COUPLED-PAIR THEORIES AND DAVIDSON-TYPE CORRECTIONS FOR QUASIDEGENERATE STATES: THE H_4 MODEL REVISITED

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

The performance of various variational and non-variational approaches to the many-electron correlation problem is examined for a simple four-electron model system consisting of two stretched hydrogen molecules in trapezoidal, rectangular and linear configurations, in which the degree of quasi-degeneracy can be continuously varied from a non-degenerate to an almost degenerate situation. In contrast to an earlier work (K. Jankowski and J. Paldus, Int. J. Quantum Chem. *18*, 1243 (1980)) we employ a double-zeta plus polarization basis and examine both single reference and multireference configuration interaction and coupled-cluster-type approaches. The performance of various Davidson-type corrections is also investigated.

It is well known that the size-consistency or size-extensivity problem for truncated variational expansions, such as used in configuration interaction (CI) approaches restricted to singly and doubly excited configuration states, arises due to the presence of unlinked contributions. These unlinked terms make these variational energies nonadditive when applied to an assembly of non-interacting systems, and similarly influence the potential energy surfaces when dissociation into smaller fragments is involved. The non-physical unlinked terms can best be eliminated *a priori* by employing a genuinely size-extensive approach, such as the finite-order many-body perturbation theory[1-3] (MBPT) or various infinite-order coupled-cluster (CC) approaches[4-6]. (For numerous reviews and monograph chapters on these subjects

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see Refs 7–20.) Although these approaches are nowadays often employed for closed-shell ground states, their use in quasidegenerate or general open shell cases is far from being routine. Consequently, one often employs the conceptually simplest variational CI approaches, where numerous recent developments[21] enable large scale computations to be carried out for general states of arbitrary multiplicity, and eliminates the unlinked terms *a posteriori* by applying various forms of Davidson--type corrections[16,22–32]. Clearly, the latter procedure can only achieve an approximate elimination of unlinked cluster contributions.

It is worth noting that the elimination of unlinked terms is equally important for the computation of various second order properties, such as polarizabilities and van der Waals coefficients[33–35]. This was clearly shown in the case of the neon dimer, where the unlinked cluster contribution amounts to about 13% of the dipole and quadrupole polarizability values and corresponding C_6 and C_8 coefficients[36].

For methods based on a non-degenerate single-determinantal closed shell reference state, the relationship between variational and perturbative approaches is well understood[16,27]. In particular, there exists an explicit relationship[27] between the CI and linear CC (LCC) approaches limited to doubly excited configurations (i.e., CI-D and LCC-D), which contains the Davidson correction as a leading term. An extension of this idea to the multi-reference (MR) case has led to a CI based approximate MR-LCC method[16], which was recently extensively exploited by Bartlett's group[37,38] and to corresponding generalizations of Davidson's correction to the multireference case[16,31,32].

In examining the suitability and performance of various approaches, it is instructive to compare them with the full CI(FCI) result representing the exact solution for a given model (cf., e.g. Ref. 39). Nowadays, as the FCI results are more easily available, this is becoming more and more the practice in testing of various methods (cf. Ref. 17). Moreover, it is useful to devise models in which the quasidegeneracy (or other studied property or characteristic) can be continuously varied over a large range, so that the effectiveness of various approaches can be systematically examined and evaluated.

Such a systematic examination of the applicability of coupled-pair theories to quasidegenerate electronic states was carried out[40] for a minimum basis set (MBS) four-electron model of two stretched hydrogen molecules with trapezoidal, rectangular and linear geometry, referred to as the H4, P4, and D4 models, respectively. By varying the trapezoidal angle in the H4 model or the distance between the hydrogen molecules in the P4 model, we can change the quasidegeneracy of the HF ground state in a continuous manner from a non-degenerate situation to an almost degenerate one as the FCI results given in Table I of Ref. 40 indicate. This study clearly showed that while the LCC-D or LCC-SD (linear CC approach with singly and doubly excited cluster components) breaks down completely in the quasidegenerate region (when the purely biexcited submatrix of the CI problem becomes singular), the

TABLE I

Total SCF (E_{SCF}) and the lowest two FCI (E_1, E_2) electronic energies (i.e., no nuclear repulsion is included) of the totally symmetric species for the H4, P4, and D4 DZP models (in a.u.). The coefficients of the most significants configurations in the corresponding FCI wavefunction are also given. The configuration (*ijkl*) represents a spin-bonded function with (*ij*) and (*kl*) singlet coupled pairs*. The orbitals labeled 1—4 represent the orbitals with the lowest orbital energy of the four D_{2h} symmetry species for the P4 model [the *i*-th orbital having $(i-1)$ nodes within the MBS subspace], and the corresponding orbitals for the other two models

α	$-E_{SCF}$	$-E_1$ $-E_2$	(1122)	(1133)	(2233)	(2213)	(1234)	(1324)	(1144)	(2244)	(3344)	(1124)
						Model H4 DZP						
0·5	4·317035	4·399367	·966	—·172	—·066	·018	·072	—·068	—·045	—·047	·019	—·015
		4·031772	·106	·605	—·283	—·624	·160	·186	—·121	·059	—·010	·294
0·4	4·326948	4·409408	·966	—·172	—·066	—·017	—·074	·068	—·045	—·047	·019	—·014
		4·042339	·106	·611	—·279	·613	—·160	—·188	—·126	·061	—·010	·306
0·2	4·412583	4·497536	·964	—·173	—·068	—·013	—·091	·064	—·053	—·046	·021	—·009
		4·157752	·121	·705	—·249	·474	—·128	—·196	—·161	·066	—·014	·349
0·1	4·496160	4·587166	·955	—·198	—·073	—·008	—·111	·064	—·062	—·042	·025	—·005
		4·327944	·173	·859	·218	·250	—·049	—·176	—·165	·049	—·020	·220
0·075	4·523104	4·617188	·948	—·222	—·073	·007	·117	—·066	—·063	—·040	·027	—·005
		4·397807	·204	·889	—·205	—·177	·030	·163	—·160	·041	—·021	·160
0·05	4·554041	4·652688	·934	—·271	—·070	·007	·123	—·071	—·061	—·038	·029	—·005
		4·482888	·260	·901	—·193	—·109	·020	·146	—·154	·031	—·019	·100
0·02	4·599715	4·709585	·868	—·435	—·047	·008	·125	—·089	—·042	—·037	·033	—·007
		4·604444	·428	·854	—·184	—·038	·032	·113	—·151	·016	—·012	·036
0·01	4·618147	4·736103	·803	—·547	·027	·006	—·121	·100	—·024	—·036	·034	·005
		4·647340	·541	·792	—·183	—·018	—·046	—·094	—·150	·009	—·007	—·017
0·005	4·628185	4·752016	·752	—·615	—·014	·004	—·116	·106	—·013	—·036	·034	·003
		4·668304	·610	·742	—·182	—·009	—·056	—·081	—·150	·005	—·004	—·008

