PHYSICAL REVIEW A VOLUME 24, NUMBER 5 NOVEMBER 1981

Symmetry-adapted coupled-pair approach to the many-electron correlation problem. II. Application to the Be atom

B. G. Adams,* K. Jankowski,† and J. Paldus‡
Quantum Theory Group, Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

(Received 26 November 1980)

The analytic forms of both the *LS*-adapted coupled-pair many-electron theory (CPMET) and its linear version (LCPMET) are applied to the ground state of the Be atom in order to examine the reliability of the analytic coupled-pair approaches. Using CPMET within a $(7s,7p,4d,3f,3g)$ set of orbitals, we obtain 97% of the experimental correlation energy. Special attention is paid to the convergence properties for both radial and angular correlation effects. By means of the partial-wave analysis of the various pair energies it is shown that the difference between LCPMET and CPMET is primarily due to the quasidegeneracy of the Be ground state. The role of different types of coupling terms for pair clusters is also examined yielding a basis for an understanding of various approximate coupled-pair theories. The results are compared with other calculations and the role of monoexcited and triexcited clusters is briefly discussed.

I. INTRODUCTION

Based on our orthogonally spin-adapted versions[1,2] of the coupled-pair many-electron theory[3] (CPMET) or its extended form[3,4] (ECPMET), we have recently formulated the orthogonally spin-*and* angular momentum adapted version[5] of the CPMET (so called *LS*-adapted CPMET) in a form suitable for application to closed-shell atoms using an analytic form for the intervening one-electron wave functions. This analytic approach has also been referred to as the algebraic approximation[6] (expansion of wave functions in a finite set of functions) as opposed to the numerical approach in which radial pair equations are solved numerically (cf., e.g., Ref. 7).

Recently, there has been a considerable revival of the coupled-pair many-electron theory, or, generally, of the coupled-cluster approach,[8] particularly for molecular systems. This renewed interest was primarily stimulated by the fact that these approaches are both "size consistent[9]" and "size extensive" (cf., e.g., Ref. 10) and by the fact that very efficient codes have been developed[9-11] for the simultaneous construction and evaluation of many-body perturbation-theory (MBPT) diagrams characterizing the coupled-pair theory,[3] at least in its spin-orbital form. There has also been a number of approximate pair theories developed,[12-16] which may be easily interrelated with a general coupled-cluster approach[3] and which will be discussed in a subsequent paper of this series.[17] Very recently the coupled-cluster approach has been successfully generalized to the open-shell systems.[18,19]

The aim of this paper is to study rather extensively the simplest possible four-electron system in which nontrivial pair interactions occur, namely, the Be atom. Since we are primarily interested in molecular applications of the CPMET we employ an analytic form (or algebraic approximation[6]) of this approach as noted above, which is closely related to the LCAO-MO approximation, which is currently unavoidable in most molecular electronic structure problems. With the numerical approach based on the solutions of coupled radial pair equations[7,19] one can obviously attain more precise results than with the analytic approach, since the basis set incompleteness or overcompleteness problems are automatically avoided. Unfortunately, these numerical methods cannot be readily extended to molecular systems for which the analytic approach is the only feasible approach at the present time.

Thus, rather than striving for the best possible wave function or energy for the Be atom, using either numerical[7,20] or analytic[21] approaches, we wish to carry out a reasonably detailed test of the CPMET approach on the simplest truly many-electron closed-shell system. The ground state of the Be atom represents an almost ideal system for this purpose since it has been well studied in the past with many different approaches and very accurate results and details of its electronic structure are available for comparison (cf., e.g., Refs. 6, 7, and 20–34). On the other hand, due to its simplicity and high symmetry we are able to use effectively large basis sets of Slater-type atomic orbitals and thus obtain highly accurate and reliable results which exceed in accuracy all other existing applications of the coupled-pair theories based on the LCAO approximation. In this way we are able to examine in detail the convergence characteristics of the correlation energy in the analytic coupled-pair approaches. We note that such investigations have often been carried out for variational approaches (cf., e.g., Refs. 21, 31, and 35) but not for the coupled-pair approaches, where a careful investigation of the convergence properties of the correlation energy is even more essential due to their nonvariational character and the lack of general results concerning the convergence. We thus examine this convergence with respect to both radial and angular correlations.

Another problem encountered by the closed-shell theories is the quasidegeneracy of the state considered. This effect is well known in the Be atom ground state which gives us the possibility to examine the performance of the coupled-pair theories in the presence of quasidegeneracy. This is particularly important for various approximate pair theories which are discussed in a subsequent paper.[36]

The structure of this paper is as follows. In Sec. II we discuss the simplifications arising when the general LS-coupled theory (paper I) is specialized to the Be atom. The resulting LS-coupled CPMET equations for this special case are given in Appendix A. In Sec. III we discuss the various numerical procedures used while in Sec. IV we present the results and their discussion. In particular, we analyze both the radial and angular convergence properties of CPMET and of its linear approximation (LCPMET), and find that they are quite similar to those of variational approaches (except for the upper bound property) such as D-CI (configuration interaction with doubly excited configurations).

We find that the convergence characteristics of the CPMET and the LCPMET, which represents the crudest approximation to the former, are quite similar. Hence, it may be expected that the regularities manifested by the present results are a general property of all coupled-pair methods including the CEPA-like approaches[12-15] which are based on less severe approximations than LCPMET. We also find that CPMET correctly accounts for the well-known quasidegeneracy in Be whereas D-CI and LCPMET do not. Finally, we analyze various approximations to CPMET obtained by using various subsets of the set of diagrams corresponding to the quadratic (nonlinear) part of the CPMET equations. These results show why several approximate coupled-pair (e.g., CEPA) approaches give correlation energies in close agreement with CPMET. Preliminary results on approximate coupled-pair theories both for the Be atom and other systems have been given elsewhere[37-39] and further results for the Be atom will be presented in a subsequent paper.[36]

II. CPMET FORMALISM FOR BERYLLIUM

The general LS-coupled CPMET equations for closed-shell atomic systems have been presented in paper I.[5] We now consider the simplifications arising in the application of these equations to Be using, for the most part, the notation of paper I.

For Be all hole-state l quantum numbers and the intermediate quantum number L_i are zero [cf., e.g., Eq. (4.18b) of paper I]. This greatly simplifies the orbital angular momentum factors appearing in the CPMET Eqs. (5.11) and (5.12) of paper I. In particular, all 6-j symbols and the 12-j symbol which appear in Tables I–VI of paper I reduce to simple factors. This follows from the identity

$$\begin{Bmatrix} a & c & e \\ b & d & 0 \end{Bmatrix} = (-1)^{c+d+e}\,[a,b]^{-1/2}\delta(a,d)\delta(b,c)\,, \qquad (2.1)$$

or graphically (cf. Appendix I of Ref. 40) from the rules for removing zero angular momentum lines from the orbital angular momentum diagrams in Fig. 4 of paper I.

It also follows that the l quantum numbers of the particle states [cf., e.g., Eq. (4.18b) of paper I] defining the t_2 matrix elements are identical. Thus, we can use the simplified notation

$$\langle n^1 n^2 l \,|\, t_2(S_i) \,|\, n_1 n_2 \rangle \equiv \langle n^1 l n^2 l \,|\, t_2(0, S_i) \,|\, n_1 0 n_2 0 \rangle \qquad (2.2)$$

for the t_2 matrix elements and a similar notation for the left-hand sides of Eqs. (5.11) of paper I. The CPMET equations for Be and the results needed to include the monoexcited states are given in Appendix A.

III. BASIS SETS USED AND COMPUTATIONAL ASPECTS

Our results for Be were obtained using Bunge's set of 7s, 7p, and 4d natural orbitals which includes the Hartree-Fock orbitals[31,32] supplemented by a set of 3f and 3g orbitals.[22] These orthonormal orbitals are defined in terms of a set of 9s, 7p, 5d, 3f, and 3g Slater orbitals.

In the study of convergence properties we essentially consider the following two classes of basis sets.

