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A Hilbert space multi-reference coupled-cluster study of the H_4 model system

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Summary. Employing the Hilbert space ansatz, a fully quadratic coupled-cluster method with a multidimensional reference space is applied to a DZP basis study of the model system, H_4. The reference space is described by two to four configurations at the level of single and double excitations, and single and double excitation operators are included in the expansions for the cluster and wave operator through quadratic terms. The performance of quadratic MRCCSD is investigated for the ground and three excited states of the H_4 system consisting of two stretched hydrogen molecules in a trapezoidal configuration where the degree of quasidegeneracy is varied from a nondegenerate situation to a completely degenerate one. Compared to full CI, in the highly degenerate region, the MRCCSD works quite well. In less degenerate regions, the accuracy is less satisfactory.

Key words: Coupled-cluster – Hilbert space ansatz – H_4 model system – MRCCSD-DZP

1. Introduction

Numerous applications of the single-reference coupled-cluster (CC) method [1, 2] during the past two decades (for reviews see [3–8] and references therein) have demonstrated the success of this method in treating the correlation problem for various properties of molecular systems. It is probably fair to say that the coupled-cluster method which combines the conceptual simplicity of the one-determinant-reference formulation with infinite-order summation of the most important dynamic correlation terms represents, for the time being, the most powerful tool for a (size)-extensive description of the electronic structure for nondegenerate states of molecules. The alternative truncated variational expan-

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*** *Permanent address*: Pedagogical University, Physics Institute, 42-200 Czestochowa, Poland sions in configuration interaction (CI) theory, which furnish an upper bound to the exact energy, are known to suffer from inextensivity, usually requiring an "a posteriori" approximate correction [9–13].

Though in many applications single-reference CC methods can describe highly degenerate electronic states of atoms and molecules, it will eventually fail when sufficiently difficult nondynamic correlation effects are encountered. This deficiency prevents exploiting nondegenerate CC theory for cases where the degree of degeneracy varies over a wide range from a completely nondegenerate situation to a nearly degenerate one, as occurs in studies of many potential energy surfaces and excited states of molecules.

Multi-reference variational CI methods are well known [14–17]; however, several attempts to extend single-determinantal many-body perturbation theory (MBPT) [18–23] and allied CC [10, 24–37] to a general multi-reference case have also been made. Nevertheless, the more intricate structure of "many-body" theories greatly complicates the solution of the problem. Depending upon the form of wave operator employed, multi-reference CC approaches can be divided into two broad classes, namely Fock space or valence-universal CC methods [24–28] and Hilbert space or state-universal CC approaches [10, 29–37]. The use of a complete active space is formally and computationally simpler, but can suffer from intruder states [38]. Recent formulations using an incomplete reference have now been developed [36, 37, 39–43]. Here, we limit ourselves to a complete model space.

Fock space multi-reference CC approaches aimed at the calculations of ionization potentials [44, 46, 47], electron affinities [46] and excitation energies [44, 46–48], are becoming routine in several groups [44–48]. However, applications of the alternative Hilbert space formulation have been limited to the linearized version of MRCC [10] with prediagonalization as presented by Laidig and Bartlett [30, 31], a related formalism of Banerjee and Simons [32], and to some more rigorous effective Hamiltonian model calculations [33, 35, 49].

The problem undertaken in this paper is a part of a wider project directed at the development and implementation of the Hilbert space multi-reference CC method for full-scale calculations of molecular systems. Here we present results obtained for the model system of H_4 [50]. These represent an extension of the earlier applications of an orthogonally spin-adapted MRCC formalism of Paldus et al. [35] as well as of a quadratic MRCCD formalism developed by Meissner et al. [33]. In our formulation we focus on the full inclusion of all quadratic terms and some higher terms in the expansion for both cluster and effective Hamiltonian operators within the single and double excitations (CCSD) approach [51], with special attention paid to the comparison of the performance for the closed- vs. open-shell model configurations included in a complete model space. Presenting results for formally a four-configurational (two of one symmetry and two of another) MRCC study of the prototype system H_4 we want to discuss some theoretical and numerical problems in our formulation connected with the convergence of nonlinear CC equations for individual model states, the choice of model space itself, and the related question of the selection of the reference starting vector.

A short synopsis of the state universal MRCCSD method is given in Sect. 2. Besides basic equations we also sketch the general derivation to show how all nonphysical terms of unlinked or disconnected character are eliminated in our formulation which differs somewhat from others [35]. Comparisons of MRCC results for the trapezoidal H_4 model system with corresponding FCI values and energies provided by other correlated methods are presented in Sect. 3.