TABLE I
(*Continued*)

α	$-E_{SCF}$	$-E_1$ / $-E_2$	(1122)	(1133)	(2233)	(1234)	(1324)	(1144)	(2244)	(3344)
					Model P4 DZP					
10	3·575250	3·651093	·970	−·076	−·077	−·153	·002	−·077	−·076	·024
		3·154471	<·001	·430	−·429	−·286	−·572	−·428	·428	<·001
4	4·111574	4·190851	·968	−·086	−·082	−·143	·024	−·085	−·060	·025
		3·721755	·023	·654	−·420	−·213	−·501	−·352	·250	−·010
2·2	4·571084	4·674745	·911	−·337	−·064	·130	−·078	−·057	−·038	·032
		4·546622	·329	·894	−·188	·020	·136	−·154	·024	−·017
2·1	4·604408	4·716935	·847	−·474	−·041	·125	−·093	−·036	−·037	·034
		4·620068	·468	·835	−·184	·037	·108	−·151	·013	−·010
2·04	4·624935	4·746977	·767	−·596	−·018	·118	−·104	−·016	−·036	·034
		4·662322	·590	·757	−·183	·053	·085	−·150	·006	−·004
2·02	4·631871	4·758225	·730	−·641	−·009	−·114	·108	−·008	−·036	·035
		4·675675	·635	·721	−·182	−·060	−·076	−·149	·003	−·002
2·01	4·635358	4·764125	·710	−·664	−·004	·112	−·109	−·004	−·035	·034
		4·682173	·658	·701	−·181	·063	·071	−·149	·002	<·001
2·002	4·638156	4·768984	·693	−·681	<·001	−·111	·111	<·001	−·035	·034
		4·687277	·676	·684	−·181	−·065	−·068	−·148	<·001	<·001

TABLE I
(*Continued*)

α	$-E_{SCF}$	$-E_1$ / $-E_2$	(1122)	(1133)	(2233)	(2213)	(1234)	(1324)	(1144)	(2244)	(1124)	(3344)
						Model D4 DZP						
6	3·695686	3·771678	·970	−·076	−·080	−·002	−·149	·009	−·078	−·073	−·001	·024
		3·280427	·002	−·298	·283	·676	·185	·358	·245	−·229	−·363	<·001
4	3·886094	3·962626	·970	−·084	−·085	−·004	·138	−·023	−·075	−·066	·003	·024
		3·511345	−·002	−·440	·342	·677	−·221	−·383	·223	−·174	−·135	·002
2	4·317035	4·399367	·966	−·172	−·066	·018	·072	−·068	−·045	−·047	−·015	·019
		4·031772	−·106	−·605	·283	·624	−·160	−·186	·121	−·059	−·294	·010
1·5	4·533522	4·625500	·956	−·233	−·049	−·037	·038	−·076	−·031	−·039	·028	·016
		4·257290	·187	·687	−·242	·566	·105	·095	−·090	·034	−·278	−·014
1	4·856511	4·965265	·939	−·302	−·036	·050	−·007	·068	−·022	−·027	·035	·012
		4·578584	·278	·785	−.179	−·444	−·029	−·006	−·061	·013	−·231	−·014

* Note that in Ref. 40 we used the pp-hh coupled states[65,66]. In this convention the sign of the first nonvanishing singlet (the only one which survives when double occupancies occur) is opposite to the standard convention[67].

CC-D and CC-SD approaches yield remarkably good results even when the ground state becomes strongly quasidegenerate. Likewise various approximate coupled-pair theories, particularly the CC-SD(4,5)[40,41] or ACCD[42,43] approach accounting for pair-coupling diagrams which are separable over one or two hole lines, yielded excellent results[44-46]. This also explains the success of various coupled-electron-pair approximation (CEPA)-type approaches[8,47-50] which consider only the most important EPV (exclusion principle violating) diagrams of the same type. On the other hand, a standard Davidson correction grossly overestimates the correlation energies in the quasidegenerate region.

The performance of the finite order non-degenerate (single reference) MBPT was investigated for this model by Wilson et al.[51]. Although the fourth order MBPT energies are much inferior when compared with the CC energies in the highly quasidegenerate region, a part of the higher order contributions can be recovered using denominator shifting or Padé approximants. However, this infinite-order resummation works only for small quasidegeneracies, since the perturbation series behaves less like a geometric series as quasidegeneracy increases.

The same model was also employed in a study of a variational formulation and gradient evaluation for CEPA by Pulay[52].* Finally, it was also investigated by Kaldor[53] using the multi-reference degenerate MBPT (cf. also Ref. 54).

