

## Applicability of Coupled-Pair Theories to Quasidegenerate Electronic States: A Model Study

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### Abstracts

The coupled-pair many-electron theory, its linear approximation, and various other approximate coupled-pair approaches based on the orthogonally spin-adapted coupled-pair theory are applied to simple model systems in which the degree of quasidegeneracy can be continuously varied over a wide range. The four-electron models studied are three *ab initio* minimum basis set models involving four hydrogen atoms in various spatial arrangements as well as the semiempirical Pariser-Parr-Pople  $\pi$ -electron model of *cis*-butadiene. The results are compared with the exact full configuration interaction results as well as with those obtained with other approximate limited configuration interaction approaches and Davidson's formula estimate, and the effect of quasidegeneracy on various approaches is discussed. We also examine the difference between the correlation energies obtained with the coupled-pair many-electron theory and its linear version and discuss the source of these differences and of the breakdown of the latter approximation in the case of very strong quasidegeneracies.

La théorie à  $N$  électrons par paires couplées, son approximation linéaire et diverses approximations basées sur la théorie des paires spin-adaptées orthogonales sont appliquées à des systèmes de modèle simples, dans lesquels le degré de quasi-dégénérescence peut être varié d'une façon continue sur un intervalle important. Les modèles à quatre électrons étudiés comprennent trois modèles *ab initio* à base minimale avec quatre atomes d'hydrogène dans des arrangements spatiaux différents ainsi que le modèle semi-empirique pour les électrons  $\pi$  de Pariser-Parr-Pople du *cis*-butadiène. Les résultats sont comparés à ceux obtenus par des interactions de configurations pleines et exactes ainsi qu'à ceux obtenus par d'autres approximations de CI's limitées et par la formule de Davidson. L'effet de la quasi-dégénérescence sur les procédés différents est discuté. Nous examinons aussi la différence entre l'énergie de corrélation des paires couplées et sa version linéaire. Nous discutons la raison de ces différences et du fait que la version linéaire ne fonctionne pas dans le cas où les quasi-dégénérescences sont très fortes.

Die Paarkopplungsvielelektronentheorie, ihre lineare Näherung und verschiedene andere auf die Theorie für orthogonal spinangepasste Paare basierende Paarkopplungsverfahren werden auf einfache Modellsysteme angewandt, in welchen der Quasi-Entartungsgrad stetig über einem breiten Intervall variiert werden kann. Die studierten Vierelektronenmodelle sind drei *ab initio* Minimalbasissatzmodelle mit vier Wasserstoffatomen in verschiedenen Raumkonfigurationen, und das semiempirische  $\pi$ -Elektronenmodell von Pariser-Parr-Pople für *cis*-Butadien. Die Ergebnisse werden mit den Resultaten von vollen exakten CI-Berechnungen, anderen angenäherten begrenzten CI-Verfahren und einer Abschätzung mittels der Davidson'schen Formel verglichen. Der Effekt der Quasi-Entartung auf verschiedene Verfahren wird diskutiert. Wir untersuchen auch den Unterschied zwischen der Korrelationsenergie der Paarkopplungsmethode und der ihrer Linearversion und diskutieren die Ursache dieser Unterschiede und den Zusammenbruch der linearen Näherung wenn die Quasi-Entartungen sehr stark sind.

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## 1. Introduction

There has been a considerable development in the nonvariational approaches to the many-fermion correlation problem during the past several decades [1]. It was soon recognized (cf. e.g., Ref. 2) that a desirable method should be "size consistent"\* [3, 4], i.e., when applied to  $N$ -noninteracting identical systems the calculated energy should be proportional to  $N$ . Evidently, such a property is crucial in any application to extended systems, like the electron gas or nuclear matter, but is also important—even though in a less severe way—in applications to finite many-fermion systems, particularly when dissociative or reactive chemical phenomena are involved. It is well known today that any size consistent theory must involve only linked terms (diagrams) when interpreted in the many-body perturbation theory language. Thus, for example, the configuration interaction (CI) limited to doubly excited configurations from the closed-shell ground state (when applied to larger than two-electron systems) or Brillouin–Wigner perturbation theory, are well known examples of non-size-consistent theories.

It is not difficult to realize (cf. e.g., Ref. 2) that a theory which will automatically possess the size consistency property may be obtained if we express the wave operator [5] in exponential form or, equivalently, if we formulate the theory in terms of the logarithm of the wave operator rather than in terms of the wave operator itself. This exponential *Ansatz* is analogous to the cluster expansion *Ansatz* exploited earlier in statistical mechanics [6] and the wave operator exponential form just mentioned is thus often referred to by the same name.

The relevance of this *Ansatz* for a many-fermion wave function (or, equivalently, a wave operator) was first inferred from the structure of the many-body perturbation theory by Hubbard [7] and this *Ansatz* was first exploited in the nuclear many-body problem by Coster and Kümmel [8]. The general procedure for obtaining the explicit equations for the cluster components in the closed-shell case was given by Čížek [9], who also formulated the most important approximation in which the cluster operator is approximated by its pair cluster component, which he termed the coupled-pair many-electron theory (CPMET). This theory represents a generalization of earlier approaches [10, 11] where the coupling of different pair clusters was accounted for only in an approximate way. Lately, there has been a considerable development in the coupled cluster approach culminating with a formulation of the cluster exponential-type *Ansatz* for the open-shell systems by Lindgren [12]. A brief review of these developments and of the historical origins and motivations may be found elsewhere [1].

With the increasing awareness of the importance of size consistency in studies of various chemical phenomena, there has been lately a considerable increase in

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\* This very appropriate term has been coined by Pople [3]. However, for finite systems, the correct  $N$ -dependence of the wave function is often combined with the requirement that the wave function describes correctly certain dissociative processes, in which the closed-shell character of the system often breaks down. In order to distinguish these two quite different requirements, Bartlett et al. [4] introduced the term "size extensivity" for the correct  $N$ -dependence.

the number of CPMET applications (cf., e.g., Refs. 4, 13–17), which was particularly stimulated by the development of algorithms [4, 13] which enable an efficient recursive evaluation of the perturbation theory diagrams characteristic of the CPMET approach. Unfortunately, it is still difficult to handle the triexcited cluster contributions [18, 19], which might be quite important in certain problems.

In spite of the remarkable success in the implementation of the CPMET to actual systems at the *ab initio* level, it seems quite unlikely that the same technique can be routinely used in the near future for larger than 10–20 electron systems or even for smaller problems requiring very extensive orbital basis sets. Consequently, it is highly desirable to develop reliable approximate coupled-pair (CP) theories, which will preserve the size consistency (size extensivity) property of the general coupled cluster approach (CCA) as well as the quantitative reliability of the CPMET. There exists already a whole spectrum of such approximate CP approaches, starting with the linear CPMET (L-CPMET), formulated by Čížek [9] as a zeroth approximation to the CPMET in which all nonlinear terms are suppressed, through several “coupled electron pair approximation” (CEPA) schemes developed by Meyer, Kutzelnigg, Ahlrichs, Lischka, and Staemmler [20–24], and recently by Hurley, Taylor, Bacskay, and Hush [17, 25, 26] where various approximations of the CPMET nonlinear part are used (note that CEPA(0) is equivalent to L-CPMET). These latter approaches have been extensively applied to actual systems and considerable experience with their reliability has been gained (for a very recent review, see Ref. 27).

As we have recently pointed out [28], many other approximations to the CPMET may be successfully devised and applied, particularly when using the orthogonally spin-adapted form of the CPMET equations [29]. At the same time, the approximations made in various existing CEPA-type approaches may be better understood when related to the exact CPMET formulation. It must be stressed here that even though the disconnected cluster contribution to the correlation energy is usually quite small, it has nevertheless a considerable effect on the numerical values of various physical and chemical observables, such as molecular equilibrium geometry or force field, and a proper account of these terms is essential if accurate and size-consistent results are desired.

There exist several studies in which the performance of various approximation schemes is compared [17, 26, 27] and their relative merits assessed [23, 24]. These studies are often based on a comparison with the experimental data available. In view of the fact that practically all quantum-chemical calculations use model Hamiltonians defined on finite-dimensional spaces, and thus share the inherent shortcomings due to the use of finite basis sets, we find it most appropriate to use the full CI result within the same basis as a benchmark, whenever possible, rather than attempting a comparison with experimental data. This viewpoint seems to be now commonly accepted (cf. e.g., Ref. 4). We must stress, however, that we address here the problem of establishing the reliability criteria of various approximate approaches, and not an exploitation of such approaches in actual chemical and physical problems.

In most existing studies just mentioned [17, 26, 27] a comparison of the correlation energies with the corresponding full CI or CPMET results within the same basis was made for one particular molecular geometry. Since these comparisons were primarily concerned with geometries close to the equilibrium one, they could not provide any information about the performance of different CEPA-like schemes in the presence of quasidegeneracy; i.e., in cases where in addition to the single-determinant reference configuration other configurations play a significant role. A proper description of quasidegeneracy effects is of vital importance in many quantum-chemical problems, especially in problems involving dissociative or reactive chemical phenomena. For example, in calculating various potential-energy surfaces for large internuclear separations, the closed-shell reference configuration often yields incorrect asymptotic behavior and additional configurations must be considered. The fact that both CPMET and CEPA-type methods may become unreliable in such cases has been realized for a long time (cf. e.g., Ref. 23). However, very few systematic studies have been devoted to this problem. Very recently, Bartlett and Purvis [16] examined the problem of a proper description of quasidegenerate states in various versions of the many-body perturbation theory (MBPT), including the CPMET approach. They demonstrated on examples of the  $N_2$  molecule and  $Be_2$  dimer that the results given by certain methods deteriorate so drastically in the presence of a strong quasidegeneracy that they lead to qualitatively incorrect behavior. These difficulties clearly stem from the fact that the closed-shell CP approaches are based on a single configuration state and/or that the essential pair interactions have been neglected.