2. Theory

2.1. Overview of the multi-reference approach

The basic concept of multi-reference coupled-cluster theory is a wave operator $\hat{\Omega}$ which operating on the model function Ψ^0 defined within a model space P generates the exact wavefunction Ψ:

$$\Psi = \hat{\Omega}\Psi^0 \tag{1}$$

The wave operator fulfills an equation, which may be looked upon as corresponding to the Schrödinger equation for the wavefunction, known as the Bloch equation [52, 53]:

$$[\hat{\Omega}, \hat{H}_0]\hat{P} = \hat{V}\hat{\Omega}\hat{P} - \hat{\Omega}\hat{P}\hat{V}\hat{\Omega}\hat{P} \tag{2}$$

Here $\hat{P}$ is a projection operator:

$$\hat{P}\Psi = \Psi^0 \tag{3}$$

$$\hat{P}^2 = \hat{P} \tag{4}$$

$$\hat{P} = \sum_{I=1}^{d} |\Phi_I\rangle\langle\Phi_I| \tag{5}$$

which defines the d-dimensional model space spanned by the zeroth-order wavefunctions Φ_I.

When substituting the exact wavefunction, Eq. (1), into the Schrödinger equation and operating from the left with a projector $\hat{P}$ we obtain the expression:

$$\hat{P}\hat{H}\hat{\Omega}\Psi^0 = \hat{H}^{\text{eff}}\Psi^0 = E\Psi^0 \tag{6}$$

which defines the effective Hamiltonian operator $\hat{H}^{\text{eff}}$. This operator has the property that while operating in the subspace of the complete Hilbert space, it gives a part of the energy spectrum of the exact Hamiltonian.

The general form of the wave operator adopted in the coupled-cluster theory is as an exponential:

$$\hat{\Omega} = e^{\hat{T}} \tag{7}$$

where $\hat{T}$ is the cluster operator defined by the expression:

$$\hat{T} = \sum_n \hat{T}_n \tag{8}$$

$$\hat{T}_n = (n!)^{-2} \sum t_{i_1 i_2 \ldots i_n}^{a_1 a_2 \ldots a_n} \hat{a}_1^+ \hat{a}_2^+ \ldots \hat{a}_n^+ \hat{i}_n \ldots \hat{i}_2 \hat{i}_1 \tag{9}$$

and $\hat{a}_k^+$, $\hat{i}_k$, are the second-quantized creation and annihilation operators, respectively. (The indices a_k, i_k and summation run over all virtual and occupied spinorbitals, respectively.)

In the multi-reference approach the unique construction of the wave operator is, according to Eqs. (7–9), no longer possible. Since the reference state contains several functions a distinction between hole and particle states is no longer obvious, as the spinorbitals occupied in one reference determinant may be empty in another. In general we have the option to assume either a fixed vacuum state, i.e., the same for all P-space reference functions, or a reference-dependent one, i.e., each of the reference functions plays, in turn, the role of the vacuum.

Out of the several originally proposed formulations of the multi-reference CC theory [24, 25, 29] two are evolving into computationally tractable schemes. These, already mentioned in the introduction, are the Fock space valence-universal approach and the Hilbert space state-universal approach. The first of these is based on the definition of the wave operator proposed by Lindgren [25] which can be expressed as:

$$\hat{\Omega} = \{e^{\hat{T}}\}\hat{P} \tag{10}$$

where the operator $\hat{T}$ is identical for all reference functions and the braces indicate that the normal-ordering operation should be applied to all operator products after expansion. The explicit form of $\hat{T}$ depends on the assumed vacuum function. The characteristic feature of valence-universal approaches is a non-commutativity of the cluster operators, hence it is convenient to impose a normal-ordering condition on the products of $\hat{T}$ operators. It is common to assume that one of the reference functions (usually the ground state) is adopted as a vacuum state, as has been done in the applications of Kaldor [44], Mukherjee [45], Bartlett [46–48] and co-workers.

In the alternative Hilbert space approach as developed by Jeziorski and Monkhorst [29], the wave operator is expressed as:

$$\hat{\Omega} = \sum_{K} e^{\hat{T}(K)}\hat{P}_K \tag{11}$$

where the ranges of the summations over a and i in Eq. (9) do not overlap and are strictly defined by the Φ_K determinant due to the fact that the vacuum is formed by the current reference function Φ_K [19, 54]. In each of the mentioned approaches a general rule is valid that none of the $\hat{T}_n$ operators can produce excitations within the model (P) space.