The main shortcoming of this simple model is the fact that the full CI space is very small and contains only one tetra-excited configuration. For this reason, Jankowski et al.[30] have extended the model to eight electrons, considering four stretched H_2 molecules in an irregular octagonal configuration, with two oppositely placed molecules being fixed and the remaining two moved while keeping them parallel to one another and perpendicular to the other pair (cf. Fig. 1 of Ref. 30). Again, the same MBS was employed. For this model, which involves up to the octuple excitations, the CC-SD or CPMET (coupled pair many-electron theory) provides again a good description of the correlation effects even in the highly quasidegenerate region (the largest error not exceeding 4·5% of the correlation energy). The authors have also tested the performance of various Davidson-type corrections which were designed for MR-CI approaches: in addition to the DDC (degenerate Davidson correction) and QDC (quasi-degenerate DC) corrections proposed earlier[16], they suggested the GDC (generalized DC) as well as the simplified scalar version of QDC (SQDC)[30], all of them yielding very encouraging results.

In severe cases of quasidegeneracy, such as found in linear metallic-like systems (e.g. cyclic polyene model[55,56] in the strongly correlated limit[57]), even the standard CPMET breaks down completely[58] when the number of electrons N exceeds 10. This breakdown can be traced to the presence of high order connected cluster contributions, mainly of the tetraexcited type (T_4). In fact, many of these clusters have

* Note that the original full CI and LCPMET results of Ref. 40 are correct while those of Ref. 52 are shifted by about 2 mH.

been shown not to possess any disconnected (i.e. $\frac{1}{2}T_2^2$) counterpart[57]. A simple procedure which implicitly accounts for these quadruply (or higher order) excited cluster components was formulated[58] and successfully used in this case[59,60]. The effectiveness of this simple procedure, referred to as the approximate coupled pair approximation with quadruples (ACPQ), can only be expected in cases when the unrestricted Hartree–Fock (UHF) approximation provides a reasonable approximation for the T_4 clusters, as its derivation clearly implies. We must also note that the ACPQ approach is very close to the CC-SD-(4, 5)[40,41] or the ACCD[42] approach, whose usefulness has been demonstrated in numerous applications[44–46] and whose potential and possible extensions based on other estimates of higher order clusters should be examined.

In this paper we consider a generalization of the H_4 MBS model by extending the basis set to a double zeta plus polarization (DZP) basis, which provides a much larger CI space with a considerable number of tetraexcited configurations. For this model we shall also investigate several new approaches, which have been developed in the meantime, namely the ACPQ approach[59], an approximate MR-LCC approach[16], as well as various MR-type Davidson corrections[16,30–32] mentioned earlier. However, we shall not examine the performance of various CEPA-type approaches except for the simplest one, CEPA(0), which is identical with the LCC-SD or LCPMET or DMBPT (∞) approaches.

THEORETICAL

We consider three H_4 models[40], representing two stretched H_2 molecules in, respectively, trapezoidal (H4), rectangular (P4) and linear (D4) arrangements. The geometry of these models is uniquely defined by a single parameter α as shown in Fig. 1. In contrast to Ref. 40, where a MBS was used, we consider a double zeta plus polarization basis (DZP), taking the 5*s* basis of Huzinaga[61] split into contracted sets of dimensions 3 and 2, and a single polarization function with exponent 0·93. We used

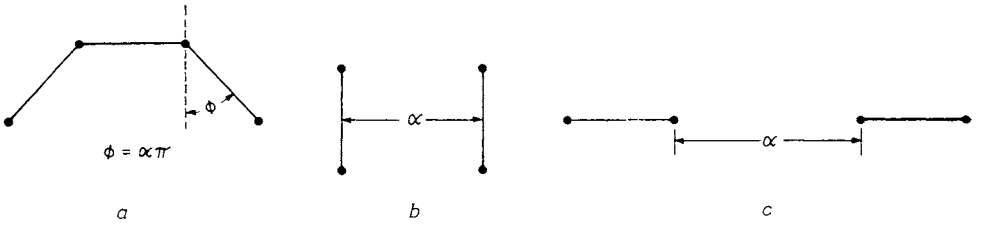

FIG. 1

Geometry of the studied models and the definition of the parameter α. The H—H internuclear separation between the sites connected by the thick lines is $2a_0$ ($a_0 = 0{\cdot}52917706 \cdot 10^{-10}$ m). *a* H4 model, *b* P4 model, *c* D4 model

system of programs ASTERIX[62] as well as ATMOL4 of Saunders and Guest[63] to generate the necessary integrals and molecular orbitals. The four MO's with the lowest orbital energies, which correspond to the MBS orbitals, are numbered 1 – 4, the first two orbitals being occupied.*

RESULTS AND DISCUSSION

In order to make a meaningful comparison of various approximate procedures and to judge their performance as a function of quasidegeneracy (as represented by the parameter α), we have first determined the exact energies for the studied DZP H_4 models using a general purpose CI program based on a spin-bonded function approach[64]. Since these models are of general interest (cf. e.g. Refs. 51 – 54) for testing the performance of various procedures, we present in Table I, a summary of the FCI results for these models with α ranging from the nondegenerate case to a highly quasidegenerate one. We also present the first excited state of the same symmetry in order to better judge the quasidegeneracy involved. Only a few coefficients which characterize the most important configurations are shown. It is easily seen that the general character of the FCI wavefunction for the DZP model is very similar to the MBS model case, except that the lowest energy tetraexcited coefficient, which corresponds to the only tetraexcited coefficient C_Q of the MBS model, increases much less with increasing quasidegeneracy than was the case for the MBS model. This is understandable in view of the fact that the quadruply excited contribution is now distributed over a large number of quadruply excited configuration states. Using the available point group symmetry, we find that the dimensions of the FCI matrices for the H4, P4 and D4 models are 3 820, 1 960 and 2 172, respectively.

Single Reference Approaches

We shall first consider standard CI and CC approaches, which are based on a single Slater determinant closed-shell reference configuration. Although these approaches are only appropriate for the lowest non-degenerate state of a given symmetry (normally the ground state), it is worthwhile to investigate their performance in quasi-degenerate situations in order to determine the limits of their applicability.