The aim of this paper is to examine the applicability of the CPMET and approximate CP theories in the presence of quasidegeneracy. Our analysis is based on numerical results obtained for simple four-electron systems, which were chosen both because of their simplicity and because they allow the degree of quasidegeneracy to be continuously varied over a large range. In view of the simplicity of these models we can also readily obtain the full CI results that are used as a reference in the discussion of quasidegeneracy effects in different methods. Our attention is mainly focused on the correlation energy, even though we also examine the validity of the cluster pair *Ansatz* for the wave function. We consider the following CP approaches: (i) CPMET, (ii) L-CPMET, (III) three different CEPA-type procedures [referred to as approximate CP (ACP) methods] and, (iv) two approximations defined by entire classes of diagrams considered (involving both EPV\* [30] and non-EPV diagrams). In addition we also consider limited CI with doubly (D-CI) and doubly and quadruply excited (DQ-CI) configurations and D-CI with Davidson's correction [31]. The model systems considered are the  $H_4$  system in three different geometrical configurations using the *ab initio* minimum basis set (MBS) model Hamiltonian, and the  $\pi$ -electron model of *cis*-butadiene described by the semiempirical Pariser-Parr-Pople (PPP) Hamiltonian [32]. We will see that both *ab initio* and semiempirical Hamiltonians lead to the same

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\* EPV designates exclusion principle violating diagrams (cf. e.g., Ref. 30).

conclusions concerning the effects of quasidegeneracy on the reliability of various methods.

## 2. Brief Review of CPMET and Approximate CP Theories

The cluster expansion *Ansatz* for closed-shell systems expresses the wave operator  $W$ , which transforms the independent particle model wave function  $|\Phi_0\rangle$  into the exact nonrelativistic wave function  $|\Psi\rangle$

$$|\Psi\rangle = W|\Phi_0\rangle, \quad \langle\Phi_0|\Psi\rangle = 1, \quad (1)$$

as an exponential of the cluster operator  $T$ ,

$$W = e^T, \quad (2)$$

with

$$T = \sum_{i=1}^n T_i, \quad (3)$$

where  $T_i$  designates the  $i$ -particle component of the cluster operator  $T$ . In the second quantization formalism we can thus write

$$T_i = (i!)^{-2} \sum_{\{A^k, A_k\}} \langle A^1 A^2 \cdots A^i | t_i | A_1 A_2 \cdots A_i \rangle_A \\ \times X_{A^1}^+ X_{A^2}^+ \cdots X_{A^i}^+ X_{A_i} \cdots X_{A_1}, \quad (4)$$

where  $\langle A^1 \cdots A^i | t_i | A_1 \cdots A_i \rangle_A$  designates the antisymmetrized  $t_i$  matrix element [cf. e.g., Eq. (5) of Ref. 29],  $X_A^+$  ( $X_A$ ) is the creation (annihilation) operator associated with spin orbital  $|A\rangle$ , and the summation extends over all spin orbital labels involved. The spin orbitals occupied in the reference configuration  $|\Phi_0\rangle$  are labeled by subscripted capitals  $A_1, A_2, \dots, A_N$  so that

$$|\Phi_0\rangle = \prod_{i=1}^N X_{A_i}^+ |0\rangle, \quad (5)$$

where  $|0\rangle$  is the true vacuum state, while those unoccupied in  $|\Phi_0\rangle$  are labeled with superscripted capitals.

The two principal advantages of this *Ansatz* stem from the basic characteristic of the exponential mapping. Thus, when two independent noninteracting systems  $A$  and  $B$ ,

$$|\Psi^X\rangle = e^{T^X} |\Phi_0^X\rangle, \quad X = A, B, \quad [T^A, T^B] = 0, \quad (6)$$

are considered as a single system (as in the “super-molecule” approach, for example), we see that the multiplicative structure of the wave function is translated into the additive structure of the cluster operator since

$$|\Psi^{AB}\rangle = e^{T^A + T^B} |\Phi_0^{AB}\rangle. \quad (7)$$

Consequently, even in the CP approximation

$$T \approx T_2, \quad (8)$$

the energy remains additive unlike in the usual limited CI-type expansion. The second important advantage, closely related to the first, arises from the possibility of approximating higher excited components of the wave function through products of lower excited components (i.e., through disconnected clusters). In particular, it is well known that for closed-shell systems

$$T_4 \ll \frac{1}{2}T_2^2, \quad (9)$$

so that the tetraexcited contribution can be well described through the nonlinear pair cluster components assuming that the monoexcited clusters  $T_1$  are very small as is usually the case. In this way, the size consistency is preserved since the pair clusters  $T_2$  are by far the most important ones.

It is well known that the cluster *Ansatz* [Eq. (2)] makes it impossible to apply the variational principle since the energy mean value expression will contain all powers of the components  $T_i$ . One thus reverts to the Schrödinger equation and finds the equations determining the  $T_i$  components by projecting it on the appropriate many-electron subspace. This is most easily done [9] using the diagrammatic method based on second quantization formalism and time-independent Wick's theorem [33], even though the derivation of the pertinent equations, particularly in the spin-orbital form, when only  $T_1$  and  $T_2$  components are retained can be easily accomplished using any formalism (cf. e.g., Refs. 25, 34–36). Thus, substituting Eqs. (1) and (2) into the Schrödinger equation, and eliminating disconnected terms (cf. e.g., Refs. 9, 29, 37) we find

$$(H_N e^T)_{\mathcal{C}} |\Phi_0\rangle = \Delta\epsilon |\Phi_0\rangle, \quad (10)$$

where  $\Delta\epsilon$  is the correlation energy  $\Delta\epsilon = E - E_0$ ,  $E_0 = \langle \Phi_0 | H | \Phi_0 \rangle$ ,  $H_N$  is the Hamiltonian in the normal product form [9, 33]:

$$H_N = H - E_0 = \sum_{A,B} \langle A | f | B \rangle N[X_A^\dagger X_B] + \frac{1}{4} \sum_{ABCD} \langle AB | v | CD \rangle_A N[X_A^\dagger X_B^\dagger X_D X_C], \quad (11)$$

$$\langle A | f | B \rangle = \langle A | z | B \rangle + \sum_{C_1} \langle AC_1 | v | BC_1 \rangle_A, \quad (12)$$

$$\langle AB | v | CD \rangle_A = \langle AB | v | CD \rangle - \langle AB | v | DC \rangle, \quad (13)$$

where  $N[\dots]$  designates the normal product with respect to  $|\Phi_0\rangle$ , and  $\mathcal{C}$  indicates the connected part. Projecting then Eq. (10) onto one-dimensional subspaces defined by appropriate configurations we obtained the desired system of equations for the components of  $T_i$ . Clearly, these equations are independent of the correlation energy  $\Delta\epsilon$  which is given by the projection on the reference configuration  $|\Phi_0\rangle$ ,

$$\begin{aligned} \Delta\epsilon &= \langle \Phi_0 | (H_N e^T)_{\mathcal{C}} | \Phi_0 \rangle \\ &= \langle \Phi_0 | H_N (T_1 + T_2 + \frac{1}{2}T_1^2) | \Phi_0 \rangle. \end{aligned} \quad (14)$$

Using approximation (8) we obtain CPMET equations in the spin orbital form [9].

For the spin-independent Hamiltonian

$$H = \sum_{a,b} \langle a|z|b \rangle \sum_{\sigma} X_{a\sigma}^{\dagger} X_{b\sigma} + \frac{1}{2} \sum_{a,b,c,d} \langle ab|v|cd \rangle \sum_{\sigma,\tau} X_{a\sigma}^{\dagger} X_{b\tau}^{\dagger} X_{d\tau} X_{c\sigma}, \quad (15)$$

used invariably in molecular electronic structure calculations, the operators  $S^2$  and  $S_z$  are constants of the motion so that the system of coupled cluster equations can be factored accordingly. This may be simply achieved by assuming that the  $t_i$  operators are spin independent [9, 34]. However, this procedure yields the cluster components associated with nonorthogonal configurations and leads thus to a cumbersome formalism when higher than biexcited clusters are considered [18]. We have, therefore, formulated the orthogonally spin-adapted form of the theory in which the clusters are associated with orthogonal spin-adapted configurations [19,29]. This formalism is advantageous even in the CPMET case, when at most pair clusters are considered, since it yields sparser matrices of coefficients appearing in the CP equations and gives a simple relationship between the coupled-cluster components and the coefficients in the CI expansion based on the same orthogonal configurations used to define the cluster components [19, 29]. Moreover, this formulation has definite advantages in devising various spin-adapted CEPA-type schemes as will be seen later.