Inserting the wave operator defined by Eq. (11) into the Bloch equation, Eq. (2), and operating on the Kth reference determinant we arrive at the general expression [29]:

$$[e^{\hat{T}(K)}, \hat{H}_0]|\Phi_K\rangle = \hat{V}e^{\hat{T}(K)}|\Phi_K\rangle - \sum_{L} e^{\hat{T}(L)}|\Phi_L\rangle\langle\Phi_L|\hat{V}e^{\hat{T}(K)}|\Phi_K\rangle \tag{12}$$

where K and L run over all reference configurations. Projecting Eq. (12) onto the subspace of the singly and doubly excited configurations with respect to Φ_K we obtain CC equations for single-:

$$\langle\Phi_i^a(K)|[e^{\hat{T}(K)}, \hat{H}_0]|\Phi_K\rangle = \langle\Phi_i^a(K)|\hat{V}e^{\hat{T}(K)}|\Phi_K\rangle - \sum_{L}\langle\Phi_i^a(K)|e^{\hat{T}(L)}|\Phi_L\rangle\langle\Phi_L|\hat{V}e^{\hat{T}(K)}|\Phi_K\rangle \tag{13}$$

and double-excitation amplitudes:

$$\langle\Phi_{ij}^{ab}(K)|[e^{\hat{T}(K)}, \hat{H}_0]|\Phi_K\rangle = \langle\Phi_{ij}^{ab}(K)|\hat{V}e^{\hat{T}(K)}|\Phi_K\rangle - \sum_{L}\langle\Phi_{ij}^{ab}(K)|e^{\hat{T}(L)}|\Phi_L\rangle\langle\Phi_L|\hat{V}e^{\hat{T}(K)}|\Phi_K\rangle \tag{14}$$

and analogous expressions for higher rank amplitudes. This provides a starting point for the derivation of explicit recursive formulae for $t_1, t_2, \ldots$ coefficients. The detailed equations, for reference spaces containing excitations through hextuples which is complete for a MRCCSD model, are presented elsewhere [55].

2.2. *General structure of the Hilbert space multi-reference CC equations*

The general CC equations, Eqs. (13, 14), are represented in terms of many-electron functions. To enable their efficient implementation it is convenient to express them in terms of t amplitudes and one- and two-electron integrals. The standard method is to rewrite all the involved operators in terms of creation-annihilation operators, to expand exponentials, and to generate all possible products of t amplitudes and integrals. Here we will only refer to some general structural features.

As was already mentioned in the introduction, the Hilbert space approach is conceptually similar to the single-reference method. If we suppress the second (the so-called renormalization) term on the right-hand side of Eqs. (13, 14), then from the point of view of the particular reference Φ_K we obtain the single-reference equations [51]. The only difference is that certain amplitudes responsible for excitations within the model space are excluded from the summation in Eq. (9). Most of the single-reference derivations are simplified by operating with the $e^{-\hat{T}}$ operator on the left-hand side of Eq. (12) to take advantage of the Hausdorff commutator formula which automatically ensures connectivity of the resulting expansion. We could follow that route also in the multi-reference derivation [29], however, we obtain the product $e^{-\hat{T}(K)} e^{\hat{T}(L)}$ which is cumbersome. Alternatively, we can work directly with Eqs. (13, 14). In this approach, however, unlinked and – in the case of Eq. (14) – also disconnected terms appear and we have to demonstrate that they vanish from the final form of the CC equations.

In doing so we observe that the unlinked terms generated by the first term on the right-hand side of Eqs. (13, 14) are of the same form as those occurring for the single-reference formulation. In that case, they are cancelled by the energy term. If we look closely at the renormalization term in Eqs. (13, 14), we see that the diagonal part of the effective Hamiltonian, i.e., the term in the summation corresponding to $L = K$ is nothing else than the familiar single-reference energy expression and the cancellation of the unlinked contributions is carried out in the same manner as in a one-determinantal CC approach [6b].

In an analogous manner we may show that the disconnected terms disappear from Eq. (14). We note that they occur both for the left-hand side and for two terms on the right-hand side of Eq. (14), since in all three situations the projection on Φ_{ij}^{ab} will give us an equivalent of either a t_{ij}^{ab} amplitude or of a product of two t_1 amplitudes (i.e. $t_i^a t_j^b - t_j^a t_i^b$). Similarly as in the case of the single-reference equations we observe that a substitution of the expression given by Eq. (13) for one of the t_1 amplitudes eliminates the disconnected terms from the $\hat{T}_2$ equation. In the present case, however, elimination is not complete and some residual disconnected contributions survive. By performing an order-by-order analysis it may be shown that those apparent disconnected terms, although formally expressed in terms of disconnected diagrams, provide important exclusion principle violating (EPV) contributions to the folded MBPT diagrams [54, 55] generated by the iteration of the renormalization part of Eq. (14).