We consider limited CI approaches with doubly excited (CI-D) and both singly and doubly excited (CI-SD) configurations as well as the corresponding CC approaches) in both the linear (LCC-D and LCC-SD) and full pair-coupling (CC-D and CC-SD approximations. Moreover, we also consider the CC-SD (4, 5) or ACP-D45 (or, simply, ACP) approximation[40-43], in which only the pair-cluster coupling diagrams that are separable over one or two hole lines are retained, and the ACPQ approxima-

* All energies are expressed in this paper in atomic units. To give them the SI expression, we treat the energy as a relative dimensionless quantity E/E_h, $E_h = 2{\cdot}6255 \cdot 10^6$ J mol^{-1}. For convenience we will also use millihartrees, 1 mH = $2{\cdot}6255 \cdot 10^3$ J mol^{-1}.

tion[58] (or ACP-D45 (9_3)), which differs from the ACP approximation by a factor of 9. This factor multiplies the non-linear coupling terms that are separable over two hole lines and involve the coupling of triplet-coupled pair clusters.

The resulting correlation energies are given in Tables II–IV. For easier reference we also indicate in parentheses the percentage errors relative to the exact FCI result. It is worth noting that while the CI-D relative correlation energy errors for the MBS model are within 3–4% over the whole range of the α values considered (and in fact slightly decrease with increasing quasidegeneracy in the strongly quasidegenerate region, cf. Tables III and IV of Ref. 40), they increase over 10% value in the DZP case.

The linear CC results, while providing a very good approximation in the nondegenerate limit, suffer again from the singular behavior in the quasidegenerate region, as might be expected. The full CC-SD results provide, however, an excellent approximation in the whole range of quasidegeneracies studied, as was the case in the MBS models. Nevertheless, in contrast to the MBS case, where the sign of the relative error in the correlation energy changes with α, both the CC-D and the CC-SD correlation energies stay above the exact value for the DZP models, just as for the variational approaches. The relative error for a given CC approach is, however, less than half the corresponding CI error. The largest relative error in the strongly quasidegenerate limit is about twice as large in the DZP case as in the MBS case, and of opposite sign, as already indicated.

It is also worth mentioning that the CI and CC approaches yield very similar monoexcited contribution to the correlation energy. In both cases this contribution increases from about 1·5% to about 2% of the total correlation energy in the strongly quasidegenerate limit (except for the D4 model where the monoexcited contribution reaches 3–4% value for small α's). Generally, the CC monoexcited contribution is about 10–15% higher than the corresponding CI value, the difference increasing with the quasidegeneracy.

The approximate CC approaches as ACP and ACPQ, which in a certain manner account for the connected quadruply excited clusters (cf. Refs 58–60 for details), do provide a slight improvement, particularly in the quasidegenerate region. While the ACP recovers up to about 1% of the total correlation energy as compared with the full CC-SD result, the additional improvement due to the ACPQ (differing only by the factor of 9 for the interacting triplet-coupled clusters) is marginal ($\sim$0·2% of the total correlation energy), as is usually the case[59,60].

Multireference Approaches

We now briefly examine the CI and the linear CC results when the biexcited configuration ($1\bar{1}3\bar{3}$) is included in the reference space. The configuration ($1\bar{1}3\bar{3}$) becomes quasidegenerate with the ground state configuration ($1\bar{1}2\bar{2}$) for small α values in the

TABLE II

Correlation energies for the H4 DZP model obtained using single reference CI and CC procedures (in mH, all signs reversed). The first column gives the exact FCI energy for comparison. The numbers in parentheses indicate the relative percentage error

α	CI-approaches			CC-approaches						
	FCI	CI-D	CI-SD	LCC-D	LCC-SD	CC-D	CC-SD	CC-D(4,5(9))	CC-SD(4,5)	ACPQ
0·5	82·333	78·579 (4·56)	79·880 (2·98)	83·868 (−1·86)	85·675 (−4·06)	80·190 (2·60)	81·631 (0·85)	80·512 (2·12)	81·909 (0·52)	81·969 (0·44)
0·2	84·953	81·078 (4·56)	82·209 (3·23)	87·173 (−2·61)	88·722 (−4·44)	82·964 (2·34)	84·201 (0·89)	83·252 (2·00)	84·451 (0·59)	84·505 (0·53)
0·1	91·006	86·321 (5·15)	87·521 (3·83)	94·899 (−4·28)	96·671 (−6·22)	88·779 (2·45)	90·110 (0·99)	89·165 (2·02)	90·459 (0·60)	90·515 (0·54)
0·05	98·647	92·461 (6·27)	93·907 (4·81)	109·265 (−10·76)	112·348 (−13·89)	95·758 (2·93)	97·398 (1·27)	96·542 (2·13)	98·146 (0·51)	98·223 (0·43)
0·02	109·870	100·498 (8·53)	102·272 (6·92)	584·730 (−432·2)	2 127·10 (−1 836)	105·331 (4·13)	107·394 (2·25)	106·981 (2·63)	108·969 (0·82)	109·110 (0·69)
0·015	113·412	102·874 (9·29)	104·723 (7·66)	−47·625 (142·0)	−29·756 (126·2)	108·247 (4·55)	110·401 (2·66)	110·044 (2·97)	112·103 (1·15)	112·267 (1·01)
0·01	117·956	105·881 (10·24)	107·808 (8·60)	32·085 (72·80)	34·818 (70·48)	111·970 (5·07)	114·214 (3·17)	113·788 (3·53)	115·912 (1·73)	116·102 (1·57)
0·005	123·831	109·769 (11·36)	111·774 (9·74)	54·414 (56·06)	55·586 (55·11)	116·808 (5·67)	119·131 (3·80)	118·355 (4·42)	120·539 (2·66)	120·759 (2·48)

TABLE III

Correlation energies for the P4 DZP model (see Table II)