(i) The set of five bases obtained by truncating the largest basis indicated above by the value of the l quantum number, namely, 7s, 7s7p, 7s7p4d, 7s7p4d3f, and 7s7p4d3f3g.

(ii) The second class of basis sets is defined as 4skp2d ($k = 1, 2, \ldots, 7$) and is used in the CPMET and LCPMET schemes when examining the radial convergence of the correlation energy. The basis 4s3p2d is used for the analysis of the role of various nonlinear terms in the CPMET approach. Although these bases are relatively small they yield rather accurate results for all quantities considered.

We have also calculated the CPMET correlation energies using Watson's $6s5p4d3f3g$ basis[22] and its various subsets obtaining also very accurate results.[41] However, we shall use this basis here only for a comparison and when discussing the extension of the CPMET.

A system of programs were written to implement the CPMET equations of Appendix A. These equations have the general form [cf. Eq. (45) of Ref. 1]

$$a_i + \sum_j b_{ij} x_j + \sum_{j\leq k} c_{ijk} x_j x_k = 0 \quad (i,j,k = 1,\ldots,N) \tag{3.1}$$

where the coefficients a_i represent the interaction matrix elements of the Hamiltonian between the ground state and the biexcited states, the linear coefficients b_{ij} and the nonlinear coefficients c_{ijk} represent the interaction matrix elements between bi-biexcited and bi-tetraexcited states, respectively. Finally, the x_i represent the distinct LS-coupled t_2 matrix elements and N their number.

The coefficients c_{ijk} were calculated and stored linearly on tape as N lower triangular (symmetric) matrices $[c_{ijk}]$, one for each value of i. Each of these matrices is sparse (typically 3–4% nonzero matrix elements for $N \sim 200$) so only the nonzero and diagonal (c_{ijj}) matrix elements were stored. In Fortran on an IBM360/75 computer the packed form for the coefficients was implemented by storing the column index k in the least significant (rightmost) two bytes of the double precision word containing each nonzero c_{ijk}.[42] The indices i and j were then controlled by program loops.

Let us recall here one of the advantages of the orthogonally spin-adapted CPMET (Refs. 1 and 2) as opposed to the nonorthogonally spin-adapted theory,[3] namely, the greater sparseness of the $[c_{ijk}]$ matrices in the former. For example, with Watson's[22] $6s5p4d3f3g$ basis ($N=169$) one obtains 4.2% nonzero c_{ijk} matrix elements (101 690 out of 2 427 685) using the nonorthogonally spin-adapted version[3] while only 3.4% (81 460 out of 2 427 685) using the orthogonally spin-adapted[1,2] version. Similarly, one also obtains fewer linear (b_{ij}) coefficients with the orthogonal version than with the nonorthogonal one (10 014 vs 12 185 out of 28 561; i.e., 34.9% vs 42.7% in the case mentioned above) even though the $[b_{ij}]$ matrix is not sparse unless a very large basis is used.

To solve the system (3.1) of nonlinear equations we used a Newton-Raphson-type procedure (cf. Appendix B for further details) and at each iteration the resulting linear system was solved by Gaussian elimination.[43] The starting iteration was chosen as the solution of the linear system

$$a_i + \sum_j b_{ij} x_j = 0\,, \quad i,j = 1,\ldots,N \tag{3.2}$$

which corresponds to neglecting the quadratic terms in (3.1) and is just the linear CPMET (LCPMET) approximation.

We note that if normalized t_2 matrix elements are used[1,2,5] then the matrix $[b_{ij}]$ in (3.1) is symmetric and in this case (3.2) and the equation

$$\Delta\epsilon = \sum_i a_i x_i \tag{3.3}$$

determining the correlation energy can be converted to the secular problem of the doubly excited CI method (D-CI) using intermediate normalization.[38,39] Thus, we have also computed the D-CI correlation energies using simple modifications of our CPMET program.[44]

IV. RESULTS AND DISCUSSION

The results which we have obtained for Be are summarized in Tables I–V. Our goal was a detailed analysis of the correlation energy $\Delta\epsilon$ in terms of pair energies and partial waves [cf. Eqs. (A5)–(A7) of Appendix A] for the CPMET, LCPMET, and D-CI approximations using various subsets of the basis mentioned above. With these results we could determine the quality of the basis, compare the three approximations, and analyze the well-known quasidegeneracy of Be arising from the closeness of the $1s^2 2s^2$ and $1s^2 2p^2$ levels.

A. Pair and total correlation energies and their convergence behavior

In Table I we list the ss, pp, dd, ff, and gg partial-wave contributions to the correlation energy using various subsets of the $7s7p4d3f3g$ basis. The breakdown of the correlation-energy contribution of each partial wave is given for the $1s^2\,{}^1S$, $2s^2\,{}^1S$, $1s2s\,{}^1S$, and $1s2s\,{}^3S$ pairs for the CPMET, LCPMET, and D-CI approximations. This table shows that all partial-wave contributions to the pair correlation energies change monotonically if the results obtained for different basis sets containing orbitals with increasing l quantum numbers are considered. For both LCPMET and CPMET all contributions increase (decrease in absolute value) and a similar behavior is observed for the D-CI contributions except perhaps for the small dd contributions to the $1s2s\,{}^3S$ pair energy. The largest differences among the partial-wave contributions obtained by the different methods for the same basis set can be observed for the pp $2s^2\,{}^1S$ contributions. These differences are due to quasidegeneracy effects[37] and are discussed in Sec. IV B.

If for a given basis set the partial-wave contributions for increasing l values are considered then starting with the pp partial waves the contributions

TABLE I. Partial-wave (PW) contributions $\epsilon^{ll}_{n_1n_2}(S_i)$ to the pair correlation energies $\epsilon_{n_1n_2}(S_i)$ for different orbital basis sets. Energies are given in μH with signs reversed.

			$1s^2\,{}^1S$			$2s^2\,{}^1S$			$1s2s\,{}^1S$			$1s2s\,{}^3S$	
PW	Basis[a]	CPMET	LCPMET	D-CI	CPMET	LCPMET	D-CI	CPMET	LCPMET	D-CI	CPMET	LCPMET	D-CI
	$7s$	13 801	13 811	13 800	3 522	3 551	3 477	1179	1181	1179	48	48	48
	$7s7p$	13 526	13 551	13 502	2 553	2 611	2 516	1176	1181	1174	44	44	44
ss	$7s7p4d$	13 489	13 517	13 465	2 546	2 607	2 505	1174	1180	1172	44	44	44
	$7s7p4d3f$	13 482	13 510	13 458	2 543	2 604	2 499	1174	1179	1172	44	44	44
	$7s7p4d3f3g$	13 480	13 508	13 456	2 541	2 603	2 498	1173	1179	1172	44	44	44
	$7s7p$	24 477	24 520	24 435	41 377	46 880	38 257	1855	1826	1856	1945	1921	1953
pp	$7s7p4d$	24 220	24 266	24 178	40 373	46 064	36 986	1852	1823	1854	1949	1925	1958
	$7s7p4d3f$	24 170	24 217	24 129	40 276	45 987	36 836	1849	1819	1851	1949	1925	1959
	$7s7p4d3f3g$	24 154	24 200	24 112	40 242	45 959	36 784	1848	1818	1850	1949	1925	1959
	$7s7p4d$	3 210	3 210	3 208	1 406	1 063	1 593	112	112	112	31	31	31
dd	$7s7p4d3f$	3 188	3 190	3 187	1 386	1 047	1 573	111	111	111	31	31	30
	$7s7p4d3f3g$	3 182	3 183	3 180	1 380	1 041	1 566	111	111	111	31	31	31
ff	$7s7p4d3f$	718	718	718	157	122	178	44	44	44	2	2	2
	$7s7p4d3f3g$	714	714	714	153	119	174	43	44	43	2	2	2
gg	$7s7p4d3f3g$	251	251	251	62	50	69	14	14	14	0	0	0

[a] All bases are subsets of the $7s7p4d3f3g$ basis (cf. text for details).