To conclude our discussion on the nature of the MRCC equations we mention the fact that although the expression $\langle \Phi_{ij}^{ab}(K) | \hat{V} e^{\hat{T}(K)} | \Phi_K \rangle$ occurring in the direct part of Eq. (14) generates both unlinked and disconnected diagrams, an analogous expression occurring in the definition of $\hat{H}^{\mathrm{eff}}$, i.e., $\langle \Phi_{\mu\nu}^{ab} | \hat{V} e^{\hat{T}(K)} | \Phi_K \rangle$ generates only connected contributions. This is due to the completeness of the model space which is equivalent to the assumption that all amplitudes have to carry at least one passive label, i.e., they are not allowed to produce excitations within the model space. Thus the final equations for t_i^a and t_{ij}^{ab} are expressed in the form:

$$D_i^a t_i^a(K) = \langle \Phi_i^a(K) | \hat{V} e^{\hat{T}(K)} | \Phi_K \rangle_C - \sum_{L \neq K} (\langle \Phi_i^a(K) | e^{\hat{T}(L)} | \Phi_L \rangle H_{LK})_C \quad (15)$$

$$D_{ij}^{ab} t_{ij}^{ab}(K) = \langle \Phi_{ij}^{ab}(K) | V e^{\hat{T}(K)} | \Phi_K \rangle_C - \sum_{L \neq K} (\langle \Phi_{ij}^{ab}(K) | e^{\hat{T}(L)} | \Phi_L \rangle H_{LK})_C$$
$$- \sum_{L \neq K} (t_i^a(K) - t_i^a(L))(\langle \Phi_j^b(K) | e^{\hat{T}(L)} | \Phi_L \rangle H_{LK})_C \quad (16)$$

where in the last term of Eq. (16), which generates apparent disconnected terms, all possible permutations of a, b and i, j labels are assumed. The letter C indicates that only connected terms are considered.

Let us define $w_{\mu\nu\ldots}^{\alpha\beta\ldots}$ amplitudes creating excitations within the model space as:

$$w_{\mu\nu\ldots}^{\alpha\beta\ldots}(K) = \langle \Phi_{\mu\nu\ldots}^{\alpha\beta\ldots}(K) | V e^{T(K)} | \Phi_K \rangle \quad (17)$$

We notice that neglecting the renormalization terms (and apparent disconnected ones in case of Eq. (16)) gives us the familiar single-reference equations for t_i^a and t_{ij}^{ab} amplitudes. An analogous formula is obtained also for w_μ^α and $w_{\mu\nu}^{\alpha\beta}$ amplitudes, with an exception that we do not include the denominator and the summation over external indices is limited to the active labels.

Since in actual applications the t amplitudes are reference dependent we need to store d sets of t_1 and t_2 amplitudes (where d is the size of the model space). The calculations are performed iteratively in the same manner as in the case of a single-reference approach. We assume starting t_i^a and t_{ij}^{ab} amplitudes (equal usually to one- and two-particle integrals divided by denominators, respectively) for each reference determinant. To complete the zeroth-order iteration we compute the whole set of w amplitudes, Eq. (17), creating an effective Hamiltonian matrix. In the next step new $t(K)$ amplitudes are evaluated on the basis of $t(K)$ amplitudes (direct part of Eqs. (15, 16)) and $t(L)$ and $w(L)$ amplitudes ($L \neq K$) (renormalization part of Eqs. (15, 16)), all of them determined in the previous iteration. We see that in each iteration we have to iterate simultaneously all sets of t amplitudes and to compute the effective Hamiltonian matrix. It should be emphasized that due to the presence of the renormalization term in Eqs. (15, 16) the amplitudes belonging to one reference determinant are coupled to those belonging to all other determinants.

In the next section the application of a MRCC model will be presented, where all possible terms, linear, quadratic, cubic, and quartic are retained in the direct term, while linear and quadratic terms are included in the renormalization term. We will refer to this as "quadratic" MRCCSD.

3. Applications

3.1. Computational details

A state-universal coupled cluster method for a complete model space is applied to study a prototypical molecular problem in which the range of quasidegeneracy of the electronic levels change in a broad spectrum from the entirely degenerate case to a nearly nondegenerate one. The problem studied is the H_4 system consisting of two stretched hydrogen molecules in a trapezoidal configuration where all nearest-neighbor internuclear separations are fixed ($a = 2$ a.u.) while the angle

$\phi = H_1H_2H_3 - \pi/2$ varies in the interval $\phi \in (0, \pi/2)$ [50]. The range of degeneracy of this model is determined by a parameter α defining the angle $\phi = \alpha\pi$.

