Valence bond corrected single reference coupled cluster approach

III. Simple model of bond breaking or formation

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Summary. The valence bond (VB) corrected single reference (SR) coupled cluster (CC) method [J. Paldus and J. Planelles, Theor. Chim. Acta 89, 13–31 (1994)] with Singly and Doubly excited cluster components (CCSD-VB) is applied to simple Pariser–Parr–Pople (PPP) model systems that are capable of simulating chemical bond breaking or formation. Dissociation into both closed and open shell type subsystems is considered. The 3- and 4-body connected cluster components are first determined by cluster analyzing simple PPP-VB wave functions [X. Li and J. Paldus, J. Mol. Structure (Theochem) 229, 249 (1991)] involving only covalent-type structures, and are subsequently employed in the CCSD-VB approach. The results are compared with the full configuration interaction (FCI) or full valence bond (FVB) solutions, representing the exact result for these models, and the potential of the CCSD-VB approach is discussed.

1. Introduction

In the first part of this series [1], further referred to as Part I, we have formulated a valence bond (VB) corrected single reference (SR) coupled cluster (CC) method, involving singly and doubly excited cluster amplitudes, designated as the CCSD-VB approach. The basic idea of this approach is to obtain approximate 3- and 4-body connected cluster components by cluster analyzing simple VB-type wave functions and to exploit them subsequently to truncate the CC chain of equations at the doubly excited level. This is achieved by explicitly evaluating the terms

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involving these higher than biexcited clusters and using them to correct the absolute term in the CCSD equations. Clearly, such a precaution is not necessary under normal circumstances, when basic assumptions for the applicability of the CCSD method hold, namely when higher than pair cluster amplitudes are negligible or, as in the case of T_3 clusters, may be properly accounted for through perturbative approaches [2]. It is well known that this is indeed the case for non-degenerate ground states of closed shell systems in their equilibrium geometries. However, when considering these systems away from their equilibrium conformations, particularly when dissociating or forming chemical bonds, the negligibility of these higher excited clusters no longer holds and the performance of the standard CCSD approach deteriorates or even breaks down (see, e.g. [3]). Of course, in such cases the general multi-reference (MR) formalism (for an overview see e.g. [4]) should be applied. However, since MRCC approaches are both conceptually and computationally rather demanding, it is worthwhile to explore the possibility of extending the SR CCSD method into regions where quasidegeneracy of the reference configuration plays a crucial role. Obviously, such an approach is not intended to provide highly accurate results, as one expects from bona fide MRCC methods, but rather to extend the utility of the SR CCSD approach well beyond its range of applicability.

In the second paper of this series [5], further referred to as Part II, we have tested the CCSD-VB approach on a number of π-electron model systems described by the Pariser–Parr–Pople (PPP) Hamiltonian. In this way we were able to explore the whole range of correlation effects by simply scaling the resonance integral β, whose reciprocal value may be regarded as a coupling constant. It is well known that when approaching the fully correlated limit ($\beta = 0$), both orbital and configurational degeneracy effects arise, which make the proper account of correlation effects very demanding. Indeed, a number of methods, including SR CCSD, often break down in this region [3, 6]. We have shown in Part II that simple VB wave functions, involving at most covalent structures, can provide a reasonable estimate of 3- and 4-body clusters which, in turn, yield the desirable corrections of the CCSD equations, so that meaningful results are obtained even in the region where the standard CCSD method gives very poor results.

In this paper we intend to exploit the same π-electron model systems in order to simulate a dissociation or formation of chemical bonds. We shall thus employ a physical (or spectroscopic) parametrization of the PPP Hamiltonian and model the dissociation process by assuming that for nonequilibrium geometries the resonance integral β is proportional to the corresponding orbital overlap S. This approximation forms the basis of the so-called Mulliken "magic formula" [7] for molecular dissociation energies and is thus often referred to by this name. Since for the spectroscopic parametrization the SR CCSD method works well in the vicinity of equilibrium nuclear conformations, we will be mainly concerned with the regions of the potential energy surface that correspond to highly stretched C–C bonds. Although this problem is less demanding than the exploration of the correlation effects in the region near the fully correlated limit, it represents a much more realistic model of the type of problems that one encounters when handling the ab initio models. In particular, we will also explore the case when the system dissociates into open shell fragments, so that the spin-adapted SR CCSD method is unable to properly describe the dissociation process.

In the next section we briefly describe the method and models employed. In Sect. 3 we present and discuss our results, while in Sect. 4 we briefly summarize the conclusions concerning the capabilities of the CCSD-VB approach.

2 Method and models employed

The essence of the SR CCSD-VB approach was briefly outlined in the Introduction and we refer the reader to Part I for more detail and explicit expressions for the relevant correcting terms. In Part II, this approach was applied to a number of aromatic, nonaromatic and antiaromatic π-electron model systems. In each case the whole range of the coupling constant, ranging from the noncorrelated to the fully correlated limit, was examined. The advantages and usefulness of these simple models was also amply discussed.

In this paper we use these models to simulate chemical bond breaking and formation. This is achieved by exploiting Mulliken's "magic formula" [7] (see Sect. 1) for the required resonance integrals β. Moreover, since the differences between the nearest neighbor and the next nearest neighbor C–C internuclear separations, involving carbon atoms in different subsystems which react (or into which a given species dissociates), tend to zero with the increasing subsystem separation, we abandon the tight binding approximation for the one-electron part of the PPP Hamiltonian. Thus, the π-electron Hamiltonian, Eq. (6), of Part II takes now a more general form

$$H_\pi = \sum_{\mu,\nu} \beta_{\mu\nu} E_{\mu\nu} + \tfrac{1}{2} \sum_{\mu,\nu} \gamma_{\mu\nu}(n_\mu - 1)(n_\nu - 1), \tag{1}$$

where the symbols are defined as in Part II, except that the resonance integrals $\beta_{\mu\nu}$ are considered between any two centers μ and ν, just as the two-electron Coulomb integrals $\gamma_{\mu\nu}$. They are determined by assuming their proportionality to overlap [7], i.e.

$$\beta_{\mu\nu} \equiv \beta(R_{\mu\nu}) = \frac{\beta(R_0)}{S(R_0)} S(R_{\mu\nu}). \tag{2}$$

Here $R_{\mu\nu}$ designates the distance between the sites μ and ν and $S(R)$ is the overlap integral between the $2p_z$ carbon atomic orbitals in π-orientation which are R(Å) apart,

$$S(R) = \tfrac{1}{15} e^{-\rho} (\rho^3 + 6\rho^2 + 15\rho + 15),$$
$$\rho = \xi R/a_0, \tag{3}$$

assuming the Slater's value for the effective nuclear charge $\xi = 1.625$ and a_0 is the Bohr radius (0.529177 Å) [8]. The reference equilibrium C–C separation is taken as $R_0 = 1.4$ Å and $\beta(R_0) = -2.4$ eV (or, in some cases, -2.5 eV) [8]. We note that since we go beyond the tight binding approximation, the PPP Hamiltonian (1) no longer possesses the alternancy symmetry. As we have seen in Part II, this symmetry is also usually broken in the CCSD-VB method, since the truncated VB wave functions are constructed using the overlap enhanced atomic orbitals (OEAOs).