The orthogonally spin-adapted formulation of the CPMET [29] is based on the *pp-hh* coupled biexcited configurations [38, 39] [cf. Eq. (17) of Ref. 29 or Eq. (16) of Ref. 39], which have definite advantages over the *ph-ph* coupled states [cf. Eqs. (19) of Ref. 39]. In fact, the former may be regarded, up to the phase, as the hole-particle version of the Gelfand-Tsetlin canonical basis of the unitary group approach to the many-body problem [40]. Since only singlet configurations are needed, the intermediate spins arising from the coupling of hole and particle states must be identical ( $S_i$ ), so that the configurations can be simply labeled by the orbitals involved in the excitation and by the intermediate spin  $S_i$ ,  $S_i = 0, 1$  as (cf. Eq. (21) of Ref. 29)

$$\left| \begin{array}{cc} a^1 & a^2 \\ a_1 & a_2 \end{array} \right\rangle_{S_i}. \quad (16)$$

They possess very simple and desirable properties given by Eqs. (22) and (23) of [29]. The doubly excited part of the CI singlet wave function  $(C_2|\Phi_0\rangle)_{S=0}$  can thus be written\*

$$\begin{aligned} (C_2|\Phi_0\rangle)_{S=0} &= \sum_{a^1 \leq a^2} \sum_{a_1 \leq a_2} \sum_{S_i} C_{a_1 a_2}^{a^1 a^2}(S_i) \left| \begin{array}{cc} a^1 & a^2 \\ a_1 & a_2 \end{array} \right\rangle_{S_i} \\ &= (T_2|\Phi_0\rangle)_{S=0} \\ &= \frac{1}{4} \sum_{S_i} \sum_{a^1, a^2, a_1, a_2} \mathcal{N}_a \langle a^1 a^2 | t_2(S_i) | a_1 a_2 \rangle \left| \begin{array}{cc} a^1 & a^2 \\ a_1 & a_2 \end{array} \right\rangle_{S_i}, \end{aligned} \quad (17)$$

\* If the coefficients or the states in Eq. (17) vanish for  $S_i = 1$  (i.e., when  $a^1 = a^2$  and/or  $a_1 = a_2$ ), we will often drop the argument or subscript  $S_i$ , implying that  $S_i = 0$  in such a case.

assuming that the  $T_1$  component vanishes and designating by  $\mathcal{N}_a$  the simple normalization factor

$$\mathcal{N}_a = (1 + \delta_{a^1 a^2})(1 + \delta_{a_1 a_2}). \quad (18)$$

The orthogonally spin-adapted CPMET equations are most easily derived [19, 29] by combining the diagrammatic method based on the time-independent Wick's theorem [9, 33] with graphical techniques of spin algebras [41–44]. Thus constructing all connected diagrams involving at most two  $T_2$  vertices\* and evaluating the corresponding spin diagrams we obtain the CPMET equations in orthogonally spin-adapted form, Eqs. (40) of Ref. 29. The general form of these equations is

$$a_i + \sum_j b_{ij} t_j + \sum_{j \leq k} c_{ijk} t_j t_k = 0, \quad (19)$$

where  $t_i$  designates the matrix elements  $\langle a^1 a^2 | t_2(S_i) | a_1 a_2 \rangle$  arranged in some definite order.

Neglecting the quadratic term, i.e., setting  $c_{ijk} = 0$ , we obtain the linear CPMET (L-CPMET). Clearly, when we approximate the quadratic term in a less drastic manner, we can generate a whole series of approximations ranging from L-CPMET to full CPMET. The most natural way of generating such approximations within the formalism used is to consider the contribution of various diagrams which give rise to the nonlinear part in Eq. (19). These diagrams are shown in Figure 1 [cf. Fig. 3(c) of Ref. 29]. In the spin-orbital form, the diagrams 1 and 2, 3, 4, and 5 correspond to the Hugenholtz diagrams 1, 2, 3, and 4 of Figure 14 of the second Ref. 9.

The role of individual terms represented by the diagrams of Figure 1 was investigated in detail for the Be atom [45]. Here we only consider two important cases characterized by diagrams 1, 2, and 3 and by diagrams 4 and 5. The essential difference between these two sets is that the latter group consists of diagrams which are separable† over one or two hole lines. It is easily seen that the contributions from the exclusion principle violating (EPV) diagrams of this type, in which the internal (i.e., summation) hole label(s) are identical with the appropriate external hole line label(s), are expressible as the product of the pertinent  $t_2$  matrix element and the energy contribution (given by the energy diagram with pertinent fixed hole labels).

Thus, in addition to the L-CPMET and CPMET schemes, in which either none or all of the diagrams of Figure 1 are accounted for, we consider also the schemes ACP-D123 and ACP-D45 in which only the above named sets of diagrams are taken into account. Further, in the spirit of the CEPA-type approaches we consider

\* As explained in Ref. 29 it is particularly convenient to use the mixed Goldstone–Hugenholtz (Brandow) form representing the interaction vertices by Goldstone diagrams and the  $T_2$  vertices by Brandow diagrams (i.e., by one Goldstone representative of a Hugenholtz diagram).

† A diagram is separable over a given set of lines if a removal (or an interruption) of these lines yields two (or more) disconnected diagrams.



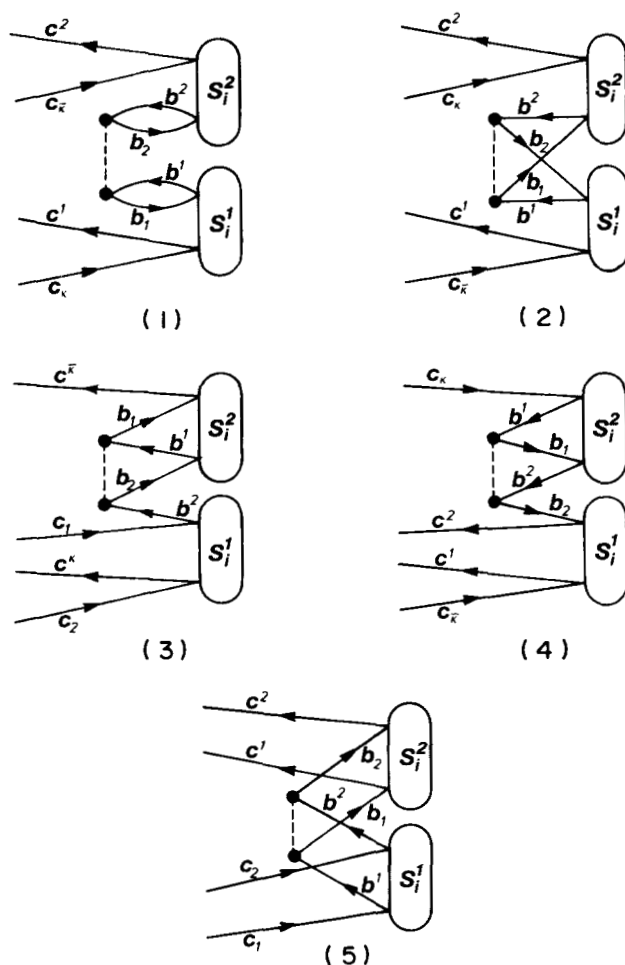


Figure 1. Goldstone versions of the resulting orbital diagrams ( $\kappa = 1, 2$ ) in the mixed Goldstone-Hugenholtz (Brandow) representation (cf. Ref. 29 for details) yielding the quadratic terms in the orthogonally spin-adapted CPMET equations [Eqs. (19)].

also the approximations in which only the EPV diagrams 4 and 5 of Figure 1 are retained in the nonlinear part of the CPMET equations (19). Since they are not identical to the conventional CEPA schemes, we refer to them as approximate coupled pair (ACP) methods. In addition to the ACP-D123 and ACP-D45 schemes defined above, we consider the following schemes:

(a) ACP-A scheme, which takes into account the terms associated with diagrams 4 and 5 of Figure 1 with  $b_1$  and  $b_2$  labels fixed to the values  $c_1$  and  $c_2$  carried by the external lines in both possible ways (i.e.,  $b_1 = c_1, b_2 = c_2$  and  $b_1 = c_2, b_2 = c_1$ ).

(b) ACP-B scheme, which in addition to the terms accounted for in the ACP-A scheme above also takes into account the terms associated with the diagram 4 of

Figure 1 in which  $b_1 \neq c_i$  ( $i = 1, 2$ ). Thus, for the contribution of diagram 4 the internal hole line label  $b_1$  is summed over all occupied states.

(c) ACP-C scheme results, finally, when all the terms by which the approximations *A* and *B* above differ are multiplied by the factor  $(\frac{1}{2})$ .

These approximations are related to but not identical with the well-known CEPA schemes. The main difference stems from the fact that the above definitions are based entirely on the diagrammatic formulation of the orthogonally spin-adapted coupled-pair theory. The CEPA-type methods, in turn, can be easily interpreted [25] in terms of the diagrams occurring in the spin-orbital formulation of the CP theory, in which spin-orbital pair energies play an essential role. However, for practical applications it is desirable to work with symmetry-adapted configurations and spin-coupled pairs. This requires a unitary transformation of the subspace of doubly-occupied configurations. Since the CEPA-type equations are not invariant with respect to these transformations, one has the option of either using the transformed equations, as in our case, or, in order to maintain the original structure of the equations, applying an averaging procedure to the spin-orbital pair energies. This latter procedure is characteristic of all CEPA-like approaches. Finally, another difference between the commonly used CEPA-type procedures and the ACP schemes described above stems from the fact that the former ones are formulated in terms of nonorthogonal orbitals (PNO's) whereas the latter ones are formulated in terms of orthogonal orbitals.