TABLE II. Pair correlation energies $\epsilon_{n_1 n_2}(S_i)$ for different orbital basis sets. Energies are given in μH with signs reversed.

	$1s^2\,{}^1S$			$2s^2\,{}^1S$			$1s2s\,{}^1S$			$1s2s\,{}^3S$		
Basis[a]	CPMET	LCPMET	D-CI	CPMET	LCPMET	D-CI	CPMET	LCPMET	D-CI	CPMET	LCPMET	D-CI
7*s*	13 801	13 811	13 800	3 522	3 551	3 477	1179	1181	1179	48	48	48
7*s*7*p*	38 002	38 071	37 936	43 930	49 490	40 773	3030	3007	3030	1989	1965	1996
7*s*7*p*4*d*	40 920	40 995	40 852	44 325	49 734	41 083	3138	3114	3138	2023	1999	2032
7*s*7*p*4*d*3*f*	41 559	41 635	41 491	44 362	49 760	41 086	3177	3154	3178	2025	2001	2035
7*s*7*p*4*d*3*f*3*g*	41 780	41 856	41 712	44 378	49 773	41 091	3190	3166	3190	2025	2001	2035
4*s*3*p*2*d*	36 963	37 027	36 896	44 491	49 735	41 513	2274	2255	2269	1130	1111	1135

[a] All bases are subsets of the 7*s*7*p*4*d*3*f*3*g* basis (cf. text for details).

to the pair correlation energies decrease. The rate of decrease (l-convergence characteristics of pair energies) is different for singlet and triplet pairs: the l convergence is faster for triplet than for singlet pairs. This is in qualitative agreement with the l^{-4} and l^{-6} behavior of singlet and triplet pairs, respectively, observed by Schwartz[45] for the ground state of He and verified by Bunge[21] for the Be atom.

Thus, the nonvariational LCPMET and CPMET methods have the same angular convergence behavior and numerical stability as the variational D-CI method since the rate of convergence is the same for all three methods. In our case, for better quantitative agreement, a larger basis would be needed to achieve a full radial convergence for each value of l.

In Table II pair correlation energies are given for all three methods and in Table III total correlation energies are given for different bases considered, as well as the differences between the full CPMET and, respectively, LCPMET and D-CI correlation energies. In Table III each correlation energy is the sum of the four pair energies in the corresponding row of Table II. Note that the correlation energy obtained with the largest basis 7*s*7*p*4*d*3*f*3*g* yields 96.9% of the total correlation energy.[21, 46] The number of biexcited clusters (i.e., the number N of t_2 matrix elements) is in this case 238.

The Tables II and III show that the pair energies and total correlation energies decrease (increase in absolute value) as the maximum l quantum number of the basis set increases. Again this l convergence is similar for all three methods. However, although the CPMET pair energies in Table II are in most cases lower than their D-CI counterparts, this need not be the case, as can be seen for the intershell $1s2s\,{}^3S$ pair, where the variational results are slightly lower than the CPMET ones.

In Table IV we summarize our results for the pair energies, the pp partial-wave contributions to the pair energies, and the total correlation energy using the bases $4skp2d$, $k = 1, 2, \ldots, 7$. The CPMET results are given below the corresponding LCPMET ones. Thus, we can examine the effect of the saturation of the radial basis (radial convergence) for p-type orbitals. Only the pp partial wave is given since it is the most sensitive to details of the selection of the p orbitals from a given subset. For all pairs except $2s^2\,{}^1S$, the pp partial-wave contributions decrease as the number of p orbitals in the basis increases, for both LCPMET and CPMET approaches, whereas almost the opposite takes place for the $2s^2\,{}^1S$ pair. Similar changes are also observed for the total pair

TABLE III. Total correlation energies obtained from CPMET, LCPMET, and D-CI for various basis sets (in μH with signs reversed). The last two columns give the differences between the CPMET energy and the LCPMET and D-CI energies, respectively (in μH).

Basis[a]	$\Delta\epsilon^{\text{CPMET}}$	$\Delta\epsilon^{\text{LCPMET}}$	$\Delta\epsilon^{\text{D-CI}}$	$\Delta\epsilon^{\text{CPMET}} - \Delta\epsilon^{\text{LCPMET}}$	$\Delta\epsilon^{\text{CPMET}} - \Delta\epsilon^{\text{D-CI}}$
$7s$	18 550	18 591	18 504	41	−46
$7s7p$	86 952	92 534	83 736	5582	−3216
$7s7p4d$	90 406	95 842	87 106	5436	−3300
$7s7p4d3f$	91 123	96 550	87 790	5427	−3333
$7s7p4d3f3g$	91 373	96 797	88 029	5424	−3344
$4s3p2d$	84 859	90 128	81 813	5269	−3046

[a] All bases are subsets of the $7s7p4d3f3g$ basis (cf. text for details).

energies. Finally, we note that the total correlation energy decreases for both LCPMET and CPMET methods as the radial saturation of the basis is approached.

The remarkable regularities indicated in Tables I–IV for LCPMET and CPMET energies, when compared with those of D-CI method, resemble the situation found in variational approaches, even though we have no upper bound property for these nonvariational approaches. These regularities could be exploited in extrapolations in much the same way as done by Bunge[21] in the case of the variational CI approach. This is a clear indication that coupled-pair methods yield not only accurate global correlation energies but they also correctly represent subtle details of the electronic structure of many-electron systems.

B. Quasidegeneracy effect

For the largest basis considered ($7s7p4d3f3g$) the difference between the linear and full CPMET correlation energies is +5.424 mH while the difference between the D-CI and full CPMET energies is −3.344 mH. These differences amount to 5.94% and −3.66% of the total correlation energy. It should be noted that while the D-CI yields smaller correlation energies (in absolute value) in agree-

TABLE IV. Analysis of radial convergence of the pp partial wave, pair energies, and correlation energy for the $4s,np,2d$ bases, $n=1,\ldots,7$. Energies are given in μH with signs reversed. The CPMET results are given below the corresponding LCPMET ones.

	pp partial wave				Pair energies				
Basis[a]	$1s^2$	$2s^2$	$1s2s\,^1S$	$1s2s\,^3S$	$1s^2$	$2s^2$	$1s2s\,^1S$	$1s2s\,^3S$	$\Delta\epsilon$
$4s,1p,2d$	13	46 305	178	0	15 729	49 881	1345	30	66 985
	16	40 960	190	0	15 720	44 818	1354	30	61 922
$4s,2p,2d$	21 627	46 101	748	763	36 994	49 695	1905	793	89 387
	21 590	40 643	774	783	36 931	44 524	1927	812	84 194
$4s,3p,2d$	21 661	46 148	1096	1082	37 027	49 735	2255	1111	90 128
	21 623	40 629	1120	1101	36 963	44 491	2274	1130	84 859
$4s,4p,2d$	23 833	46 139	1391	1486	39 112	49 722	2549	1514	92 897
	23 790	40 549	1421	1509	39 042	44 409	2574	1537	87 562
$4s,5p,2d$	24 186	46 099	1648	1758	39 448	49 689	2811	1786	93 733
	24 142	40 462	1678	1782	39 377	44 328	2837	1810	88 351
$4s,6p,2d$	24 266	46 092	1818	1921	39 524	49 683	2983	1949	94 139
	24 221	40 422	1847	1945	39 452	44 290	3007	1973	88 722
$4s,7p,2d$	24 332	46 096	1823	1927	39 587	49 686	2988	1955	94 217
	24 288	40 423	1853	1952	39 515	44 291	3012	1980	88 797

[a] All bases are subsets of the $7s7p4d3f3g$ basis (cf. text for details).

TABLE V. Percentage breakdown of the differences between the CPMET and LCPMET energies and between the CPMET and D-CI energies (values in parentheses) into various pair and partial-wave contributions.