As the source of the 3- and 4-body connected cluster amplitudes we again rely on the PPP-VB method [9]. Only covalent structures are employed throughout this study.

Similarly as in Part II, we start with the simplest model involving only T_4 clusters, namely the dissociation of the π-electron model of butadiene into the two ethylenic fragments (Fig. 1(a)). In this way we simulate the simultaneous breaking of two single bonds. Considering, next, breaking of a single bond in this model, we gradually decrease the complement θ of the $C_1C_2C_3$ and $C_2C_3C_4$ angles from $\pi/2$ to 0 (Fig. 1(b)). Finally, we examine two possible dissociation pathways for the benzene π-electron model: one leading to butadienic and ethylenic fragments
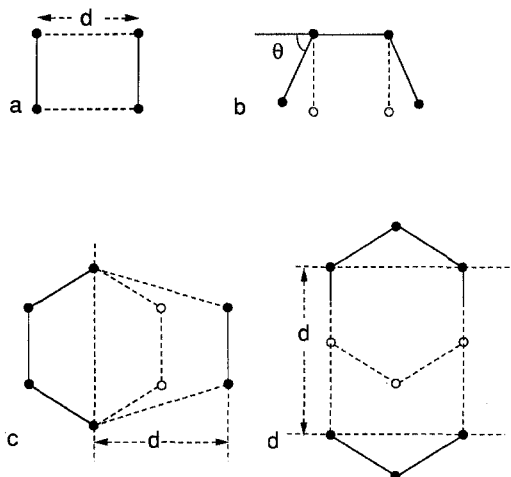
Fig. 1. A schematic representation of nuclear configurations and the definition of the parameter d for the PPP models of cyclobutadiene dissociation into the ethylenic fragments (a) and ring opening (b), as well as benzene dissociation into the closed shell (Diels–Alder mode) (c) and open shell (radicaloid mode) (d) fragments

(Diels–Alder mode) and the other one leading to two allylic fragments (radicaloid mode). The latter example is designed to test the dissociation process involving open shell fragments. The geometry of both models is depicted in Figs. 1(c) and 1(d).

3 Results and discussion

3.1 Cyclobutadiene

3.1.1 Simultaneous opening of two bonds. We first investigate the π-electron model of cyclobutadiene separation into the two ethylenic fragments or, equivalently, the interaction of two ethylenes, assuming a rectangular geometry of the nuclear framework shown in Fig. 1(a). We note that $T_1 = T_3 = 0$ at all times in this model, so that only one t_4 amplitude intervenes. Also, we have that CCD $\equiv$ CCSD $\equiv$ CCSDT. For the reference resonance integral corresponding to unstretched C–C bonds we take $\beta(R_0) = -2.5$ eV and $R_0 = 1.4$ Å. The VB description employed is always in terms of two Kekulé structures.

Now, with the exception of the square configuration, when the separation between the ethylenic fragments d (Fig. 1(a)) equals the C–C "equilibrium" bond length $R_0 = 1.4$ Å, i.e., when $d = R_0$, we have two distinct C–C "bonds" in our model characterized by distinct resonance integrals $\beta_0 = \beta(R_0) = -2.5$ eV and $\beta_1 = (\beta_0/S(R_0))S(d)$. Thus, even when involving only the nearest neighbors in the OEAO basis, we should associate different parameters with these distinct bonds. There are several ways how to account for this fact. We have thus examined the following possibilities [which we designate by the acronyms indicated in square brackets]: (a) As a crude first approximation we use only one mixing parameter throughout [VB(2K, 1ε)]. (b) We keep the mixing parameter associated with each ethylenic fragment frozen at its optimal value corresponding to the equilibrium geometry and optimize only the second mixing parameter ε_2 for each d [VB(2K; 1ε, 1ε̄)]. This approximation will be particularly useful when considering larger systems. (c) We optimize both mixing parameters [VB(2K, 2ε)].

For our simple 4-electron model, the last approach (c) leads to an almost perfect agreement with the FCI model. For example, choosing $d = 2$ Å, the FCI correlation

energy is $E_{corr}^{FCI} = -5.9154$ eV, while VB($2K$, 2ε) approach gives $E_{corr}^{VB(2\varepsilon)} = -5.9150$ eV (with $\varepsilon_1^{opt} = 0.325$ and $\varepsilon_2^{opt} = 0.064$). Using the first approximation (a) above, we will get $E_{corr}^{VB(1\varepsilon)} = -5.3772$ eV (with $\varepsilon_1^{opt} \approx 0.296$). In view of these facts we only explore the crudest appoximation (a), since the two-parameter descriptions will yield results that are almost indistinguishable from the exact FCI solutions. We shall see that even the very rough approximation (a) leads to a satisfactory description within the CCD-VB formalism.

The t_4 amplitudes obtained with the simplest PPP-VB($2K$, 1ε) approach are compared with their FCI counterparts in Table 1. We see that even this crudest approximation, which gives a rather poor energetic description of our model (see below), provides us with a reasonable estimate of the t_4 cluster amplitudes, which in fact remain to be rather small throughout the range of geometries considered. We note that the PPP-VB ($2K$, 2ε) approximation yields amplitudes (and energies; see above) that are very close to the FCI ones. Thus, for $d = 2$ Å, we get $t_4^{VB(2\varepsilon)} = -0.00012$.

Carrying out next the CCD-VB calculations with the PPP-VB($2K$, 1ε) amplitudes, we obtain a significant improvement in the vicinity of square geometry as Fig. 2 demonstrates. As expected, the two Kekulé one ε structure VB description is very appropriate for the square geometry, but significantly deteriorates for larger intersystem separations d. On the other hand, the standard CCD approach performs very well in the dissociated limit, since it involves two closed shell subsystems and the method is size extensive, but suffers in the vicinity of the square geometry, where the reference configuration becomes degenerate with the lowest lying biexcited one (see also analogous H_4 models [3a, 10]). The resulting poorer performance of the standard CCD in this region is then almost completely corrected by the CCD-VB approach exploiting the crudest estimate of the t_4 amplitude given in Table 1. Of course, in view of the poor performance of the PPP-VB($2K$, 1ε) approximation for large d values, CCD-VB energy is slightly worse than the standard CCD one for larger separations ($d = 2$ Å). As already pointed out, this disparity could be removed by considering two-parameter PPP-VB corrections.

