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Different forms of the zeroth-order Hamiltonian in second-order perturbation theory with a complete active space self-consistent field reference function

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Summary. A new one-particle zeroth-order Hamiltonian is proposed for perturbation theory with a complete active space self-consistent field (CASSCF) reference function. With the new partitioning of the Hamiltonian, reference functions dominated by a closed-shell configuration, on one hand, and an open-shell configuration, on the other hand, are treated in similar and balanced ways. This leads to a better description of excitation energies and dissociation energies. The new zeroth-order Hamiltonian has been tested on CH_2, SiH_2, NH_2, CH_3, N_2, NO, and O_2, for which full configuration interaction (FCI) results are available. Further, excitation energies and dissociation energies for the N_2 molecule have been compared to corresponding multireference (MR) CI results. Finally, the dissociation energies for a large number of benchmark molecules containing first-row atoms (the "G1" test) have been compared to experimental data. The computed excitation energies compare very well with the corresponding FCI and MRCI values. In most cases the errors are well below 1 kcal/mol. The dissociation energies, on the other hand, are in general improved in the new treatment but have a tendency to be overestimated when compared to other more accurate methods.

Key words: Zeroth-order Hamiltonian – Perturbation theory – Complete active space self-consistent field

1 Introduction

The use of perturbation theory for treating electron correlation in atoms and molecules is by now well established. From Kelly's pioneering work [1] in the 1960s to the present-day program packages [2], perturbation theory applied to chemical problems has gained widespread use. There are many reasons for this. First, the property of size extensivity, which is easily achieved with perturbation methods, makes perturbation theory suitable for application to larger molecules and is convenient in computing accurate dissociation energies. Second, the calculation of the second-order correction to the self-consistent field (SCF) energy is only a trivial supplement to the SCF code and recovers in many cases the major part of the correlation energy.

In formulating a perturbation method the crucial step is the choice of thezeroth-order Hamiltonian. Already in 1934 Møller and Plesset [3] proposed to take the Hartree–Fock (HF) approximation as the zeroth-order approximation to the exact theory. This turned out to be a brilliant choice and later efforts to formulate alternative zeroth-order Hamiltonians for the closed-shell reference state have not been fruitful [4]. Several suggestions of a perturbation method for the open-shell case have been made especially during the last few years [5–7]. What most of these theories have in common is the attempt to retain some of the features of Møller–Plesset (MP) many-body perturbation theory (MBPT) [8]. The spin contamination of the spin-unrestricted HF wave function and the somewhat slower convergence of the perturbation series have directed a lot of research toward a restricted formalism.

Though successful, the perturbation methods described above are limited to cases where the HF wave function provides a valid starting point. If the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are almost degenerate the perturbation expansion suffers from apparent slow convergence or no convergence at all. A considerable part of the near-degeneracy correlation effects can be effectively treated by the multiconfigurational (MC) SCF method [9]. With this method it is also possible to obtain electronic wave functions that are qualitatively correct at all geometries. A particular kind of MCSCF method is the complete active space (CAS) SCF method [9] which was introduced in 1980 by Roos and has since become a valuable tool for describing the electronic structure of molecular systems in ground and excited states. An obvious continuation of improving the description of the electronic structure is to include the remaining dynamical electron correlation effects perturbatively. Already in 1982, Roos et al. [10] made an attempt to implement second-order perturbation theory with a CASSCF wave function as the reference function. At the time one had to make some severe approximations to bypass the need for higher-order density matrices. Ten years later these matrices could be efficiently calculated and a complete second-order perturbation theory was implemented [11, 12]. This approach, denoted CASPT2, has been successfully applied to a large number of chemical problems, in particular to molecular structure, electronic spectra, and transition metal chemistry (see Refs. [13] and [14] and references therein). The method seems to be reliable for a broad range of problems in chemistry and one might wonder about the necessity of formulating alternative zeroth-order Hamiltonians. In a systematic test of geometries and binding energies of 32 molecules containing first-row atoms [15], it was noticed that wave functions dominated by an open-shell configuration were favoured over wave functions dominated by a closed-shell configuration. This led to dissociation energies underestimated with between 3 and 6 kcal/mol times the number of extra electron pairs formed. It would be desirable to treat these two kinds of wave functions in a similar and more balanced way. We have made an attempt to modify the zeroth-order Hamiltonian to achieve this and simultaneously retain all the nice properties of the original operator. This will be discussed in Section 2. In Section 3 numerous test applications are presented for different forms of the zeroth-order Hamiltonian. Comparison of results is made to either full configuration interaction (FCI), multireference (MR) CI, or experimental data. Finally, in Section 4 the conclusions are given.

