ_S is a diagonal $L \times L$ matrix and U is a $M \times L$ matrix, where $L = \dim V_{SD}$. In cases with near-linear dependence $L < \dim V_{SD}$. As was mentioned previously, the simple structure of the matrix F_D and therefore also of the matrix $\tilde{F}_D$ makes the diagonalization of $\tilde{F}_D$ practicable

$$\Lambda_D = W^\dagger \tilde{F}_D W. \qquad (16)$$

This diagonalization will simplify the procedure of solving the system of linear equations (14) somewhat. The final form of Eq. (14) now is

$$[\Lambda_D + \tilde{\tilde{F}}_N - E_0 1]\tilde{\tilde{C}} = -\tilde{\tilde{V}}, \qquad (17)$$

where $\tilde{\tilde{F}}_N = \Omega^\dagger F_N \Omega$, $\Omega\tilde{\tilde{C}} = C$, $\tilde{\tilde{V}} = \Omega^\dagger V$, and $\Omega = U\Lambda_S^{-1/2}W$. It should be mentioned that the two diagonalizations above are nothing else but rotations of double replacement states consisting of identical collections of inactive and/or secondary indices. The large number of elements equal to zero in F_N will therefore remain zero after the transformation. Finally, once we have obtained the solution $\tilde{\tilde{C}}$ to Eq. (17), we can calculate the second-order energy easily since

$$E_2 = \langle 0|\hat{H}|\Psi_1\rangle = V^\dagger C = \tilde{V}^\dagger \tilde{C} = \tilde{\tilde{V}}^\dagger \tilde{\tilde{C}}. \qquad (18)$$

The complicated structure of F_N, and consequently of $\tilde{\tilde{F}}_N$, makes it difficult to solve Eq. (17). It can be shown that

$$(F_N)_{ij} \neq 0$$

$$\text{for some } (|i\rangle, |j\rangle), (|j\rangle, |i\rangle) \in \{(V_A, V_B),$$
$$(V_A, V_D), (V_B, V_E), (V_C, V_D), (V_C, V_F),$$
$$(V_D, V_E), (V_D, V_G), (V_E, V_H), \qquad (19)$$
$$(V_F, V_G), (V_G, V_H)\}$$

and that $(F_N)_{ij} = 0$ otherwise. However, as experienced in several test cases, $\tilde{\tilde{F}}_N$ is usually small compared to $\Lambda_D - E_0 1$ and for such cases an iterative procedure to solve Eq. (17) will converge rather quickly.

III. SOME TEST APPLICATIONS

Two series of test calculations have been carried out in order to examine the performance of the present perturbation approach. The purpose of the first series was to compare the results with full CI results obtained with the same basis set. The existing full CI results, though, correspond to rather limited basis sets that are incapable of yielding very accurate results for the properties studied. For this reason, a second series of calculations, using more extended basis sets, were performed. For these calculations, the corresponding MRCI + Q results are included for comparison. The results from the second-order perturbation calculations will be denoted CASPT2D and CASPT2N. CASPT2D corresponds to the calculations where a zeroth-order Hamiltonian with a diagonal one-particle operator has been used whereas

CASPT2N corresponds to a nondiagonal one-particle operator. The acronym CASPT2 will also be used, meaning either of the two perturbation methods.

A. Spectroscopic constants for the ground states of N_2, NO, and O_2

In a first set of calculations, we studied the bond breaking process of N_2, NO, and O_2, which all have electron dense multiple bonds. We will report not only the spectroscopic parameters (r_e, ω_e, D_e) (Tables I–III), but also the energetics of the bond breaking process (Tables IV–VI). The results can be compared directly to the full CI results of Bauschlicher and Langhoff.[12] A double-zeta polarization (DZP) basis was used and only the $2p$ electrons were correlated. In the CASSCF calculations, the $2p$ orbitals and electrons were active. The $1s$ and $2s$ orbitals were optimized in the CASSCF calculations, but were uncorrelated in the CASPT2 calculations to allow comparison with the full CI results. The spectroscopic parameters r_e and ω_e were computed using three points with $0.05a_0$ separation fit to a second-degree polynomial in $1/R$.

