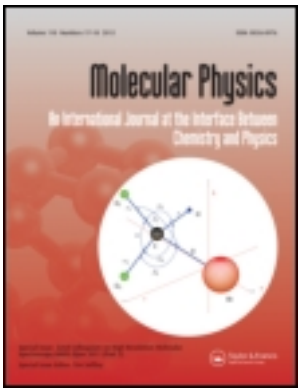
This article was downloaded by: [University Of Pittsburgh]
On: 02 August 2013, At: 06:46
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Physics: An International Journal at the Interface Between Chemistry and Physics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tmph20

Third-order multireference perturbation theory The CASPT3 method

HANS-JOACHIM WERNER

Published online: 03 Dec 2010.

To cite this article: HANS-JOACHIM WERNER (1996) Third-order multireference perturbation theory The CASPT3 method, Molecular Physics: An International Journal at the Interface Between Chemistry and Physics, 89:2, 645-661

To link to this article: http://dx.doi.org/10.1080/002689796173967

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused

arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

MOLECULAR PHYSICS, 1996, VOL. 89, NO. 2, 645–661

Third-order multireference perturbation theory The CASPT3 method

By HANS-JOACHIM WERNER
Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

(*Received 13 January 1996; accepted 22 February 1996*)

Rayleigh–Schrödinger perturbation theory is applied to compute second and third-order correlation energies using complete active space self-consistent field (CASSCF) zeroth-order wavefunctions. The first-order wavefunction is expanded in a basis of internally contracted configurations. The zeroth-order Hamiltonian is a sum of one-electron effective Fock operators, which are invariant to unitary transformations among the active orbitals. Comparisons with FCI data are made for the singlet–triplet splitting of CH_2 and the barrier height and exothermicity of the $F + H_2$ reaction. Potential energy functions and spectroscopic data are computed for C_2, CN, CO, CF, N_2, NO, O_2, and F_2 using large basis sets. It is demonstrated that the third-order results (CASPT3) are significantly more accurate than the second-order (CASPT2) ones. The equilibrium distances and harmonic frequencies obtained with CASPT3 are found to be as accurate as MRCI and RCCSD(T) values, while dissociation energies are generally somewhat too small. Modifications of the zeroth-order Hamiltonian as recently proposed by Andersson are found to have a much smaller effect on the third-order energies than on the second-order ones.

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

1. Introduction

One of the simplest and most popular methods for treating electron correlation effects is second-order Møller–Plesset perturbation theory (MP2) [1]. This works quite well for non-degenerate ground states of closed-shell molecules, but in its simplest form it is restricted to closed-shell single determinant reference functions. Open-shell cases can be treated most easily with UHF reference functions [2, 3], but then often suffer from spin-contamination problems [4–7]. More recently, various spin-adapted open-shell Møller–Plesset perturbation theories have been developed [8–18]. The application of such methods is limited to cases in which the wavefunction is strongly dominated by a single configuration. Problems may arise in the case of near degeneracies or in the presence of low lying excited states, which may lead to poor convergence or even divergence of the Møller–Plesset perturbation expansion [6, 9, 10, 14, 17].

It is therefore generally desirable to generalize Møller–Plesset perturbation theory to multiconfiguration reference functions, which are properly spin adapted and account for strong non-dynamical correlation effects. Many variants of quasi-degenerate multireference perturbation theory [19–26] have been proposed in the past, but the success of such methods has been quite limited. This is due to the difficulty of practical implementation, and also to the so called intruder-state problem, which causes singularities when one or more reference states become (nearly) degenerate with a state in the complementary configuration space.

A simpler approach has been suggested in 1982 by Roos *et al.* [27]. They used a

0026–8976/96 $12·00 © 1996 Taylor & Francis Ltd

CASSCF wavefunction as zeroth-order approximation, and expanded the first-order wavefunction in the space of internally contracted configurations [28–32], which are obtained by applying spin-coupled single and double excitation operators to the complete CASSCF reference function. From the first-order wavefunction the second-order correlation energy was computed. The complete set of singly and doubly excited internally contracted configurations spans exactly the first-order interacting space [28], but in the original work of Roos *et al.* [27] only double excitations with two electrons in external (secondary) orbitals have been considered. The zeroth-order Hamiltonian was constructed from an averaged Fock-matrix and assumed to be diagonal in the configuration space. In 1987, Wolinski and Pulay [33, 34] developed a generalized Møller–Plesset perturbation (GMP) theory which is similar to the method of Roos *et al.* [27], but also included the important semi-internal and internal configuration spaces. A non-diagonal zeroth-order Hamiltonian was used, and the first-order wavefunction was obtained by solving a linear set of equations. Their implementation was restricted to cases with two reference determinants and was called GMP2 (generalized second-order Møller–Plesset perturbation theory). Third-order energies (GMP3) were computed for some two-electron systems [33]. In 1990, Andersson *et al.* [35] generalized the earlier method of Roos *et al.* [27] by also including the internal and semi-internal configuration spaces using CASSCF reference functions. Initially, a diagonal zeroth-order Hamiltonian was employed, but this restriction was lifted at a later stage [36]. Their method has become well known as CASPT2 and has been successfully used in many applications.

It has even recently been argued [37] that non-diagonal zeroth-order Hamiltonians are disadvantageous, since very large sets of linear equations must be solved. This is not quite so, however. Firstly, the equations can easily be solved iteratively in a direct way, and the cost for each iteration is low since only one-electron matrix elements are required. Secondly, the zeroth-order Hamiltonian can be brought to a sparse block-diagonal form (see section 2), which makes convergence very fast (5–10 iterations). A major advantage of using a non-diagonal operator is that it only depends on the density of the reference wavefunction and is invariant to unitary transformations among certain orbital subsets. This applies to the inactive, active or virtual subspaces when complete active space (CASSCF) reference functions are used. Therefore, also the second-order and higher-order energies are invariant with respect to such transformations. Serious problems can occur when such invariance properties are not fulfilled, in particular for cases with degenerate open-shell orbitals [38, 39].

Even though the CASPT2 method of Roos *et al.* [27, 35, 36] and the GMP2 method of Wolinski and Pulay [33, 34] are not considered as degenerate perturbation theories, they allow the treatment of molecules and states for which the wavefunction is dominated by several configurations. This makes it possible to describe the dissociation of molecular bonds correctly and to compute global potential energy surfaces. Murphy and Messmer [40, 41] developed a closely related method, which differs from the GMP2 and CASPT2 methods by expanding the first-order wavefunction in a set of uncontracted configurations. These were obtained by applying excitation operators to each individual reference configuration. Second-order (GMP2) and third-order (GMP3) energies were computed for H_2O, CH_2 [40], N_2, and O_2^{++} [41] using small basis sets. It was found that the third-order corrections are in some cases quite sizeable, in particular for the singlet-triplet splitting of CH_2. Other second-order multireference perturbation methods, which use uncontracted configurations and diagonal zeroth-order Hamiltonians, have been proposed by Hirao

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

[42–44] and Kozlowski and Davidson [37, 45, 46]. The disadvantage of using uncontracted configurations is that the size of the configuration space increases strongly with the number of reference configurations. On the other hand, the internally contracted configurations as used in [33–36] are non-orthogonal and have a very complicated structure. Orthogonalization is necessary at least at an intermediate stage and may be difficult for the internal- and semi-internal configurations, since in these cases the overlap matrices may become very large.