2 Theory

The greater complexity of multiconfigurational MBPT compared to single-configurational MBPT makes it necessary to choose a zeroth-order Hamiltonian with a simple structure, i.e., preferably a one-particle operator. In our previous work [11, 12], the following operator was suggested:

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_K \hat{F} \hat{P}_K + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \hat{P}_{TQ..} \hat{F} \hat{P}_{TQ..}, \tag{1}$$

where $\hat{P}_X$ are projection operators onto various N-particle spaces, namely the space spanned by the reference state, the rest of the CASSCF CI space, the singly and doubly excited interacting space, etc. The Fock operator, $\hat{F}$, is a one-particle operator defined in the following way:

$$\hat{F} = \sum_{pq} f_{pq} \hat{E}_{pq}, \tag{2}$$

where

$$f_{pq} = h_{pq} + \sum_{rs} D_{rs} [(pq|rs) - \tfrac{1}{2}(pr|sq)], \tag{3}$$

$\hat{E}_{pq}$ are the spin-averaged excitation operators, $\boldsymbol{h}$ is the matrix representation of the core Hamiltonian operator, $\boldsymbol{D}$ is the density matrix, and $(pq|rs)$ are two-electron integrals. For the closed-shell (single determinant) reference state $\hat{F}$ reduces to the well-known Fock operator from Hartree–Fock theory. $\hat{H}_0$ is thus a generalization of the zeroth-order Hamiltonian in Møller–Plesset MBPT. Here it is also appropriate to mention that a restricted formalism (one set of orbitals) is used and that both the zeroth-order wave function (the CASSCF reference state) and the first-order correction to the wave function are eigenfunctions to the spin operators $\hat{S}^2$ and S_z. Further, the Fock operator, $\hat{F}$, is invariant to orbital rotations within the inactive, active, and secondary subspaces, respectively.

In order to justify a modification of the zeroth-order Hamiltonian above it is well motivated to study high-spin open-shell Hartree–Fock theory. Here the Fock operator is defined by

$$\hat{f} = \hat{h} + \sum_{b} [\hat{J}_b - \hat{K}_b], \tag{4}$$

where b refers to occupied spin orbitals, $\hat{h}$ is the core Hamiltonian operator, and $\hat{J}_b$ and $\hat{K}_b$ are coulomb and exchange operators, respectively. The matrix representation of $\hat{f}$ in the spin α and spin β orbital spaces is given by

$$\begin{aligned} f^{\alpha}_{pq} = h^{\alpha}_{pq} &+ \sum_{r=1}^{N^{\beta}} [(\phi^{\alpha}_p \phi^{\alpha}_q|\phi^{\alpha}_r \phi^{\alpha}_r) + (\phi^{\alpha}_p \phi^{\alpha}_q|\phi^{\beta}_r \phi^{\beta}_r) - (\phi^{\alpha}_p \phi^{\alpha}_r|\phi^{\alpha}_r \phi^{\alpha}_q)] \\ &+ \sum_{r=N^{\beta}+1}^{N^{\alpha}} [(\phi^{\alpha}_p \phi^{\alpha}_q|\phi^{\alpha}_r \phi^{\alpha}_r) - (\phi^{\alpha}_p \phi^{\alpha}_r|\phi^{\alpha}_r \phi^{\alpha}_q)], \end{aligned} \tag{5}$$

$$\begin{aligned} f^{\beta}_{pq} = h^{\beta}_{pq} &+ \sum_{r=1}^{N^{\beta}} [(\phi^{\beta}_p \phi^{\beta}_q|\phi^{\beta}_r \phi^{\beta}_r) + (\phi^{\beta}_p \phi^{\beta}_q|\phi^{\alpha}_r \phi^{\alpha}_r) - (\phi^{\beta}_p \phi^{\beta}_r|\phi^{\beta}_r \phi^{\beta}_q)] \\ &+ \sum_{r=N^{\beta}+1}^{N^{\alpha}} (\phi^{\beta}_p \phi^{\beta}_q|\phi^{\alpha}_r \phi^{\alpha}_r), \end{aligned} \tag{6}$$

where $\boldsymbol{h}^{\alpha}$ and $\boldsymbol{h}^{\beta}$ are the matrix representations of $\hat{h}$ in the spin α and spin β orbital spaces, the N^{α} electrons of α spin are described by the spatial orbitals ϕ^{α}_p, and the N^{β} electrons of β spin are described by the spatial orbitals ϕ^{β}_p.

For the high-spin open-shell (single determinant) reference state the Fock matrix in Eq. (3) can be written as

$$f_{pq} = h_{pq} + \sum_{r=1}^{N^\beta} [2(pq|rr) - (pr|rq)] + \sum_{r=N^\beta+1}^{N^\alpha} [(pq|rr) - \tfrac{1}{2}(pr|rq)]. \tag{7}$$

Apart from the different sets of orbitals used in Eqs. (5)–(7) the largest difference between f_{pq}, f_{pq}^α, and f_{pq}^β is to be found in the last summation. Although f_{pq} is defined as an interpolation of the negatives of ionization potentials and electron affinities [11, 12] one can interpret it, by comparing Eqs. (5)–(7) as some sort of an average of f_{pq}^α and f_{pq}^β. While this seems to be a good compromise for the inactive–inactive and secondary–secondary blocks of f it might not be the best choice for the active–active block. This block consists of the open-shell orbitals filled with spin α electrons. Our proposal is to let this block resemble f_{pq}^α instead of an average of f_{pq}^α and and f_{pq}^β. One motivation for this proposal is that for the hydrogen atom the orbital energy of the occupied orbital will then contain the core Hamiltonian contribution only and no contributions from two-electron integrals.