Partial wave	$1s^2\,{}^1S$	$2s^2\,{}^1S$	$1s2s\,{}^1S$	$1s2s\,{}^3S$
s	0.52	1.14	0.11	0
	(0.72)	(1.29)	(0.03)	(0)
p	0.85	105.40	−0.55	−0.44
	(1.25)	(103.41)	(−0.06)	(−0.30)
d	0.02	−6.25	0	0
	(0.06)	(−5.56)	(0)	(0)
f	0	−0.63	0.02	0
	(0)	(−0.63)	(0)	(0)
g	0	−0.22	0	0
	(0)	(−0.21)	(0)	(0)

ment with its variational character, the LCPMET yields typically the overcorrelated results. These differences, however, may be shown to correspond to the same effect which manifests itself in the opposite direction in the correlation energies for the LCPMET and D-CI approaches. Indeed, the partial-wave analysis of these differences clearly indicates that they originate in the p wave of the $2s^2$ pair, and may thus be associated with the quasidegeneracy of the Be ground state with the biexcited configuration resulting from the $2s^2 \rightarrow 2p^2$ promotion. [Note that the coefficient of the latter configuration is about 0.3 in the intermediate normalization while the next largest coefficient is one order of magnitude smaller (cf., e.g., Refs. 21, 22).] The next largest contribution to these differences comes from the d wave of the $2s^2$ pair compensating for the overshoot due to the p wave.

These contributions are most clearly apparent from Table V where the percentage breakdown of the differences between the CPMET and LCPMET energies and between the CPMET and D-CI (values in parentheses) energies into different pair and partial-wave contributions is given for the $7s7p4d3f3g$ basis. This table also clearly displays a completely parallel behavior in the two differences (note that the actual energy differences have opposite signs).

This parallel behavior may be easily understood if we recall the close relationship between the LCPMET and D-CI methods: They both exploit the same information, namely, the D-CI matrix of the Hamiltonian. However, while this matrix is diagonalized in the variational procedure, in order to guarantee the upper bound property unlinked diagram contributions are introduced. They are eliminated in the nonvariational LCPMET approach where a linear system of algebraic equations is solved for the biexcited clusters (cf., e.g., Ref. 38 for details) to obtain a size extensive result. The size extensivity (proportionality of the energy of a noninteracting system to the particle number) will not play a crucial role in only a four-electron system. Thus, the main defect of both LCPMET and D-CI wave functions will be due to the neglect of the quasidegeneracy of the Be ground state which is accounted for to a large extent by the disconnected tetraexcited contribution in the CPMET [for a more satisfactory treatment one has to exploit the degenerate (open-shell) theory, cf. Ref. 47]. This is also consistent with the fact that with the $7s$ basis we obtain very small differences in the pair-energy contributions (cf., also Tables II and III) among all three methods considered since with such a poor basis not containing any p orbitals the quasidegeneracy effects cannot arise (cf. also Ref. 6).

These results concerning the quasidegeneracy effects have also been recently corroborated by a detailed study on minimum basis set models for the various H_4 systems and on the semiempirical π-electron model of *cis*-butadiene.[39] In these models the quasidegeneracy could be varied over a wide range, up to the almost real degeneracies. It is remarkable that even under these conditions the CPMET yielded an excellent agreement with the exact full CI results for these models even though one would expect its breakdown in almost degenerate cases.

Finally, it should be mentioned that the quasidegeneracy found in the Be ground state is very significant when compared with the situation encountered in most molecular systems near their equilibrium geometries. Thus, out of 26 systems studied by Pople *et al.*[9] this system displayed the largest relative difference (cf. Ref. 37) between the LCPMET and CPMET correlation energies. It must be stressed, however, that these were relatively small systems (3–10 electrons). In fact, for the three-dimensional electron gas model studied by Freeman[48] (considering only direct and some exchange ring diagrams in the CPMET and LCPMET equations) and by Bishop and Lührmann[49] who obtained the exact analytical solution for the t_2 matrix elements in the ring approximation, the difference between the full and linearized versions of the CPMET were of the order of 8–15 % of the total correlation energy obtained in this approximation in the range of r_s values between 1 and 10. In the Be case this difference only amounts to about 6% while in most molecular cases it is less than 1%. Clearly, these effects can be expected to be much more significant for large metalliclike molecular systems.

C. Basis for approximate coupled-pair theories: Analysis of individual coupling terms

In order to examine the relative importance of various nonlinear terms coupling the different pair clusters in the CPMET approach, we consider in Table VI the contribution of individual nonlinear diagrams and classes of these diagrams to the total correlation energy and the *pp* partial-wave contribution to the $2s^2$ pair energy using the $4s3p2d$ basis. These results were obtained by solving the system of Eqs. (3.1) using only those terms in the nonlinear part arising from the sets of diagrams indicated in the table [diagrams 1–5 correspond, respectively, to those in Figs. $3(i_\kappa)$–(v) of paper I]. Thus, the first entry in Table VI is the LCPMET result (no nonlinear diagrams) and the last is the CPMET result (all nonlinear diagrams). Our first observation is that the results show significant differences for different combinations of diagrams. Other partial-wave contributions will also change significantly but are less important in the description of quasidegeneracy effects. Also the effect of different diagrams on the correlation energy when compared to the LCPMET result is to a certain extent additive.

These types of approximations to CPMET where only selected nonlinear terms in (3.1) are included are referred to as approximate coupled-pair (ACP) methods and are studied in greater detail in a subsequent paper.[36, 50] Thus, for example, the selection of diagrams 1, 2, and 3 is referred to as ACP-*D*123. We note that ACP-*D*123 gives $\Delta\epsilon = -90.091$ mH whereas ACP-*D*45 gives $\Delta\epsilon = -84.885$ mH. The former is close to the LCPMET value (−90.128 mH) while the latter is close to the CPMET value (−84.859 mH). Therefore the contribution of diagrams 1, 2, and 3 together is quite small so in effect they almost cancel among themselves since their individual contributions (cf. ACP-*D*1, ACP-*D*2, and ACP-*D*3 values) are large. This compensation is due mainly to the cancellation of the contributions of "nonenergetic" EPV terms (those EPV terms which cannot be expressed as the product of a pair energy and a t_2 matrix element when summation indices are freed). This cancellation of relatively large contributions does not occur when the diagrams are considered separately. The remaining small effect of diagrams 1, 2, and 3 arises from the non-EPV terms and these give relatively small contributions.

TABLE VI. Diagram contributions to the correlation energy and the *pp* partial-wave contribution to the $2s^2\,{}^1S$ pair energy. Energies are given in μH with signs reversed. See text for details.

Diagrams	$\Delta\epsilon$[a]	*pp* PW $2s^2\,{}^1S$	Diagrams	$\Delta\epsilon$	*pp* PW $2s^2\,{}^1S$
	90 128	46 148	123	90 001	46 103
1	92 260	48 452	124	83 405	39 207
2	92 204	48 404	125	113 475	71 484
3	86 841	42 598	134	80 683	36 294
4	81 507	37 178	135	95 412	51 699
5	98 924	55 535	145	86 173	42 037
12	94 845	51 269	234	80 649	36 269
13	88 364	44 232	235	95 350	51 645
14	82 427	38 150	245	85 131	42 004
15	104 037	61 117	345	82 731	38 351
23	88 317	44 195	1 234	81 488	37 156
24	82 390	38 127	1 235	98 855	55 458
25	103 944	61 031	1 245	87 601	43 583
34	79 910	35 479	1 345	83 757	39 442
35	92 733	48 796	2 345	83 719	39 413
45	84 885	40 658	12 345	84 859	40 629

[a] All results are reported for the $4s3p2d$ subset of the $7s7p4d3f3g$ basis.

On the other hand, diagrams 4 and 5 give almost the exact CPMET result. As in the ACP-*D*123 case all of the nonenergetic EPV terms effectively cancel and both diagrams 4 and 5 must be present to achieve this cancellation (cf. ACP-*D*4 and ACP-*D*5 values). Also, the non-EPV terms again have a very small effect. However, all of the "energetic" EPV terms (those which can be expressed as the product of a pair energy and a t_2 matrix element) arise only from diagrams 4 and 5 (cf. Refs. 35 and 38).