In the present work we use a compromise of both methods, which appears to be computationally most efficient. The doubly external configurations, which represent the largest part of the configuration space but are easily orthogonalized [30–32], are internally contracted. On the other hand, the internal and semi-internal configuration spaces are left uncontracted. The same strategy is used in our internally contracted MRCI program [32, 47], which forms the basis for the present implementation. Our method is applicable to arbitrary MCSCF reference wavefunctions and allows the computation of second-order (GMP2) and third-order (GMP3) energies. For the case in which CASSCF reference functions are used, as is the case for all applications presented in this paper, the method is denoted CASPT3. With a single closed-shell reference determinant, the method reduces to standard MP3. In section 2 we will define our first-order wavefunction and zeroth-order Hamiltonian. The method has been applied to the calculation of spectroscopic properties of a number of diatomic molecules using large basis sets. In section 3 we will compare the CASPT2 and CASPT3 results to MRCI (multireference configuration interaction) and MR-ACPF (multireference averaged coupled pair functional) [48, 49] calculations performed with exactly the same one-electron and many-electron basis sets. It will be demonstrated that the third-order results obtained with CASSCF reference functions are significantly more accurate than the second-order ones. The equilibrium distances and harmonic frequencies obtained with CASPT3 are found to be as accurate as MRCI and CCSD(T) (coupled-cluster with perturbative corrections for triple excitations) values.

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

2. Theory

As is usual practice, we partition the orbital space into *closed-shell* (inactive), *active*, and *external* (secondary) orbitals according to their occupancies in the reference wavefunction. External orbitals are unoccupied and closed-shell orbitals are doubly occupied in all reference configurations, while all kinds of excitations are allowed within the active space. In all calculations reported in this paper, we use complete active space (CAS) reference functions, even though our method is not restricted to this case. The inactive and active orbitals together form the *internal* orbital space and are denoted by indices $i, j, k \ldots$. External orbitals are denoted by the indices $a, b, c \ldots$, and any orbitals by $r, s, t \ldots$

Accordingly, the configuration space can be partitioned into *internal* configurations $|I\rangle \equiv \Phi_I$, singly external configurations $|S^a\rangle \equiv \Phi_S^a$, and doubly external configurations $|P^{ab}\rangle \equiv \Phi_P^{ab}$, where S and P denote N-1 and N-2 electron hole states, respectively, in the internal space. The reference configurations $|R\rangle \equiv \Phi_R$ form a subset of the internal configuration space. The N-2 electron configurations P are obtained by annihilation of two electrons from any of the reference configurations. Subsequently, the N-1 electron configurations S are generated by adding one electron to an internal orbital of the P configurations. The internal single and double

excitations Φ_I are finally obtained by adding one electron to the S configurations. All possible spin couplings for each orbital occupancy are included.

For the multireference perturbation treatment, it appears natural to include in the first-order wavefunction only configurations which interact directly with the reference function via the complete Hamiltonian. As has been shown by Meyer [28], the interacting space is *exactly* spanned by a linearly independent subset of the *internally contracted* configurations $\Phi_{su}^{tt} = E_{rs}E_{tu}|0\rangle$, where

$$|0\rangle \equiv \Psi^{(0)} = \sum_R c_R^{(0)}|R\rangle \tag{1}$$

is the normalized reference wavefunction and $\hat{E}_{rs}$ are the usual spin-coupled one-particle excitation operators. The internally contracted configurations can be expressed as linear combinations of uncontracted CSFs with the same external but different internal parts. For a given number of correlated orbitals, the number of contracted functions is independent of the number of reference configurations, and for cases with many reference configurations much smaller than the complete set of uncontracted CSFs [28–32]. Efficient internally contracted MRCI methods have been developed by the present author together with Reinsch [30] and Knowles [32, 47, 49, 50]. It has been shown in numerous applications of these methods that the internal contraction has very little effect on the results, but significantly reduces the computational effort and the storage requirements. In the context of multireference perturbation theory, internally contracted configurations have been used by Roos *et al.* [27], Wolinski and Pulay [33, 34], Andersson *et al.* [35, 36], and Dyall [51].

A complication arises from the fact that the contracted configurations are in general non-orthogonal and may also be linearly dependent [28–32]. Defining the doubly external configurations as

$$\Phi_{ijp}^{ab} = \tfrac{1}{2}(\hat{E}_{ai}\hat{E}_{bj} + p\hat{E}_{bi}\hat{E}_{aj})|0\rangle \text{ with } i \geqslant j,\ a \geqslant b,\ p = \pm 1, \tag{2}$$

where $p = \pm 1$ denotes singlet and triplet coupling, respectively, of the external electrons, the overlap is determined by the second-order density matrix of the reference function [30–32]

$$S_{ij,kl}^{(p)} = \langle 0|\hat{E}_{ik,jl} + p\hat{E}_{il,jk}|0\rangle. \tag{3}$$

An orthogonal set of doubly external configurations $|D^{ab,p}\rangle$ can be obtained, for example, by symmetrical orthogonalization

$$|D^{ab,p}\rangle = \sum_{i \geqslant j} |\Phi_{ijp}^{ab}\rangle T_{ij,D}^{(p)} \tag{4}$$

with $\mathbf{T}^{(p)} = [\mathbf{S}^{(p)}]^{-1/2}$. If the matrix $\mathbf{S}^{(p)}$ has zero or very small eigenvalues, a corresponding number of redundant pairs (ijp) is eliminated. It should be noted that the $|D^{ab,p}\rangle$ are not normalized [31, 32].

The orthogonalization procedure is less simple for the contracted internal and singly external configurations, since then the overlap matrices depend on the third- and fourth-order density matrices and may become very large. Therefore, as in our internally contracted MRCI method [32, 49, 50], but different from the GMP2 method of Wolinski and Pulay [34] and the CASPT2 method of Andersson *et al.* [35, 36], we decided to use uncontracted functions for the internal and singly external configuration

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

spaces. This avoids the orthogonalization problem and simplifies the calculation of the Hamiltonian matrix elements, but may introduce contributions of CSFs in the first-order wavefunction that do not interact directly with the reference function. As a consequence, the second- and third-order energies are not exactly identical to the ones which would be obtained using the contracted configuration space. However, as will be demonstrated in section 3, the differences are usually very small and are not expected to have any significant effect on practical applications.

In the Rayleigh–Schrödinger perturbational treatment, the reference wavefunction $|0\rangle \equiv \Psi^{(0)}$ is taken as zeroth-order wavefunction, and the first-order wavefunction is expanded as

$$\Psi^{(1)} = \sum_{I \neq R} c_I^{(1)} |I\rangle + \sum_S \sum_a c_a^S |S^a\rangle + \sum_D \sum_p \sum_{a \geq b} C_{ab}^{Dp} |D^{ab,p}\rangle, \quad (5)$$

with $C_{ab}^{Dp} = pC_{ba}^{Dp}$. Since the reference wavefunction is an eigenfunction of $\hat{H}$ in the space of all reference configurations, the latter do not interact with the reference, i.e., $\langle R|H - E_0|0\rangle = 0$, and are therefore normally excluded from the first-order wavefunction. Small higher-order contributions to the reference configurations can arise, however, via their coupling with the other internal and singly external configurations. Optionally, they can therefore be included, and then the orthogonality restriction,

$$\langle \Psi^{(1)} | \Psi^{(0)} \rangle = \sum_R c_R^{(0)} c_R^{(1)} = 0, \quad (6)$$

must be fulfilled. In all test calculations performed so far we found that inclusion of the reference configurations in the first-order wavefunction leads only to negligible changes of the energies and potential energy functions.