Table 1. A comparison of approximate (PPP-VB with 2 Kekulé structures and one mixing parameter ε_1 OEAO basis) and exact (FCI) 4-body connected cluster amplitudes (t_4) characterizing the fragmentation of the π-electron model of cyclobutadiene as a function of the ethylenic subsystem separation parameter d (in Å) (see Fig. 1(a)). The optimal values of the mixing parameter ε_1 as well as the differences Δ of the PPP-VB and FCI t_4 amplitudes are also given

|		t_4		
d(Å)	$\varepsilon_1^{(opt)}$	PPP-VB($2K$, 1ε)	FCI	Δ
1.30	0.2778	-0.011572	-0.008555	-0.003017
1.35	0.2635	-0.033078	-0.024969	-0.008108
1.40	0.2549	-0.070274	-0.070688	0.000414
1.45	0.2513	-0.038521	-0.030237	-0.008284
1.50	0.2519	-0.017306	-0.013698	-0.003608
1.55	0.2560	-0.005439	-0.006716	0.001277
1.60	0.2623	-0.000650	-0.003498	0.002848
1.65	0.2693	-0.000144	-0.001880	0.001736
1.70	0.2758	-0.001577	-0.001008	-0.000569
1.80	0.2856	-0.005582	-0.000222	-0.005360
2.00	0.2958	-0.011370	0.000164	-0.011534
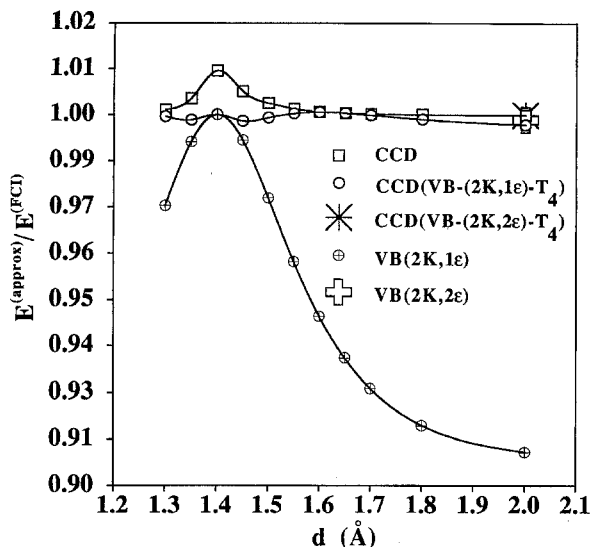
Fig. 2. Relative correlation energy $E^{(approx)}/E^{FCI}$ as a function of the intersystem separation d (in Å), (see Fig. 1(a)) for the cyclobutadiene dissociation into the ethylenic fragments, obtained with the standard and VB-corrected CCD approaches, as well as with the variational PPP-VB approach. The VB-based approaches always employ two Kekulé structures (2K) and one-parameter OEAOs (1ε). For one value of $d(d=2\text{ Å})$, the result obtained with two-parameter OEAOs (2ε) is also indicated. The label T_4 indicates that $T_1 = T_3 = 0$ in this case. See the text for more detail

To conclude, we find that even the crudest VB approximation is capable of improving the performance of the standard CCD method in the critical region of geometries.

3.1.2 Breaking of a single bond. We next explore a single bond dissociation mode in cyclobutadiene, rotating appropriately the terminal bonds as indicated in Fig. 1(b). The molecular orbitals are no longer determined by the symmetry of the model and both T_1 and T_3 no longer vanish. Since this is the simplest model in which all three correcting terms (i.e., T_3, T_4 and $T_1 T_3$) give nonvanishing contributions, we first study their role using their exact values as provided by the cluster analysis of the FCI wave function. The cluster amplitudes for two different values of the resonance integral β (−2.4 and −1 eV) are shown in Figs. 3(a) and 3(b), respectively. We also note that due to the alternancy symmetry breaking in the PPP Hamiltonian (non-tight-binding approximation), the number of t_1 and t_3 amplitudes is doubled as compared to their number for the corresponding tight binding model. We see from Figs. 3(a), (b) that the importance of T_4 clusters is again most prominent in the vicinity of the square geometry, namely for $\theta > 80°$. In contrast, both T_1 and T_3 components vanish for the square geometry, $\theta = 90°$, and are in fact rather small in the whole range of geometries involved. Nonetheless, we shall see that they play a nonnegligible role, particularly when T_4 becomes prominent.

In order to see the role of individual correcting terms in the CCSD-VB approach, we employ the exact FCI or FVB amplitudes and examine the differences in correlation energy relative to the FCI exact result as shown in Fig. 4. Thus, when considering all three correcting terms simultaneously, we recover the exact
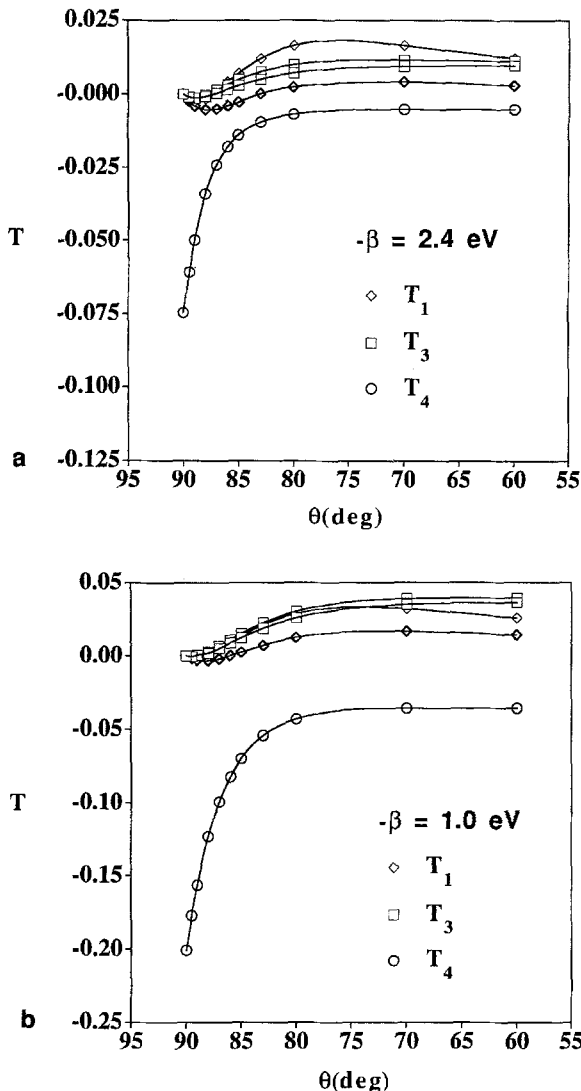
Fig. 3a, b. The exact one, three and four-body connected cluster components obtained by cluster analysis of the FCI wave function modelling the cyclobutadiene ring opening as a function of the angle θ (in degrees), (cf. Fig. 1(b)). Two values of the resonance integral characterizing the equilibrium C–C bond are considered: -2.4 eV (a) and -1 eV (b)