Nevertheless, if the approximations (a), (b), and (c) above were interpreted in terms of spin-orbital diagrams, we would obtain the schemes corresponding to (in Kutzelnigg's classification [23]) the CEPA (2), Kelly's CEPA [46], and CEPA (1) methods, respectively. Even though this relationship does not hold exactly in the spin-adapted case as explained above, there is nevertheless a correspondence between the ACP and CEPA-type schemes when basic approximations involved are considered. Indeed, this correspondence can be symbolically expressed as follows:

$$\text{ACP-A} \leftrightarrow \text{CEPA (2) [23], CPA' [25],}$$

$$\text{ACP-B} \leftrightarrow \text{Kelly's CEPA [23], CEPA (3) [27], CPA'' [25],}$$

$$\text{ACP-C} \leftrightarrow \text{CEPA (1) [23].}$$

The general character of the numerical results obtained by our method seems to support this correspondence.

### 3. Model Description and Computational Details

In order to investigate the quasidegeneracy effects we have looked for a model in which the strength of the quasidegeneracy can be continuously varied and which is simple enough to enable the computations using many different approaches at an affordable cost. We have thus decided to consider several four-electron systems using both *ab initio* and semiempirical model Hamiltonians.

The first group of models consists of four hydrogen atoms arranged in the isosceles trapezoidal (H4), rectangular (P4), and linear (D4) configurations as shown in Figure 2. In order to vary the degree of quasidegeneracy, we vary a single parameter  $\alpha$  in each model, as indicated in Figure 2. Thus, in the H4 model, all

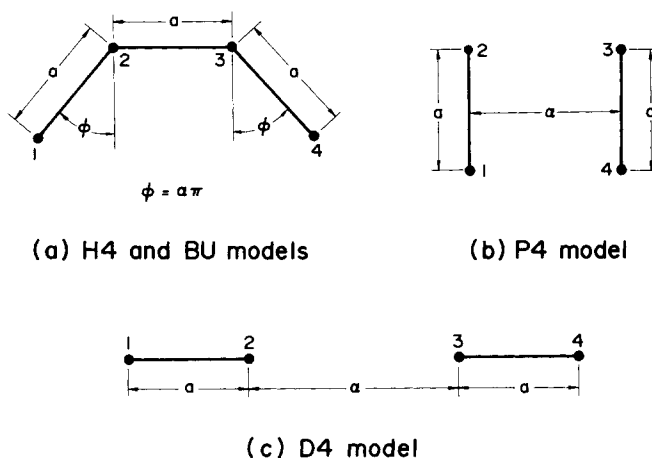


Figure 2. Nuclear configurations and definitions of the model parameter  $\alpha$  for the models used.

nearest-neighbor internuclear separations are fixed ( $a = 2$  a.u.) while the angle  $\phi \equiv H_1 H_2 H_3 - \pi/2$  varies in the interval  $\phi \in (0, \pi/2)$ . We thus characterize this model by the parameter  $\alpha$  defining this angle, i.e.,  $\phi = \alpha\pi$ . This model closely parallels the  $\pi$ -electron model of *cis*-butadiene (see later). The P4 model consists of two parallel hydrogen molecules, with a fixed (stretched) bond length  $a$  with the nuclei in a rectangular arrangement. The geometry of this model is thus simply determined by the distance  $\alpha$  between the two molecules, as is also the case in the linear D4 model [cf. Fig. 2(c)].

Finally, we also consider the  $\pi$ -electron model of *cis*-butadiene described by the Pariser–Parr–Pople (PPP) Hamiltonian, in which the  $C_1 C_2 C_3$  angle is again varied as in the corresponding H4 model [cf. Fig. 1(a)]. The fixed CC bond length for all CC bonds was chosen to be 1.4 Å.

For all  $H_4$  models we use the minimum basis set (MBS) represented as a linear combination of three  $s$ -type Gaussians with exponents 4.50038, 0.681277, and 0.151374 and (unnormalized) coefficients 0.07048, 0.40789, and 0.64767, respectively [47]. For the  $H_2$  molecule this basis yields the energy  $-1.09379$  a.u. at the equilibrium bond length 1.605 a.u. These values should be compared with the Hartree–Fock limit values  $-1.13363$  and 1.4 a.u., respectively. For  $a = 2$  a.u., the  $H_2$  energy is  $-1.075482$  a.u. using MBS.

In the PPP Hamiltonian [32] defining the  $\pi$ -electron *cis*-butadiene model (further referred to as BU model) we use Mataga–Nishimoto parametrization [48]

of the two-electron two-center Coulomb integrals and the I-A approximation [32] for the one-center Coulomb integral ( $\gamma_{00} = 10.84$  eV). Further, in view of the structure of our model for  $\alpha \rightarrow 0$  we refrain from using the tight binding approximation as is usual but consider the resonance integrals  $\beta_{\mu\nu}$  between all centers. We choose  $\beta = -2.4$  eV for the C—C distance of 1.4 Å and calculate all other resonance integrals using "Mulliken's magic formula"  $\beta = S(\beta_0/S_0)$  where  $\beta_0 = -2.4$  eV, and  $S$  and  $S_0$  are the overlap integrals of the Slater carbon  $2p_z$  atomic orbitals for the given and "equilibrium" (1.4 Å) C—C nuclear separations, respectively.

In each case we first find the SCF-MO-LCAO solution using the system of programs ASTERIX [49] in the *ab initio* case. After transforming the one- and two-electron integrals into the SCF-MO basis\* we calculated the full and limited CI results as well as the CPMET, L-CPMET, and various ACP results using a set of programs specially developed for this purpose.

The MO's  $\phi_i$ ,  $i = 1, 2, 3, 4$  are labeled according to increasing orbital energy. Except for the special value of the parameter  $\alpha$  corresponding to a square nuclear configuration in the H4 model and for the rectangular P4 models, these MO's are either symmetric or antisymmetric with respect to one twofold symmetry operation. Thus, the full CI wave function involves only two mono- and two triexcited, six biexcited, and one tetraexcited configurations. Since the MBS is used, only the matrix elements up to the biexcited configurations (cf. Ref. 39) are needed in view of the hole-particle symmetry. The mono-, tri-, and tetraexcited configurations are uniquely defined by the orbital occupancies while for the biexcited configurations we use the *pp-hh* coupled states [39]. We can thus write the full CI wave function as follows:

$$\begin{aligned}
 |\Psi\rangle = & C_0|\Phi_0\rangle + \sum_{i=3}^4 \sum_{j=1}^2 C_i^j \left| \begin{matrix} j \\ i \end{matrix} \right\rangle \\
 & + \sum_{S_i=0}^1 \sum_{i,k=3}^4 \sum_{j,l=1}^2 C_{ik}^{jl}(S_i) \left| \begin{matrix} j & l \\ i & k \end{matrix} \right\rangle_{S_i} \\
 & + \cdots + C_Q \left| \begin{matrix} 33 & 44 \\ 11 & 22 \end{matrix} \right\rangle, \quad (20)
 \end{aligned}$$

where  $C_2^3 = C_1^4 = C_{12}^{33}(S_i) = C_{11}^{34}(S_i) = \cdots = 0$ , due to the symmetry of the model. In addition to full CI (F-CI) we also calculate the limited CI containing in addition to the ground-state configuration  $|\Phi_0\rangle$  all doubly excited (D-CI) and all doubly and a quadruple (DQ-CI) configurations. Moreover, for the rectangular nuclear conformation (model P4) all mono- and triexcited configurations are absent from  $|\Psi\rangle$  [Eq. (20)], so that in this case the DQ-CI results are equivalent with F-CI results.

\* We are greatly obliged to Dr. I. Shavitt and Dr. M. Benard for providing us with the two-electron integral transformation routines.

#### 4. Results and Discussion

We have carried out a detailed study of each model for a wide range of parameter values  $\alpha$ . As may be expected, the quasidegeneracy, particularly in the H4, P4, and BU models, becomes most pronounced when the parameter  $\alpha$  approaches values corresponding to a square configuration ( $\alpha \rightarrow 0$  in H4 and BU models and  $\alpha \rightarrow a = 2.0$  a.u. in P4 model). It is well known from a simple MO theory that in this case the highest occupied (HOMO) and the lowest unoccupied (LUMO) MO's become degenerate. However, when the interelectronic repulsion is accounted for, this is not the case. The problem of HOMO and LUMO energy crossing and its relationship to the nonsinglet instability [50] of the corresponding SCF solutions of a rectangular H4 MBS model was discussed in detail by Fukutome [51]. He showed that in contrast to a simple MO theory the orbital energy crossing (when the orbital energies are considered as functions of the reaction coordinate corresponding to the  $H_2 + H_2$  exchange reaction) is shifted away from the square configuration due to the interelectronic repulsion terms. In fact, the orbital energy behavior is asymmetric with respect to the square configuration unless the biexcited configuration  $|_{22}^{33}\rangle$  is chosen as a reference configuration on one side of the square nuclear arrangement and  $|\Phi_0\rangle$  on the other side. Indeed, one can see easily that for the parameter range  $\alpha \in (a, \infty)$  of the P4 model considered the HOMO and LUMO will not cross (in fact their separation is never smaller than 0.34 a.u. in this whole range). However, should one consider the configuration  $|_{22}^{33}\rangle$  as a reference state, the HOMO and LUMO orbital energies will cross in this interval.