The zeroth-order Hamiltonian is chosen to be

$$\hat{H}^{(0)} = \hat{P}\hat{F}\hat{P} + \hat{Q}\hat{F}\hat{Q}, \quad (7)$$

where the N-electron operator,

$$\hat{F} = \sum_{rs} f_{rs} \hat{E}_{rs} \quad (8)$$

is constructed from an effective one electron Fock matrix $\mathbf{f}$ with elements

$$f_{rs} = h_{rs} + \sum_{ij} \langle 0|\hat{E}_{ij}|0\rangle \left[(rs|ij) - \frac{1}{2}(ri|js) \right]. \quad (9)$$

The operators $\hat{P} = |0\rangle\langle 0|$ and $\hat{Q} = 1 - \hat{P}$ project onto the reference wavefunction and its orthogonal complement within the space of all configurations defined above. Due to this simple construction, the reference function $\Psi^{(0)}$ is an eigenfunction of $H^{(0)}$ with eigenvalue $E^{(0)} = \langle 0|F|0\rangle$. The zeroth-order Hamiltonian $H^{(0)}$ is invariant with respect to unitary transformations among the active or inactive orbitals of a CASSCF reference function, and therefore the same is true for the CASPT2 and CASPT3 energies. For the case of closed-shell single reference functions, $\mathbf{f}$ becomes identical to the closed-shell Fock matrix, and the method reduces to ordinary Møller–Plesset perturbation theory.

Similar zeroth-order Hamiltonians have been used by Wolinski and Pulay [33, 34], Andersson *et al.* [35, 36], and Murphy and Messmer [40, 41, 52]. They all used the

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

same operator $\hat{F}$, but somewhat different choices of projection operators. Wolinski and Pulay have neglected all couplings between the single and double excitations, i.e., the zeroth-order Hamiltonian was written as

$$\hat{H}^{(0)} = \hat{P}\hat{F}\hat{P} + \hat{Q}_S\hat{F}\hat{Q}_S + \hat{Q}_D\hat{F}\hat{Q}_D \tag{10}$$

where $\hat{Q}_S$ and $\hat{Q}_D$ project onto the subspaces of single and double excitations, respectively. The coupling between singles and doubles was also absent in the original CASPT2 method of Andersson *et al.* [35] (later denoted CASPT2D [36]), since the off-diagonal elements of $\mathbf{f}$ (in a pseudo-canonical basis) were neglected. Later the off-diagonal blocks were added, leading to the CASPT2N version [36]. A further minor difference concerns the orthogonal complement of the reference wavefunction in the subspace of all reference CSFs. Since this space does not interact directly with the reference function it has been explicitly excluded from the first-order wavefunction by Andersson *et al.* [35, 36]. As discussed above, we normally exclude this configuration space as well. In their GMP2 method, Wolinski and Pulay have included all internally contracted internal configurations $E_{ij}|0\rangle$ and $E_{ij}E_{kl}|0\rangle$ (orthogonalized on $|0\rangle$ and among themselves), while Murphy and Messmer [40] used an uncontracted configuration space obtained by applying these operators to each individual reference configuration, with exclusion of configurations contained in the reference set.

Other forms of the zeroth-order Hamiltonian have been discussed extensively in the literature [37, 42–46, 51, 53]. In many of these methods, correction terms are added to the one-electron Fock operator (equation (9)), with the aim of improving the convergence of the perturbation expansion in open-shell cases. Here we consider only the modifications recently proposed by Andersson [53], which were denoted by g_1, g_2, and g_3. These have the effect of enlarging the energy gap between the active and virtual orbitals, in particular for states with many open shells. It was demonstrated for several examples that these modifications may lead to improved CASPT2 results. We coded all three versions and will present third-order (CASPT3) results in section 3. It will be shown that the third-order results are much less sensitive to the choice of $\hat{H}^{(0)}$ than the second-order ones.

The coefficients of the first-order wavefunction are obtained by solving the set of linear equations

$$r_I = \langle I|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle + \langle I|\hat{H} - E_0|0\rangle = 0, \tag{11}$$

$$r_a^S = \langle S^a|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle + \langle S^a|\hat{H}|0\rangle = 0, \tag{12}$$

$$R_{ab}^{Dp} = \langle D^{ab,p}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle + \langle D^{ab,p}|\hat{H}|0\rangle = 0, \tag{13}$$

subject to the auxiliary condition (6) (which is automatically fulfilled if the reference configurations are excluded from the first-order wavefunction). The reference energy E_0 and the second and third-order correlation energies are given by

$$E_0 = E^{(0)} + E^{(1)} = \langle\Psi^{(0)}|\hat{H}|\Psi^{(0)}\rangle, \tag{14}$$

$$E_{\text{corr}}^{(2)} = \langle\Psi^{(1)}|\hat{H}|\Psi^{(0)}\rangle, \tag{15}$$

$$E_{\text{corr}}^{(3)} = \langle\Psi^{(0)} + \Psi^{(1)}|\hat{H} - E_0|\Psi^{(0)} + \Psi^{(1)}\rangle. \tag{16}$$

The linear equations (11)–(13) are solved iteratively using the Gauss–Seidel procedure. Convergence can be improved, for example, by DIIS (direct inversion of the iterative subspace) [54]. In each iteration, the residuals r_I, r_a^S, and R_{ab}^{Dp} must be computed. The explicit expressions of these quantities are quite simple and can easily be obtained from the corresponding MRCI equations given by Werner and Knowles [32]. Only a few

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

additional remarks will be made here. In matrix notation, the internal–internal, single–single, and pair–pair contributions in equations (11)–(13) are given by

$$r_I = \sum_{ij} f_{ij} \sum_{I'} \langle I|\hat{E}_{ij}|I'\rangle c_{I'}^{(1)} + \ldots, \tag{17}$$

$$\mathbf{r}^S = \mathbf{f}\cdot\mathbf{c}^S + \sum_{ij} f_{ij} \sum_{S'} \langle S|\hat{E}_{ij}|S'\rangle \mathbf{c}^{S'} + \ldots, \tag{18}$$

$$\mathbf{R}^{Dp} = \mathbf{f}\cdot\mathbf{C}^{Dp} + \sum_{D'} \gamma^{(p)}_{D,D'} \mathbf{C}^{D'p} + \ldots. \tag{19}$$

The matrices $\mathbf{f}$, $\mathbf{R}^{Dp}$, $\mathbf{C}^{Dp}$ and vectors $\mathbf{r}^S$, $\mathbf{c}^S$ are defined in the external orbital subspace only. Since the energy is invariant with respect to unitary transformations in the external space, the external orbitals can be chosen such that $\mathbf{f}$ is diagonal. If a complete active space reference is used, one can also diagonalize the active–active and inactive–inactive parts of the Fock matrix f_{ij}. Thus, if both i and j refer to either active or inactive orbitals, only diagonal contributions $i = j$, $I = I'$, and $S' = S$ will survive in equations (17) and (18). Furthermore, the matrix,

$$\gamma^{(p)}_{D,D'} = \sum_{i\geqslant j} T^{(p)}_{ij,D} \sum_{k\geqslant l} T^{(p)}_{kl,D'} \sum_{mn} f_{mn} \langle 0|\hat{E}_{ik,jl,mn} + p\hat{E}_{jk,il,mn}|0\rangle, \tag{20}$$

can be precomputed and diagonalized (separately for each p). Then a new set of orthogonal doubly external configurations can be defined by

$$[\mathbf{U}^{(p)\dagger}\boldsymbol{\gamma}^{(p)}\mathbf{U}^{(p)}]_{D,D'} = \delta_{D,D'}\tilde{\gamma}_D \tag{21}$$

$$\tilde{\mathbf{T}}^{(p)} = \mathbf{T}^{(p)}\cdot\mathbf{U}^{(p)}, \tag{22}$$

$$|\tilde{D}^{ab,p}\rangle = \sum_{i\geqslant j} |\Phi^{ab}_{ijp}\rangle \tilde{T}^{(p)}_{ij,D} \tag{23}$$

which also makes the pair-pair block $\langle \tilde{D}^{ab,p}|\hat{H}^{(0)}|\tilde{D}'^{cd,q}\rangle$ diagonal. These block diagonalizations not only reduce the computational effort, but also considerably speed up the convergence. A similar blocking technique has been used by Andersson *et al.* [36]. It should be noted, however, that our program is completely general and does neither require CASSCF reference functions, nor a block diagonal Fock matrix.