The CASPT2 results for the equilibrium bond distance r_e and the harmonic vibrational frequency ω_e are all in agreement with the full CI results. This is not surprising since the results also at the CASSCF level of approximation are good. The CASSCF wave function therefore proves a good starting point for a perturbation calculation for all three molecules. This can be seen especially for the N_2 molecule, where the error in r_e is reduced from 0.0035 to 0.0004 a.u. The deviation in total energy from the FCI value around equilibrium is almost the same for all three molecules. This is most striking for the more accurate perturbation method (CASPT2N), where the error is 0.0049, 0.0052, and 0.0048 a.u. for N_2, NO, and O_2, respectively—CASSCF plus CASPT2 is able to recover about 97% of the correlation energy at equilibrium. At infinite separation, however, there is no such agreement. The total energy for the nitrogen atom is almost identical to the FCI result, while the total energy for the oxygen atom differs more from the FCI result. The deviations are 0.0001 and 0.0028 a.u., respectively, for CASPT2N. This leads to a small overestimation of the dissociation energy D_e for O_2 and an underestimation of D_e for N_2. Tables IV and V show that somewhere halfway up the potential curve, the molecules are changing character, i.e., the bonds are breaking. For N_2, this critical point occurs for an internuclear distance between 3 and 4 a.u. The energy

differences from the full CI value are very different to the left- and the right-hand sides of this point for all three methods, indicating that the present perturbation approach is sensitive to changes in the spin coupling of the electrons. Nevertheless, CASPT2 reduces the error in D_e considerably. With CASPT2N, it is reduced from 0.42 to 0.13 eV for N_2, from 0.85 to 0.06 eV for NO, and from 0.96 to 0.02 eV for O_2. From Tables IV–VI, one might get the impression that CASPT2D is a better method than CASPT2N since, for most cases in this set of calculations, it gives better total energies than CASPT2N, but we get more insight into the accuracy of the two methods by studying the parameters r_e and ω_e in Tables I–III. CASPT2N yields better results than CASPT2D for these parameters and from this point of view, we conclude that CASPT2N is somewhat more accurate than CASPT2D.

B. The CH_3 radical

In a second set of test calculations, we have studied the process of simultaneously stretching three single bonds. The results, presented in Table VII, can be compared to the full CI calculations of Bauschlicher and Taylor.[13] The basis set used in the calculations was segmented contracted and had the size $(C/4s,2p,1d /H/2s,1p)$. CH_3 was taken as planar and symmetric and calculations were performed at r_e, $1.5*r_e$, and $2.0*r_e$, where r_e is the equilibrium bond distance (for details, see Ref. 13). Only the seven valence electrons were correlated and two different active spaces were used. In the first set of calculations, the valence orbitals of carbon and hydrogen formed the active space [(4120), where the four numbers represent the number of active orbitals in the four different symmetries a_1, b_1, b_2, and a_2]. The error in total energy is reduced significantly for all three bond distances

TABLE II. Spectroscopic constants for NO. A comparison between CASPT2 and full CI.

Method	r_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
FCI[a]	2.2196	1922	5.753
CASSCF-FCI	0.0036	− 24	− 0.853
CASPT2D-FCI	0.0021	− 6	− 0.021
CASPT2N-FCI	0.0017	− 5	− 0.061

[a] The FCI results have been obtained using the FCI energies given in Ref. 12.

TABLE I. Spectroscopic constants for N_2. A comparison between CASPT2 and full CI.

Method	r_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
FCI[a]	2.1227	2342	8.748
CASSCF-FCI	− 0.0035	0	− 0.415
CASPT2D-FCI	− 0.0004	− 1	− 0.113
CASPT2N-FCI	− 0.0004	− 1	− 0.126

[a] The FCI results have been obtained using the FCI energies given in Ref. 12.

TABLE III. Spectroscopic constants for O_2. A comparison between CASPT2 and full CI.

Method	r_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
FCI[a]	2.3182	1608	4.637
CASSCF-FCI	0.0041	− 42	− 0.959
CASPT2D-FCI	0.0023	− 1	+ 0.061
CASPT2N-FCI	0.0014	− 1	+ 0.021

[a] The FCI results have been obtained using the FCI energies given in Ref. 12.