There are many possible ways to define a Fock operator for a general CASSCF reference state with the property described above for the high-spin open-shell (single determinant) wave function. Our first trial was the operator whose matrix representation is

$$f' = f + g_1, \tag{8}$$

where

$$g_1 = -\tfrac{1}{4}[\boldsymbol{DKd} + \boldsymbol{dKD}], \tag{9}$$

$$K_{pq} = \sum_{rs} (\boldsymbol{Dd})_{rs}(pr|sq), \tag{10}$$

$$\boldsymbol{d} = 2\boldsymbol{I} - \boldsymbol{D}, \tag{11}$$

and f is the Fock matrix defined in Eq. (3). The multiple use of the particle and hole density matrices $\boldsymbol{D}$ and $\boldsymbol{d}$ in the definition of g_1 is due to their projection properties. The matrix product $\boldsymbol{Dd}$ has nonzero elements for only the active–active subblock. Further, the sandwich formula $\boldsymbol{DKd} + \boldsymbol{dKD}$ simply makes the inactive–inactive and secondary–secondary subblocks of g_1 zero and g_1 symmetric. For the high-spin open-shell (single determinant) reference state the active–active subblock of g_1 reduces to

$$(g_1)_{pq} = -\frac{1}{2} \sum_{r=N^\beta+1}^{N^\alpha} (pr|rq), \tag{12}$$

just as is desired from the discussion above.

The matrix g_1 introduces nonzero elements in the inactive–secondary subblock of f'. Those elements are zero in f for a converged CASSCF wave function. This is, however, a small cosmetic disadvantage which may be removed by replacing g_1 by g_2 defined by

$$g_2 = -\tfrac{1}{2}(\boldsymbol{Dd})^{1/2}\boldsymbol{K}(\boldsymbol{Dd})^{1/2} \tag{13}$$

Only the active–active subblock of g_2 is nonzero, and for the high-spin open-shell (single determinant) reference state this block reduces to that of g_1 in Eq. (12). g_1

and g_2 have the same power dependence in $\boldsymbol{D}$ (and $\boldsymbol{d}$). However, this power dependence is not the only possible choice. In this work we have tested a third Fock operator by taking g_3 defined by

$$g_3 = -\tfrac{1}{2}(\boldsymbol{Dd})\boldsymbol{K}(\boldsymbol{Dd}) \tag{14}$$

instead of g_1 in Eq. (8). Again only the active–active subblock of g_3 is nonzero, and for the high-spin open-shell (single determinant) reference state this block reduces to that of g_1 in Eq. (12). The greater power dependence in $\boldsymbol{D}$ (and $\boldsymbol{d}$) usually will make g_3 contribute less to f' than g_1 and g_2 for a general CASSCF reference function.

The major effect of the introduction of a correction to the Fock matrix is an enlarged energy gap between the active and secondary orbitals. The enlargement is small for CASSCF wave functions dominated by a closed-shell configuration and larger for other kinds of wave functions. Since the correction does not affect the inactive–inactive and secondary–secondary subblocks of the Fock matrix the energy gap between the inactive and active orbitals consequently will be reduced. The enlarged energy gap between the active and secondary orbitals will lead to larger energy denominaters for the more important contributions to the second-order energy. The result is smaller absolute values of the second-order energy for reference functions with many open shells. However, if inactive orbitals high in energy are present then the decreased energy gap between them and the active orbitals may lead to contributions to the second-order energy with small energy denominaters. This phenomenon has actually been observed in test calculations on the CrF_6 molecule.

In this work all these suggestions g_1, g_2, and g_3 of a correction to the Fock matrix, f, have been tested. As is illustrated in the next section the final results are almost independent on the choice of the correction while the presence of a correction has a great impact of the quality of the results.

3 Test applications

For testing the new zeroth-order Hamiltonian we have calculated excitation energies and dissociation energies for various systems. The new partitioning of the Hamiltonian is expected to have the largest effect on these properties, although other properties will be discussed as well. The acronyms CASPT2[0], CASPT2[g_1,], CASPT2[g_2], and CASPT2[g_3] will be used for the second-order perturbation theory calculations with a CASSCF reference state. The symbols in brackets refer to the correction made to the Fock matrix, f. In all CASPT2 calculations the full corrected Fock matrix was used except in the CASPT2[g_1] calculations where the inactive–secondary subblock was left out.

3.1 The singlet–triplet splitting in CH_2

The adiabatic $^1A_1$–$^3B_1$ separation in CH_2 exhibits large differential correlation effects and is therefore a good candidate for testing correlation methods. For comparison we have used the FCI results of Bauschlicher and Taylor [16]. The basis set is of the double zeta plus polarization (DZP) type and for details we refer to Ref. [16].

Table 1. The singlet–triplet separation in CH_2. A comparison between CASPT2 and FCI

Method[a]	Energy (a.u.)		Exc. energy (kcal/mol)
	$^1A_1$	$^3B_1$	
FCI[b]	−39.027182	−39.046259	11.97
(3210)			
CASSCF	−38.945529	−38.965954	12.82
CASPT2[0]	−39.013078	−39.037664	15.43
CASPT2[g_1]	−39.012868	−39.033906	13.20
CASPT2[g_2]	−39.012895	−39.033643	13.02
CASPT2[g_3]	−39.013049	−39.033686	12.95
CASPT2[0]–FCI	0.014104	0.008595	
CASPT2[g_1]–FCI	0.014314	0.012353	
CASPT2[g_2]–FCI	0.014287	0.012616	
CASPT2[g_3]–FCI	0.014133	0.012573	
(4220)			
CASSCF	−38.968726	−38.982741	8.79
CASPT2[0]	−39.017092	−39.038660	13.53
CASPT2[g_1]	−39.016998	−39.036392	12.17
CASPT2[g_2]	−39.016996	−39.036249	12.08
CASPT2[g_3]	−39.017078	−39.036296	12.06
(6331)			
CASSCF	−39.007032	−39.025395	11.52
CASPT2[0]	−39.023749	−39.043334	12.29
CASPT2[g_1]	−39.023721	−39.043024	12.11
CASPT2[g_2]	−39.023709	−39.042993	12.10
CASPT2[g_3]	−39.023743	−39.043013	12.09