In order to compare correlation energies from our fully quadratic MRCCSD calculations with results provided by other variational and non-variational methods we have implemented both the minimal and DZP basis set used by Paldus et al. [35, 49] in his studies on this topic [57]. For the same reason the reference space in our applications is formally spanned by four configurations, namely the closed-shell singlet model functions biexcited with respect to each other (vectors included in Paldus studies), and two open-shell configurations of a different symmetry, resulting in two-block diagonal matrices. Both N-electron and $N-2$ electron (QRHF [58]) references have been adopted as alternative choices of a starting vector, with respect to which a set of creation and annihilation operators may be defined. To accelerate the convergence of the iterative scheme for the solution of the nonlinear equations, the zeroth-order one-particle energies are shifted [56, 59] to make the gap between active space and core and particle subspaces, respectively, more pronounced. We have tested several alternative ways of solving Eqs. (15, 16) with the best results provided when both direct and renormalization terms are calculated in each iteration. As already emphasized, all $\hat{T}$ amplitudes that constitute the upper vertices in the renormalization diagrams refer to the current intermediate model state with the consequence that we retrieve the amplitudes assigned to it and use those as t coefficients in the algebraic formulae.

All CC calculations are performed with the ACES package of electronic structure codes [60] and exact correlation energies are calculated using a direct full CI program [61]. (Results for some geometries are already published [49] but for completeness we reproduce all of them here.)

4. Results and discussion

During the past decade the H_4 model system has been investigated by a variety of variation and perturbation methods using minimal [35, 50, 62–65] and DZP [49] basis sets. (See also the accompanying article in the present volume [66]). In order to shed light on the subtle interplay between dynamic and nondynamic correlation effects the main focus has been on the performance of the methods in situations where a different degree of degeneracy of electronic levels occurs. Our study represents a natural extension of this effort reporting results from the complete Hilbert space MRCCSD approach with the inclusion of all terms both in the direct and all quadratic terms in the renormalization part of Eqs. (15, 16).

Previous studies on the topic [49, 50, 62–65] have pointed out that a single-reference CC approach with a satisfactorily flexible cluster expansion can be applied even for the description of highly degenerate situations. When we look at the efficacy of such calculations, however, the question arises of how to achieve a balanced truncation of the expansions for the cluster amplitudes and the effective Hamiltonian. The first step in answering this question is the extension of the single-determinantal model space to include in the reference the first excited state of the same symmetry (which becomes quasidegenerate with the ground state for parameter $\alpha \to 0$). Formally, the complete model space comprises also two open-shell configurations of a different symmetry, which in our formalism provides an opportunity to study the convergence for both closed- and open-shell correlation problems.

Table 1. Comparison of the minimal basis set FCI and MRCC correlation energies for the H_4 model as a function of the parameter α (all energies in mH). The MRCC values indicate the difference of CC energies from corresponding FCI values

α	X^1A_1[a]		$^3B_1$[a]		$^1B_1$[a]		$^1A_1$[a]	
	FCI	MRCC[b]	FCI	MRCC[b]	FCI	MRCC[b]	FCI	MRCC[b]
0.0	−117.621	0.046 0.041		−111.392[c]	31.676	−0.066	−7.268	0.002 0.000
0.05	−76.428	−0.045 −0.245	−29.177	0.313	131.638	−0.006	118.949	0.062 0.041
0.1	−65.321	−0.209 −0.702	27.541	0.920	211.379	−0.079	221.429	−0.662 −0.749
0.15	−60.039	−0.605 −1.401	65.062	1.368	268.828	−0.073	280.305	−2.445 −2.595
0.2	−57.260	−1.070 −2.089	88.713	1.677	307.525	−0.020	310.718	−4.390 −4.468
0.3	−54.775	−1.703 −2.804	111.328	2.048	347.156	0.106	333.482	−6.523 −6.711
0.4	−53.905	−1.928 −2.902	118.359	2.224	360.307	0.194	337.505	−7.001 −7.195
0.5	−53.689	−1.975 −2.883	119.824	2.275	363.143	0.224	337.644	−7.039 −7.234

[a] Despite the higher symmetry for the square ($\alpha = 0.0$) and linear ($\alpha = 0.5$) structures, we use the C_{2v} symmetry notation for all geometries