FCI result. We see that in the case of physical parametrization ($\beta = -2.4$ eV), the standard CCSD method gives excellent results up to $\theta \sim 75°$. We also see that the $T_1 T_3$ correcting term gives an almost negligible effect, the CCSD-VB($T_1 T_3$) energies hardly differing from the standard CCSD ones for both resonance integral values considered. The role of T_3 and T_4 corrections are very interesting. Both are very small for the spectroscopic parametrization in the nondegenerate region, i.e. for $\theta < 80°$, and working against each other. Indeed, we can say that in this region of geometries both corrections practically compensate, although when applied simultaneously, they do improve the CCSD result yielding practically the FCI result. For example, for the geometry corresponding to cis-butadiene ($\theta = 60°$), we have that the standard CCSD and $T_1 T_3$, T_3, T_4 and ($T_3 + T_4$) corrected CCSD-VB correlation energies are -1.4110, and -1.4106, -1.4162, -1.4047, and
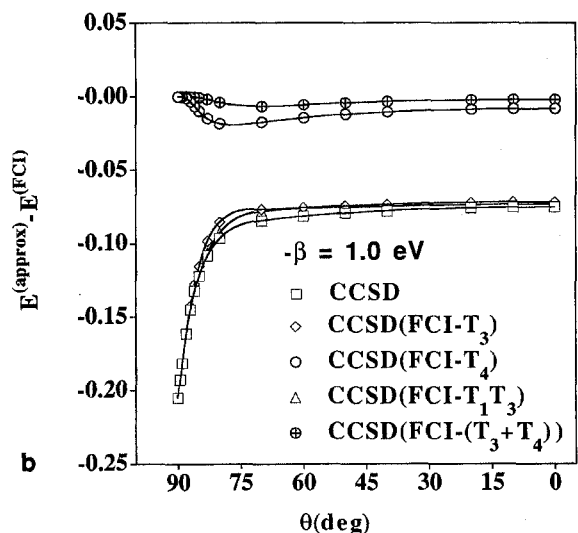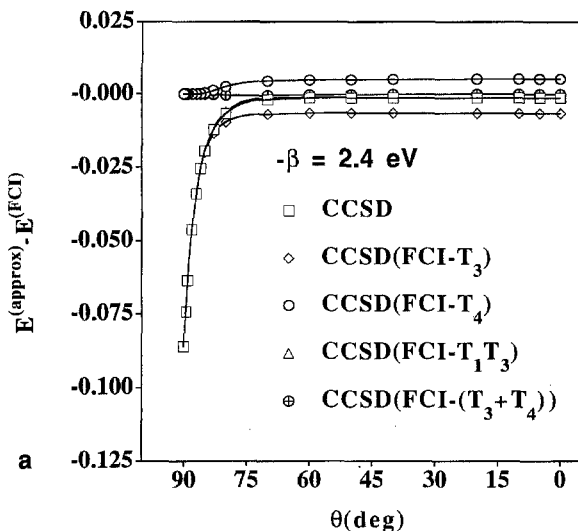
Fig. 4a, b. Correlation energy (relative to the FCI energy) (in eV) of the cyclobutadiene ring opening model, obtained with the standard and VB-corrected CCSD approaches, as a function of the angle θ (in degrees) (see Fig. 1(b)). The CCSD-VB approaches, involving $T_3, T_4, T_1 T_3$ and $T_3 + T_4$ correcting terms, employ the exact FCI cluster amplitudes. The results for equilibrium resonance integral values of -2.4 eV (a) and -1 eV (b) are shown

-1.4099 eV, respectively. The corresponding FCI value is -1.4096 eV. For $\theta > 80°$, when the prominence of T_4 clusters rapidly increases with θ, we see practically no effect of T_1 and T_3 clusters (both of which tend to zero in the $\theta = 90°$ limit), so that T_4 corrected CCSD-VB gives a practically exact result. For the $\beta = -1$ eV case, where the correlation effects are more prominent, we see again a small effect of $T_1 T_3$ and T_3 corrections by themselves, although now T_3 and T_4 corrections work in the same direction. We also see that around $\theta \sim 75°$ their contributions are clearly nonadditive. These results should be also compared with the ab initio results concerning the H_4 model [11]. Although very different methodology was used in both cases, since the T_3 or T_4 corrected CCSD equations are very different from the CCSDT or CCSDQ ones, the similar behavior of the 3- and 4-body effects resulting in both cases is interesting.

After exploring the role of individual correcting terms we are now ready to examine how well these corrections can be accomplished using approximate VB wave functions. We used again 2 Kekulé structures and two distinct nearest neighbor parameters: one for the C–C bonds of fixed bond length (ε_1) and one for the C–C bond being broken (ε_1'). Optimizing both parameters we see that ε_1 does not change very much (being 0.25 at $\theta = 90°$, 0.29 at $\theta = 80°$ and 0.31 at $\theta = 0$, while ε_1' rapidly decreases as θ changes from 90° to 80° (from 0.25 at $\theta = 90°$ to 0.039 at $\theta = 80°$ reaching zero at $\theta = 75°$). We could thus keep ε_1 fixed at the appropriate optimal value (see Fig. 2 of Part II) and optimize only ε_1' (approximation (b) above). We also note that the highly strained cyclobutadiene structure is rather untypical in that it leads to the smallest value of the mixing parameter of all the π-electron systems studied earlier (for the corresponding tight binding study see [9a]). For $\theta < 80°$, ε_1' is almost zero. Thus, for $\theta < 70°$, ε_1' was set equal to zero and only ε_1 was optimized. The t_3 and t_4 cluster amplitudes obtained from these PPP-VB wave functions are compared with the exact FCI amplitudes in Fig. 5. Although the absolute value of these amplitudes are overestimated, an overall cluster structure seems to be reasonably reproduced.