[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. [16]

Only the six valence electrons were correlated and three different active spaces were used. The results are presented in Table 1. For the smallest active space (all valence orbitals active) the CASSCF value is in a very good agreement with the FCI result differing with less than 1 kcal/mol. At the CASPT2[0] level of theory, however, the situation is severely worsened. What happens is that the triplet state is favoured energetically over the singlet state leading to an overestimation of the excitation energy. The new zeroth-order Hamiltonian is designed to treat this situation correctly. The singlet state dominated by a closed-shell configuration should be hardly affected by the new operator while the triplet ground state dominated by a high-spin open-shell configuration should be noticeably increased in energy. As is demonstrated in Table 1 the total energy hardly changes for the $^1A_1$ state but considerably for the $^3B_1$ state. The error in the excitation energy is reduced from 3.5 to 1.2 kcal/mol when the g_1 correction is added to the Fock matrix. However, an improvement over the CASSCF value cannot be obtained with any of the corrections.

An analysis of the first-order correction to the wave function gave a hint of other choices of the active space, namely the (4220) and (6331) active spaces (see Table 1). The (4220) active space is only slightly larger than the valence orbital space but the CASSCF value of the excitation energy drops down considerably indicating that the result obtained with the smaller active space was fortuitously good. All CASPT2 results are in better agreement with the FCI value now and especially those with a correction added to the Fock matrix are in an excellent agreement with FCI. The error is only 0.2 kcal/mol with the g_1 correction. Also with the largest active space, (6331), CASPT2 with a corrected Fock matrix is superior to CASPT2[0].

In addition, one can mention that the CASPT2[0] results are similar to the MROPT1 results of Kozlowski and Davidson [17] and that the CASPT2[g_1], CASPT2[g_2], and CASPT2[g_3] results are similar to their MROPT3 and MROPT4 results.

3.2 The three lowest-lying states of SiH$_2$

The electronic structure of SiH_2 is similar to that of CH_2 except that the $^1A_1$ state is lower in energy than the $^3B_1$ state. Third in energy is the $^1B_1$ state. FCI calculations on these three states have been reported by Bauschlicher and Taylor [18] and information about basis sets and geometries can be found in Ref. [18]. Only the six valence electrons were correlated and the active space consisted of the valence orbitals of silicon and hydrogen. The results are presented in Table 2.

All three states are different in character: the $^1A_1$ state is dominated by a closed-shell configuration, the $^3B_1$ state is dominated by a high-spin open-shell configuration, and the $^1B_1$ state is dominated by a low-spin open-shell configuration. In designing the new zeroth-order Hamiltonian the attention was directed toward the closed-shell and the high-spin open-shell wave functions. Here we have a possibility to investigate the functioning of the new operator on other types of wave functions, namely the low-spin open-shell wave function.

As was the case for the CH_2 molecule, the CASSCF method is able to predict the excitation energies for SiH_2 fairly well. The errors are about 1 kcal/mol. Also here the situation is severely worsened at the CASPT2[0] level of theory because of the unbalanced treatment of the three states. The open-shell states (B_1) are

Table 2. The three lowest-lying states of SiH_2. A comparison between CASPT2 and FCI

Method[a]	Energy (a.u.)			Exc. energy (kcal/mol)	
	$^1A_1$	$^3B_1$	$^1B_1$	$^3B_1$–$^1A_1$	$^1B_1$–$^1A_1$
FCI[b]	− 290.110207	− 290.082313	− 290.036639	17.50	46.16
CASSCF	− 290.042911	− 290.016813	− 289.967938	16.38	47.05
CASPT2[0]	− 290.095397	− 290.071304	− 290.025231	15.12	44.03
CASPT2[g_1]	− 290.095257	− 290.068643	− 290.021907	16.70	46.03
CASPT2[g_2]	− 290.095260	− 290.068506	− 290.021843	16.79	46.07
CASPT2[g_3]	− 290.095375	− 290.068543	− 290.021940	16.84	46.08
CASPT2[0]–FCI	0.014810	0.011009	0.011408		
CASPT2[g_1]–FCI	0.014950	0.013670	0.014732		
CASPT2[g_2]–FCI	0.014947	0.013807	0.014796		
CASPT2[g_3]–FCI	0.014832	0.013770	0.014699		

[a] The valence orbitals are active in the CASSCF and CASPT2 calculations

[b] FCI results from Ref. [18]

favoured over the closed-shell ground state ($^1A_1$) leading to too small excitation energies. The errors are larger than 2 kcal/mol. The new zeroth-order Hamiltonian is able to correct the situation and to treat all three states in a more balanced way. The difference in results for the three different corrections is only minor and with the g_1 correction added to the Fock matrix the error in the $^3B_1$–$^1A_1$ splitting is 0.8 kcal/mol and that for the $^1B_1$–$^1A_1$ splitting only 0.1 kcal/mol. Only the valence orbital active space was applied for this molecule since an analysis of the first-order wave function did not motivate a slight enlargement of the active space.