In any case the energy of the  $|_{22}^{33}\rangle$  configuration approaches that of the ground state  $|\Phi_0\rangle$  as we approach the square nuclear arrangement, as may be anticipated, so that the quasidegeneracy becomes very strong in this limit. We shall see that in fact this quasidegeneracy will cause a complete breakdown of the L-CPMET approximation in the vicinity of geometries corresponding to certain critical value  $\bar{\alpha}$  of the parameter  $\alpha$ , which is always close to the parameter value of  $\alpha$  characterizing the square nuclear arrangement. We will see that this critical value  $\bar{\alpha}$  is determined by the singularity of the matrix of the linear part of the CPMET equations [i.e., matrix  $[b_{ij}]$ , Eq. (19)].

Since we are mainly interested in the quasidegeneracy effects, we will present our results primarily for the region of geometries close to that defined by  $\bar{\alpha}$ . In the remaining region of  $\alpha$  values studied we only select a few typical points since the qualitative behavior of the results depends very little on the actual value of the structural parameter  $\alpha$  outside the critical region mentioned.

##### A. Wave Function and Cluster Expansion Analysis

The extent of the quasidegeneracy present in the studied systems may be estimated from the weight of the reference configuration  $|\Phi_0\rangle$  in the normalized F-CI wave function given in Table I (the coefficients of mono- and triexcited configurations are small and are not included in this table). We find that for the H4, P4, and BU models the  $C_0$  coefficient [Eq. (20)] decreases considerably with decreasing  $\alpha$ . At the same time we observe a sharp increase in the coefficient  $C_{22}^{33}$

TABLE I. The coefficients of an even number times excited configurations in the F-CI normalized wave function for all models considered. Spin-adapted configurations defined in Ref. 39 were used. Last column gives the disconnected component  $T_2^2$  of the quadruply excited coefficient obtained by a cluster analysis.

MODEL	$\alpha$	$c_0$	$c_{11}^{33}$	$c_{11}^{44}$	$c_{22}^{33}$	$c_{22}^{44}$	$c_{12(0)}^{34}$	$c_{12(1)}^{34}$	$c_Q$	$c_Q^D$
H4	0.500	.967	.064	.051	.193	.041	.126	-.057	.022	.024
	0.200	.962	.068	.053	.200	.053	.143	-.056	.027	.028
	0.100	.950	.075	.051	.234	.063	.165	-.057	.034	.035
	0.050	.922	.072	.048	.317	.061	.181	-.065	.042	.045
	0.020	.848	.046	.047	.473	.039	.190	-.084	.051	.064
	0.015	.821	.037	.047	.525	.031	.190	-.089	.053	.071
	0.005	.742	.014	.046	.633	.012	.187	-.100	.060	.094
P4	10.000	.968	.088	.087	.087	.088	.175	-.002	.033	.033
	4.000	.967	.091	.067	.105	.095	.177	-.017	.034	.034
	2.200	.893	.064	.048	.386	.057	.192	-.072	.047	.054
	2.100	.827	.040	.047	.514	.034	.192	-.088	.054	.070
	2.020	.724	.009	.046	.653	.008	.186	-.102	.062	.100
	2.002	.693	.001	.045	.686	.001	.183	-.105	.064	.110
D4	6.0	.968	.091	.083	.089	.088	.175	-.006	.033	.033
	4.0	.969	.096	.073	.099	.082	.172	-.016	.032	.032
	2.0	.967	.063	.051	.193	.041	.126	-.057	.022	.024
	1.5	.957	.040	.044	.257	.024	.092	-.064	.018	.020
	1.0	.938	.021	.035	.330	.011	.053	-.055	.015	.017
BU	0.500	.926	.070	.097	.259	.073	.220	-.062	.060	.066
	0.200	.927	.070	.097	.256	.076	.220	-.062	.059	.066
	0.100	.922	.071	.094	.266	.083	.226	-.062	.063	.068
	0.050	.904	.071	.088	.310	.090	.238	-.065	.071	.078
	0.020	.850	.054	.082	.434	.075	.247	-.084	.086	.102
	0.015	.827	.046	.081	.478	.064	.247	-.092	.091	.112
	0.005	.744	.019	.078	.603	.027	.239	-.117	.103	.150
	0.001	.692	.004	.076	.663	.006	.231	-.129	.109	.177

indicating the participation of one of the two leading doubly excited configurations. However, the coefficient of the second leading configuration,  $C_{12}^{34}(0)$ , although appreciable and often larger than  $C_{22}^{33}$ , changes very little with  $\alpha$ . A significant increase is also observed for the coefficient  $C_{12}^{34}(1)$ . However, this coefficient remains relatively insignificant in the whole range of  $\alpha$  values. Hence, we can state that in general the quasidegeneracy becomes more pronounced as the parameter  $\alpha$  decreases, and manifests itself most strongly when the model approaches the square conformation. This is, of course, a direct consequence of the fact that a single-determinant reference configuration is inadequate in this case.

To get an idea about the “strength” of the quasidegeneracy in the model cases considered here let us recall the situation in the beryllium ground state which is usually regarded as a typical quasidegenerate system. In this case Watson [52] found for the ground-state coefficient  $C_0 = 0.9576$  while for the coefficients of the three leading doubly excited configurations he obtained the values 0.2845, 0.0262 and 0.0232. For the three models discussed so far we find that only for  $\alpha = 0.5$  and 0.2 in case of the H4 model and for  $\alpha = 10.0$  and 4.0 in case of the P4 model is the coefficient  $C_0$  slightly larger than for the Be atom. Hence, in the case of the H4, P4, and BU models we always deal with a rather strong quasidegeneracy. For the limiting small values of the model parameter  $\alpha$  the values of  $C_0$  and  $C_{22}^{33}$  are almost equal indicating that we are approaching a true degeneracy involving the reference state  $|\Phi_0\rangle$  and the doubly excited configuration  $|_{22}^{33}\rangle$ . Thus, the H4, P4, and BU models enable a continuous variation of the quasidegeneracy effects over a large range so that we can investigate the reliability of various CP approaches in the presence of this effect.

The D4 model represents, in turn, a somewhat different situation. For large  $\alpha$  values we observe an equal participation of all configurations  $|_{aa}^{ii}\rangle$ , while the coefficient  $C_{12}^{34}(0)$  of the singlet coupled interpair configuration  $|_{12}^{34}\rangle_0$  is roughly twice as large as  $C_{aa}^{ii}$  and  $C_{12}^{34}(1)$  almost vanishes. A similar situation also occurs in the P4 model for very large  $\alpha$ . On the other hand, we find that for the D4 model with  $\alpha = 1$  the doubly excited configuration  $|_{22}^{33}\rangle$  is again the most important, similarly as in the Be case.

In order to find out how well the basic assumption [Eq. (9)] of the CPMET approach is satisfied in these cases, we have also carried out the cluster analysis of the F-CI wave functions. In the MBS four-electron case studied we can directly use the equations and analysis described in detail in Ref. 53. Since there is only one tetraexcited configuration present in the models studied, we can simply compare the value of the F-CI tetraexcited coefficient  $C_Q$  [Eq. (20)] with its disconnected part  $C_Q^D$  obtained from the cluster analysis [53]. Both these coefficients are given in the last two columns of Table I. We see from this table that for the H4, P4, and BU models the agreement between  $C_Q$  and  $C_Q^D$  is very good in the intermediate quasidegeneracy range but deteriorates rapidly when strong quasidegeneracy is present. For the D4 model the agreement is satisfactory for the whole range of parameter values, even though the best agreement occurs for large  $\alpha$  values when no clearly dominant doubly-excited configuration is present.

In order to get a better insight into the structure of the wave function both in the CI and CP approaches, we present in Table II the coefficients of all nonvanishing doubly-excited configurations together with the corresponding  $t_2$  matrix elements obtained with various approaches for the H4 model. The results of the CI calculations are also presented in the intermediate normalization ( $C_0 = 1$ ) for easier comparison. We observe that the F-CI and DQ-CI coefficients differ very little indicating that the singly- and triply-excited configurations have a negligible effect. On the other hand we find a much more noticeable difference between the D-CI and DQ-CI wave functions which indicates that the quadruply-excited configuration is next in importance to the doubly-excited ones.

TABLE II. Coefficients of the doubly-excited configurations (intermediate normalization) and of the corresponding  $t_2$  matrix elements for the H4 models obtained with various CI and CP schemes.