Thus, we conclude that among the nonlinear terms in (3.1) only the energetic EPV ones are important. These facts seem to justify the reliability of the well-known CEPA-type approximations to CPMET which arise when the nonlinear terms are approximated by some selection of the energetic EPV terms. We have considered two such approximations for Be (Ref. 39) and further results have been presented elsewhere.[37,38]

D. Comparison with other results

The overall accuracy and reliability of the analytic coupled-pair many-electron theory can be best judged by a comparison of the results obtained here with very accurate results for the Be atom obtained by either variational (CI) approaches by Bunge[21] or with recently published numerical coupled-cluster results of Lindgren and Salomonson.[7] These results are summarized in Table VII for individual pair-energy contributions as well as the total correlation energies. For the sake of comparison we also include some results based on many-body perturbation theory and MCHF (multiconfiguration Hartree-Fock) approximation.

We first observe that the total correlation energy

TABLE VII. Pair and total correlation energies for Be obtained with various methods (in μH with signs reversed).

			Pair energies			Correlation
Method	$1s^2\,{}^1S$	$2s^2\,{}^1S$	$1s2s\,{}^1S$	$1s2s\,{}^3S$	$1s2s$	energy
D-CI[a]	41 712	41 091	3190	2035	5225	88 029
LCPMET[a]	41 856	49 773	3166	2001	5167	96 797
ACP-*D*45[a]	41 781	44 414	3187	2014	5191	91 416
CPMET[a]	41 780	44 378	3190	2025	5215	91 373
numer. CPMET[b]	42 630	44 780			5540	92 960
DPMET[c]	42 083	44 381				
PT(Kelly)[d]	42 120	44 880			4966	91 970
PT(BJ)[e]	42 470	44 820			5240	92 530
PT(SWB)[f]	41 110	44 770			6040	91 920
MCHF[g]	42 143	46 161			4126	92 845[h]
CI(180)[i]	40 869	45 104			5240	91 204
corrected[i, j]	42 610	45 500			5300	93 404
CI(650)-s.a[k,l]	42 564	46 731			6016	94 421[m]
CI(650)-abs.[k,n]	42 537	46 560			5416	94 421
"Experiment"[o]						94 407[p]
						94 283[q]
						93 894[r]
						93 367[s]
						94 305 ± 25[t]

[a] This work using $7s7p4d3f3g$ basis.

[b] Reference 7, using numerical CPMET procedure.

[c] Reference 26, decoupled-pair many-electron theory.

[d] Reference 24, numerical many-body perturbation theory (including continuum states).

[e] Reference 28, variation-perturbation theory to the fifth order in energy applied to decoupled-electron pairs using the Hylleraas type trial functions.

[f] Reference 6, many-body perturbation theory to the third order with shifted denominators using only discrete $10s9p7d$ basis.

[g] Reference 20, numerical MCHF procedure.

[h] This correlation energy also includes the $1s2p$ pair contribution of 416 μH arising in view of the multideterminantal reference state used in this approach.

[i] Reference 31, 180-term CI expansion using $7s7p4d$ basis.

[j] Corrected for the *spd* limit and higher l contributions.

[k] Reference 21, 650-term CI expansion using $10s9p8d7f5g3h1i$ basis.

[l] Symmetry-adapted pairs.

[m] Pair energies do not add up to the total correlation energy for symmetry-adapted pairs in this method.

[n] Absolute pairs.

[o] Nonrelativistic estimates.

[p] Reference 51.

[q] Reference 26.

[r] Reference 27.

[s] Reference 31.

[t] Reference 21.

obtained with the largest basis considered ($7s7p4d3f3g$), −91.373 mH, compares favorably with the numerically obtained result of Lindgren and Salomonson,[7] −92.960 mH, the main difference (0.85 mH) being in the $1s^2$ pair correlation energy due to the limitation in our basis. We note that Bunge's extrapolated value for the *spdfg* limit[21] gives[46] the correlation energy 93.947 a.u. Our basis thus yields 97.3% of this limit, which is a very plausible value in view of the incompleteness of our basis and neglect of monoexcited and triexcited clusters. We also note a very good agreement between our D-CI correlation energy (88.03 mH) and the corresponding doubly excited *spd* limit (87.79 mH).[6] It is also interesting in this context to mention the CPMET results obtained earlier[41, 52] with the Watson's $6s5p4d3f3g$ basis yielding the total correlation energy 90.151 mH and the pair energies 41.352 mH for $1s^2$, 44.036 mH for $2s^2$, 3.081 mH for $1s2s\,{}^1S$, and 1.690 mH for $1s2s\,{}^3S$

pairs.

Let us also briefly discuss the effect of other than doubly excited connected clusters. The monoexcited clusters, whose main contribution comes via their interaction with doubly excited clusters (cf., Table VIII) and whose number is small relative to other cluster types, can be easily taken into account using the equations given in Appendix A (we neglect terms like T_1T_2, T_1^2, T_3^2, etc., in the cluster expansion which contribute for the first time in the fifth and higher orders in energy; cf. Ref. 53). The triexcited clusters on the other hand are much more difficult to include,[2] primarily due to the large number of these clusters.

The contribution of monoexcited and triexcited clusters to the correlation energy of Be can be estimated on the basis of CI results[21] even though these contributions are very much basis dependent (cf., e.g., Ref. 32). The extensive CI results of Bunge[21] indicate that monoexcited and triexcited contributions amount to about 0.35% and 1.1% of the total correlation energy, i.e., significantly less than the tetraexcited contribution which amounts to about 3.3% (note, however, that in the *spd* limit[6] the monoexcited contribution represents 0.6% of the correlation energy).

We have carried out a preliminary examination of the singly and triply excited clusters for a small basis set $4s2p1d$ obtained as a subset of Bunge's basis.[31, 32] For a very similar $4s2p1d$ basis (called BeG2 in their paper) an almost full (82 term) CI was carried out by Olympia and Smith[32] yielding the total energy −14.655 341 2 a.u. This corresponds to the correlation energy of 82.355 mH ($E_{\mathrm{HF}} = -14.572\,986$ a.u. for this basis). With the CPMET and its extended versions we obtain correlation energies given in Table VIII. Thus, the ECPMET including both singly and triply excited clusters yields the result which is very close to an almost full CI result of Olympia and Smith,[32] namely, −14.655 426 a.u.

The results in Table VIII also indicate that the correlation-energy contributions of singly and triply excited clusters are independent of one another and are thus additive to a high degree of accuracy. This effect was observed earlier in the case of the BH_3 molecule[4] and seems thus to be a rather universal property. In the Be case we thus obtain for the monoexcited cluster contribution in the absence and presence of the triply excited clusters the values 443 and 448 μH, respectively. Similarly, the triply excited contributions calculated in the absence and in the presence of singly excited clusters are 262 and 267 μH, respectively. Unfortunately, we do not know the monoexcited and triply excited contributions in the CI wave function in this case where the ECPMET result indicates a larger role of monoexcited rather than triexcited clusters. However, this reversal may be due to the relatively small number of triexcited clusters which occur in this case (4 t_1, 23 t_2, and 32 t_3 matrix elements).

TABLE VIII. Correlation energies $\Delta\epsilon$ for Be obtained with CPMET and its extended versions involving monoexcited and/or triexcited clusters with the $4s2p1d$ basis (in μH with signs reversed). The one- and two-electron components $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are defined by Eqs. (A10) and (A5), respectively. The first column indicates the type of clusters considered.

(E)CPMET version	$\Delta\epsilon_1$	$\Delta\epsilon_2$	$\Delta\epsilon = \Delta\epsilon_1 + \Delta\epsilon_2$
t_2		81 730	81 730
t_2, t_3		81 992	81 992
t_1, t_2	30	82 204	82 173
t_1, t_2, t_3	31	82 471	82 440

We can thus conclude that, as in an earlier study of a simple 8-electron molecular system,[4] the CPMET and, in particular, its extended versions[2-4] yield correlation energies which are in an excellent agreement with those obtained by variational CI procedures involving quadruply excited configurations. We note that while a minimum basis set was used in our BH_3 study a rather extensive basis set has been used in this paper for the Be atom. Since in each case an excellent agreement was obtained with the corresponding variational results, one can hope that this behavior will be generally valid.