In order to compute the third-order energy, it is necessary to evaluate the matrix element $\langle \Psi^{(1)}|H|\Psi^{(1)}\rangle$. Since the off-diagonal blocks need to be computed only once, the computational effort is somewhat less than for one iteration of the MRCI. The explicit expressions needed can be found in reference [32]. An efficient method of evaluating the coupling coefficients and density matrices has been described in reference [47].

3. Applications

The method described in the previous section has been implemented into the MOLPRO [55] package of *ab initio* programs by modifying the existing MRCI code [32, 47]. In this section we present some preliminary applications and investigate the accuracy of the second-order and third-order energies by comparison with full configuration interaction (FCI) and MRCI results.

As a first test, we computed energies of the lowest $^1A_1$ and $^3B_1$ states of CH_2 using a double-zeta plus polarization (DZP) basis set, for which the FCI results of Bauschlicher and Taylor [56] are available. Using the same basis set, Andersson *et al.* [36, 53] performed CASPT2 calculations with various different active reference spaces.

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

They found that the CASPT2 with full-valence CASSCF reference functions give a singlet-triplet splitting that is almost 4 kcal mol^{-1} larger than the FCI result. The CASPT2 excitation energy converged only rather slowly to the FCI result when the reference space was increased. Messmer and Murphy [40] have carried out GMP2 and GMP3 calculations using the full valence reference spaces, and found that the third-order contribution reduces the splitting by almost 3 kcal mol^{-1}, bringing it into much better agreement with the FCI value. In table 1 our results are compared to the previous calculations. First we notice that for all active spaces our CASPT2 energies are very close to the ones of Andersson *et al.* [36, 53], despite the fact that we use a partly uncontracted basis. As expected, our CASPT2 energies are slightly lower than the CASPT2N values of reference [36], but not as low as the GMP2 energies of Messmer and Murphy [40], who used a completely uncontracted basis. Somewhat unexpectedly, our third-order energies are lower than the GMP3 values. This might be due to contributions of the non-interacting spin-couplings of singly external configurations, which are included in our calculation but not in the GMP3. Nevertheless, the computed GMP3 and CASPT3 energy splittings are in close agreement.

We have also performed calculations using various larger reference spaces. It is found that the CASPT3 energies and energy splittings converge towards the FCI results considerably faster than the CASPT2 ones, but more slowly than the MRCI values. The best CASPT3 values (obtained with up to 9786 reference CSFs) are within about 1 mH of the FCI energies, and in no case are the CASPT2 or CASPT3 energies lower than the FCI energies. Surprisingly, this was the case for a calculation with a diagonal $H^{(0)}$ in [40], but not in the corresponding CASPT2D calculation of [36].

Recently, Andersson [53] has proposed three different modifications (denoted g_1, g_2, and g_3) of the zeroth-order Hamiltonian, which considerably improved the CASPT2 energy splittings. We have carried out CASPT3 calculations with these modified Hamiltonians using the same active spaces as in [53]. Our computed CASPT2 energy splittings agree with the ones given in [53] within 0·01 kcal mol^{-1} for all three versions and all active spaces. The CASPT3(g_i) (i = 1–3) differ by only 0·02–0·05 kcal mol^{-1}, and therefore only results for the g_1 version are presented in table 1. It is found that the CASPT3(g_1) energy splittings are in better agreement with the FCI values than the ones obtained without the modification, but the effect is much smaller than in second order. For instance, for the smallest active space the g_1 operator reduces the second-order energy splitting by 2·2 kcal mol^{-1}, while in third-order the effect is only 0·4 kcal mol. Calculations for CH_2 with other zeroth-order Hamiltonians have been performed by Hirao [43], Kozlowski and Davidson [46, 37], and Dyall [51]. The results are quite similar to the present CASPT2(g_1) values and we refer to the literature for a comparison.

Secondly, we have computed potential energy functions for a number of diatomic molecules with quite different electronic structure (open- and closed-shell, single, double and triple bonds). In all cases the correlation consistent valence quadruple zeta (cc-pVQZ) basis sets of Dunning [57] have been used. These include [5s4p3d2f1g] contracted functions for the first-row atoms. For N_2, F_2, and O_2 additional calculations with the quintuple zeta basis sets (cc-pV5Z, [6s5p4d3f2g1h]) have been performed. Full valence CASSCF reference functions have been used in all cases. For comparison, MRCI and MR-ACPF [48, 49]) calculations with the same basis sets and configuration spaces, as well as spin-restricted single reference coupled cluster (RCCSD(T)) [58, 59] calculations have been carried out. The 1s core orbitals were not correlated. For each

Table 1. Comparison of different correlation treatments[a] for the $^1A_1$ and $^3B_1$ states of CH_2.

Method	Reference	Energy (au) $^1A_1$	Energy (au) $^3B_1$	Exc. Energy (kcal mol^{-1})
Active space (3210)[b]				
CASSCF		−38·945529	−38·965954	12·82
CASPT2		−39·013092	−39·037695	15·44
CASPT2	[36, 53]	−39·013078	−39·037664	15·43
CASPT2(g_1)		−39·012883	−39·033939	13·21
CASPT2(g_1)	[53]	−39·012868	−39·033906	13·20
CASPT3		−39·023374	−39·043766	12·80
CASPT3(g_1)		−39·023397	−39·043155	12·40
GMP2	[40]	−39·01331	−39·03794	15·45
GMP3	[40]	−39·02322	−39·04338	12·65
MRCI		−39·025362	−39·044360	11·92
FCI[c]		−39·027284	−39·046348	11·96
Active space (4220)[b]				
CASSCF[d]		−38·968726	−38·982741	8·79
CASPT2		−39·017120	−39·038707	13·54
CASPT2	[36, 53]	−39·017092	−38·038660	13·53
CASPT2(g_1)		−39·017026	−39·036436	12·18
CASPT2(g_1)	[53]	−39·016998	−39·036392	12·17
CASPT3		−39·024593	−39·044195	12·30
CASPT3(g_1)		−39·024599	−39·043671	11·97
MRCI		−39·026429	−39·045366	11·88
FCI[c]		−39·027284	−39·046355	11·97
Active space (7331)[b]				
CASSCF		−39·007032	−39·025395	11·52
CASPT2		−39·023760	−39·043345	12·29
CASPT2	[53]	−39·023749	−39·043334	12·29
CASPT2(g_1)		−39·023732	−39·043036	12·11
CASPT2(g_1)	[53]	−39·023721	−39·043024	12·11
CASPT3		−39·025954	−39·045359	12·18
CASPT3(g_1)		−39·025951	−39·045299	12·14
MRCI		−39·027223	−39·046303	11·97
FCI[c]		−39·027286	−39·046362	11·97

[a] Basis set and geometries (see [56]).

[b] The numbers in parenthesis are the number of active orbitals in the a_1, b_2, b_1, and a_2 symmetries, respectively. The $1a_1$ orbital is inactive and uncorrelated in all cases.

[c] FCI results obtained with the corresponding CASSCF orbitals. The energies for the different space differ slightly due to different $1a_1$ orbitals, which are not correlated.

[d] In this case a lower CASSCF energy for the $^3B_1$ state could be obtained, depending on the starting orbitals. The given energy corresponds to the one in [36] but is a local minimum.

molecule, energies have been computed for at least 10 geometries, and spectroscopic constants have been obtained from polynomial fits of ninth degree to these points. Variations of the degree or the number of points had virtually no effect on the computed spectroscopic constants. For the multireference methods, dissociation energies have been computed as difference of the energy at a very large distance and

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

Table 2. Spectroscopic constants for closed-shell diatomic molecules[a].