α	CI-approaches			CC-approaches					
	FCI	CI-D	CI-SD	LCC-D	LCC-SD	CC-D	CC-SD	CC-SD(4,5)	ACPQ
10	75·843	72·645 (4·22)	73·698 (2·83)	77·010 (−1·54)	78·288 (−3·22)	74·678 (1·54)	75·841 (0·003)	75·841 (0·003)	75·840 (0·004)
4	79·277	75·836 (4·34)	76·895 (3·00)	80·624 (−1·70)	81·925 (−3·34)	77·987 (1·63)	79·161 (1·46)	79·143 (0·17)	79·144 (0·17)
2·2	103·662	96·163 (7·23)	97·786 (5·67)	134·972 (−30·20)	140·487 (−35·52)	100·181 (3·36)	102·043 (1·56)	103·184 (0·46)	103·281 (0·37)
2·1	112·527	102·277 (9·11)	104·098 (7·49)	−66·191 (158·8)	−51·416 (145·7)	107·551 (4·42)	109·660 (2·55)	111·348 (1·05)	111·504 (0·91)
2·04	122·043	108·579 (11·03)	110·555 (9·41)	50·597 (58·54)	51·751 (57·60)	115·340 (5·49)	117·629 (3·62)	119·159 (2·36)	119·370 (2·19)
2·02	126·354	111·454 (11·79)	113·483 (10·19)	59·098 (53·23)	60·092 (52·44)	118·909 (5·89)	121·253 (4·04)	122·440 (3·10)	122·671 (2·92)
2·01	128·767	113·083 (12·18)	115·139 (10·58)	62·238 (51·67)	63·205 (50·92)	120·928 (6·09)	123·296 (4·25)	124·222 (3·53)	124·463 (3·34)
2·002	130·828	114·488 (12·49)	116·563 (10·90)	64·387 (50·79)	65·344 (50·05)	122·666 (6·24)	125·052 (4·41)	125·717 (3·91)	125·966 (3·72)

TABLE IV

Correlation energies for the D4 DZP model (see Table II)

α	CI-approaches			CC-approaches					
	FCI	CI-D	CI-SD	LCC-D	LCC-SD	CC-D	CC-SD	CC-SD(4,5)	ACPQ
6	75·991	72·779 (4·23)	73·833 (2·84)	77·853 (−2·45)	78·433 (−3·21)	74·812 (1·55)	75·976 (0·02)	75·974 (0·02)	75·974 (0·02)
4	76·532	73·269 (4·26)	74·327 (2·88)	77·646 (−1·46)	78·933 (−3·14)	75·264 (1·66)	76·435 (0·13)	76·440 (0·12)	76·441 (0·12)
2	82·333	78·579 (4·56)	79·880 (2·98)	83·868 (−1·86)	85·675 (−4·06)	80·190 (2·60)	81·631 (0·85)	81·909 (0·52)	81·969 (0·44)
1·5	91·978	86·744 (5·69)	88·872 (3·38)	94·152 (−2·36)	97·766 (−6·29)	88·409 (3·88)	90·929 (1·14)	91·465 (0·56)	91·576 (0·44)
1	108·755	100·948 (7·18)	104·237 (4·15)	113·325 (−4·20)	120·080 (−10·41)	103·106 (5·19)	107·216 (1·42)	108·200 (0·51)	108·317 (0·40)

H4 and D4 models (cf. Table I). In view of the symmetry of our model systems, this two-dimensional reference space is complete when we assume the lowest orbital to be a core orbital and the next two quasidegenerate orbitals to span the active space.

We have used the same CI program[64] to obtain the MR-CI-SD correlation energies, using the ground state SCF molecular orbitals and the two-dimensional reference space just mentioned. The dimensionality of these CI problems was 406, 217 and 264 for the H4, P4 and D4 models, respectively, using all available symmetry. In spite of this large reduction in the dimensionality, the MR-CI-SD approach provides truly excellent results in this case, as can be seen from Tables V – VII. We particularly note a very small relative change (see the percentage figures enclosed in parentheses) across the whole range of geometries which were examined.

The linear CC approach which we employed[16] represents an approximate version of this method. Although the basic equations, Eq. (87) of Ref. 16, are consistent, they nevertheless still contain some unlinked cluster contributions. We have presently formulated[68] a fully linked version of this approach for the special case of two

TABLE V

Correlation energy for the H4 DZP model (in mH, all signs reversed) as obtained with FCI, multireference CI and linear CC approaches limited to single and double excitations. Two-dimensional reference space is employed. Percentage errors relative to the FCI result are shown in parentheses

α	FCI	MR-CI-SD	MR-LCC-SD
0·5	82·333	81·438 (1·09)	83·894 (−1·90)
0·2	84·953	83·914 (1·22)	87·006 (−2·42)
0·1	91·006	89·729 (1·40)	93·857 (−3·13)
0·05	98·647	97·140 (1·53)	102·061 (−3·46)
0·02	109·870	108·164 (1·55)	113·412 (−3·22)
0·015	113·412	111·671 (1·54)	116·930 (−3·10)
0·01	117·956	116·185 (1·50)	121·436 (−2·95)
0·005	123·831	122·037 (1·45)	127·264 (−2·77)

TABLE VI

Correlation energy for the P4 DZP model. See Table V for details

α	FCI	MR-CI-SD	MR-LCC-SD
10	75·843	74·927 (1·21)	78·947 (−4·09)
4	79·277	78·264 (1·28)	82·731 (−4·36)
2·2	103·662	102·018 (1·59)	107·408 (−3·61)
2·1	112·527	110·785 (1·55)	116·104 (−3·18)
2·04	122·043	120·252 (1·47)	125·496 (−2·83)
2·02	126·354	124·555 (1·42)	129·771 (−2·70)
2·01	128·767	126·965 (1·40)	132·167 (−2·64)
2·002	130·828	129·026 (1·38)	134·216 (−2·59)

TABLE VII

Correlation energy for the D4 DZP model. See Table V for details

α	FCI	MR-CI-SD	MR-LCC-SD
6	75·991	75·051 (1·24)	79·150 (−4·16)
4	76·532	75·605 (1·21)	79·632 (−4·05)
2	82·333	81·438 (1·09)	83·894 (−1·90)
1·5	91·978	91·072 (0·99)	93·044 (−1·16)
1	108·755	107·922 (0·77)	109·681 (−0·85)

closed-shell-type references, as in the model case considered here. This study is in progress and the results will be reported elsewhere[69]. An extensive *ab initio* implementation of the approach of Ref. 16 for several quasidegenerate systems was recently published by Laidig, Saxe and Bartlett[38], showing its viability. These authors have found[38] that for general open-shell systems it is essential that MCSCF (or MR-SCF) orbitals are employed. This has not been done in our study, which is entirely based on MO's obtained with the single-determinant closed shell reference. The use of MR-SCF orbitals should provide improved results.