[b] The current MRCC results are obtained from fully-quadratic multi-reference calculations while the prior MRCCSD applications [35] for the A_1 states included only the $\hat{T}_2^2/2$ quadratic contribution (first and second line, respectively)

[c] The corresponding FCI results are not available

Table 1 compares results of our minimal basis set two-configurational MRCCSD study of H_4 in comparison with available correlation energies provided by the Hilbert space orthogonally spin-adapted CC method of Paldus et al. [35]. It should be emphasized, that in our calculations, at least all quadratic contributions are included in both (direct and renormalization) terms on the right-hand side of Eqs. (15, 16), while the Paldus et al. application only incorporates the $\hat{T}_2^2/2$ quadratic terms in the CC equations. In order to make a meaningful test of the performance of our formulation all results are compared with exact FCI energies.

Two facts are immediately apparent when comparing the MRCCSD energy values for closed-shell model configurations in Table 1. Considering the sign of deviations from the FCI values, the correlation energies from both MRCC methods approach the exact energies from below with the largest differences for the nondegenerate regions of the energy surface (Fig. 1). As far as absolute values of the correlation energies are concerned, the application with full inclusion of quadratic terms provides a better approximation to the exact FCI energies over the whole spectrum of geometries studied. In the vicinity of complete degeneracy ($\alpha = 0$) there is excellent agreement between the two MRCC approaches, while moving towards the nondegenerate region increases the differences. This can be attributed to the relatively higher importance of singly excited states for nondegenerate situations which affects the size of the $\hat{T}_1^2/2$ and $\hat{T}_1\hat{T}_2$

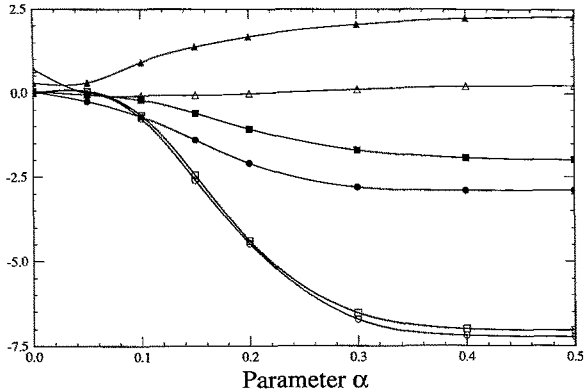

Fig. 1. Differences of minimal basis set MRCCSD correlation energies from exact FCI values ΔE, $\Delta E = E - E_{\mathrm{FCI}}$, for the ground and three excited states of the model system H_4 (all deviations in mH) as a function of α (see text). The methods are identified as follows: fully-quadratic MRCCSD; (■) root X^1A_1; (□) root $^1A_1$; (▲) root $^3B_1$; (△) root $^1B_1$; MRCCSD including only the $\hat{T}_2^2/2$ quadratic contribution [35]; (●) root X^1A_1; (○) root $^1A_1$

quadratic contributions, not included in Paldus et al. calculations [35]. It should be emphasized, however, that already incorporating the $\hat{T}_2^2/2$ terms into the linear CCSD expansion qualitatively improves the convergence of the MRCC correlation problem, which is affected by intruder states, and provides a good approximation to the fully quadratic MRCCSD method. Contrary to the closed-shell MRCC results, the multi-reference correlation energies for open-shell configurations approach the exact energies from above.

The open-shell states, $^3B_1$ and $^1B_1$, have a somewhat different behavior. The absolute deviations from FCI energies for the $^3B_1$ configuration vary with respect to the degeneracy occurring with the best convergence for the quasidegenerate situations (Fig. 1), while the open-shell singlet, $^1B_1$, energies are in very close agreement with the corresponding FCI energies for the whole range of geometries. The importance of open-shell singlets in chemistry and their inability to be adequately described in single-reference theories (unlike $^3B_1$) makes MRCC methods especially relevant.

As mentioned previously, to investigate the use of other orbital choices, besides the N-electron orbitals we have implemented the MRCC method with orbitals taken from an $N-2$ (QRHF) electron reference [67]. For all the situations studied, the QRHF orbitals are seen to provide worse convergence of the multi-reference CCSD expansion, with the deviations from the FCI energies increased about 30–40% compared to the results corresponding to the N-electron reference set.

It is well known [49] that the main insufficiency of the minimal basis set H_4 model is the fact that the complete configuration space is spanned by a very few configurations (e.g. it contains only one tetra-excitation). In order to decide whether the semiquantitative agreement of MRCCSD results with the exact FCI energies (see Table 1) is caused mainly by mutual cancellation of the limitations in our calculations we have decided to investigate also an extended double zeta plus polarization basis (DZP) for H_4, suggested by Paldus et al. [49].