Method	$E(r_e)$ (hartree)	r_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (eV)
$C_2(X^1\Sigma_g^+)$:							
CASPT2	−75·793288	1·2479	1·804	0·0174	1844·9	12·83	6·27
CASPT3	−75·793858	1·2443	1·815	0·0171	1870·0	12·64	6·08
MRCI	−75·794412	1·2469	1·807	0·0173	1851·4	12·80	6·24
MRCI+Q	−75·801903	1·2475	1·805	0·0175	1845·3	13·00	6·18
MRACPF	−75·800260	1·2474	1·806	0·0175	1846·6	12·96	6·19
Experiment		1·2425	1·820	0·0176	1854·7	13·34	6·32
$N_2(X^1\Sigma_g^+)$:							
CASPT2	−109·384689	1·1023	1·982	0·0174	2332·6	14·51	9·37
CASPT3	−109·397249	1·1011	1·986	0·0171	2350·7	14·09	9·59
MRCI	−109·389591	1·1011	1·986	0·0171	2349·5	14·14	9·71
MRCI+Q	−109·403917	1·1021	1·983	0·0172	2341·6	14·23	9·66
MRACPF	−109·401682	1·1019	1·983	0·0172	2342·5	14·22	9·67
Experiment		1·0977	1·998	0·0173	2358·6	14·32	9·90
$CO(X^1\Sigma^+)$:							
CASPT2	−113·164707	1·1328	1·916	0·0176	2151·4	13·45	10·84
CASPT3	−113·178416	1·1322	1·918	0·0173	2161·9	13·15	10·97
MRCI	−113·171903	1·1321	1·919	0·0173	2163·3	13·10	11·13
MRCI+Q	−113·186224	1·1333	1·914	0·0173	2154·5	13·15	11·07
MRACPF	−113·184070	1·1332	1·915	0·0173	2155·4	13·15	11·07
Experiment		1·1283	1·931	0·0175	2169·8	13·29	11·22
$F_2(X^1\Sigma_g^+)$:							
CASPT2	−199·340289	1·4216	0·878	0·0131	888·2	11·54	1·57
CASPT3	−199·343373	1·4118	0·890	0·0135	911·4	12·67	1·43
MRCI	−199·318874	1·4162	0·885	0·0136	892·9	12·43	1·46
MRCI+Q	−199·352133	1·4158	0·885	0·0130	909·5	11·91	1·56
MRACPF	−199·349884	1·4163	0·885	0·0130	908·4	11·82	1·56
Experiment		1·4119	0·890	0·0138	916·6	11·24	1·64

[a] Using basis cc-pVQZ [57].

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

the fitted energy minimum. In the single reference cases, the asymptotic energies have been obtained from separate atomic calculations.

The results for the closed-shell and open-shell molecules are presented in tables 2 and 3 respectively. The errors in the harmonic frequencies ω_e and equilibrium distances r_e relative to the experimental data are shown in fig. 1. It is found that in all cases the CASPT3 results are significantly more accurate than the CASPT2 ones. The values of r_e, ω_e and anharmonicity constants $\omega_e x_e$ are generally in very close agreement with the MRCI values and in excellent agreement with experiment. With the exception of C_2, the deviations between theory and experiment for ω_e are smaller than 10 cm^{-1}. The root mean square (rms) errors for r_e are 0·0058 Å (CASPT2), 0·0028 Å (CASPT3), 0·0035 Å (MRCI), 0·0049 Å (MR-ACPF), and 0·0023 Å [RCCSD(T)]. The rms errors for ω_e are 20·7 cm^{-1} (CASPT2), 8·4 cm^{-1} (CASPT3), 10·1 cm^{-1} (MRCI), 11·8 cm^{-1} (MR-ACPF), and 8·8 cm^{-1} [RCCSD(T)]. These values should not be taken too literally, since neither the basis set is fully converged, nor are core-valence correlation effects taken into account.

Table 3. Spectroscopic constants for open-shell diatomic molecules[a].

Method	$E(r_e)$ (hartree)	r_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (eV)
$CN(X^2\Sigma^+)$:							
CASPT2	−92·579438	1·1781	1·880	0·0173	2041·2	13·09	7·56
CASPT3	−92·586143	1·1753	1·889	0·0172	2061·9	12·93	7·58
MRCI	−92·581339	1·1757	1·887	0·0172	2058·9	12·98	7·69
MRCI+Q	−92·592928	1·1766	1·885	0·0173	2053·0	13·07	7·65
MRACPF	−92·590857	1·1764	1·885	0·0173	2054·0	13·06	7·65
Experiment		1·1718	1·900	0·0174	2068·6	13·09	7·89
$NO(X^2\Pi)$:							
CASPT2	−129·737292	1·1558	1·690	0·0178	1880·6	14·40	6·31
CASPT3	−129·745201	1·1531	1·698	0·0173	1907·9	13·93	6·34
MRCI	−129·732230	1·1534	1·697	0·0174	1905·0	14·02	6·41
MRCI+Q	−129·752906	1·1550	1·693	0·0174	1894·3	14·05	6·44
MRACPF	−129·750368	1·1549	1·693	0·0174	1894·8	14·06	6·43
Experiment		1·1508	1·672	0·0171	1904·2	14·08	6·73
$CF(X^2\Pi)$:							
CASPT2	−137·617577	1·2753	1·409	0·0185	1304·3	11·16	5·31
CASPT3	−137·630359	1·2760	1·408	0·0182	1304·9	10·89	5·43
MRCI	−137·618625	1·2751	1·410	0·0181	1311·2	10·79	5·53
MRCI+Q	−137·639439	1·2793	1·401	0·0180	1294·3	10·57	5·58
MRACPF	−137·637240	1·2792	1·401	0·0181	1294·6	10·67	5·57
Experiment		1·2718	1·417	0·0184	1308·1	11·10	5·83
$O_2(X^3\Sigma_g^+)$:							
CASPT2	−150·163783	1·2126	1·434	0·0158	1566·1	11·84	5·12
CASPT3	−150·159563	1·2076	1·446	0·0159	1590·9	12·04	4·89
MRCI	−150·142947	1·2091	1·442	0·0158	1583·8	11·93	4·91
MRCI+Q	−150·170306	1·2117	1·436	0·0158	1573·8	11·81	4·98
MRACPF	−150·167722	1·2118	1·436	0·0158	1573·2	11·81	4·97
Experiment		1·2075	1·446	0·0159	1580·2	11·98	5·21

[a] Using basis cc-pVQZ [57].

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

The results for the dissociation energies D_e are less conclusive than for the bond distances and frequencies. In most cases CASPT3 improves the results relative to CASPT2, but this is not the case for C_2, F_2, and O_2. Interestingly, these are the cases in which the CASPT2 dissociation energies are in best agreement with the experimental values. On the other hand, in the case of N_2, the CASPT2 dissociation energy is much too small, and quite significantly improved by CASPT3 (+0·22 eV). This may indicate that in the former cases the perturbation expansion of correlation energies shows an oscillatory behaviour as well known from single-reference Møller–Plesset theory. In all cases the computed dissociation energies are smaller than the experimental values. The errors of the CASPT3 values amount to 0·2–0·3 eV for the closed-shell molecules and to 0·3–0·4 eV for the open-shell ones. Part of the deviations are due to basis set deficiencies, but these are certainly not the only source of error. The MRCI, MRCI+Q and MR-ACPF values are larger than the CASPT3 ones by 0·07–0·15 eV,