$\alpha$	METHOD	$C_{11}^{33}$	$C_{11}^{44}$	$C_{22}^{33}$	$C_{22}^{44}$	$C_{12}^{34}(0)$	$C_{12}^{34}(1)$
0.500	F-CI	.0657	.0528	.1995	.0429	.1302	-.0588
	D-CI	.0655	.0512	.1936	.0427	.1281	-.0565
	DQ-CI	.0671	.0527	.1961	.0437	.1307	-.0576
	L-CPMET	.0670	.0538	.2140	.0428	.1366	-.0601
	CPMET	.0672	.0529	.1965	.0438	.1309	-.0577
	ACP-D45	.0692	.0522	.1983	.0434	.1307	-.0564
0.100	F-CI	.0793	.0536	.2464	.0661	.1736	-.0602
	D-CI	.0758	.0524	.2429	.0627	.1674	-.0592
	DQ-CI	.0785	.0542	.2487	.0649	.1725	-.0609
	L-CPMET	.0737	.0573	.3039	.0600	.1851	-.0685
	CPMET	.0787	.0543	.2490	.0650	.1729	-.0610
	ACP-D45	.0797	.0539	.2557	.0636	.1730	-.0594
0.020	F-CI	.0543	.0548	.5650	.0463	.2242	-.0990
	D-CI	.0497	.0537	.5523	.0428	.2157	-.0962
	DQ-CI	.0546	.0557	.5634	.0467	.2243	-.0987
	L-CPMET	-.5483	.2085	4.4186	-.4588	.6463	-.6733
	CPMET	.0561	.0562	.5665	.0477	.2267	-.0994
	ACP-D45	.0527	.0562	.5995	.0419	.2282	-.0993
0.015	F-CI	.0452	.0573	.6394	.0385	.2319	-.1086
	D-CI	.0401	.0553	.6274	.0346	.2230	-.1059
	DQ-CI	.0455	.0572	.6380	.0388	.2319	-.1083
	L-CPMET	1.7217	-.3514	10.0381	1.4361	-.8869	.7358
	CPMET	.0450	.0579	.6416	.0403	.2351	-.1091
	ACP-D45	.0435	.0578	.6741	.0342	.2359	-.1087
0.005	F-CI	.0185	.0619	.8525	.0157	.2522	-.1354
	D-CI	.0115	.0600	.8455	.0102	.2427	-.1334
	DQ-CI	.0186	.0619	.8521	.0157	.2523	-.1353
	L-CPMET	.3470	-.0130	1.2673	.2869	-.0449	-.1690
	CPMET	.0227	.0630	.8559	.0190	.2579	-.1365
	ACP-D45	.0180	.0620	.8722	.0138	.2551	-.1332

The  $t_2$  matrix elements of the CPMET are very close to the results of the DQ-CI calculation for all values of  $\alpha$ . This is particularly the case for the dominant  $t_2$  matrix elements and corresponding CI coefficients [cf. Eq. (17)]. When comparing the CP results among themselves one can see that for  $\alpha = 0.5$  and  $0.1$ , i.e., in the presence of an intermediate quasidegeneracy, all three approaches yield very close results. However, for small  $\alpha$  values (the last three entries in Table II), when the quasidegeneracy becomes very strong, the L-CPMET approximation clearly breaks down. The largest errors are observed when  $\alpha$  approaches the value  $\bar{\alpha}$  defined above. We shall discuss the reasons of this behavior in greater detail in Sec. 4 D. On the other hand, a comparison of the  $t_2$  matrix elements obtained with the CPMET and ACP-D45 approaches clearly indicates that the latter method is a reliable approximation to the CPMET irrespective of the quasidegeneracy present.



### B. Correlation Energies

The correlation energies obtained for all four models are compiled in Tables III–VI. Each table presents a set of results obtained both by the CI-type procedures, involving different sets of configurations, and by the CP-type methods including the CPMET and various approximate schemes. In addition, results obtained by the D-CI method corrected by Davidson's formula [31] are also displayed.

TABLE III. Correlation energies for the H4 model obtained by means of various CI- and CP-type methods (in mH, all signs reversed; NC indicates no convergence of the system of equations in the region of physical interest).

$\alpha$	F-CI	D-CI DQ-CI	CPMET	L-CPMET ACP-D123	ACP-B ACP-D45	ACP-A ACP-C	D-CI + Davidson's Correction
0.500	53.690	52.515 53.511	53.572	56.260 56.086	53.276 53.756	54.884 54.054	55.759
0.200	57.260	52.727 57.163	57.233	60.553 60.374	56.836 57.417	58.933 57.844	59.815
0.100	65.321	63.340 65.227	65.318	71.017 70.566	64.824 65.691	68.273 66.448	69.252
0.050	76.429	73.785 76.401	76.635	91.829 90.990	76.113 77.507	83.125 79.240	84.268
0.020	92.148	88.781 92.124	93.034	320.410 NC	92.265 94.195	111.728 99.937	112.667
0.015	96.711	93.220 96.686	97.900	-517.543 NC	96.872 98.763	121.474 106.305	122.538
0.005	109.196	105.552 109.188	111.355	-8.129 NC	109.062 110.369	148.182 123.484	152.316

Let us first discuss the CI-type results shown in the second and third columns of Tables III–VI. The F-CI and DQ-CI correlation energies differ very little: for the H4, D4, and BU models the largest difference occurs for  $\alpha = 0.5$  in the BU model and amounts to less than 0.5% of the F-CI result used as a reference throughout this paper. For most other parameter values this difference is much smaller and becomes negligible in the strongly quasidegenerate limit. In the P4 model the agreement between the F-CI and DQ-CI is exact since odd number of times excited states cannot contribute due to the symmetry of this model. These results indicate that singly- and triply-excited configurations contribute very little to the total correlation energy, so that the basic assumptions of the CPMET ( $T_1, T_3 \ll T_2$ ) are

TABLE IV. Correlation energies for the P4 model obtained by means of various CI- and CP-type methods (in mH, all signs reversed; NC indicates no convergence, see Table III).

$\alpha$	F-CI	D-CI DQ-CI	CPMET	L-CPMET ACP-D123	ACP-B ACP-D45	ACP-A ACP-C	D-CI + Davidson's Correction
10.000	54.650	53.013 54.650	54.650	56.507 56.507	54.225 54.650	56.022 55.095	56.100
4.000	57.269	55.504 57.268	57.258	59.364 59.381	56.785 57.243	58.766 57.742	56.889
2.200	84.443	81.300 84.443	84.897	125.211 NC	84.352 86.152	96.449 89.373	96.859
2.100	95.815	92.339 95.815	96.967	-787.233 NC	96.002 97.926	119.945 105.164	120.532
2.020	112.069	108.421 112.069	114.467	2.473 NC	111.778 112.870	154.101 127.319	159.470
2.002	117.035	113.385 117.035	119.824	13.770 NC	116.386 117.060	163.847 133.759	171.886

TABLE V. Correlation energies for the D4 model obtained by means of various CI- and CP-type methods (in mH, all signs reversed).

$\alpha$	F-CI	D-CI DQ-CI	CPMET	L-CPMET ACP-D123	ACP-B ACP-D45	ACP-A ACP-C	D-CI + Davidson's Correction
6.0	54.718	53.076 54.714	54.714	56.572 56.577	54.285 54.710	56.083 55.154	56.165
4.0	54.754	53.105 54.698	54.697	56.555 56.551	54.261 54.700	56.029 55.116	56.156
2.0	53.690	52.515 53.512	53.572	56.260 56.086	53.276 53.756	54.884 54.054	55.759
1.5	58.517	56.790 57.572	57.644	62.001 61.787	57.462 57.890	59.060 58.236	61.128
1.0	70.896	67.575 68.213	68.255	76.704 76.452	68.211 68.537	69.597 68.885	74.645

TABLE VI. Correlation energies for the BU model obtained by means of various CI- and CP-type methods (in eV, all signs reversed; NC indicates no convergence; see Table III).

$\alpha$	F-CI	D-CI DQ-CI	CPMET	L-CPMET ACP-D123	ACP-B ACP-D45	ACP-A ACP-C	D-CI + Davidson's Correction
0.500	1.4279	1.3564 1.4214	1.4294	1.5997 1.6116	1.4049 1.4244	1.5149 1.4556	1.5319
0.200	1.4048	1.3335 1.3983	1.4060	1.5714 1.5890	1.3811 1.4002	1.4885 1.4307	1.5049
0.100	1.4342	1.3563 1.4264	1.4342	1.6236 1.6438	1.4077 1.4287	1.5271 1.4624	1.5417
0.050	1.5715	1.4796 1.5652	1.5750	1.9012 1.9451	1.5447 1.5720	1.7171 1.6212	1.7265
0.020	1.8393	1.7294 1.8385	1.8609	4.2490 NC <sup>a</sup>	1.8206 1.8572	2.1905 1.9690	2.1731
0.015	1.9242	1.8101 1.9239	1.9537	-34.632 NC <sup>a</sup>	1.9081 1.9450	2.3770 2.0895	2.3464
0.005	2.1813	2.0624 2.1810	2.2421	0.526 NC <sup>a</sup>	2.1695 2.1968	2.9854 2.4660	2.9593
0.001	2.3350	2.2179 2.3350	2.4168	0.831 NC <sup>a</sup>	2.3216 2.3368	NC 2.6843	3.3610

also fulfilled for the models considered. The only two instances where these states are of some importance are found for the D4 model with  $\alpha = 1.0$  and 1.5.