TABLE IV. Total energies for N_2 in a DZP basis (in a.u.). A comparison between CASPT2 and full CI.

Method	2.05[b]	2.10	2.15	2.50	3.00	4.00	50.0
FCI[a]	− 109.146 91	− 109.150 64	− 109.150 49	− 109.087 32	− 108.957 53	− 108.842 21	− 108.829 52
CASSCF-FCI	0.055 61	0.055 90	0.056 14	0.057 08	0.057 12	0.048 10	0.040 74
CASPT2D-FCI	0.004 93	0.004 96	0.004 99	0.004 91	0.003 68	− 0.000 52	0.000 80
CASPT2N-FCI	0.004 88	0.004 91	0.004 94	0.004 87	0.003 65	− 0.000 83	0.000 26

[a] The FCI results from Ref. 12.
[b] Internuclear distances in atomic units.

compared to CASSCF. Using CASPT2N, the error at r_e is reduced from 0.0964 to 0.0125 a.u. and this method is therefore able to yield 92% of the correlation energy at the equilibrium bond distance. The difference between the two perturbation approaches is only minor for this active space, but CASPT2N gives more uniform results for the three bond distances.

Correlation of the electron in the carbon π orbital at the CASSCF level can be improved by adding one more π orbital in the active space giving, in total, the active space (4220). The uniformity of the total energies for the three bond distances now becomes slightly better at the CASPT2 level.

In Ref. 10, the CASPT2D results for stretching the two OH bonds in H_2O were reported—the CASPT2N results are similar to these and will therefore not be published. The results for CH_3 are in agreement with the results for H_2O, even though we are not able to reach neither the same accuracy nor the same uniformity for CH_3. A reason for the former could be that three bonds are stretched in CH_3 while only two are stretched in H_2O. A reason for the latter could be that the oxygen atom can be described equally well in a bonding situation as a separate atom with a rather small active space (see also Table VI).

C. The singlet–triplet splitting in CH_2

In a third set of test calculations, we have studied the singlet–triplet splitting in the methylene radical. Again the results can be compared to the full CI results of Bauschlicher and Taylor.[14] The basis set used is the same as the one used in the CH_3 calculations. All six valence electrons were correlated and three different active spaces were used. In the first set of calculations, only the valence orbitals of carbon and hydrogen formed the active space (3120). The results,

which are presented in Table VIII, are rather disappointing. One would hope that the excitation energy, which at the CASSCF level of approximation already is in very good agreement with the full CI result, would change only slightly when the perturbation correction is added. This is not the case. The two states $^1A_1$ and $^3B_1$ are treated in an unbalanced way at the correlated level, which increases the excitation energy. Calculations with a second active space (4220) were therefore performed in order to see whether this active space could give a more balanced treatment of the dynamical correlation effect for the two states. The excitation energy computed with the CASSCF wave functions with this active space is no longer in good agreement with the full CI result, indicating that the CASSCF result obtained with the smaller active space (3120) was fortuitously good. At the CASPT2 level of approximation, the excitation energy is also changed dramatically, but for the better. Compared to the smaller active space, the excitation energy is lowered by 2 kcal/mol. Calculations with a third active space (6240) were also performed. For this active space, the CASPT2 results for the excitation energy are in good agreement with the full CI result and also with the third-order result obtained by Murphy et al.[20] The conclusion is that in order to get a balanced treatment of the two states $^1A_1$ and $^3B_1$, we have to have a rather large active space. And again we notice that the difference between the two perturbation approaches is minor, especially with the largest active space.

D. The polarizability of F^-

As a final test in the first series of calculations, we have studied the second-order perturbation correction to an electric property—the polarizability of F^-. The correlation contribution to this property is substantial and therefore it is interesting to see how much a second-order perturbation approach is able to recover. Bauschlicher and Taylor have

TABLE V. Total energies for NO in a DZP basis (in a.u.). A comparison between CASPT2 and full CI.