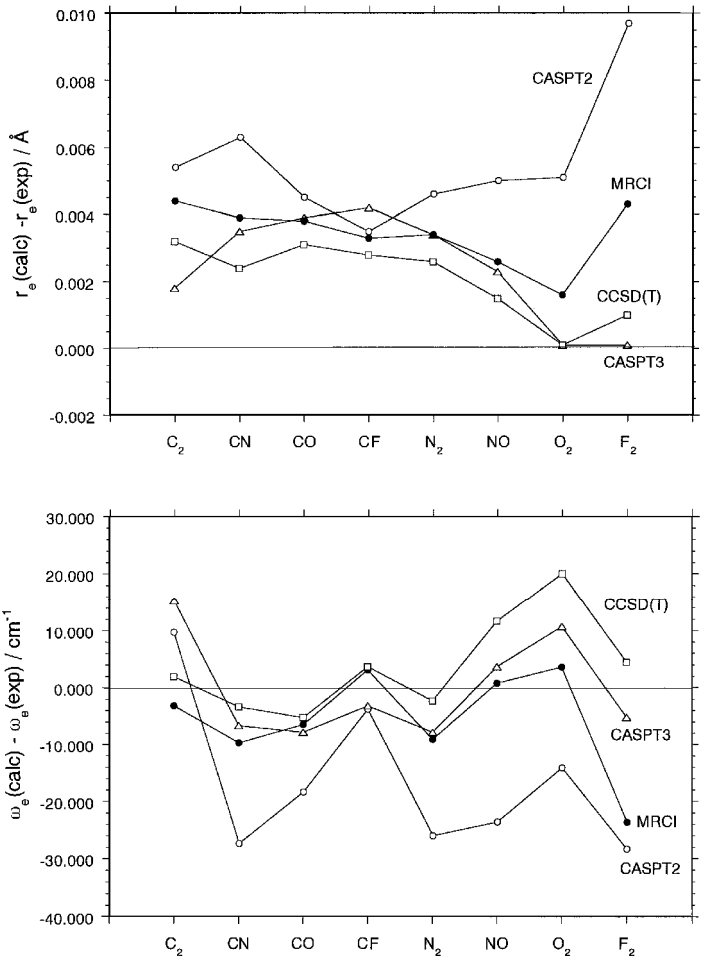


Figure 1. Differences of computed and experimental equilibrium distances r_e (upper panel) and harmonic frequencies ω_e (lower panel). Open circles: CASPT2, open triangles: CASPT3, open squares: RCCSD(T), full circles: MRCI.

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

indicating that higher orders of perturbation theory would give significant contributions, even without extending the configuration space to higher excitations.

Rather similar results have been obtained in an extensive CASPT2 study of geometries and binding energies by Andersson and Roos [60]. In most cases (with the exception of NO) their equilibrium distances are slightly longer than ours, and the dissociation energies are somewhat smaller. This is attributed to the fact that their basis sets did not include *g*-functions. Furthermore, the 2s-orbitals of nitrogen, oxygen, and fluorine were inactive in the CASSCF reference functions.

Table 4 shows a comparison of single-reference coupled-cluster calculations and various multi-reference methods for the homonuclear diatomics N_2, O_2, and F_2, using the larger cc-pV5Z basis. The improvement of the basis set slightly reduces the r_e values, bringing them into better agreement with experiment. The harmonic frequencies ω_e are increased, and for O_2 and F_2 they now become somewhat larger than the experimental data. For N_2 it is well known [61, 62] that core-valence correlation effects increase ω_e by about 8–9 cm^{-1}, and if this is taken into account,

Table 4. Comparison of correlation treatments for diatomic molecules[a].

Method	$E(r_e)$ (hartree)	r_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (eV)
$N_2(X^1\Sigma_g^+)$:							
CCSD	−109·393470	1·0922	2·018	0·0160	2440·0	12·94	9·37
CCSD(T)	−109·414195	1·0994	1·992	0·0170	2360·0	13·95	9·77
CASPT2	−109·396180	1·1016	1·984	0·0175	2335·6	14·57	9·46
CASPT2(g_1)	−109·395796	1·1012	1·986	0·0174	2341·3	14·39	9·86
CASPT3	−109·406705	1·1002	1·989	0·0171	2355·5	14·10	9·71
CASPT3(g_1)	−109·406840	1·1004	1·989	0·0172	2352·9	14·21	9·66
MRCI	−109·398595	1·1003	1·989	0·0172	2353·6	14·19	9·80
MRACPF	−109·411085	1·1011	1·986	0·0172	2346·5	14·27	9·76
Experiment		1·0977	1·998	0·0173	2358·6	14·32	9·90
$O_2(X^3\Sigma_g^+)$:							
RCCSD	−150·165493	1·1936	1·480	0·0141	1698·3	10·26	4·74
RCCSD(T)	−150·188179	1·2067	1·448	0·0151	1602·5	11·02	5·14
CASPT2	−150·181158	1·2119	1·435	0·0158	1566·6	11·84	5·17
CASPT2(g_1)	−150·176947	1·2088	1·443	0·0155	1590·8	11·49	5·62
CASPT3	−150·173841	1·2061	1·449	0·0158	1598·9	11·92	4·94
CASPT3(g_1)	−150·174056	1·2082	1·444	0·0161	1579·2	12·14	4·95
MRCI	−150·156534	1·2080	1·445	0·0158	1587·3	11·91	4·96
MRACPF	−150·182192	1·2109	1·438	0·0157	1575·7	11·79	5·03
Experiment		1·2075	1·446	0·0159	1580·2	11·98	5·21
$F_2(X^1\Sigma_g^+)$:							
CCSD	−199·359280	1·3885	0·921	0·0103	1021·8	8·76	1·33
CCSD(T)	−199·380987	1·4110	0·891	0·0125	926·5	11·49	1·64
CASPT2	−199·364452	1·4198	0·880	0·0131	892·5	11·63	1·59
CASPT2(g_1)	−199·363927	1·4163	0·885	0·0123	912·0	10·80	1·71
CASPT3	−199·364617	1·4091	0·894	0·0133	920·0	12·62	1·47
CASPT3(g_1)	−199·364916	1·4106	0·892	0·0136	911·7	12·99	1·44
MRCI	−199·338720	1·4137	0·888	0·0136	899·7	12·48	1·49
MRACPF	−199·371094	1·4141	0·888	0·0129	914·9	11·93	1·53
Experiment		1·4119	0·890	0·0138	916·6	11·24	1·64

[a] Using basis cc-pV5Z [57].

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

a harmonic frequency which is slightly too large is obtained. The dissociation energies are very slowly converging with basis set size and are still considerably too small. Also shown in table 4 are CASPT2(g_1) and CASPT3(g_1) results obtained with the modified zeroth-order Hamiltonian as proposed by Andersson [53]. While the modification tends to reduce the r_e values and increase the frequencies at the CASPT2 level, the opposite is true for CASPT3. It appears that the CASPT3(g_1) r_e and ω_e values are slightly more accurate than the unmodified CASPT3 ones. Similar results were obtained for all other molecules shown in tables 2 and 3. The situation is different for the dissociation energies, however. While at the CASPT2 level the D_e values are overestimated when the g_1 operator is used [53], in most cases (with the exceptions of C_2 and O_2) the CASPT3(g_1) dissociation energies are slightly reduced. The RCCSD(T) results are of similar accuracy as CASPT3 or MRCI ones, but single-reference

Table 5. Computed collinear barrier heights[a] and exothermicities for the $F+H_2$ reaction.

Method	Barrier (kcal mol^{-1})	Exothermicity (kcal mol^{-1})
Basis A:		
CASPT2	3·339	29·00
CASPT2(g_1)	2·826	29·02
CASPT3	3·657	28·01
CASPT3(g_1)	4·278	28·00
MRCI[b]	3·496	28·24
MRCI+Q[b]	3·171	27·86
FCI[c]	3·169 ± 0·045	27·91 ± 0·02
Basis B:		
CASPT2	2·553	31·66
CASPT2(g_1)	2·030	31·88
CASPT3	2·836	31·44
CASPT3(g_1)	3·485	31·44
MRCI[b]	2·623	31·81
MRCI+Q[b]	1·918	31·30
Experiment		31·73

[a] Basis sets, geometries and other details, see text and [65].
[b] Results from [65].
[c] Results from [64].