The MR-LCC method as implemented here exploits the MR-CI matrix, as suggested in Ref. 16. After diagonalizing the reference space 2×2 submatrix and accordingly transforming the corresponding rows (columns) of the CI matrix in order to achieve the de-coupling of the LCC system relative to each reference configuration, we shift the diagonal relative to the reference space energy ε_i (given in the columns labeled REF-CI of Tables VIII–X) and solve the linear system of equations (of the dimension of the corresponding MR-CI problem minus 2) with the transformed columns providing the right-hand-side (i.e. the absolute term; cf. the non-degenerate case, Ref. 27). The resulting correlation energy is then shifted back by the reference space energy ε_i. The results obtained with this technique are shown in the last column of Tables V–VII. The singular behavior, which plagues the LCC approach in the single reference case, is clearly removed. Typically for the LCC results, the correlation energies are overestimated by about 3–4%. We shall investigate the role of the remaining unlinked terms (which arise due to the fact that some configurations have a different excitation order relative to the two references) and the effect of different molecular orbital bases elsewhere[69].

Davidson-Type Corrections

We finally investigate various forms of the Davidson-type corrections to the MR-CI-SD energy, which can be regarded as an approximate way of estimating the LCC energies, as has been clearly shown in the single reference case[27]. In addition to the degenerate (DDC) and quasi-degenerate (QDC) Davidson corrections, which were proposed in Ref. 16, we also consider the generalized Davidson correction (GDC), suggested by Jankowski et al.[30]. In addition to these "matrix" corrections, which construct an effective Hamiltonian that must be subsequently diagonalized (except in the QDG case based on the pre-diagonalized LCC version), we also consider scalar versions of these corrections as suggested by Bruna, Peyerimhoff and Buenker[28,29] and Meissner[31,32].

For easier reference we briefly summarize the definition of the multi-reference Davidson-type corrections which we employ. We write the MR-CI-SD matrix in the following block form

$$\boldsymbol{H}_{\mathrm{MR}}^{(\mathrm{SD})} = \begin{bmatrix} \boldsymbol{z} & \boldsymbol{a}^{+} \\ \boldsymbol{a} & \boldsymbol{b} \end{bmatrix}, \qquad (1)$$

TABLE VIII

Correlation energy for the H4 DZP model (in mH, all signs reversed) obtained by using various Davidson-type corrections (see text for details). For easier reference we also give the FCI energies as well as the reference space energies (REF-CI) obtained by diagonalizing the 2 × 2 reference space CI submatrix. Percentage errors relative to the FCI result are shown in parentheses

α	CI-results		Davidson corrections						
			single reference		multiple reference				
	FCI	REF-CI	DC	RDC	DDC	QDC	GDC	SQDC	SGDC
0·5	82·333	15·773 (80·84)	84·734 (−2·92)	85·048 (−3·30)	85·433 (−3·77)	83·851 (−1·84)	84·158 (−2·22)	85·810 (−4·22)	82·208 (0·15)
0·2	84·953	13·504 (84·10)	87·552 (−3·06)	87·923 (−3·50)	87·429 (−2·91)	86·869 (−2·26)	86·718 (−2·08)	88·559 (−4·24)	84·734 (0·26)
0·1	91·006	12·227 (86·56)	94·364 (−3·69)	94·945 (−4·33)	94·194 (−3·50)	93·589 (−2·84)	93·567 (−2·81)	94·798 (−4·17)	90·624 (0·42)
0·05	98·647	14·438 (85·36)	103·946 (−5·37)	105·147 (−6·59)	102·498 (−3·90)	101·708 (−3·10)	101·697 (−3·09)	102·826 (−4·24)	98·147 (0·51)
0·02	109·870	22·405 (79·61)	121·047 (−10·17)	125·269 (−14·02)	114·330 (−4·06)	113·081 (−2·92)	113·055 (−2·90)	114·676 (−4·37)	109·319 (0·50)
0·015	113·412	25·470 (77·54)	127·140 (−12·10)	133·246 (−17·49)	118·035 (−4·08)	116·623 (−2·83)	116·588 (−2·80)	118·418 (−4·41)	112·868 (0·48)
0·01	117·956	29·573 (74·93)	135·367 (−14·76)	144·831 (−22·78)	122·792 (−4·10)	121·166 (−2·72)	121·117 (−2·68)	123·224 (−4·47)	117·434 (0·44)
0·005	123·831	35·058 (71·69)	146·625 (−18·41)	162·414 (−31·16)	128·950 (−4·13)	127·039 (−2·59)	126·975 (−2·54)	129·446 (−4·53)	123·352 (0·39)