Correlation energies relative to the FCI energies, that result by applying the above obtained T_3 and T_4 corrections ($T_1 T_3$ corrections always remain very small), are shown in Fig. 6. We see that the approximate T_3 and T_4 corrections have very much similar effect as do the exact ones and, since the approximate amplitudes overestimate the exact ones, the corrections are larger as well. Again, however, there is a mutual compensation of the tri- and tetra-excited effects so that in either case, only the total $T_3 + T_4$ corrections improve the standard CCSD result. Close to the square geometry ($85° < \theta < 90°$), the T_3 component being almost zero has practically no effect on the CCSD energy so that the whole contribution is practically due to the T_4 clusters. Nonetheless, we must conclude that the standard CCSD method performs very well over the whole region of θ and only near the quasidegenerate square configuration may be substantially improved by implementing the VB based corrections.
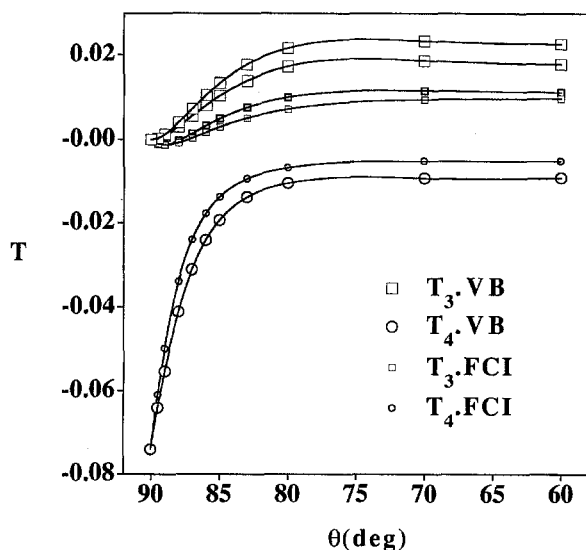

Fig. 5. A comparison of the exact and approximate 3- and 4-body connected cluster amplitudes, as obtained with the FCI and PPP-VB procedures, respectively, as a function of the cyclobutadiene model ring opening parameter θ (in degrees) (see Fig. 1(b)). The PPP-VB procedure involved two Kekulé structures and nearest neighbor mixing parameters OEAO basis (see the text for details)
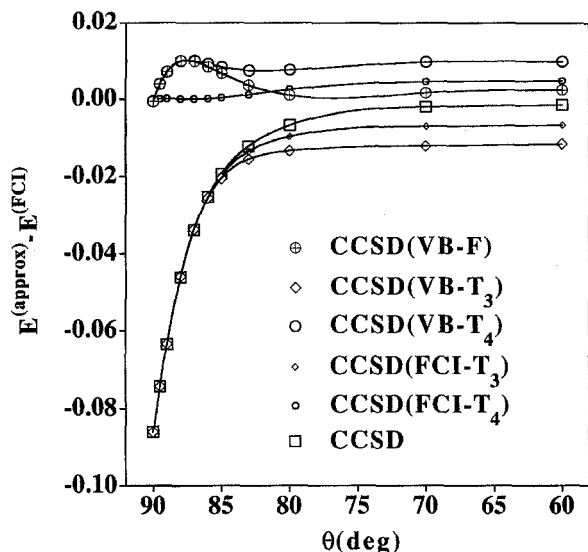
Fig. 6. Correlation energy (relative to the FCI energy) (in eV) of the cyclobutadiene ring opening model obtained with the standard and VB corrected CCSD methods, as a function of the ring opening parameter θ (in degrees) (see Fig. 1(b)). The CCSD-VB method employs the approximate PPP-VB based cluster components (see the text and Fig. 5). For the sake of comparison, the results employing the exact (FCI) T_3 and T_4 corrections are also shown. The symbol F (full) indicates that all three correction terms $(T_3, T_4, T_1 T_3)$ were applied. The corresponding FCI result [i.e., CCSD (FCI-F)], yielding the exact FCI energy, is not shown

3.2 Benzene

In considering both modes of separation of benzene into the two fragments, we employ parametrization described in Sect. 2 with $\beta_0 = -2.4$ eV and C–C bond length of 1.4 Å. The nearest neighbor mixing parameters, determining the OEAOs, were fixed at their optimal values corresponding to the benzene equilibrium geometry for all bonds whose bond length remained constant in the separation process (ε_1), and only those parameters associated with bonds being broken were optimized for each separation distance d (cf. Figs. 1(c) and 1(d)). In the case of 2 Kekulé structure VB wave function, the fixed mixing parameter has the value $\varepsilon_1^{(2K)} = 0.3329$ and when all 5 covalent structures are considered, $\varepsilon_1^{(5c)} = 0.3310$. Note that in each case all resonance integrals between any pair of carbon atomic sites are considered. (For the sake of comparison, $\varepsilon_1^{(2K)}$ in the case of the tight binding approximation equals 0.341.)

3.2.1 Diels–Alder mode.
Considering the Diels–Adler dissociation mode and defining the geometry of intermediate nuclear conformations using a single parameter d (Fig. 1(c)) by keeping the dissociating fragments rigid, we first determined corresponding PPP-VB energies and wave functions by optimizing the variable mixing parameter ε_1' for both 2 Kekulé and 5 covalent structure cases. The resulting optimal parameter values, as well as the corresponding PPP-VB energies, are given in Table 2, together with corresponding exact energies given by the FCI or FVB procedures.

Table 2. Correlation energies obtained with the FCI and PPP-VB approaches involving two Kekulé (2K) and five covalent (5c) structures for the Diels-Alder mode of dissociation of the π-electron model of benzene as a function of the separation parameter d (in Å) (see Fig. 1(c)). The OEAO basis employed in PPP-VB calculations involved one fixed mixing parameter ($\varepsilon_1 = 0.3329$ for 2K and $\varepsilon_1 = 0.3310$ for 5c cases) for nearest neighbors with the fixed internuclear separation and an analogous parameter ε_1' for nearest neighbors involving variable internuclear separation. The optimal values of the latter parameter are also shown