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

MP2–MP4 calculations performed with the same basis set (not shown in table 4) gave very unsatisfactory agreement with experiment, in particular for N_2.

The computation times for the CASPT2/CASPT3 calculations are rather small. For instance, for the N_2 calculation with V5Z basis (182 contractions, D_{2h} symmetry) and full-valence reference function (176 reference CSFs) one iteration of the CASPT2 takes 1·30 s on an SGI PowerChallenge (R8000/75 MHz processor). The corresponding MRCI takes 36·1 s per iteration, i.e., 28 times longer. Both calculations require 7 iterations, yielding a total of 260 s for MRCI and 13·3 s for CASPT2 (including initialization and integral transformation). Evaluation of the third-order energy takes 31·6 s, yielding a total of 45 s for CASPT3. The total time for a single-reference CCSD(T) calculation (8 iterations) is 133 s (all times obtained with the MOLPRO [55] package).

In general, the CASPT2 and CASPT3 energies are not exactly size extensive [38, 63], i.e., the energy of two fragments A and B evaluated at a very large distance is not identical to the sum of the individually computed fragment energies, even if this is the case for the reference function. This is due to the projection operators in the zeroth-order Hamiltonian, which make $H^{(0)}(AB) \neq H^{(0)}(A)+H^{(0)}(B)$, and consequently, $\Psi^{(1)}(AB) \neq \Psi^{(0)}(A)\,\Psi^{(1)}(B)+\Psi^{(1)}(A)\,\Psi^{(0)}(B)$ [63]. However, the size extensivity errors (evaluated as difference of the molecular energies at R = 100 bohr and the sum of the separately computed atomic energies) are very small: for the calculations in table 4, they amount to (−0·0023/+0·0086) eV, (−0·00034/+0·00084) eV, and (−0·00053/+0·00041) eV (CASPT2/CASPT3) for N_2, O_2, and F_2, respectively. These values can be further reduced (but in general not completely eliminated) by projecting out the non-interacting contributions of the uncontracted configurations. However,

we believe that for any practical application the size consistency errors are unimportant and can be safely neglected.

As a final test of the CASPT3 method, we computed the collinear barrier height and exothermicity for the $F+H_2$ reaction using the same basis sets and configuration spaces as in our recent studies of this reaction [64, 65]. The active space (denoted [622/2] in [64, 65]) included the fluorine 2p, 3p and hydrogen 1s orbitals. The orbitals from CASSCF[622/2] were used and 9 electrons were correlated (for details of the orbital optimization see [65]). Two basis sets have been used: Basis A ([4s3p1d/2s1p]) is of double-zeta plus polarization quality with additional diffuse s and p functions optimized for F^-. For this basis, full CI results are available [64]. Basis B is much larger ([7s6p4d3f2g/6s4p2d]) and should yield results quite close to the basis set limit [65]. This basis has been used to compute a global MRCI+Q potential energy surface [65], which has been successfully used in various dynamics calculations [66–70]. It is found that the CASPT2 and CASPT3 barrier heights are considerably larger than the MRCI+Q or FCI values. In fact, the CASPT3 value is worse than the CASPT2 one. This effect is even more pronounced when the g_1 correction [53] is used. Most likely, higher excitations and higher orders of perturbation theory are necessary to reproduce the barrier height correctly. As for the dissociation energies of some molecules discussed above, it appears that the perturbation expansion shows an oscillatory behaviour in this case. In contrast to the barrier height, the CASPT3 exothermicity is much more accurate than the CASPT2 one. For the small basis set, the CASPT2 value is 1 kcal mol^{-1} larger than the FCI value, while the CASPT3 exothermicity agrees with the FCI value within 0·1 kcal mol^{-1}. The g_1 correction has almost no effect on the CASPT3 exothermicity. For the larger basis, the differences between CASPT2 and CASPT3 are somewhat smaller. Taking into account that further improvements of the basis would increase the exothermicity by about 0·4 kcal mol [65], the basis set limit for CASPT3 is likely to be very close to the experimental value.

Our CASPT2 results are similar to those obtained in a recent CASPT2 study of Gonzáles-Luque, Merchán, and Roos [71], but not exactly comparable since different basis sets were used.

4. Conclusions

It has been demonstrated that third-order multireference perturbation theory yields highly accurate results at moderate cost. For a number of diatomic molecules it has been found that the equilibrium distances, harmonic and anharmonic frequencies are of similar accuracy as those obtained in full MRCI calculations. The dissociation energies, however, are generally too low, and not always improved relative to CASPT2. The barrier height of the $F+H_2$ reaction is overestimated at the CASPT3 level, while the exothermicity of this reaction is reproduced very accurately. These results indicate that in some cases the perturbation expansion of correlation energies might show an oscillatory behaviour, even though this is probably less pronounced than in single reference cases. Modifications of the Fock matrix used in the zeroth-order Hamiltonian as recently proposed by Andersson [53] have also been tested. While equilibrium distances and harmonic frequencies appear to be slightly improved when the modified operator is used, the CASPT3 barrier height of $F+H_2$ is overestimated even more than without the correction.

The remaining errors in the CASPT3 energies are likely to be due to the omission of higher excitations, which would contribute only to the fourth and higher order energies. Nevertheless, the CASPT3 method appears to be promising and cost effective

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

for many applications. Further calculations will be necessary to investigate how the method performs for larger molecules and electronically excited states. A difficulty in excited state calculations is the intruder-state problem. This may also occur, though much less likely, in ground state calculations [72]. This problem is reduced when a modified zeroth-order Hamiltonian is used [53, 51], or can be circumvented using level-shift techniques [72]. Another problem is the fact that in certain cases dynamical and non-dynamical correlation effects are quite strongly coupled. This effect is not accounted for in the first-order wavefunction if only a single reference state is used. Our method is also capable of using multiple-state references, as required in near degeneracy situations, using techniques similar to those described in reference [50]. Results for such cases will be presented in a future publication.

The author thanks P. J. Knowles, P.-Å. Malmquist, P. Pulay, and B. O. Roos for helpful discussions. This work has been supported by the German Fonds der Chemischen Industrie.