TABLE IX

Correlation energy for the P4 DZP model. See Table VIII for details

α	CI-results		Davidson correction						
			single reference		multiple reference				
	FCI	REF-CI	DC	RDC	DDC	QDC	GDC	SQDC	SGDC
10	75·843	3·945 (94·80)	77·710 (−2·46)	77·941 (−2·77)	79·188 (−4·41)	78·837 (−3·95)	80·245 (−5·80)	79·255 (−4·50)	75·693 (0·20)
4	79·277	4·276 (94·61)	81·256 (−2·50)	81·518 (−2·83)	82·668 (−4·28)	82·415 (−3·96)	80·977 (−2·14)	82·947 (−4·63)	79·094 (0·23)
2·2	103·662	16·488 (84·09)	110·984 (−7·06)	113·043 (−9·05)	107·959 (−4·15)	107·010 (−3·23)	106·996 (−3·22)	108·198 (−4·38)	103·114 (0·53)
2·1	112·527	24·403 (78·31)	125·577 (−11·60)	131·161 (−16·56)	117·146 (−4·10)	115·780 (−2·89)	115·747 (−2·86)	117·507 (−4·43)	111·978 (0·49)
2·04	122·043	33·325 (72·69)	143·153 (−17·30)	156·783 (−28·47)	127·078 (−4·13)	125·255 (−2·63)	125·196 (−2·58)	127·556 (−4·52)	121·548 (0·41)
2·02	126·354	37·446 (70·36)	151·671 (−20·04)	171·039 (−35·36)	131·600 (−4·15)	129·563 (−2·54)	129·495 (−2·49)	132·124 (−4·57)	125·898 (0·36)
2·01	128·767	39·773 (69·11)	156·578 (−21·60)	179·878 (−39·69)	134·131 (−4·17)	131·974 (−2·49)	131·901 (−2·43)	134·681 (−4·59)	128·334 (0·34)
2·002	130·828	41·742 (68·09)	160·848 (−22·95)	187·981 (−43·69)	136·295 (−4·18)	134·033 (−2·45)	133·959 (−2·39)	136·869 (−4·62)	130·418 (0·31)

TABLE X

Correlation energy for the D4 DZP model. See Table VIII for details

α	CI-results		Davidson correction						
			single reference		multiple reference				
	FCI	REF-CI	DC	RDC	DDC	QDC	GDC	SQDC	SGDC
6	75·991	3·767 (95·04)	77·853 (−2·45)	78·085 (−2·76)	79·189 (−4·21)	78·980 (−3·93)	80·276 (−5·64)	79·386 (−4·47)	75·818 (0·23)
4	76·532	4·482 (94·14)	78·353 (−2·38)	78·584 (−2·68)	79·653 (−4·08)	79·400 (−3·75)	80·404 (−5·06)	79·957 (−4·48)	76·375 (0·21)
2	82·333	15·771 (80·84)	84·730 (−2·91)	85·044 (−3·29)	84·420 (−2·53)	83·851 (−1·84)	84·158 (−2·22)	85·810 (−4·22)	82·208 (0·15)
1·5	91·978	26·804 (70·86)	95·746 (−4·10)	96·322 (−4·72)	93·898 (−2·09)	93·071 (−1·19)	94·080 (−2·29)	95·559 (−3·89)	91·859 (0·13)
1	108·755	44·099 (59·45)	115·194 (−5·92)	116·481 (−7·10)	110·870 (−1·94)	109·659 (−0·83)	109·952 (−1·10)	112·276 (−3·24)	108·678 (0·07)

where the first diagonal block $\mathbf{z}$ corresponds to the chosen reference space $\mathscr{V}_0$, dim $\mathscr{V}_0 = M$. Designating the diagonal matrix consisting of the first M eigenvalues of $\boldsymbol{H}_{\mathrm{MR}}^{(\mathrm{SD})}$ by $\boldsymbol{\lambda}$, and the rectangular matrix whose columns represent the corresponding eigenvectors by $\boldsymbol{U}$, we can write

$$\boldsymbol{H}_{\mathrm{MR}}^{(\mathrm{SD})}\boldsymbol{U} = \boldsymbol{U}\boldsymbol{\lambda}\,, \quad \boldsymbol{\lambda} = [\lambda_i\delta_{ij}]\,, \quad \boldsymbol{U} = \begin{bmatrix}\boldsymbol{u}_0\\ \boldsymbol{u}_2\end{bmatrix}, \tag{2}$$

where $\boldsymbol{u}_0$ is the $M \times M$ square matrix formed by the reference space components of the respective MR-CI eigenvectors. The approximate MR-LCC equations take form[16]

$$\boldsymbol{a} + \boldsymbol{b}\boldsymbol{t} = \boldsymbol{t}\mathbf{z}\,,$$
$$\boldsymbol{H}'_{\mathrm{eff}} := \mathbf{z} + \boldsymbol{a}^{+}\boldsymbol{t}\,, \tag{3}$$

where $\boldsymbol{H}'_{\mathrm{eff}}$ designates the effective Hamiltonian, whose eigenvalues provide the desired correlated energies.

The following Davidson-type corrections to the MR-CI energies result by applying an analogous procedure as in the single reference case[27] to the effective Hamiltonian $\boldsymbol{H}'_{\mathrm{eff}}$ based on an approximate MR-LCC equations (*3*).

(i) *Degenerate Davidson correction* (DDC)[16]: We calculate an approximate inverse $\mathbf{g}$ of the effective Hamiltonian as

$$\mathbf{g} = \boldsymbol{u}_0^{+}\boldsymbol{\lambda}^{-1}\boldsymbol{u}_0\,, \quad \boldsymbol{\lambda}^{-1} = [\lambda_i^{-1}\delta_{ij}]\,, \tag{4}$$

and diagonalize,

$$\mathbf{g}\boldsymbol{w} = \boldsymbol{w}\boldsymbol{\gamma}\,, \quad \boldsymbol{\gamma} = [\gamma_i\delta_{ij}]\,. \tag{5}$$

Then the corrected energy is

$$E'_i = 1/\gamma_i\,. \tag{6}$$

The values E'_0 are shown in Tables VIII–X under the heading DDC.

(ii) *Quasidegenerate Davidson correction* (QDC)[16]: We first diagonalize the model space submatrix $\mathbf{z}$,

$$\mathbf{z}\boldsymbol{v} = \boldsymbol{v}\boldsymbol{\alpha}_0\,, \quad \boldsymbol{\alpha}_0 = [\alpha_i\delta_{ij}]\,. \tag{7}$$

Then, for the i-th eigenvalue we define the shifted MR-CI energy

$$\lambda'_i = \lambda_i - \alpha_i\,, \tag{8}$$

and rotate accordingly the k-th MR-CI eigenvector as

$$\boldsymbol{u}'_k = \boldsymbol{v}^+ \boldsymbol{u}_k \,, \tag{9}$$

for $k = 1, \ldots, M$, successively, and calculate the renormalized Davidson correction in the standard way, i.e.

$$(\lambda''_i)^{-1} = \frac{|u'_{i0}|^2}{\lambda'_i} \,, \quad E''_i = \alpha_i + \lambda''_i \,. \tag{10}$$

The values E''_0 are shown in Tables VIII–X under the heading QDC.