ACKNOWLEDGMENTS

This work was supported by the Natural Science and Engineering Research Council of Canada Grants-in-Aid of Research (J.P. and B.G.A.) which are hereby gratefully acknowledged. One of us (B.G.A.) would like to acknowledge the receipt of an NSERC University Research Fellowship, 1980-1983, and another (K.J.) would like to express his sincere thanks to the Department of Applied Mathematics of the University of Waterloo, and in particular to J. Čížek and his co-author (J.P.) for their warm hospitality, unceasing help, and stimulating discussions provided to him during his visit.

APPENDIX A: *LS*-COUPLED CPMET EQUATIONS FOR Be

For Be the left-hand sides of Eqs. (5.11) of paper I reduce to

$$\langle \tilde{n}^1 \tilde{n}^2 \tilde{l} \,|\, \Lambda^{2,0}(\tilde{S}_i) \,|\, \tilde{n}_1 \tilde{n}_2 \rangle = \sum_{\kappa=1}^{2} \mathfrak{L}_1 \mathcal{S}_1^{I} (-1)^{\kappa} R^{\tilde{l}} (\tilde{n}^{\bar{\kappa}} \tilde{l} \tilde{n}_1 0 \,|\, \tilde{n}^{\kappa} \tilde{l} \tilde{n}_2 0) \,, \qquad \text{(A1a)}$$

$$\begin{aligned}
\langle \tilde{n}^1\tilde{n}^2\tilde{l}\,|\,\Lambda_{L}^{2\,2}(\tilde{S}_i)\,|\,\tilde{n}_1\tilde{n}_2\rangle
&=\sum_{\kappa=1}^{2}\sum_{S_i}\Big(\sum_{n^1}\mathcal{S}_1^{\mathrm{II}}\langle \tilde{n}^{\kappa}\tilde{l}\,|f\,|n^1\tilde{l}\rangle\langle n^1\tilde{n}^{\tilde{\kappa}}\tilde{l}\,|\,\tau_2(S_i)\,|\,\tilde{n}_{\kappa}\tilde{n}_{\tilde{\kappa}}\rangle-\sum_{n_1}\mathcal{S}_2^{\mathrm{II}}\langle n_1 0\,|f\,|\tilde{n}_{\kappa}0\rangle\langle \tilde{n}^{\kappa}\tilde{n}^{\tilde{\kappa}}\tilde{l}\,|\,\tau_2(S_i)\,|\,n_1\tilde{n}_{\tilde{\kappa}}\rangle\Big)\\
&\quad+\sum_{S_i}\Big(\sum_{ln^1n^2}\mathcal{S}_3^{\mathrm{II}}G(\tilde{n}^1\tilde{l}n^1l\,|\,\tilde{n}^2\tilde{l}n^2l)\langle n^1n^2l\,|\,\tau_2(S_i)\,|\,\tilde{n}_1\tilde{n}_2\rangle+\sum_{n_1n_2}\mathcal{S}_4^{\mathrm{II}}R^0(n_1 0\tilde{n}_1 0\,|\,n_2 0\tilde{n}_2 0)\langle \tilde{n}^1\tilde{n}^2\tilde{l}\,|\,\tau_2(S_i)\,|\,n_1n_2\rangle\Big)\\
&\quad+\sum_{\kappa,\lambda=1}^{2}\sum_{S_i}\sum_{n^1n_1}(-1)^{\kappa+\lambda+1}\{\mathcal{S}_5^{\mathrm{II}}R^0(\tilde{n}^{\kappa}\tilde{l}n^1\tilde{l}\,|\,n_1 0\tilde{n}_{\tilde{\lambda}}0)-[\tilde{l}]^{-1}\mathcal{S}_6^{\mathrm{II}}R^{\tilde{l}}(\tilde{n}^{\kappa}\tilde{l}\tilde{n}_{\tilde{\lambda}}0\,|\,n_1 0n^1\tilde{l}\}\langle \tilde{n}^1\tilde{n}^{\tilde{\kappa}}\tilde{l}\,|\,\tau_2(S_i)\,|\,\tilde{n}_{\lambda}n_1\rangle\,,
\end{aligned}\tag{A1b}$$

$$\begin{aligned}
\langle \tilde{n}^1\tilde{n}^2\tilde{l}\,|\Lambda_{NL}^{2\,2}(S_i)\,|\,\tilde{n}_1\tilde{n}_2\rangle
&=\sum_{S_i^1}\sum_{S_i^2}\sum_{n_1n_2}\sum_{ln^1n^2}R^l(n_1 0n^1l\,|\,n_2 0n^2l)\\
&\qquad\times\Big(\sum_{\kappa=1}^{2}(-1)^{\tilde{\kappa}}[\delta(l,\tilde{l})\mathcal{L}_2\mathcal{S}_1^{\mathrm{III}}\langle \tilde{n}^1n^1\tilde{l}\,|\,\tau_2(S_i^1)\,|\,\tilde{n}_{\kappa}n_1\rangle\langle \tilde{n}^2n^2\tilde{l}\,|\,\tau_2(S_i^2)\,|\,\tilde{n}_{\tilde{\kappa}}n_2\rangle\\
&\qquad\qquad+\delta(l,\tilde{l})\mathcal{L}_2\mathcal{S}_2^{\mathrm{III}}\langle \tilde{n}^1n^1\tilde{l}\,|\,\tau_2(S_i^1)\,|\,\tilde{n}_{\tilde{\kappa}}n_2\rangle\langle \tilde{n}^2n^2\tilde{l}\,|\,\tau_2(S_i^2)\,|\,\tilde{n}_{\kappa}n_1\rangle\\
&\qquad\qquad-\delta(l,\tilde{l})\mathcal{L}_2\mathcal{S}_3^{\mathrm{III}}\langle n^2\tilde{n}^{\kappa}\tilde{l}\,|\,\tau_2(S_i^1)\,|\,\tilde{n}_1\tilde{n}_2\rangle\langle \tilde{n}^{\tilde{\kappa}}n^1\tilde{l}\,|\,\tau_2(S_i^2)\,|\,n_1n_2\rangle\\
&\qquad\qquad-\mathcal{L}_3\mathcal{S}_4^{\mathrm{III}}\langle \tilde{n}^1\tilde{n}^2\tilde{l}\,|\,\tau_2(S_i^1)\,|\,\tilde{n}_1\tilde{n}_2\rangle\langle \tilde{n}^1\tilde{n}^2\tilde{l}\,|\,\tau_2(S_i^2)\,|\,n_1n_2\rangle]\\
&\qquad+\tfrac{1}{2}\mathcal{L}_3\mathcal{S}_5^{\mathrm{III}}\langle n^1n^2l\,|\,\tau_2(S_i^1)\,|\,\tilde{n}_1\tilde{n}_2\rangle\langle \tilde{n}^1\tilde{n}^2\tilde{l}\,|\,\tau_2(S_i^2)\,|\,n_1n_2\rangle\Big)\,.
\end{aligned}\tag{A1c}$$

In addition to the notations and definitions given in paper I and Sec. II for the radial integrals, τ_2 matrix elements, and spin factors we have defined

$$\mathcal{L}_1=(-1)^{\tilde{l}}[\tilde{l}]^{-1/2}\,,\tag{A2a}$$

$$\mathcal{L}_2=(-1)^{\tilde{l}}[\tilde{l}]^{-3/2}\,,\tag{A2b}$$

$$\mathcal{L}_3=(-1)^{l}[l]^{-1/2}\,,\tag{A2c}$$

and

$$G(n^1l^1n^2l^2\,|\,n^3l^1n^4l^2)=\sum_k[l^1,l^2]^{-1/2}C^k(l^1l^2\,|\,l^1l^2)R^k(n^1l^1n^2l^2\,|\,n^3l^1n^4l^2)\,.\tag{A3}$$