3.3 The doublet–doublet separation in NH_2

In this test calculation the energy splitting between two states of similar character has been investigated, namely that of the $^2B_1$ and $^2A_1$ states of NH_2. Both states are doublet states dominated by a high-spin open-shell configuration. FCI calculations of Bauschlicher et al. [19] are available and information about basis sets and geometries can be found in the same paper. The seven valence electrons were correlated and the valence orbitals of nitrogen and hydrogen constituted the active space.

As is demonstrated in Table 3 the excitation energy obtained with the CASSCF method is 3.6 kcal/mol larger than the FCI value. All CASPT2 methods are able to reduce that error to below 0.3 kcal/mol. The relative unimportance of the correction to the Fock matrix in this particular example is due to the similar character of the two states $^2B_1$ and $^2A_1$.

3.4 The potential surface of CH_3

The total energy of the CH_3 molecule has been calculated at three geometries and compared to the FCI results of Bauschlicher and Taylor [20]. CH_3 was taken as

Table 3. The doublet–doublet separation in NH_2. A comparison between CASPT2 and FCI

Method[a]	Energy (a.u.)		Exc. energy (kcal/mol)
	$^2B_1$	$^2A_1$	
FCI[b]	– 55.742620	– 55.688762	33.80
CASSCF	– 55.620752	– 55.561066	37.45
CASPT2[0]	– 55.730183	– 55.676791	33.50
CASPT2[g_1]	– 55.727933	– 55.674402	33.59
CASPT2[g_2]	– 55.727747	– 55.674225	33.59
CASPT2[g_3]	– 55.727784	– 55.674255	33.59
CASPT2[0]–FCI	0.012437	0.011971	
CASPT2[g_1]–FCI	0.014687	0.014360	
CASPT2[g_2]–FCI	0.014873	0.014537	
CASPT2[g_3]–FCI	0.014836	0.014507	

[a] The valence orbitals are active in the CASSCF and CASPT2 calculations
[b] FCI results from Ref. [19]

Table 4. Total energies (in a.u.) of CH_3 at three geometries. A comparison between CASPT2 and FCI

Method[a]	r_e	$1.5*r_e$	$2.0*r_e$
FCI[b]	– 39.7212	– 39.4829	– 39.3031
SCF[b]–FCI	0.1547	0.1989	0.2901
CASSCF–FCI	0.0964	0.0737	0.0651
CASPT2[0]–FCI	0.0125	0.0079	0.0058
CASPT2[g_1]–FCI	0.0147	0.0114	0.0107
CASPT2[g_2]–FCI	0.0148	0.0113	0.0108
CASPT2[g_3]–FCI	0.0147	0.0109	0.0101

[a] The valence orbitals are active in the CASSCF and CASPT2 calculations
[b] FCI and SCF results from Ref. [20]

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 information about basis sets and geometries see Ref. [20]. The seven valence electrons were correlated and the valence orbitals of carbon and hydrogen formed the active space. The results are presented in Table 4.

The deviation from the FCI potential curve is increased when a correction is added to the Fock matrix in the CASPT2 calculation. However, the size of the deviation is not of importance but the uniformity of it at all geometries is. Without a correction (CASPT2[0]) the deviation is reduced 54% when going from r_e to $2*r_e$ while with the g_1 correction the same reduction is only 27%. Therefore, a correction to the Fock matrix enables CASPT2 to create potential surfaces that are more parallel to the FCI surface. This is of importance in the calculation of equilibrium bond distances and harmonic frequencies.

3.5 Dissociation energies for N_2, NO, and O_2

Dissociation energies provide another test of the new zeroth-order Hamiltonian since here we have to compare total energies of electronic states of molecules and their fragments. The electronic ground state of a molecule is usually dominated by a closed-shell configuration or a high-spin open-shell configuration with a few open shells. The electronic structure of the fragments, on the other hand, is usually a configuration with several open shells.

We will report the dissociation energies D_e of N_2, NO, and O_2. The results presented in Table 5 can be directly compared to the FCI results of Bauschlicher and Langhoff [21]. For basis sets and other computational details see Ref. [21]. Only the $2p$ electrons were correlated. The $1s$ and $2s$ orbitals were optimized in the CASSCF calculations, but were uncorrelated in the CASPT2 calculations to allow comparison with the FCI results. Two sets of calculations were performed: one with the $2p$ orbitals active and another with a doubling of the active space.