Method	2.15[b]	2.20	2.25	3.30	4.40	50.0
FCI[a]	− 129.476 83	− 129.479 32	− 129.479 06	− 129.321 24	− 129.272 73	− 129.268 10
CASSCF-FCI	0.105 89	0.105 75	0.105 56	0.094 38	0.077 94	0.074 31
CASPT2D-FCI	0.004 25	0.004 15	0.004 04	0.001 69	0.002 50	0.003 33
CASPT2N-FCI	0.005 27	0.005 19	0.005 10	0.002 45	0.002 11	0.002 92

[a] The FCI results from Ref. 12.
[b] Internuclear distances in atomic units.

TABLE VI. Total energies for O_2 in a DZP basis (in a.u.). A comparison between CASPT2 and full CI.

Method	2.25[b]	2.30	2.35	100.0
FCI[a]	− 149.875 15	− 149.876 95	− 149.876 69	− 149.706 68
CASSCF-FCI	0.143 25	0.143 17	0.143 00	0.107 88
CASPT2D-FCI	0.003 74	0.003 64	0.003 55	0.005 85
CASPT2N-FCI	0.004 88	0.004 82	0.004 76	0.005 60

[a] The FCI results from Ref. 12.
[b] Internuclear distances in atomic units.

made two sets of full CI calculations of the polarizability of F^-.[15] In the first, only the $2p$ electrons were correlated and in the second, the correlation treatment was extended to also include the $2s$ electrons. The basis set used by them was segmented contracted with the size $(5s,3p,2d)$. The polarizability was obtained as the second derivative of the energy with respect to the electric field strength. In the finite difference estimation of the second derivative of the energy, a small electric field of strength 0.005 a.u. was used. Our calculations were done under the same conditions and the results are presented in Table IX. For each of the two problems of correlating either the $2p$ electrons or the $2s$ and $2p$ electrons, two different active spaces were used. In the case of correlating the $2p$ electrons, the polarizability increases from 13.663 to 15.269 a.u. for CASPT2N when increasing the active space. The difference from the full CI value is therefore only 0.094 a.u. with the larger active space. The same improvement is not obtained when increasing the active space and correlating both the $2s$ and the $2p$ electrons. The polarizability calculated with the two active spaces gives almost the same results 15.190 and 15.258 a.u., respectively, for CASPT2N. As a curious fact, these results can actually be improved by making the $2s$ orbital inactive instead of active. We then get the results 16.412 and 15.912 a.u. with the smaller and the larger active spaces, respectively, for CASPT2N—for CASPT2D, the corresponding results are 13.823 and 15.706 a.u., respectively.

TABLE VII. Comparison of total energies from CASPT2 and full CI for CH_3 in a DZP basis (in a.u.).

Method[a]	r_e	$1.5*r_e$	$2.0*r_e$
FCI[b]	− 39.7212	− 39.4829	− 39.3031
SCF[b]-FCI (4120)	0.1547	0.1989	0.2901
CASSCF-FCI	0.0964	0.0737	0.0651
CASPT2D-FCI	0.0142	0.0079	0.0054
CASPT2N-FCI (4220)	0.0125	0.0079	0.0058
CASSCF-FCI	0.0847	0.0633	0.0597
CASPT2D-FCI	0.0126	0.0076	0.0061
CASPT2N-FCI	0.0113	0.0071	0.0062

[a] The numbers within parentheses are the number of active orbitals used in the CASSCF and CASPT2 calculations given in symmetry order a_1, b_1, b_2, and a_2.
[b] FCI and SCF results from Ref. 13.