Thus, the LS-coupled CPMET equations for Be are given by substituting (A1) into Eqs. (5.4) and (5.5) of paper I. Corresponding to Eq. (5.12) of paper I the correlation energy is given by

$$\Delta\epsilon_2=\tfrac{1}{2}\sum_{S_i}\sum_{n_1n_2}\sum_{ln^1n^2}\mathcal{L}_3\mathcal{S}_1^{\mathrm{IV}}R^l(n_1 0n^1l\,|\,n_2 0n^2l)\langle n^1n^2l\,|\,\tau_2(S_i)\,|\,n_1n_2\rangle\,.\tag{A4}$$

In the discussion of our results in Sec. III it is useful to consider the pair-energy and partial-wave expansion of the correlation energy. Thus, using normalized t_2 matrix elements[1,2,5] we can write

$$\Delta\epsilon_2=\tfrac{1}{2}\sum_{S_i=0}^{1}\sum_{n_1n_2}\omega_{n_1n_2}^{-1}\epsilon_{n_1n_2}(S_i)\,,\tag{A5}$$

where

$$\epsilon_{n_1n_2}(S_i)=(-1)^{1+S_i}[S_i]^{1/2}\omega_{n_1n_2}\sum_{l}\sum_{n^1n^2}(-1)^l[l]^{-1/2}R^l(n_1 0n^1l\,|\,n_2 0n^2l)N_n^{-1}\langle n^1n^2l\,|\,t_2(S_i)\,|\,n_1n_2\rangle\,,\tag{A6a}$$

$$\omega_{n_1n_2}=[1+\delta(n_1,n_2)]^{-1}\,,\tag{A6b}$$

$$N_n=\{[1+\delta(n_1,n_2)][1+\delta(n^1l,n^2l)]\}^{-1/2}\,.\tag{A6c}$$

Each $\epsilon_{n_1n_2}(S_i)$ is a pair energy and for $(n_1n_2S_i)=(110)$, (220), (120), (121), respectively, we obtain the $1s^2\,{}^1S$, $2s^2\,{}^1S$, $1s2s\,{}^1S$, and $1s2s\,{}^3S$ pair energies. Finally, we can write (A6a) in the form

$$\epsilon_{n_1n_2}(S_i)=\sum_l\epsilon_{n_1n_2}^{ll}(S_i)\,,\tag{A7}$$

where $\epsilon_{n_1n_2}^{ll}(S_i)$ is the ll partial-wave contribution to the pair energy.

For completeness we also give the results (cf. Appendix of paper I) needed to include the monoexcited states using the notation

$$\langle n^1 | t_1(0) | n_1 \rangle = \langle n^1 0 | t_1(0) | n_1 0 \rangle \tag{A8}$$

for the t_1 matrix elements. Thus,

$$\langle \tilde{n}^1 | \Lambda^{1,0}(0) | \tilde{n}_1 \rangle = \sqrt{2}\, \langle \tilde{n}^1 0 | f | \tilde{n}_1 0 \rangle , \tag{A9a}$$

$$\begin{aligned} \langle \tilde{n}^1 | \Lambda^{1,1}(0) | \tilde{n}_1 \rangle ={}& \sum_{n^1} \langle \tilde{n}^1 0 | f | n^1 0 \rangle \langle n^1 | t_1(0) | \tilde{n}_1 \rangle - \sum_{n^1} \langle n_1 0 | f | \tilde{n}_1 0 \rangle \langle \tilde{n}^1 | t_1(0) | n_1 \rangle \\ &+ \sum_{n^1 n_1} [2R^0(\tilde{n}^1 0 \tilde{n}_1 0 | n_1 0 n^1 0) - R^0(\tilde{n}^1 0 n^1 0 | n_1 0 \tilde{n}_1 0)] \langle n^1 | t_1(0) | n_1 \rangle , \end{aligned} \tag{A9b}$$

$$\begin{aligned} \langle n^1 | \Lambda^{1,2}(0) | n_1 \rangle = \sum_{S_i} \sum_{n_1} \sum_{l n^1} \Big(& - \sum_{n_2} \delta(l,0) \mathcal{S}_1^{\mathrm{V}} R^0(n_1 0 n^1 0 | n_2 0 \tilde{n}_1 0) \langle n^1 \tilde{n}^1 0 | \tau_2(S_i) | n_1 n_2 \rangle \\ & + \sum_{n^2} \mathcal{L}_3 \mathcal{S}_2^{\mathrm{V}} R^l(\tilde{n}^1 0 n^2 l | n_1 0 n^1 l) \langle n^1 n^2 l | \tau_2(S_i) | n_1 \tilde{n}_1 \rangle \\ & + \delta(l,0) \mathcal{S}_3^{\mathrm{V}} \langle n^1 0 | f | n^1 0 \rangle \langle n^1 \tilde{n}^1 0 | \tau_2(S_i) | n_1 \tilde{n}_1 \rangle \Big) , \end{aligned} \tag{A9c}$$

$$\begin{aligned} \langle \tilde{n}^1 \tilde{n}^2 \tilde{l} | \Lambda^{2,1}(\tilde{S}_i) | \tilde{n}_1 \tilde{n}_2 \rangle = \sum_{\kappa,\lambda=1}^{2} (-1)^{\kappa+\lambda+1} \Big(& \sum_{n_1} \delta(\tilde{l},0) \mathcal{S}_1^{\mathrm{VI}} R^0(n_1 0 \tilde{n}_\lambda 0 | \tilde{n}^{\bar{\kappa}} 0 \tilde{n}_{\bar{\lambda}} 0) \langle \tilde{n}^\kappa | t_1(0) | n_1 \rangle \\ & - \tfrac{1}{2} \sum_{n^1} \mathcal{L}_1 \mathcal{S}_2^{\mathrm{VI}} R^{\tilde{l}}(\tilde{n}^\lambda \tilde{l} n^1 0 | \tilde{n}^{\bar{\lambda}} \tilde{l} \tilde{n}_{\bar{\kappa}} 0) \langle n^1 | t_1(0) | \tilde{n}_\kappa \rangle \Big) , \end{aligned} \tag{A9d}$$

$$\begin{aligned} \Delta\epsilon_1 ={}& \sqrt{2} \sum_{n^1 n_1} \langle n_1 0 | f | n^1 0 \rangle \langle n^1 | t_1(0) | n_1 \rangle \\ & + \tfrac{1}{2} \sum_{n_1 n_2} \sum_{n^1 n^2} [2R^0(n_1 0 n^1 0 | n_2 0 n^2 0) - R^0(n_1 0 n^2 0 | n_2 0 n^1 0)] \langle n^1 | t_1(0) | n_1 \rangle \langle n^2 | t_1(0) | n_2 \rangle . \end{aligned} \tag{A10}$$

APPENDIX B: NEWTON-RAPHSON METHOD FOR CPMET (REFS. 3 AND 4)

As mentioned in Sec. III we used the Newton-Raphson (NR) method to solve the CPMET Eqs. (3.1). In general the NR method is a quadratically convergent iterative method for finding solutions of a nonlinear system of equations of the form

$$f_i(x_i, \ldots, x_N) = 0 , \quad i = 1, \ldots, N . \tag{B1}$$

If we write $f = (f_1, \ldots, f_N)$ and $x = (x_1, \ldots, x_N)$, this system has the compact form $f(x) = 0$. Using the first two terms of the Taylor series expansion of f we obtain

$$f(x + \Delta x) \approx f(x) + J(x) \Delta x , \tag{B2}$$

where $J(x)$ is the Jacobian matrix whose matrix elements are

$$J(x)_{ij} = \frac{\partial f_i(x)}{\partial x_j} . \tag{B3}$$

Let $x^{(n)} = x$ and $x^{(n+1)} = x + \Delta x$ and define a sequence $\{x^{(n)}\}$ of approximate solution vectors to $f(x) = 0$ by

$$f(x^{(n)}) + J(x^{(n)})(x^{(n+1)} - x^{(n)}) = 0 . \tag{B4}$$

Then we expect under fairly general conditions that the sequence $\{x^{(n)}\}$ will converge to a solution of $f(x) = 0$. In general there may be many solutions and the actual one obtained depends on the initial guess $x^{(0)}$. For each iteration (B4) is a linear system having the matrix form

$$J(x^{(n)}) x^{(n+1)} + a^{(n)} = 0 , \tag{B5}$$

where

$$a^{(n)} = f(x^{(n)}) - J(x^{(n)}) x^{(n)} . \tag{B6}$$

Given $x^{(n)}$ this system can be solved for $x^{(n+1)}$.