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013

References

[1] Møller, C., and Plesset, M. S., 1934, *Phys. Rev.*, **46**, 618.
[2] Pople, J. A., and Nesbet, R. K., 1954, *J. chem. Phys.*, **22**, 571.
[3] Krishnan, R., Frisch, M. J., and Pople, J. A., 1980, *J. chem. Phys.*, **72**, 4244.
[4] Handy, N. C., Knowles, P. J., and Somasundram, K., 1985, *Theor. chim. Acta*, **68**, 87.
[5] Knowles, P. J., Somasundram, K., Handy, N. C., and Hirao, K., 1985, *Chem. Phys. Lett.*, **113**, 8.
[6] Nobes, R. H., Pople, J. A., Radom, L., Handy, N. C., and Knowles, P. J., 1987, *Chem. Phys. Lett.*, **138**, 481.
[7] Andrews, J. S., Jayatilaka, D., Bone, R. G. A., Handy, N. C., and Amos, R. D., 1991, *Chem. Phys. Lett.*, **183**, 423.
[8] Hubač, I., and Čársky, P., 1980, *Phys. Rev.* A, **22**, 2392.
[9] Amos, R. D., Andrews, J. S., Handy, N. C., and Knowles, P. J., 1991, *Chem. Phys. Lett.*, **185**, 256.
[10] Knowles, P. J., Andrews, J. S., Amos, R. D., Handy, N. C., and Pople, J. A., 1991, *Chem. Phys. Lett.*, **186**, 130.
[11] Lauderdale, W. J., Stanton, J. F., Gauss, J., Watts, J. D., and Bartlett, R. J., 1991, *Chem. Phys. Lett.*, **187**, 21.
[12] Murray, C. W., and Davidson, E. R., 1991, *Chem. Phys. Lett.*, **187**, 451.
[13] Murray, C. W., and Davidson, E. R., 1992, *Int. J. quantum Chem.*, **43**, 755.
[14] Murray, C. W., and Handy, N. C., 1992, *J. chem. Phys.*, **97**, 6509.
[15] Lee, T. J., and Jayatilaka, D., 1993, *Chem. Phys. Lett.*, **201**, 1.
[16] Andrews, J. S., Murray, C. W., and Handy, N. C., 1993, *Chem. Phys. Lett.*, **201**, 458.
[17] Tozer, D. J., Handy, N. C., Amos, R. D., Pople, J. A., Nobes, R. H., Xie, Y., and Schaefer, H. F., 1993, *Molec. Phys.*, **79**, 777.
[18] Lee, T. J., Rendell, A. P., Dyall, K., and Jayatilaka, D., 1993, *J. chem. Phys.*, **100**, 7400.
[19] Brandow, B. H., 1967, *Rev. mod. Phys.*, **39**, 771.
[20] Brandow, B. H., 1977, *Adv. quantum Chem.*, **10**, 187.
[21] Kaldor, U., 1975, *J. chem. Phys.*, **63**, 2199.
[22] Durand, P., and Malrieu, J.-P., 1987, *Adv. chem. Phys.*, **67**, 321, and references therein.
[23] McDouall, J. J. W., Peasley, K., and Robb, M. A., 1988, *Chem. Phys. Lett.*, **148**, 183.
[24] Kucharski, S., and Bartlett, R. J., 1988, *Int. J. quantum Chem. Symp.*, **22**, 383.
[25] Nakano, H., 1993, *J. chem. Phys.*, **99**, 7983.
[26] Nakano, H., 1993, *Chem. Phys. Lett.*, **207**, 372.
[27] Roos, B. O., Linse, P., Siegbahn, P. E. M., and Blomberg, M. R. A., 1982, *Chem. Phys.*, **66**, 197.
[28] Meyer, W., 1977, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (New York: Plenum).

[29] Siegbahn, P. E. M., 1980, *Int. J. quantum Chem.*, **18**, 1229.
[30] Werner, H.-J., and Reinsch, E. A., 1982, *J. chem. Phys.*, **76**, 3144.
[31] Werner, H.-J., 1987, *Adv. chem. Phys.*, **69**, 1.
[32] Werner, H.-J., and Knowles, P. J., 1988, *J. chem. Phys.*, **89**, 5803.
[33] Wolinski, K., Sellers, H. L., and Pulay, P., 1987, *Chem. Phys. Lett.*, **140**, 225.
[34] Wolinski, K., and Pulay, P., 1989, *J. chem. Phys.*, **90**, 3647.
[35] Andersson, K., Malmquist, P.-A., Roos, B. O., Sadley, A. J., and Wolinski, K., 1990, *J. Phys. Chem.*, **94**, 5483.
[36] Andersson, K., Malmquist, P.-A., and Roos, B. O., 1992, *J. chem. Phys.*, **96**, 1218.
[37] Kozlowski, P. M., and Davidson, E. R., 1994, *J. chem. Phys.*, **100**, 3672.
[38] Malmquist, P.-Å., 1995, *Chem. Phys. Lett.*, **241**, 429.
[39] Davidson, E. R., 1995, *Chem. Phys. Lett.*, **241**, 432.
[40] Murphy, R. B., Messmer, R. P., 1991, *Chem. Phys. Lett.*, **183**, 443.
[41] Murphy, R. B., and Messmer, R. P., 1992, *J. chem. Phys.*, **97**, 4170.
[42] Hirao, K., 1992, *Chem. Phys. Lett.*, **190**, 374.
[43] Hirao, K., 1992, *Chem. Phys. Lett.*, **196**, 397.
[44] Hirao, K., 1993, *Chem. Phys. Lett.*, **201**, 59.
[45] Kozlowski, P. M., and Davidson, E. R., 1994, *Chem. Phys. Lett.*, **222**, 615.
[46] Kozlowski, P. M., and Davidson, E. R., 1994, *Chem. Phys. Lett.*, **226**, 440.
[47] Knowles, P. J., and Werner, H.-J., 1988, *Chem. Phys. Lett.*, **145**, 514.
[48] Gdanitz, R. J., and Ahlrichs, R., 1988, *Chem. Phys. Lett.*, **143**, 413.
[49] Werner, H.-J., and Knowles, P. J., 1990, *Theor. chim. Acta*, **78**, 175.
[50] Knowles, P. J., and Werner, H.-J., 1992, *Theor. chim. Acta*, **84**, 95.
[51] Dyall, K. G., 1995, *J. chem. Phys.*, **102**, 4909.
[52] Murphy, R. B., and Messmer, R. P., 1993, *J. chem. Phys.*, **98**, 10102.
[53] Andersson, K., 1995, *Theor. chim. Acta*, **91**, 31.
[54] Pulay, P., 1980, *Chem. Phys. Lett.*, **73**, 393.
[55] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, C. Hampel, R. Lindh, W. Meyer, A. Nicklass, P. Palmieri, K. A. Peterson, R. M. Pitzer, H. Stoll, A. J. Stone, and P. R. Taylor.
[56] Bauschlicher, C. W., and Taylor, P. R., 1986, *J. chem. Phys.*, **85**, 6510.
[57] Dunning, T. H., 1989, *J. chem. Phys.*, **90**, 1007.
[58] Hampel, C., Peterson, K. A., and Werner, H.-J., 1992, *Chem. Phys. Lett.*, **190**, 1.
[59] Knowles, P. J., Hampel, C., and Werner, H.-J., 1993, *J. chem. Phys.*, **99**, 5219.
[60] Andersson, K., and Roos, B. O., 1993, *Int. J. quantum Chem.*, **45**, 591.
[61] Werner, H.-J., and Knowles, P. J., 1993, *J. chem. Phys.*, **94**, 1264.
[62] Bauschlicher, C. W., and Partridge, H., 1994, *J. chem. Phys.*, **100**, 4329.
[63] This was pointed out by P.-Å. Malmquist at the symposium on 'Electron Correlation in Atoms and Molecules, New Methods and Applications', Bratislava, Slovak Republic (1994). The author thanks Dr Malmquist for communicating this material to him.
[64] Knowles, P. J., Stark, K., and Werner, H.-J., 1991, *Chem. Phys. Lett.*, **185**, 555.
[65] Stark, K., and Werner, H.-J., 1996, *J. chem. Phys.*, **104**, 6515.
[66] Manolopoulos, D. E., Stark, K., Werner, H.-J., Arnold, D. W., Bradforth, S. E., and Neumark, D. M., 1993, *Science*, **262**, 1852.
[67] Aoiz, F. J., Bañares, L., Herrero, V. J., Sáez Rábanos, V., Stark, K., and Werner, H.-J., 1994, *Chem. Phys. Lett.*, **223**, 215.
[68] Aoiz, F. J., Bañares, L., Herrero, V. J., Sáez Rábanos, V., Stark, K., and Werner, H.-J., 1994, *J. phys. Chem.*, **98**, 10665.
[69] Aoiz, F. J., Bañares, L., Herrero, V. J., Sáez Rábanos, V., Stark, K., and Werner, H.-J., 1995, *J. chem. Phys.*, **102**, 9248.
[70] Castillo, J., Manolopoulos, D. E., Stark, K., and Werner, H.-J., 1996, *J. chem. Phys.*, **104**, 6531.
[71] González-Luque, R., Merchán, M., and Roos, B. O., 1993, *Chem. Phys.*, **171**, 107.
[72] Roos, B. O., and Andersson, K., 1995, *Chem. Phys. Lett.*, **245**, 215.

Downloaded by [University Of Pittsburgh] at 06:46 02 August 2013