E. The nitrogen molecule

A number of calculations have been carried out for various states of N_2 using different basis sets. The purpose of the calculations was to illustrate the performance of the second-order perturbation approach for different basis sets. In doing that, we have calculated the spectroscopic constants (r_e, ω_e, D_e), where r_e and ω_e were obtained by a fit to a second-degree polynomial in $1/R$ using three points with $0.05a_0$ separation. Since the basis sets used were all of moderate size and since the method in obtaining ω_e is quite inaccurate, comparison with experimental data is inappropriate. Therefore, corresponding calculations using the MRCI method have been carried out, for comparison. In all calculations, the ten valence electrons were correlated. In the CAS calculations, the $2s$ and the $2p$ orbitals formed the active space, while in the MRCI calculations, the $2s$ orbitals were inactive and the $2p$ orbitals active. The MRCI expansion consisted of all single and double excitations out of all configurations obtained by distributing the remaining six electrons in the $2p$ orbitals. With the $2s$ electrons inactive in the reference configurations, only double excitations from this orbital space are included, which leads to an imbalance in the treatment of the dissociation. As suggested by Almlöf et al.,[16] this is compensated by the inclusion of the multireference Davidson correction. The results for the ground state are presented in Table X. For this state, three different basis sets were used. The first thing to notice is that the CASSCF method gets saturated more quickly with the size of the basis set than the more accurate methods. It is then not surprising that the CASSCF results are closer to experimental data than the results from the other methods for smaller basis sets and that, as a matter of fact, we get a deterioration of the CASSCF results when we add the perturbation correction. If we compare the CASPT2 results with the MRCI + Q results for r_e and ω_e, we see that this should also be the case. Actually, the CASPT2 results for these parameters agree well with the corresponding MRCI + Q results. A second thing to notice is that we cannot achieve the same accuracy in the dissociation energy with CASPT2. The difference between the MRCI + Q and the CASPT2N results are for the three basis sets 0.243, 0.257, and 0.280 eV. For this property, CASPT2 will be saturated for a smaller basis set than MRCI + Q. We also realize that even with a large basis set, we will never *with the present active space* reach the neighborhood of the experimental value for D_e with CASPT2. The reason for this is that CASPT2 seems to recover a larger fraction of the correlation energy for the nitrogen atom than for the nitrogen molecule.

TABLE VIII. The singlet–triplet separation in CH_2. A comparison between CASPT2 and full CI.

Method[a]	Energy (a.u.)		Exc. energy (kcal/mol)
	$^1A_1$	$^3B_1$	
FCI[b]	− 39.027 182	− 39.046 259	11.97
(3120)			
CASSCF	− 38.945 529	− 38.965 954	12.82
CASPT2D[c]	− 39.011 773	− 39.036 804	15.71
CASPT2N	− 39.013 078	− 39.037 664	15.43
CASPT2D-FCI	0.015 409	0.009 455	
CASPT2N-FCI	0.014 104	0.008 595	
(4220)			
CASSCF	− 38.968 726	− 38.982 741	8.79
CASPT2D	− 39.016 704	− 39.038 658	13.78
CASPT2N	− 39.017 092	− 39.038 660	13.53
CASPT2D-FCI	0.010 478	0.007 601	
CASPT2N-FCI	0.010 090	0.007 599	
(6240)			
CASSCF	− 38.999 566	− 39.012 166	7.91
CASPT2D	− 39.022 300	− 39.042 413	12.62
CASPT2N	− 39.022 170	− 39.042 165	12.55
CASPT2D-FCI	0.004 882	0.003 846	
CASPT2N-FCI	0.005 012	0.004 094	

[a] The numbers within parentheses are the number of active orbitals used in the CASSCF and CASPT2 calculations given in symmetry order a_1, b_1, b_2, and a_2.
[b] FCI results from Ref. 14.
[c] The results published in Ref. 10 differ from these since erroneously all electrons were correlated.

The results for the first and second excited states of N_2 are presented in Tables XI and XII, respectively. As is indicated in these tables, the second-order perturbation theory breaks down for the largest basis set. This can be explained by the fact that with the given zeroth-order Hamiltonian, each of the two states are accidentally near degenerate, and for excited states, this is indeed often the case. For the smaller basis sets, the two excited states are probably not well separated from other states either and an indication of this is given by comparing Tables XI and XII with Table X. The agreement with MRCI + Q for the bond length is much better for the ground state than for the excited states. The problem of near degeneracy can to some extent be avoided by choosing another active space. In this set of calculations, it was easily identified that single excitations from the active space to the $2\pi_g$ orbitals—including an orbital rotation in the active space—was the cause of the problems. These excitations gave rise to positive contributions to the second-order energy. Furthermore, since we are not able to calculate the occupation numbers—by diagonalizing the one-particle density matrix using the sum of the zeroth-order wave function and the first-order wave function—because of the need of the four-particle density matrix, we simply diagonalized

TABLE IX. The polarizability of F^-. A comparison between CASPT2 and full CI.