	ε_1'		E_{corr}(eV)		
d (Å)	2K	5c	2K	5c	FCI
1.20	0.3370	0.3350	−11.53478	−11.56115	−11.85023
1.2124	0.3329	0.3310	−11.42513	−11.45163	−11.73936
1.25	0.3204	0.3185	−11.11606	−11.14278	−11.42484
1.30	0.3031	0.3016	−10.75493	−10.78173	−11.05278
1.35	0.2853	0.2843	−10.44767	−10.47463	−10.73146
1.40	0.2671	0.2668	−10.18910	−10.21653	−10.45703
1.45	0.2488	0.2492	−9.97322	−10.00159	−10.22480
1.50	0.2307	0.2318	−9.79397	−9.82372	−10.02971
1.60	0.1959	0.1982	−9.52309	−9.55659	−9.73091
1.70	0.1642	0.1673	−9.33857	−9.37629	−9.52462
1.80	0.1364	0.1397	−9.21309	−9.25472	−9.38301
1.90	0.1125	0.1157	−9.12782	−9.17271	−9.28610
2.00	0.0923	0.0952	−9.06996	−9.11740	−9.21995
2.50	0.0323	0.0334	−8.96704	−9.01981	−9.10073
3.00	0.0105	0.0109	−8.95387	−9.00743	−9.08469
3.50	0.0033	0.0034	−8.95240	−9.00605	−9.08257
4.00	0.0009	0.0010	−8.95225	−9.00591	−9.08219
5.00	0.0001	0.0001	−8.95223	−9.00590	−9.08201
6.00	0.0000	0.0000	−8.95223	−9.00590	−9.08196

We next applied the T_3, T_4 and $T_1 T_3$ corrections to the standard CCSD procedure using the FCI as well as the PPP-VB cluster components obtained by cluster analyzing corresponding wave functions. The correlation energies relative to the FCI values as a function of the subsystem separation distance are shown in Figs. 7(a)–(c). First, we note that the CCSD method yields excellent results in this case, which again is connected with the fact that the dissociation involves closed shell systems. Only in the region of d values lying between the equilibrium geometry $[d = 1.21244$ Å $= (\sqrt{3}/2)\,(1.4$ Å$)]$ and $d = 2.5$ Å do we find a small deviation from the FCI energy. We also see that even when considering the FCI based corrections (Fig. 7(a)), no individual correction will improve the CCSD result. Only when simultaneously considering both T_3 and T_4 corrections, do we find an improvement. Of course, including also $T_1 T_3$ correction (which seems to be fairly well additive though small) we recover the FCI result.

When considering CCSD-VB energies employing approximate cluster components obtained from PPP-VB wave functions involving 2 Kekulé (Fig. 7(b)) or 5 covalent (Fig. 7(c)) structures, the effect of individual corrections is magnified, most likely thanks to the overestimate of T_3 and T_4 cluster components. In this case even the combined total correction does not improve the standard CCSD result, except in a small part of the region where CCSD deviates from FCI (1.5 Å $< d <$ 2.0 Å). For the geometries close to the equilibrium one, standard CCSD gives better results.
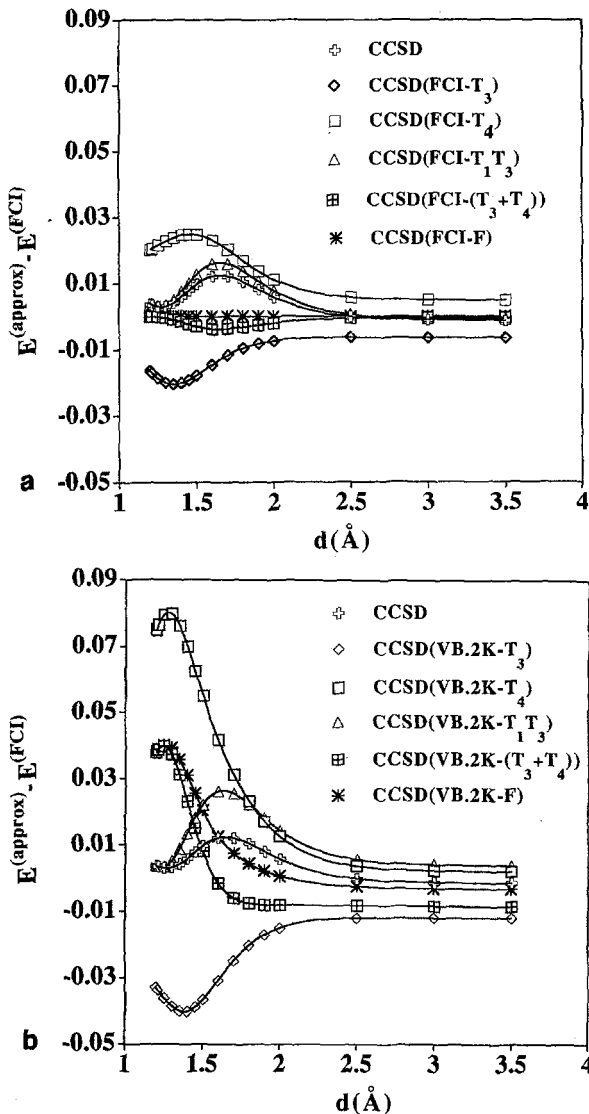
Fig. 7a–c. Correlation energy (relative to the FCI energy, see Table 2) (in eV) for the Diels–Alder mode of dissociation of the π-electronic model of benzene, obtained with the standard and VB-corrected CCSD approaches, as a function of the separation parameter d (cf. Fig. 1(c)). The CCSD-VB approaches, considering both individual correction terms $(T_3, T_4, T_1 T_3)$ as well as their combinations $[T_3 + T_4$ and $T_3 + T_4 + T_1 T_3$, the latter designated as F (full)], exploit the exact FCI cluster amplitudes (a), as well as the approximate ones obtained by cluster analyzing PPP-VB wave functions obtained with two Kekulé (2K) (b) and all five covalent (5c) (c) structures. Note that the CCSD (FCI-F) approach yields the exact FCI energy

In this regard it is interesting that the corrections derived from the energetically inferior 2 Kekulé structure VB solution yield better results than those involving all 5 covalent structures, although the latter account better for the T_3 clusters. Since both approximate VB wave functions lead to very similar T_4 corrections, it must be
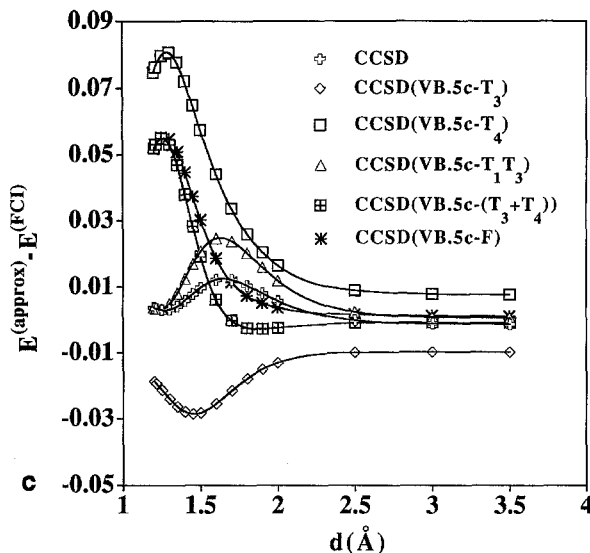
a mutual compensation of errors that leads to a slightly better performance of the simple 2 Kekulé structure solution.