With the small active space CASPT2 without a correction to the Fock matrix gives excellent results for all molecules. For NO and O_2 the error in dissociation energy is less than 0.1 eV. When a correction is added to the Fock matrix the situation is worsened. The dissociation energy is now overestimated with between 0.1 and 0.3 eV for all three molecules. This failure can be explained in the following

Table 5. Dissociation energies D_e (in eV) for N_2, NO, and O_2. A comparison between CASPT2 and FCI

Method	N_2	NO	O_2
FCI[a]	8.748	5.753	4.637
2*p* active			
CASSCF–FCI	− 0.415	− 0.853	− 0.959
CASPT2[0]–FCI	− 0.126	− 0.061	0.021
CASPT2[g_1]–FCI	0.128	0.230	0.306
CASPT2[g_2]–FCI	0.126	0.226	0.301
CASPT2[g_3]–FCI	0.129	0.212	0.252
2*p*, 3*p* active			
CASSCF–FCI	− 0.250	− 0.381	− 0.453
CASPT2[0]–FCI	− 0.057	− 0.038	− 0.024
CASPT2[g_1]–FCI	0.026	0.045	0.054
CASPT2[g_2]–FCI	0.027	0.040	0.052
CASPT2[g_3]–FCI	0.028	0.039	0.037

[a] The FCI results have been obtained using the FCI energies given in Ref. [21]

way. At equilibrium distances the CASSCF wave function consists of many configurations and CASPT2 is able to give a fairly good value of the total energy. At infinite distance, on the other hand, the CASSCF wave function is essentially one configuration. The smaller flexibility of the CASSCF wave function gives CASPT2 energies that are too high in energy. The result is an overestimated value of the dissociation energy. The MRCI + Q method also gives overestimated dissociation energies (see Ref. [21]), but the error is an order of magnitude less than what we obtain here. Werner and Knowles [22] have also shown that with the internally contracted MRCI method the error in the total energy is larger at infinite separation than at equilibrium bond distances for the nitrogen molecule.

The fact that CASPT2[0] gives such excellent results can be explained by its favouring of systems with many open shells. At infinite distance we have many open shells and we therefore get an artificial lowering of the total energy. This lowering seems to compensate (at least for the NO and O_2 molecules) for the unflexibility of the CASSCF wave function at this geometry. However, these two anomalous effects may not always cancel each other.

With the enlarged active space the uncorrected and corrected CASPT2 methods all give errors of the same order of magnitude. Interesting to notice is that the value for the dissociation energy of O_2 is not improved at the CASPT2[0] level of theory by doubling the active space. This may indicate a fortuitously good result with the small active space.

These calculations also made possible the determination of the equilibrium bond distances. These were hardly affected by the correction to the Fock matrix. They were modified by less than 0.005 au.

3.6 *The nitrogen molecule*

Excitation energies and spectroscopic constants have been calculated for the nitrogen molecule using an extended basis set of the atomic natural orbital (ANO) type of the size (5*s*4*p*3*d*2*f*). Here no FCI data are available so comparison is made with the experimental data and results obtained at the MRCI level of theory. In all calculations the ten valence electrons were correlated. In the CASSCF and CASPT2 calculations the 2*s* and 2*p* orbitals formed the active space while in the MRCI calculations the 2*s* orbitals were inactive and the 2*p* 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 2*p* orbitals. With the 2*s* 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. [23] this is compensated by the inclusion of the multireference Davidson correction (MRCI + Q).

Some spectroscopic constants obtained with the MRCI and CASPT2[0] methods for the three lowest-lying states of N_2 have already been reported [12]. In that work the equilibrium bond distance (r_e) and the harmonic vibrational frequency (w_e) were obtained by a fit to a second-degree polynomial in $1/R$ using three points with 0.05 a.u. separation. These results are included in Table 6. The results for the two excited states are unsatisfactory at the CASPT2[0] level of theory. As a matter of fact it is the appearance of singularities close to equilibrium that deteriorates the potential curves giving in particular erroneous values of w_e.

The CASSCF and CASPT2 calculations were repeated, now with the g_1 correction added to the Fock matrix. Many more points on the potential surface were calculated for an accurate determination of the spectroscopic constants. The results are exposed in Table 6. With the g_1 correction there are no singularities in

Table 6. Spectroscopic constants for N_2 with an ANO(5*s*4*p*3*d*2*f*) basis set. A comparison between CASPT2, MRCI, and experiment

Method[a]	r_e (Å)	D_e (eV)	w_e (cm^{-1})	$w_e\chi_e$ (cm^{-1})	B_e (cm^{-1})
$X^1\Sigma_g^+$, the ground state					
CASSCF	1.105	9.192	2336	12.82	1.974
CASPT2[0]	1.103	9.224	2306		
CASPT2[g_1]	1.102	9.618	2332	13.25	1.981
MRCI + Q	1.104	9.504	2308		
Expt.[b]	1.098	9.905	2359	14.32	1.998
$A^3\Sigma_u^+$, the first excited state					
CASSCF	1.302	2.760	1416	13.97	1.420
CASPT2[0]	1.281	3.331	3867		
CASPT2[g_1]	1.291	3.540	1445	14.00	1.444
MRCI + Q	1.296	3.456	1426		
Expt.[b]	1.287	3.680	1461	13.87	1.455
$B^3\Pi_g$, the second excited state					
CASSCF	1.230	3.974	1679	14.14	1.593
CASPT2[0]	1.206	4.601	2294		
CASPT2[g_1]	1.214	5.059	1732	14.16	1.632
MRCI + Q	1.222	4.879	1710		
Expt.[b]	1.213	4.896	1733	14.12	1.637

[a] The 2*s* orbitals are active in the CASSCF and CASPT2 calculations and inactive in the MRCI + Q calculations

[b] Experimental data from Ref. [26]