To estimate the importance of the quadruply-excited configuration let us examine the differences between the DQ-CI and D-CI correlation energies. For the H4 and P4 models these differences amount to about 3–3.5% of the F-CI result. They are larger in the BU model reaching up to 5.9%. In contrast, the smallest effect is found for the D4 model with  $\alpha = 1.0$  and 1.5. We recall that in these latter cases we observed the largest contribution of singly- and triply-excited configurations. It is also interesting to note that for the H4, P4, and BU models the quadruply-excited configuration gives largest energy contribution in the vicinity of the singular point  $\bar{\alpha}$ , in which the L-CPMET energy contribution changes its sign.

We shall next examine the CP theories starting with a comparison of the CPMET and F-CI results. We find that for all models considered the CPMET correlation energies are slightly lower than the exact values for strongly quasidegenerate cases and slightly larger for large  $\alpha$  values. For the intermediate range of  $\alpha$  values the difference between both results is very small and does not exceed 0.2% of the F-CI correlation energy. Finally, in the case of very strong quasidegeneracies (almost real degeneracy) these differences increase to about 2 to 3.5%. The fact that the CPMET performs so well even in the case of almost real degeneracies, at

least in the model cases studied, is truly surprising not only in view of the quasidegeneracies present but also in view of the cluster analysis discussed in Sec. 4A.

The D4 model for  $\alpha = 1.0$  and 1.5 again requires a special consideration. Since in these cases the importance of singly- and triply-excited configurations is relatively significant, we should compare the CPMET results with the DQ-CI energies rather than with the F-CI ones. If we do so, we find again a remarkable agreement.

Let us now proceed to the discussion of the approximate coupled pair methods defined above: For the medium quasidegeneracy effects the results of the L-CPMET and ACP-D123 methods are very close again confirming our conclusion [45] that a mutual compensation of contributions from the diagrams 1, 2, and 3 of Figure 1 is almost complete. The differences between these two and the CPMET results amount to about 5–10% of the F-CI correlation energies in the region of not very strong quasidegeneracies. The L-CPMET and ACP-D123 energies are always lower than the CPMET energies in agreement with findings reached by several authors [13, 16, 17, 25, 27] for other many-electron systems. Invariably, the differences, between the CPMET and the L-CPMET results obtained by these authors are considerably smaller than those obtained here. This is because cases considered by these authors the quasidegeneracy was less pronounced than in the model systems considered here.

When proceeding to strong quasidegeneracy cases we see from Tables III, IV, and VI that the L-CPMET approximation breaks down completely. In these cases we were also unable to find any solution of the equations for the ACP-D123 approximation, since the iterative procedure used (Newton–Raphson) always diverged. This complete breakdown of the L-CPMET approximation in the presence of a strong quasidegeneracy is in agreement with the conclusions reached by Bartlett and Purvis [4] in their study of the beryllium dimer potential curve. We will discuss the origins of this breakdown in Sec. 4D.

The most reliable approximations of the CPMET are undoubtedly obtained with the ACP-B and ACP-D45 schemes. We can see from Tables III–VI that these two methods yield correlation energies that are very close to those given by the CPMET method, *regardless the degree of quasidegeneracy present*. For intermediate quasidegeneracies the ACP-D45 method yields energies that are closer to their CPMET counterparts than those obtained with the ACP-B method whereas the opposite holds for very strong quasidegeneracies. The ACP-D45 method yields lower values of the correlation energies than the ACP-B method, the difference in most cases being less than 1% of the F-CI value. Only when the model parameters take values close to  $\bar{\alpha}$  does this difference increase to 2%.

The ACP-A correlation energies are always lower than their CPMET counterparts. This difference amounts to about 3–6% of the F-CI value in the case of intermediate quasidegeneracies and to as much as 40% in strongly quasidegenerate cases. This behavior is consistent with the observation of Taylor et al. [16] that the CEPA-A scheme (corresponding to our ACP-A) overestimates the contribution from the disconnected clusters as the interatomic distance increases (increasing quasidegeneracy),

The last approximate CP method considered, referred to as the ACP-C scheme, represents an intermediate case between the ACP-B and ACP-A schemes. This is also clearly demonstrated by the results given in Tables III–VI. The differences between the correlation energies obtained with the ACP-C and CPMET approaches are of the order of 1–2% for intermediate quasidegeneracies and increase to 11.5% in the case of a strong quasidegeneracy. Since the ACP-B and ACP-C methods involve the same computational effort, it is obvious that the former one should be preferred.

Considering, finally, the D-CI results corrected using Davidson's formula [31] we find that they are slightly inferior to the ACP-A results. The difference between these two approaches increases slightly with increasing quasidegeneracy.

### C. Pair-Energy Analysis

To get a better insight into the structure of the total correlation energies discussed above we present in Table VII the pair correlation energies obtained by the CP methods used in this paper. We have chosen the D4 model with  $\alpha = 1.0$  since it is characteristic of an intermediate quasidegeneracy involving only one doubly-excited configuration as in the beryllium ground state. We see from Table VII that the pair energies obtained with various approximate CP methods are very similar to the CPMET results. Moreover, an analysis of the results obtained with the L-CPMET and ACP-D123 schemes, for which the errors in the total correlation energies are large, indicates that the bulk of this error is due to a poor description

TABLE VII. Pair energies for the D4( $\alpha = 1.0$ ) model. All energies are in mH with signs reversed. Numbers in parentheses give the difference with respect to corresponding CPMET pair energies.

Method	Pair Correlation Energies			Correlation Energy
	(1,1)	(1,2)	(2,2)	
CPMET	5.322	9.335	53.598	68.255
L-CPMET	5.218 (-0.104)	9.846 (0.511)	61.641 (8.043)	76.704 (8.449)
ACP-D123	5.092 (-0.230)	9.974 (0.639)	61.385 (7.787)	76.452 (8.197)
ACP-B	5.332 (0.010)	9.228 (-0.107)	53.650 (0.052)	68.211 (-0.044)
ACP-D45	5.461 (0.139)	9.225 (-0.110)	53.850 (0.252)	68.536 (0.281)
ACP-A	5.347 (0.025)	9.586 (0.251)	54.664 (1.066)	69.597 (1.342)
ACP-C	5.340 (0.018)	9.402 (0.067)	54.143 (0.545)	68.885 (0.630)

of the (2, 2) pair which is involved in the strongly interacting configuration  $|_{22}^{33}\rangle$ . Thus, for example, in the L-CPMET case we find that the errors in the (1, 1), (1, 2), and (2, 2) pair energies represent, respectively, -1.2%, 6%, and 95.2% of the error in the total correlation energy. Thus, we find a very similar behavior as for the beryllium atom [28, 45].

#### D. L-CPMET Breakdown

Let us analyze in greater detail the breakdown of the L-CPMET approximation. We first recall that the L-CPMET scheme is equivalent to the MBPT when we restrict ourselves to linked perturbation theory diagrams with only doubly-excited intermediate states. This is easily seen when we write the CPMET equations (19) in the iterative form [cf. Eq. (47) of Ref. 29]

$$\begin{aligned} t_i &= -(b_{ii}^{(d)})^{-1} \left( a_i + b'_{ii}t_i + \sum_{j(\neq i)} b_{ij}t_j + \sum_{j \leq k} c_{ijk}t_jt_k \right), \\ b_{ii} &= b_{ii}^{(d)} + b'_{ii}, \end{aligned} \quad (21)$$

where  $b_{ii}^{(d)}$  designates the appropriate orbital energy difference associated with the  $i$ -th biexcited state, and when we realize that the linear coefficients  $b_{ij}$  represent the CI matrix elements between biexcited states. It should be noted that we usually employ a different normalization convention for the  $t_2$  matrix elements than for the corresponding CI coefficients, as also implied by Eq. (17). However, there is a very simple relationship between these two normalizations given by Eq. (32) of Ref. 29. Thus using the normalized  $t_2$  matrix elements as defined by Eq. (17), the matrix  $\mathbf{B} = [b_{ij}]$  of the linear part of the CPMET equations (19) will be a symmetric (Hermitian) matrix representing the doubly-excited part of the CI matrix obtained with the same spin-adapted configurations which were used to define the spin-adapted  $t_2$  matrix elements (cf., Ref. 29). Similarly, the column matrix  $\mathbf{a} = [a_i]$  of the absolute terms in Eqs. (19) represents the interaction part of the CI matrix between the reference ground-state configuration  $|\Phi_0\rangle$  and doubly-excited configurations considered. Thus, the D-CI matrix has the form

$$\begin{bmatrix} 0 & \mathbf{a}^\dagger \\ \mathbf{a} & \mathbf{B} \end{bmatrix}, \quad (22)$$

while the L-CPMET approximation is defined by the corresponding linear system of algebraic equations obtained from Eqs. (19) by setting  $c_{ijk} = 0$ , which in the matrix form we can write as follows:

$$\mathbf{B}\mathbf{t} = -\mathbf{a}, \quad \mathbf{t} = -\mathbf{B}^{-1}\mathbf{a} \quad (23)$$

where  $\mathbf{t} = [t_i]$  designates the column vector of L-CPMET  $t_i$  matrix elements. In the second Eq. (23) we clearly assumed the matrix  $\mathbf{B}$  to be nonsingular. We thus observe that the D-CI and L-CPMET are very closely related and involve the same set of matrix elements; however, while the former approach involves a matrix diagonalization, the second one requires the solution of a linear algebraic set of equations.