We can thus conclude that since the CCSD method works so well in this "closed-shell case", it is extremely difficult to improve its performance by exploiting approximate wave functions. In fact, it is remarkable that these corrections work as well as they do in view of their very approximate nature, as the results summarized in Fig. 8 demonstrate.

This figure compares the correlation energies (relative to FCI) of approximate PPP-VB wave functions involving 2 Kekulé and 5 covalent structures and the corresponding energies obtained with the standard CCSD and CCSD-VB
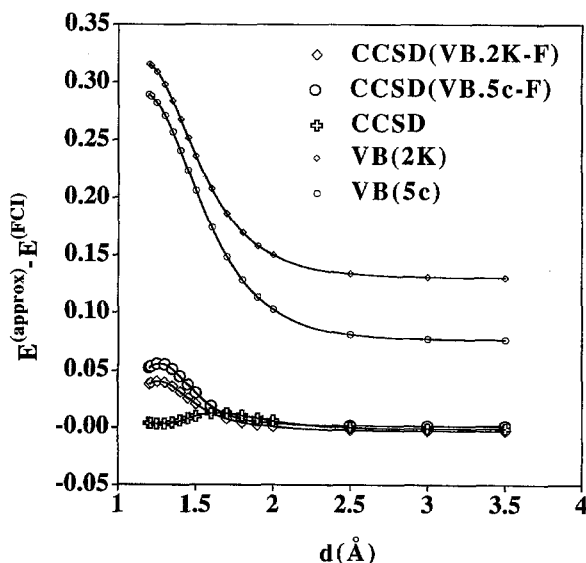

Fig. 8. Comparison of the PPP-VB, standard and VB corrected CCSD correlation energies (relative to the FCI energy, see Table 2) (in eV) as a function of the separation parameter d (cf. Fig. 1c) for the Diels–Alder mode of benzene model dissociation. Both 2 Kekulé (2K) and 5 covalent (5c) variational PPP-VB and corresponding VB corrected CCSD energies are shown

methods. We see that in only a very small region of intersystem separations the VB corrected CCSD works better than the standard CCSD, although all methods give very good results.

3.2.2 Radicaloid mode. A much more severe test of the proposed method than can be afforded by systems involving only closed shell type subsystems is that involving open shell subsystems. In order to carry out such a test we consider a recombination of two allylic radicals as schematically represented in Fig. 1(d). We shall proceed in the same manner as in the preceding section.

Table 3. Same as Table 2 for the radicaloid mode of benzene ring separation. See Fig. 1(d) for the definition of the subsystem separation parameter d (in Å)

| d (Å)	ε'_1		E_{corr}(eV)		
	2K	5c	2K	5c	FCI
1.35	0.3579	0.3519	− 11.95227	− 11.97976	− 12.27364
1.40	0.3329	0.3310	− 11.42513	− 11.45163	− 11.73936
1.45	0.3093	0.3104	− 10.95027	− 10.97866	− 11.25863
1.50	0.2871	0.2901	− 10.52489	− 10.55758	− 10.82797
1.55	0.2658	0.2703	− 10.14608	− 10.18498	− 10.44401
1.60	0.2456	0.2510	− 9.81086	− 9.85736	− 10.10343
1.70	0.2081	0.2141	− 9.25878	− 9.32281	− 9.53963
1.80	0.1744	0.1801	− 8.84334	− 8.92547	− 9.11157
2.00	0.1187	0.1229	− 8.32211	− 8.43460	− 8.56751
2.50	0.0400	0.0414	− 7.92149	− 8.06513	− 8.14323
3.00	0.0124	0.0128	− 7.87246	− 8.02052	− 8.09093
4.00	0.0010	0.0011	− 7.86707	− 8.01553	− 8.08456
5.00	0.0001	0.0001	− 7.86710	− 8.01549	− 8.08433
6.00	0.0000	0.0000	− 7.86714	− 8.01549	− 8.08426
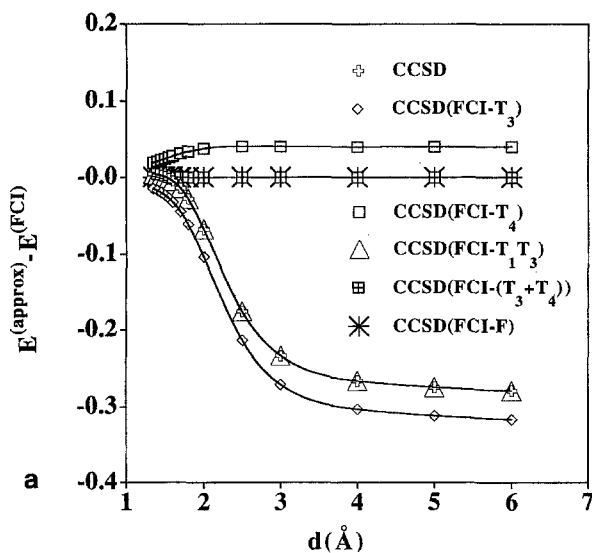
Fig. 9a–c. Same as Fig. 7 for the radicaloid mode of benzene ring opening (see Fig. 1(d) for the definition of the separation parameter d)