Table 7. Excitation energies T_e between the three lowest-lying states of N_2 obtained with an ANO(5*s*4*p*3*d*2*f*) basis set. A comparison between CASPT2, MRCI, and experiment

Method[a]	Energy (a.u.)			$A^3\Sigma_u^+ - X^1\Sigma_g^+$ (eV)	$B^3\Pi_g - X^1\Sigma_g^+$ (eV)
	$X^1\Sigma_g^+$	$A^3\Sigma_u^+$	$B^3\Pi_g$		
CASSCF	− 109.139354	− 108.902978	− 108.842695	6.43	8.07
CASPT2[0]	− 109.372697	− 109.155799	− 109.112911	5.90	7.07
CASPT2[g_1]	− 109.372379	− 109.149013	− 109.112482	6.08	7.07
MRCI + Q	− 109.396080	− 109.173691	− 109.135436	6.05	7.09
Expt.[b]	—	—	—	6.22	7.39

[a] The 2*s* orbitals are active in the CASSCF and CASPT2 calculations and inactive in the MRCI + Q calculations

[b] Experimental data from Ref. [26]

the potential curve for any of the three states. The harmonic frequencies are in a very good agreement with experimental results and also with those obtained with the MRCI method. Also an improvement of the equilibrium bond distances is achieved with g_1 added to the Fock matrix, especially for the two excited states. The great improvement of the r_e and w_e values due to g_1 for the excited states can be explained by the removal of singularities. With no singularities present, as for the ground state, the impact of g_1 is less. The dissociation energy (D_e) is the parameter that should be most affected by g_1. CASPT2[0] underestimates the dissociation energy with between 0.12 and 0.28 eV and CASPT2[g_1] overestimates it with between 0.08 and 0.18 eV compared to MRCI. This is in accordance with the results obtained for N_2, NO, and O_2 with a smaller basis set. With a correction to the Fock matrix, CASPT2 thus has a tendency to overestimate dissociation energies when compared to more accurate methods like FCI and MRCI. Compared to experimental data, CASPT2[0] underestimates the dissociation energy for the three lowest-lying states of N_2 with between 0.30 and 0.68 eV. The errors at the CASPT2[g_1] level of theory is between − 0.16 and 0.29 eV, and D_e for the two lowest-lying states is underestimated. This is due to the deficiency of the basis set. The molecule requires a larger basis set at equilibrium than at infinite separation for saturated values of the total energy. In conclusion, in many cases one can expect the largest basis set errors at equilibrium distances and the largest errors due to deficiencies of the CASPT2 method at infinite distances. These two sources of errors may sometimes cancel each other to give accurate values of the dissociation energy. We will return to this point in the next subsection.

As an outcome of the calculations the excitation energies (T_e) between the three lowest-lying states of N_2 can be determined. The results are presented in Table 7. The excitation energies obtained with CASPT2[g_1] are in almost complete accordance with the MRCI values. The CASPT2[0] values are included in Table 7 even though a comparison with other methods is questionable because of the deterioration of the potential curves of the two excited states.

3.7 Dissociation energies for some benchmark molecules

The dissociation energies obtained with CASPT2[0] of a large number of molecules containing first-row atoms have already been reported [15]. These molecules were originally included in a systematic test by Pople and co-workers of their Gaussian-1 (G1) theory [24]. With CASPT2[0] large errors of the dissociation energy are expected, especially when the difference of the number of electron pairs in the molecule and in its fragments differ. A typical example is the N_2 molecule where the difference in pairs is three and the error of the dissociation energy is 17.8 kcal/mol compared to the experiment.

The calculations were repeated for some of the molecules, now with the g_1 correction added to the Fock matrix. The results are presented in Table 8 together with those obtained with CASPT2[0] for comparison. ANO type basis sets of the size (Li-F, $5s4p3d2f$) and (H,$3s2p1d$) were used. The core orbitals were uncorrelated and the active spaces were formed by the hydrogen $1s$ orbital, the Li–C $2s$ and $2p$ orbitals, and the N–F $2p$ orbitals. Other computational details can be found in Ref. [15].

Although the number of molecules in this test is small one can conclude that the error of the dissociation energy compared to experiment is independent of the difference of the number of electron pairs in the molecule and in the atoms. We seem to have removed the systematic error proportional to this difference but we have not removed all errors. We still have errors due to deficiencies of the basis sets which usually lead to underestimated dissociation energies and errors due to the quality of the CASSCF wave function which usually lead to overestimated values. O_2 is a typical example of this last source of errors.

There is something else of interest to notice from Table 8. First, when the difference in the number of electron pairs is zero the errors with CASPT2[0] and CASPT2[g_1] are similar as one would expect them to be. Second, also for the H_2, LiH, and Li_2 molecules the errors are similar for the two methods even though the difference of the number of electron pairs is one. This is due to the fact that at infinite separation the CASSCF wave function is the exact wave function for the given basis set and at equilibrium distances these three molecules are closed-shell species giving minor differences between CASPT2[0] and CASPT2[g_1].

The most annoying result in Table 8 is the highly overestimated result of the dissociation energy of O_2. However, it is in accordance with the result obtained in Sect. 3.5. A doubling of the active space brings the error to a reasonable size, namely -0.1 kcal/mol. CASPT2[0], on the other hand, underestimates the value by 5.4 kcal/mol compared to the experiment with the enlarged active space.