The D-CI problem is clearly invariant to any unitary transformation of the configurations involved, in particular to a unitary transform of the doubly-excited configurations. Consider, thus, a unitary transformation

$$\mathbf{V} = \begin{bmatrix} 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{U} \end{bmatrix}, \quad (24)$$

where  $\mathbf{U}$  is a unitary matrix diagonalizing the doubly-excited part of the D-CI matrix (22), namely

$$\mathbf{BU} = \mathbf{Ub} \quad \text{or} \quad \mathbf{U}^\dagger \mathbf{BU} = \mathbf{b}, \quad (25)$$

where  $\mathbf{b} = [b_i \delta_{ij}]$  is a diagonal matrix with the eigenvalues of  $\mathbf{B}$  along the main diagonal. Applying now the unitary transformation (24) to the D-CI matrix (22), we obtain

$$\mathbf{V}^\dagger \begin{bmatrix} 0 & \mathbf{a}^\dagger \\ \mathbf{a} & \mathbf{B} \end{bmatrix} \mathbf{V} = \begin{bmatrix} 0 & (\mathbf{a}')^\dagger \\ \mathbf{a}' & \mathbf{b} \end{bmatrix}, \quad (26)$$

where  $\mathbf{a}' = \mathbf{U}^\dagger \mathbf{a}$ . We now see easily that also the L-CPMET approximation is invariant to this transformation. Indeed, the L-CPMET equations implied by the transformed D-CI matrix with diagonal biexcited part read

$$\mathbf{bt}' = -\mathbf{a}' \quad \text{or} \quad \mathbf{t}' = -\mathbf{b}^{-1} \mathbf{a}', \quad (27)$$

where  $\mathbf{t}'$  designates the column matrix of corresponding  $t_2$  matrix elements, so that both L-CPMET problems [Eqs. (23) and (27)] yield the same correlation energy since

$$\begin{aligned} \Delta \varepsilon'_{\text{L-CPMET}} &= (\mathbf{a}')^\dagger \mathbf{t}' = -(\mathbf{a}')^\dagger \mathbf{b}^{-1} \mathbf{a}' = -\mathbf{a}^\dagger \mathbf{U} \mathbf{b}^{-1} \mathbf{U}^\dagger \mathbf{a} \\ &= -\mathbf{a}^\dagger \mathbf{B}^{-1} \mathbf{a} = \mathbf{a}^\dagger \mathbf{t} = \Delta \varepsilon_{\text{L-CPMET}}. \end{aligned} \quad (28)$$

However, since  $\mathbf{b}$  is diagonal, the solution of the transformed L-CPMET problem may be given in an explicit form, namely

$$t'_i = -a'_i / b_i, \quad (29)$$

so that

$$\Delta \varepsilon_{\text{L-CPMET}} = \sum_i \frac{(a'_i)^2}{b_i}. \quad (30)$$

We thus find that using the appropriate linear combinations of doubly-excited configurations, which diagonalize the doubly-excited part of the CI problem, namely the eigenvectors of  $\mathbf{B}$  [Eq. (25)] as the basis of the subspace spanned by the doubly-excited configurations, we obtain the L-CPMET result already in the second order of perturbation theory. In this form the relationship between the L-CPMET and the MBPT becomes particularly transparent.

Moreover, we also see immediately from this formulation when the L-CPMET approximation will break down. This will clearly be the case when the lowest eigenvalue  $b_i$  of  $\mathbf{B}$  vanishes. Clearly, when  $b_i = 0$ , the matrix  $\mathbf{B}$  becomes singular

and the L-CPMET approximation breaks down. This is exactly the case that occurs in our models H4, P4, and BU for the geometries characterized by the critical value  $\bar{\alpha}$  of the parameter  $\alpha$ .

This behavior is illustrated on the BU model in Figure 3, where we have plotted the F-CI, CPMET, and L-CPMET correlation energies as a function of the parameter  $\alpha$ , as well as the lowest eigenvalue and the determinant of the **B** matrix. We see

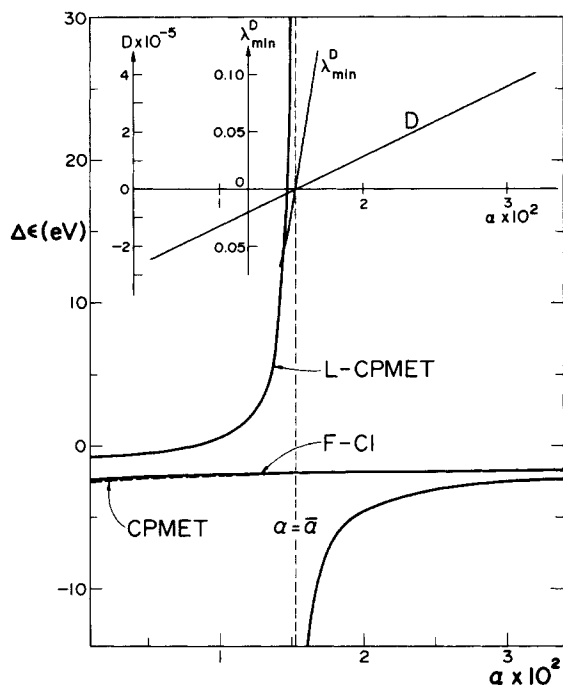


Figure 3. Dependence of the L-CPMET, CPMET, and F-CI correlation energies on the model parameter  $\alpha$  for the BU model. Dependence of the lowest eigenvalue  $\lambda_{\min}^D$  and of the determinant  $D$  of the doubly-excited submatrix **B** of the D-CI matrix (22) on the same parameter  $\alpha$  are also shown in the upper part of the figure (note different scale for each quantity). Vertical dashed line, defined by the singularity of the **B** matrix, indicates the critical value  $\bar{\alpha}$  of the model parameter  $\alpha$  in this case.

very clearly that while the CPMET energies are very close to the F-CI results (in the energy scale employed both curves almost coincide) throughout the whole range of  $\alpha$  values, the L-CPMET energy displays a clear singularity at  $\alpha = \bar{\alpha}$ , which is defined by the singularity of the **B** matrix. The latter follows from the plots of the lowest eigenvalue and of the determinant of **B** both of which vanish at  $\alpha = \bar{\alpha}$ .

## 5. Conclusions

We have applied a variety of CP methods to simple model systems with quasidegenerate ground states. The extent of this quasidegeneracy could be



widely varied from intermediate to almost degenerate cases. Consequently, these models are particularly useful in the study of the applicability of various CP methods in the presence of the quasidegeneracy.

It should be mentioned here that we measure the quasidegeneracy by the proximity of the energy (energies) of the doubly-excited configuration(s) to the ground-state HF configuration, used as a reference state. This proximity clearly depends to some extent on the choice of the basis in the doubly-excited subspace. For example, using the basis which diagonalizes the Hamiltonian in *this* subspace leads to an exact degeneracy for  $\alpha = \bar{\alpha}$ . However, since the actual CI- and CP-type calculations usually employ the basis consisting of (possibly spin-adapted) biexcited configurations constructed by promoting two electrons at a time from the HF sea into the virtual orbital space, we use in our discussion as the criterion of the quasidegeneracy the proximity of the energies of these configurations relative to the energy of the reference configuration  $|\Phi_0\rangle$ .

The results of our study indicate that even though the formulation of the closed-shell CPMET is based on a single-determinant nondegenerate reference configuration, it yields surprisingly accurate results even in cases when intermediate or even strong quasidegeneracy is present. Even in cases of very strong quasidegeneracies, which are close to a real degeneracy (and in fact correspond to an exact degeneracy at  $\alpha = \bar{\alpha}$  if the biexcited configurations are transformed to the “principal axes”), this method yields quite reliable results, at least for the models studied here. This is also true for the much simpler methods, ACP-B and ACP-D45, which seem to represent very accurate approximations to the CPMET.

All other approximate schemes, also quite accurate for weak and intermediate quasidegeneracy cases, are much less reliable when a strong quasidegeneracy is present. This is especially true for the L-CPMET and ACP-D123 schemes, which break down completely in strongly quasidegenerate cases. We have shown that the L-CPMET breakdown corresponds in fact to an exact degeneracy in the transformed biexcited basis which diagonalizes the Hamiltonian in the subspace of doubly-excited configurations. It is interesting to note that for the critical value  $\alpha = \bar{\alpha}$  of our model parameter, which is determined by the singularity of the biexcited CI submatrix  $\mathbf{B}$  [Eq. (22)], we also find that: (i) the L-CPMET correlation energy has a discontinuity, (ii) the quadruple configuration gives the largest contribution to the correlation energy, and (iii) the difference between the ACP-B and ACP-D45 schemes is maximal.

Our results also clearly indicate that the discrepancy between the CPMET and its linear approximations stems primarily from the presence of a quasidegeneracy and is almost exclusively contained in the pair energy associated with the quasidegenerate configuration(s). This feature could certainly be of practical use when truncating the doubly-excited subspace for an approximate treatment of the nonlinear contribution in the CPMET approach, as will be shown elsewhere [45].

We can thus conclude that even though we have only examined the minimum basis set models in this study, we hope that the presented results provide useful information for a better understanding of the CP theories and may serve as a guideline in future, more extensive, calculations. This work has also certain

pedagogical values since it illustrates the performance of various CP approaches on very simple model systems.

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