The optimal values of the variable mixing parameter ε_1' as well as the PPP-VB and FCI energies are listed in Table 3. The correlation energies (relative to FCI) obtained with the FCI and PPP-VB corrected as well as with the standard CCSD methods are given in Figs. 9(a)–(c). We see that in this case the CCSD energy approaches an incorrect limit when the open shell subsystems are formed. Again, the $T_1 T_3$ terms have practically no effect while the T_3 and T_4 terms work in opposite directions, both effects being fairly additive. The main effect originates from the T_4 corrections, the T_3 contribution being much smaller. When T_3 and T_4 corrections are applied simultaneously, one obtains practically the FCI result.
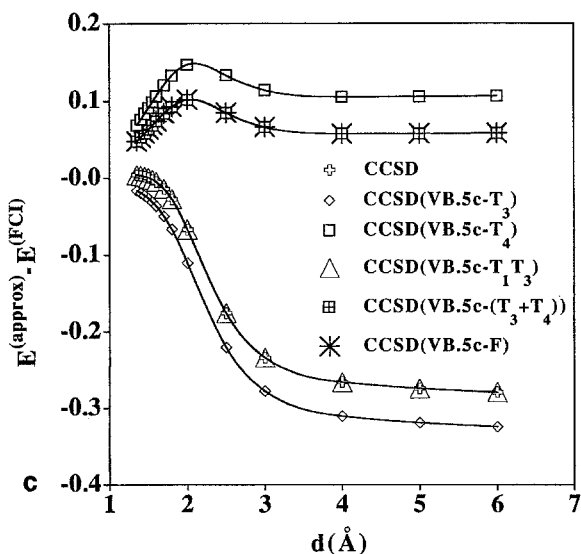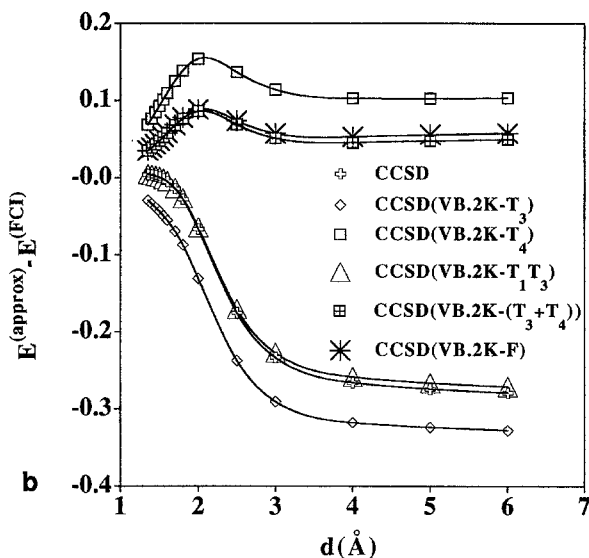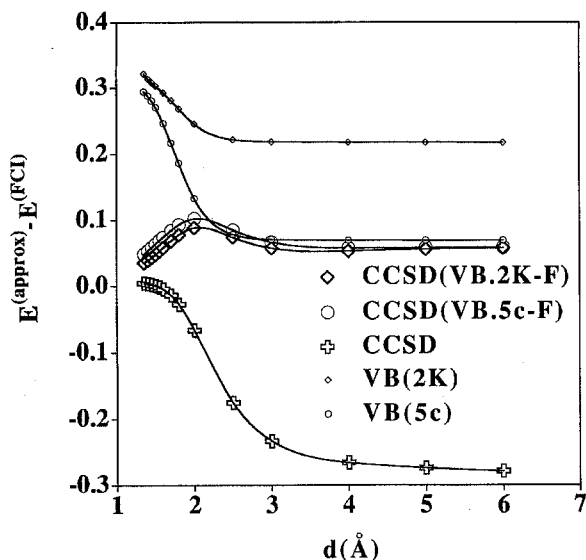

Fig. 9. Continued

Fig. 10. Same as Fig. 8 for the radicaloid mode of benzene ring opening (see Fig. 1(d) for the definition of the separation parameter d)

Employing approximate cluster components derived from VB wave functions involving 2 Kekulé and 5 covalent structures, we obtain very similar results. Both are capable of correcting the erroneous behavior of the standard CCSD approach in the open shell region.

Again, it is remarkable that the 2 Kekulé structure VB wave function is capable of providing such good corrections in view of its inferiority from the energetical viewpoint. This is illustrated in Fig. 10 where we plot correlation energies (relative to FCI) resulting from using the PPP-VB procedure with 2 Kekulé and 5 covalent structures, the correspondingly VB corrected CCSD method and the standard CCSD method. This figure should also be compared with the analogous one for the Diels–Alder dissociation mode (Fig. 8). We see that independently of the dissociation (or association) mode, the CCSD-VB energies provide a very good approximation to the FCI exact result for all the nuclear conformations that are explored.

4 Conclusions

The results of this paper corroborate our expectations concerning the usefulness of correcting the standard SR CCSD equations by exploiting the approximate values of the 3- and 4-body connected cluster amplitudes, obtained by cluster analysis of very simple VB wave functions. In this way a satisfactory decoupling of the CC chain of equations at the CCSD level may be achieved even in quasidegenerate or degenerate situations, where the standard approach often fails. Although such corrections do very little in standard non-degenerate cases, when the CCSD method provides an excellent approximation, and can even slightly degrade the quality of the CCSD energies in such cases, there is no doubt about their usefulness in situations where the higher order than pair clusters play an important role. Thus, from a practical viewpoint, one should revert to the CCSD-VB approach only in cases for which the T_3 and/or T_4 clusters are prominent, based on the cluster

analysis of the approximate VB wave function being employed. In cases where these clusters turn out to be small, it is just as well to leave the CCSD results uncorrected. In this way, the usefulness of the standard CCSD method may be extended to situations where otherwise this approach would fail, including cases when the system dissociates into the open shell fragments.

It is quite remarkable that even very simple VB wave functions are capable of appropriately correcting the CCSD equations, so that much improved results (and certainly the qualitatively correct dissociation limit) are achieved. This is particularly the case for physical (spectroscopic) parametrizations, when the variational energy that is associated with these simple VB wave functions, involving only Kekulé structures, is much inferior to the CCSD energies (cf. Figs. 8 and 9). Thus, the present study of various model systems, simulating the dissociation (or association) processes, supports our conclusions that were drawn on the basis of our study of the CCSD-VB capabilities in strongly correlated regimes (cf. Part II).

Another interesting result of these studies is the manifestation of the roles of the 3- and 4-body connected clusters in various situations. We have seen that in many cases the 3- and 4-body terms work "against each other", similarly as it was found in an earlier ab initio study of the H_4 model system [11], where these effects were accounted for by solving appropriately enlarged CC systems of equations. However, in a number of situations (see especially Part II), particularly when CCSD leads to poor results or even breaks down, the 3- and 4-body corrections may contribute in the same direction. In such situations we also usually find that their contributions are highly nonadditive, so that even when the T_3 contribution is very small, it may be essential that it is accounted for simultaneously with the T_4 contribution in order to achieve a satisfactory result (see e.g. the highly correlated regime in cyclic polyenes), at least within the CCSD-VB scheme considered.

Admittedly, the models employed in this study are too simple and restricted to allow us to make general conclusions concerning the CCSD-VB approach. Additional developments both at formal and computational levels will be required in order to test this approach at the ab initio level. Nonetheless, the examples presented in Parts II and III of this series seem to clearly indicate that further exploration of the possibilities offered by this approach, including the search for other sources of approximate higher order cluster amplitudes, are worthwhile.

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