(iii) *Generalized Davidson correction* (GDC)[30]: We compute an effective matrix $\boldsymbol{G}_{\mathrm{MR}}$,

$$\boldsymbol{G}_{\mathrm{MR}} = \boldsymbol{u}_0 \boldsymbol{\lambda} \boldsymbol{u}_0^{-1} \,, \tag{11}$$

and its correction $\boldsymbol{\Delta}_{\mathrm{GDC}}$,

$$\boldsymbol{\Delta}_{\mathrm{GDC}} = [(\boldsymbol{u}_0^{-1})^+ (\boldsymbol{u}_0)^{-1} - \boldsymbol{1}] (\boldsymbol{G}_{\mathrm{MR}} - \boldsymbol{z}) \,. \tag{12}$$

The desired energies result from the diagonalization of the effective Hamiltonian $\boldsymbol{H}'''_{\mathrm{eff}}$,

$$\boldsymbol{H}'''_{\mathrm{eff}} = \boldsymbol{G}_{\mathrm{MR}} + \boldsymbol{\Delta}_{\mathrm{GDC}} \,. \tag{13}$$

The lowest eigenvalue is shown in Tables VIII–X under the heading GDC.

To compute these "matrix"-type corrections we need as many eigenvalues and corresponding eigenvectors as is the dimensionality M of the reference space $\mathscr{V}_0$. This might be computationally a very costly requirement when M is relatively large and when only the lowest few eigenstates are of practical interest. In such cases it is useful to derive the "scalar"-type MR Davidson corrections[28–32]. We consider two corrections of this type:

(iv) *Scalar* QDC (SQDC)[28]:

$$\delta' = (1 - q)(E_{\mathrm{MR}} - E_{\mathrm{SCF}}) \,, \tag{14}$$

where

$$q = \sum_{j=1}^{M} |u_{ij}|^2 \tag{15}$$

is the sum of the squares of the reference space amplitudes for the eigenstate in question, and

(v) *Scalar* GDC (SGDC)[31,32]:

$$\delta = \frac{1 - q}{q} (E_{\mathrm{MR}} - E_{\mathrm{SCF}}) \frac{(N - 2)(N - 3)}{N(N - 1)} \,, \tag{16}$$

where the electron number N dependent factor was introduced to account for the fact that no correction is required for two and three electron systems as first noted and implemented by Pople[70].

The corrected correlation energies obtained with (*iv*) and (*v*) for the ground state of the studied models are given in Tables VIII–X under the headings SQDC and SGDC, respectively.

We see immediately that while the single reference corrections grossly overestimate the correlation energy in the quasidegenerate region, all the MR-type corrections provide a good result. All the corrections, which are not adjusted for the particle number dependence, overestimate the correlation energy by about 3–5%, as in the single reference case (note that the factor $(N-2)(N-3)/N(N-1)$ equals $1/6$ for $N = 4$).

We note that QDC and GDC yield values very close to one another while the overestimate is slightly larger in the DDC case. While the GDC and QDC provide correlation energies which are closer to the exact values than the DDC energies, the latter ones may be nevertheless preferable since the relative error is almost constant across the whole range of quasidegeneracies studied.

It is worth noting that a similar effect is also found for the H_8 model studied by Jankowski et al.[30]: while the GDC correction gives the smallest relative error with respect to the FCI result, particularly in the strongly quasidegenerate limit, it is in fact the DDC correction which provides the most constant shift in the whole studied region (when α changes from 10^{-1} to 10^{-4}, the absolute error changes from 4·5 to 0·3 mH (4·2 mH change) for GDC, from 5·7 to 1·2 mH (4·5 mH change) for QDC, and from 5 to 1·7 mH (3·3 mH change) for DDC) and, consequently, would lead to the least distortion of the pertinent potential energy surface.

CONCLUSIONS

Although the correlation effects are much more significant for our DZP models than for the MBS ones investigated earlier[40] (by a factor of 2–3), the performance of single reference approaches is very similar in both cases. In particular the LCC approach suffers from the singular behavior of the doubly excited CI submatrix, while the full CC approach provides an excellent approximation in the whole range of the quasi-degeneracies studied, although its accuracy (less than 1% of the total correlation energy in the non-degenerate case and 4–5% in the quasi-degenerate region) also deteriorates with increasing quasi-degeneracy. An approximate account of quadruply-excited clusters through the ACPQ approach reduces this error by a factor of two to three in the region of intermediate quasi-degeneracies, but much less (a factor of 1/6–1/3) in the almost degenerate limit.

The error of the corresponding CI approaches, when compared with the exact FCI result for these models, is greater by a factor of 3 than for the corresponding CC

approaches in the whole range of quasi-degeneracies examined. The MR-CI approach gives excellent results, showing a very small percentage variation across the whole range of quasi-degeneracies that were examined indicating that we would need a larger system in order to study more effectively the role of unlinked contributions in the multireference case. While the variational results provide an upper bound to the exact FCI energies, the LCC energies are systematically below the exact result, as is usually the case. This overestimate amounts typically to about 4% of the correlation energy in the non-degenerate situations and decreases to about 2–3% in the degenerate limit. The effect of the remaining unlinked cluster contributions in the approximate MR-LCC approach as well as the role of different MO bases (MR-SCF vs single-reference SCF) are currently being investigated[69].

The various Davidson-type corrections provide results of a very similar overall quality. Although the scalar type correction of Meissner[31,32] (SGDC) provides the smallest absolute error (since particularly in the present case the particle-number dependent factor is rather small and thus significantly reduces the typical overestimate due to either LCC or the related Davidson corrections), other corrections may provide a better representation of the actual shape of the potential energy surface.

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