In addition to the dissociation energies we obtained the equilibrium bond distances in these calculations. As in Sect. 3.5 they are modified by only a few thousands of an Ångström when going from CASPT2[0] to CASPT2[g_1]. Usually, the geometries are slightly improved with CASPT2[g_1].

4 Conclusions

A new one-particle zeroth-order Hamiltonian is proposed for a perturbation theory with a CASSCF reference wave function. The new partitioning of the Hamiltonian is designed to treat reference functions dominated by a closed-shell configuration, on the one hand, and an open-shell configuration, on the other hand, in similar and balanced ways. This leads to better descriptions of excitation energies and dissociation energies. Since these are the properties that are mostly affected by the new partitioning they have been extensively studied in this article. Excitation energies are considerably improved by the new partitioning while dissociation energies are in general improved but in some cases overestimated. The

Table 8. Dissociation energies (in kcal/mol) for some benchmark molecules. A comparison between CASPT2 and experiment

Molecule	CASSCF	CASPT2[0]	CASPT2[g_1]	Expt.[a]	Error[0][b]	Error[g_1][c]	Pairs[d]
BeH ($X^2\Sigma^+$)	44.1	46.9	46.7	46.9	0.0	0.2	0
BeH ($^2\Pi$)[e]	39.3	49.4	50.1	52.5	3.1	2.4	0
H_2 ($X^1\Sigma_g^+$)	89.2	99.8	99.8	103.3	3.5	3.5	1
LiH ($X^1\Sigma^+$)	53.2	54.6	54.6	56.0	1.4	1.4	1
Li_2 ($X^1\Sigma_g^+$)	23.3	23.5	23.5	24.0	0.5	0.5	1
LiF ($X^1\Sigma^+$)	121.3	132.6	132.9	137.6	5.0	4.7	1
NH ($X^3\Sigma^-$)	58.5	73.2	74.5	79.0	5.8	4.5	1
OH ($^2\Pi$)[e]	78.9	97.7	99.0	101.3	3.6	2.3	1
HF ($X^1\Sigma^+$)	108.9	132.7	134.2	135.2	2.5	1.0	1
F_2 ($X^1\Sigma_g^+$)	16.2	34.5	37.2	36.9	2.4	− 0.3	1
O_2 ($X^3\Sigma_g^-$)	88.7	114.0	124.5	118.0	4.0	− 6.5	1
NO ($^2\Pi$)[e]	117.8	139.9[f]	151.6	150.1	10.2[f]	− 1.5	2
CN ($X^2\Sigma^+$)	156.7	165.1	171.7	176.6	11.5	4.9	2
CO ($X^1\Sigma^+$)	246.0	244.2	250.0	255.8	11.6	5.8	2
N_2 ($X^1\Sigma_g^+$)	201.0	207.3	216.5	225.1	17.8	8.6	3
CO_2	348.1	365.5	381.5	381.9	16.4	0.4	3

[a] Experimental data from Ref. [15]

[b] Difference between the experimental value and the CASPT2[0] result

[c] Difference between the experimental value and the CASPT2[g_1] result

[d] Difference between the number of electron pairs in the molecule and in the atoms

[e] The π_x and π_y orbitals were restricted to be identical

[f] Singularity in the potential curve

computed excitation energies for the CH_2, SiH_2, NH_2, and N_2 molecules compare very well with corresponding FCI and MRCI values. In most cases studied the errors are well below 1 kcal/mol.

The dissociation energies, on the other hand, have a tendency to be overestimated in the new treatment when compared to other more accurate methods. However, basis set deficiencies usually will lead to underestimated values of the dissociation energies when compared to experimental data. In a test comprising 15 molecules we were able to show that the error in dissociation energy compared to experiment no longer is proportional to the difference between the number of electron pairs in the molecule and in the atoms. A nice illustration of this is the CO_2 molecule where the difference between the number of electron pairs is three and CASPT2[0] gives an error of 16.4 kcal/mol. With the new zeroth-order Hamiltonian the error is brought down to 0.4 kcal/mol. We seem to have removed the systematic error described above but we certainly have not removed all errors. In our test of 15 molecules the error is within ± 10 kcal/mol. Previously the error was between 0 and 20 kcal/mol.

The main effect of the new partitioning of the Hamiltonian can be summarized as an enlargement of the energy gap between the active and secondary orbitals. The enlargement is small for CASSCF wave functions dominated by a closed-shell configuration. For many systems, like the two lowest-lying excited states of N_2, the increment of the energy gap causes singularities in the potential curves to disappear. The same phenomenon has been noticed for the chromium dimer. While the potential curve computed with CASPT2[0] is cluttered with singularities, the one obtained with CASPT2[g_1] only contains a few of them. These findings will be reported elsewhere [25]. However, an enlargement of the energy gap between the active and secondary orbitals is not always beneficial. If inactive orbitals high in energy are present then the decreased energy gap between them and the active orbitals may lead to the introduction of new singularities. This has actually been observed in test calculations on the CrF_6 molecule. The zeroth-order Hamiltonian introduced here therefore does not constitute the ultimate choice of a zeroth-order Hamiltonian in multiconfigurational second-order perturbation theory. But the operator presented here has the advantage of being simple in structure and causes only minor modifications of our present computer implementation of CASPT2.

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