Applications of the MRCISD approach and LMRCC method [49] for the larger DZP basis demonstrate both merits and shortcomings of the multi-reference model. In the case of variational approaches, MRCISD provides truly

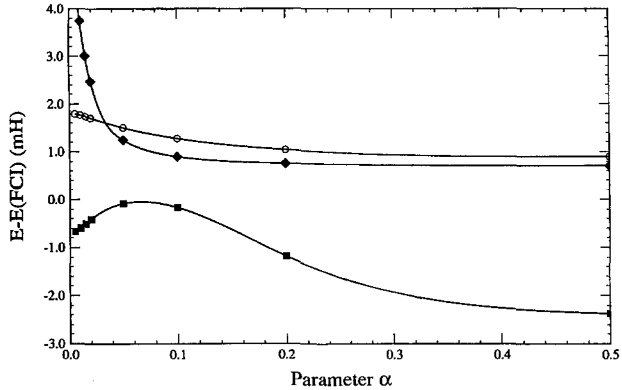

Fig. 2. The single- and multi-reference CC and CI relative energies $\Delta E = E - E_{\mathrm{FCI}}$, (in mH) as a function of α (see text) for the ground state of the DZP H_4 model system. The various methods are identified as follows: (◆) CCSD; (○) MRCISD; (■) fully-quadratic MRCCSD

satisfactory results (in comparison with single-reference CI models) with relatively small differences from the exact energies across the whole range of quasidegeneracies studied (Fig. 2). The application [49] of an approximate linear MRCC method [10, 30] provides expected results where the linear CCSD correlation energies approach the exact FCI energies from below with the largest deviations in the nearly degenerate region. Considering the analogy to the single-reference CCSD approach, we can expect that employing our extensive fully-quadratic MRCCSD model should improve the linear multi-reference CC description over the whole spectrum of geometries studied.

Table 2 summarizes results of the DZP four-configurational fully quadratic MRCC study of the H_4 model system. Comparing MRCCSD correlation energies for the ground state with the exact FCI results, we can observe an overestimation analogous to that for the minimal basis H_4 model (Fig. 2). However, when we look more closely at the multi-reference DZP values for all geometries we can distinguish two regions that differ by the convergence pattern for restricted CCSD expansions for the cluster operator and effective Hamiltonian, respectively. In the degenerate region characterized by $\alpha \leqslant 0.05$, MRCCSD correlation energies represent an excellent approximation to the exact energies. For the nondegenerate situation, however, the deviations of the multi-reference CCSD energies from the exact values increase monotonically, contrary to single-determinantal CCSD results which asymptotically approach the FCI limit from above (see Fig. 2).

The explanation for this behavior can be found when observing the differences between the exact energies for the two model states in Table 2. For instance, for point $\alpha = 0.005$ the energy gap between the first and second root is 0.083712 a.u., with the rest of the Q space fairly well separated (the energy difference between the second and third FCI root being 0.19845 a.u. e.g.). For the nondegenerate case ($\alpha = 0.5$) the situation is just the opposite, with the difference between the energies of the model states (0.367595 a.u.) being 8.2 times higher than the energy gap between the second and the third root. Moreover, the excited model state does not correspond to the second root in the FCI solution when an open-shell excited state of the same symmetry lies 0.044755 a.u. below the first closed-shell excited configuration. Because of an apparent intruder state problem (as already discussed in [35]) the single-reference description of the ground state with the second configuration being included in the Q space is more successful for the nondegenerate region than the two-configuration model

Table 2. Energies for the DZP H_4 model obtained using fully-quadratic MRCCSD for four model configurations (all values in mH). The deviations of the multi-reference results from FCI energies are shown for the MRCCSD method. The first result for each α corresponds to using N-electron SCF orbitals while the second employs $N-2$ electron orbitals