Method	Polarizability[a] (a.u.)	
	Correlating $2p$	Correlating $2s2p$
SCF[b]	9.894	9.894
FCI[b]	15.363	16.295
	(2220)	(4220)
CASSCF	16.903	13.905
CASPT2D	13.543	14.788
CASPT2N	13.663	15.190
	(3330)	(6330)
CASSCF	14.878	13.974
CASPT2D	14.899	14.932
CASPT2N	15.269	15.258

[a] The numbers within parentheses are the number of active orbitals used in the CASSCF and CASPT2 calculations given in symmetry order a_1, b_1, b_2, and a_2.
[b] SCF and FCI results from Ref. 15.

TABLE X. Spectroscopic constants[a] for N_2 ($X\,^1\Sigma_g^+$) with various methods and basis sets.[b]

Method	r_e (Å)	ω_e (cm^{-1})	D_e (eV)
	ANO [$4s,2p,1d$] basis		
MRCI + Q	1.1242	2318	8.661
CASSCF	1.1160	2363	8.989
CASPT2D	1.1245	2312	8.375
CASPT2N	1.1238	2316	8.418
	ANO [$4s,3p,2d,1f$] basis		
MRCI + Q	1.1095	2315	9.295
CASSCF	1.1069	2333	9.126
CASPT2D	1.1094	2310	9.003
CASPT2N	1.1086	2314	9.038
	ANO [$5s,4p,3d,2f$] basis		
MRCI + Q	1.1036	2308	9.504
CASSCF	1.1048	2320	9.192
CASPT2D	1.1039	2302	9.185
CASPT2N	1.1031	2306	9.224
Expt.[c]	1.0977	2359	9.905

[a] Calculated spectroscopic constants from a fit to a second-degree polynomial in $1/R$.
[b] ANO type basis sets with a ($14s,9p,4d,3f$) primitive set.
[c] From Ref. 17.

TABLE XI. Spectroscopic constants[a] for N_2 ($A\,^3\Sigma_u^+$) with various methods and basis sets.[b]

Method	r_e (Å)	ω_e (cm^{-1})	D_e (eV)
ANO [$4s,2p,1d$] basis			
MRCI + Q	1.3169	1422	2.967
CASSCF	1.3078	1451	2.678
CASPT2D	1.3163	1422	2.920
CASPT2N	1.3163	1423	2.895
ANO [$4s,3p,2d,1f$] basis			
MRCI + Q	1.3005	1424	3.342
CASSCF	1.3032	1425	2.709
CASPT2D	1.2975	1423	3.303
CASPT2N	1.2978	1423	3.275
ANO [$5s,4p,3d,2f$] basis			
CASSCF	1.3022	1426	2.761
CASPT2D	c	c	c
CASPT2N	1.2813	3867	3.331
CASSCF[d]	1.2999	1423	2.610
CASPT2D[d]	1.2960	1410	3.241
CASPT2N[d]	1.2953	1409	3.298
Expt.[e]	1.2866	1461	3.680

[a] Calculated spectroscopic constants from a fit to a second-degree polynomial in $1/R$.
[b] ANO type basis sets with a ($14s,9p,4d,3f$) primitive set.
[c] These numbers could not be obtained because of a deterioration of the potential curve due to near degeneration.
[d] The $2\pi_g$ orbitals are included in the active space.
[e] From Ref. 17.

TABLE XII. Spectroscopic constants[a] for N_2 ($B\,^3\Pi_g$) with various methods and basis sets.[b]