α	X^1A_1[a]		$^3B_1$[a]		$^1B_1$[a]		$^1A_1$[a]	
	FCI	MRCCSD	FCI	MRCCSD	FCI	MRCCSD	FCI	MRCCSD
0.0	−131.361	−0.687	−142.530	0.058	−47.637	1.327	−49.680	3.370
		−0.322		0.339		1.159		3.003
0.005	−123.831	−0.664	−133.667	0.048	−37.917	1.385	−40.119	3.356
		−0.308		0.326		1.181		2.994
0.01	−117.956	−0.594	−125.045	0.030	−28.293	1.420	−29.192	3.299
		−0.260		0.304		1.218		2.955
0.015	−113.412	−0.503	−116.715	0.048	−18.754	1.433	−17.275	3.228
		−0.199		0.318		1.233		2.907
0.02	−109.870	−0.408	−108.627	0.059	−9.351	1.462	−4.729	3.160
		−0.135		0.323		1.264		2.865
0.05	−98.647	−0.084	−65.377	0.217	43.759	1.671	71.152	3.060
		0.032		0.460		1.507		2.882
0.1	−91.006	−0.172	−11.021	0.600	117.575	2.070	168.217	3.491
		−0.236		0.839		2.012		3.293
0.12	−89.169	−0.322	5.526	0.740	141.866	2.238	194.947	3.585
		−0.463		0.986		2.234		3.310
0.15	−87.121	−0.714	25.765	0.945	173.024	2.498	224.624	3.462
		−0.900		1.204		2.582		3.039
0.2	−84.953	−1.186	49.710	1.145	212.255	2.889	254.831	2.767
		−1.744		1.426		3.129		2.132
0.3	−83.042	−1.995	73.250	1.412	254.429	3.490	279.104	1.721
		−3.108		1.714		4.023		0.997
0.4	−82.460	−2.305	80.832	1.535	269.301	3.810	284.609	1.652
		−3.786		1.840		4.538		1.041
0.5	−82.333	−2.375	82.481	1.571	272.710	3.907	285.262	1.723
		−3.983		1.876		4.701		1.173

[a] See footnote (a) in Table 1

space approach. An alternative (and more general) way to improve the MRCCSD results for the nondegenerate situation lies in extending the limited singles and doubles formulation to include tri- and tetra-excitations within the model space (which is now in progress).

Finally we present a comparison of quadratic MRCCSD results for four model functions with exact FCI energies (Fig. 3). As was already mentioned the deviations of the multi-reference ground state energies from the FCI limit vary with respect to parameter α with the smallest differences being obtained for energies at $\alpha = 0.05$. The same convergence pattern can also be found for the lowest triplet state; however, comparing with the minimal basis set results, the deviations of the $^3B_1$ correlation energies from the FCI values are smaller than the ground state ones. Comparing the results for the excited states we can see (Fig. 3) that the sum of deviations for the corresponding B_1 and A_1 roots for a given geometry is fairly constant for all points studied (with the excitation

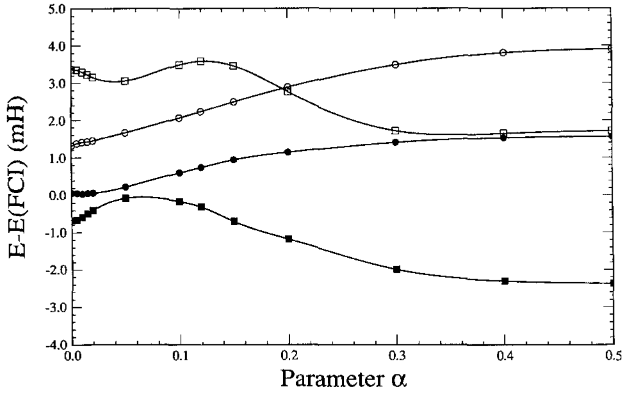

Fig. 3. Differences of N-electron reference based DZP MRCCSD correlation energies from exact FCI values for the ground and three excited states of the model system H_4 (all deviations in mH) as a function of α (see text). The curves are identified as follows: (■) X^1A_1; (□) $^1A_1$; (●) $^3B_1$; (○) $^1B_1$

energies overestimated by about 0.003–0.004 a.u. (A_1) and 0.0015–0.0025 a.u. (B_1) in comparison with FCI values).

The same trends can also be observed when N-2 electron orbitals are used (Table 2). The results for the closed-shell (open-shell) correlation problem are systematically overestimated (underestimated) compared to the N-electron reference based values, except for the ground and B_1 singlet state correlation energies in the degenerate region (Table 2) where the results are improved. In general, the energy differences between corresponding A_1 and B_1 states are comparable with those for the N-electron reference.

Generally, in contrast to the minimal basis set MRCCSD results, correlation energies for the excited closed-shell model functions are systematically underestimated with respect to the exact energy values, and also the corresponding deviations for the open-shell singlet configuration are much larger (Table 2). Clearly, the larger DZP basis introduces many more configurations and introduces much more correlation than in the minimum basis. Our results attest to the danger of drawing conclusions based on the small basis. A focus of our next study will be to assess whether the errors in our results are a consequence of the multi-reference formulation in general or rather a result of the limitations in our approach.

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