Method	r_e (Å)	ω_e (cm^{-1})	D_e (eV)
ANO [$4s,2p,1d$] basis			
MRCI + Q	1.2406	1727	4.413
CASSCF	1.2351	1740	3.865
CASPT2D	1.2380	1728	4.210
CASPT2N	1.2382	1727	4.170
ANO [$4s,3p,2d,1f$] basis			
MRCI + Q	1.2257	1722	4.801
CASSCF	1.2303	1710	3.949
CASPT2D	1.2194	1723	4.658
CASPT2N	1.2200	1722	4.612
ANO [$5s,4p,3d,2f$] basis			
CASSCF	1.2296	1703	3.974
CASPT2D	1.2020	3996	4.623
CASPT2N	1.2063	2294	4.601
CASSCF[c]	1.2226	1709	3.820
CASPT2D[c]	1.2179	1713	4.560
CASPT2N[c]	1.2184	1704	4.594
Expt.[d]	1.2126	1733	4.896

[a] Calculated spectroscopic constants from a fit to a second-degree polynomial in $1/R$.
[b] ANO type basis sets with a ($14s,9p,4d,3f$) primitive set.
[c] The $2\pi_g$ orbitals are included in the active space.
[d] From Ref. 17.

the one-particle density matrix in the secondary orbital subspace in order to get an idea of how large the occupation numbers for the secondary orbitals might be. This approximation shows that the occupation numbers for the $2\pi_g$ orbitals are substantial. An obvious modification of the active space is therefore to include the $2\pi_g$ orbitals in it. Calculations with this new active space were only performed with the largest basis set, since the necessity of another zeroth-order Hamiltonian was most apparent here. The results have been included in Tables XI and XII. The corresponding MRCI calculations were not performed—because they would be too lengthy—but comparing the results with the results obtained with the smaller basis sets show that they are quite satisfactory.

IV. DISCUSSION

In the present study, we have tried to illustrate with a few examples the capabilities of a second-order perturbation method based on a CASSCF reference function. With these examples, we have also tried to show how the results from the two perturbation methods with a diagonal and a full one-electron operator, respectively, might differ. No matter which of the two one-electron operators we use, the second-order perturbation method gives satisfactory results for most of the test calculations. However, in order to get accurate results for energy differences between electronic states that are either distinct, as in the singlet–triplet separation of CH_2, or very different because of a large change in some parameter, as for the ground state of N_2 at equilibrium and at infinite separation, it is important that the two states are equally well described at the zeroth-order level. By extend-

ing the active space, this is possible to achieve, as was illustrated in the calculations of the singlet–triplet separation of CH_2. In the case of N_2, a larger active space would probably give a better value of the dissociation energy. This recipe is, of course, not a panacea since the increase of the active space might not always be practical.

In the applications presented in this article, the method with a full one-particle operator gives in most cases the better results, although the difference in the results for the two perturbation methods is only minor. However, preliminary results for ozone show that the difference in the results for the two methods can be significant.[18] With a [$4s,3p,2d,1f$] atomic natural orbital (ANO) basis set, the following results for the equilibrium geometry and the harmonic frequencies of ozone were obtained: (1.288 Å, 115.9°, 1082, 693, and 1068 cm^{-1}) with CASPT2D and (1.280 Å, 116.5°, 1106, 706, and 1109 cm^{-1}) with CASPT2N. For all these properties, the CASPT2N values are in better agreement with the experimental data (1.272 Å, 116.8°, 1135, 716, and 1089 cm^{-1})[19] than the corresponding CASPT2D values.

To give an idea of the efficiency of the method, we will give the total CPU time on an IBM 3090-17S computer for the calculation of one point on the potential curve for the ground state of N_2. With 92 functions in the basis set, the total CPU time with the MRCI method was 3397 s. The corresponding number with the CASPT2N method was 635 s, which is less than 20% of the CPU time consumed in the MRCI calculation. The ratio between the input/output (I/O) times is, however, not so favorable, since rather long CI vectors have to be written and read also in the CASPT2N calculations. CASPT2D is computationally more efficient than CASPT2N and especially the I/O handling will be

more limited for CASPT2D. For many of the calculated properties, we have obtained fairly accurate results if we compare them to the results given by either the full CI or the MRCI methods. Thus, we conclude that CASPT2 is capable of giving accurate results for many molecular properties with a considerably reduced computational effort. The CASPT2 method becomes an especially interesting alternative in cases so large that reliable MRCI calculations no longer can be performed. In forthcoming publications, we intend to give illustrations of the performance of the method in such cases, both for ground and excited states properties.

ACKNOWLEDGMENTS

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