For CPMET the function f_i in (B1) is given by the left-hand side of Eq. (3.1), Sec. III. Thus, the Jacobian matrix is easily calculated and the linear systems (B5) have the form

$$a_i^{(n)} + \sum_j b_{ij}^{(n)} x_j^{(n+1)} = 0 , \quad i,j = 1, \ldots, N \tag{B7}$$

where

$$a_i^{(n)} = a_i - \sum_{j \leq k} c_{ijk} x_j^{(n)} x_k^{(n)} , \tag{B8}$$

$$b_{ij}^{(n)} = b_{ij} + \sum_{\substack{k \\ (k \geq j)}} c_{ijk} x_k^{(n)} + \sum_{\substack{k \\ (k \leq j)}} c_{ijk} x_k^{(n)} . \tag{B9}$$

If we choose $x^{(0)}=0$ as our initial guess, then $b_{ij}^{(0)}=b_{ij}$, $a_i^{(0)}=a_i$, and the first iteration gives the LCPMET approximation $x^{(1)}$ which is just the solution of the linear system (3.2) of Sec. III. This choice of starting approximation is based on our assumption that the quadratic terms in (3.1) are much smaller than the linear ones. The iteration process is continued until convergence.

As a measure of convergence we chose the difference in correlation energies for successive iterations. For our $7s, 7p, 4d, 3f, 3g$ basis [$N=238$ in (B7)] only three iterations (beginning with LCPMET: $x^{(1)}$) were required to obtain convergence using the precision $|\Delta\epsilon^{(n+1)}-\Delta\epsilon^{(n)}|\leq 1$ μH. In Table IX the results of this iteration procedure are given representing a typical case. The quadratic convergence of the NR method is its main advantage over the simple iterative approach [cf. Eqs. (47) of Ref. 1] which may not converge at all unless convergence acceleration methods are used. In fact we have found[54, 55] that in some cases for Be the simple iterative approach gives correlation energies and t_2 matrix elements which oscillate in a symmetric manner about the corresponding CPMET values as the iteration process is continued and that these oscillations do not die out fast enough to obtain the above mentioned precision. The advantage of the simple iterative approach is that each iteration is less time consuming since we correct only one t_2 matrix element at a time and avoid solving a linear system at each iteration. Thus, it is clear that further work needs to be done to improve the convergence of the simple iterative approach. Finally, we note that for larger systems of equations the simple Gaussian elimination method which we have used in the NR approach becomes unmanageable due to increased core requirements and it is then necessary to use an iterative "row by row" procedure.

TABLE IX. Convergence of Newton-Raphson iteration scheme for CPMET using the $7s7p4d3f3g$ basis. Energies are given in μH with signs reversed (cf. text for details).

Iteration number	τ[a]	$\Delta\epsilon_\tau$[b]	$\Delta\epsilon$
1 (LCPMET)	−0.694 099	46 173	96 797
2	−0.604 079	40 184	91 439
3	−0.602 889	40 105	91 373
4	−0.602 888	40 105	91 373

[a] Value of largest τ_2 (unnormalized) matrix element $\tau=\langle 111|\tau_2(0)|22\rangle$. The normalization factor is $N=\frac{1}{2}$.

[b] $\Delta\epsilon_\tau$ is the contribution of τ to the total correlation energy $\Delta\epsilon$.

---

*Present address: Department of Chemistry, University of New Brunswick, Bag Service No. 45222, Fredericton, N. B., E3B 6E2, Canada.

†Permanent address: Institute of Physics, Nicholas Copernicus University, 87-100 Torun, Poland.

‡Also at Department of Chemistry and Guelph-Waterloo Center for Graduate Work in Chemistry, Waterloo Campus, University of Waterloo, Waterloo, Ontario, Canada.

[1] J. Paldus, J. Chem. Phys. 67, 303 (1977).

[2] B. G. Adams and J. Paldus, Phys. Rev. A 20, 1 (1979).

[3] J. Čížek, J. Chem. Phys. 45, 4256 (1966); Adv. Chem. Phys. 14, 35 (1969); J. Čížek and J. Paldus, Int. J. Quantum Chem. 5, 359 (1971).

[4] J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A 5, 50 (1972).

[5] B. G. Adams and J. Paldus, Phys. Rev. A 24, 2302 (1981) (further referred to as paper I).

[6] D. M. Silver, S. Wilson, and C. F. Bunge, Phys. Rev. A 19, 1375 (1979).

[7] I. Lindgren and S. Salomonson, Phys. Scr. 21, 335 (1980).

[8] For a brief outline of the development of this approach, see, e.g., J. Čížek and J. Paldus, Phys. Scr. 21, 251 (1980).

[9] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. 14, 545 (1978).

[10] R. J. Bartlett and G. D. Purvis III, Phys. Scr. 21, 255 (1980).

[11] R. J. Bartlett and G. D. Purvis III, Int. J. Quantum Chem. 14, 561 (1978); G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. 68, 2114 (1978); L. T. Redmon, G. D. Purvis III, and R. J. Bartlett, *ibid*. 69, 5386 (1978).

[12] W. Meyer, J. Chem. Phys. 58, 1017 (1972).

[13] R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, J. Chem. Phys. 62, 1225 (1974).

[14] W. Kutzelnigg, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), p. 129.

[15] R. Ahlrichs, Comput. Phys. Commun. 17, 31 (1979).

[16] P. R. Taylor, G. B. Bacskay, N. S. Hush, and A. C. Hurley, Chem. Phys. Lett. 41, 444 (1976); J. Chem. Phys. 69, 1971 4669 (1978).

[17] A. C. Hurley, *Electron Correlation in Small Molecules* (Academic, New York, 1976).

[18] I. Lindgren, Int. J. Quantum. Chem. Symp. 12, 33 (1978).

[19] I. Lindgren and J. Morrison, Atomic Many-Body Theory (Springer, New York, in press).

[20] C. Froese Fischer, *The Hartree-Fock Method for Atoms: A Numerical Approach* (Wiley, New York, 1977), p. 186; C. Froese Fischer and K. M. S. Saxena, Phys. Rev. A 9, 1498 (1974).

[21] C. F. Bunge, Chem. Phys. Lett. 42, 141 (1976); Phys. Rev. 14, 1965 (1976); At. Data Nucl. Data Tables 18,

293 (1976).

[22] R. E. Watson, Phys. Rev. 119, 170 (1960).

[23] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[24] H. P. Kelly, Phys. Rev. 131, 684 (1963).

[25] D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. 41, 2677 (1964).

[26] M. Geller, H. S. Taylor, and H. B. Levine, J. Chem. Phys. 43, 1727 (1965).

[27] R. K. Nesbet, Phys. Rev. 155, 51 (1967).

[28] F. W. Byron, Jr. and C. J. Joachain, Phys. Rev. 157, 7 (1967).

[29] L. Szasz and J. Byrne, Phys. Rev. 158, 34 (1967).

[30] J.-M. Lechercq, Int. J. Quantum Chem. 3, 3 (1969); in particular, p. 6, Table I.

[31] C. F. Bunge, Phys. Rev. 168, 92 (1968).

[32] P. L. Olympia, Jr. and D. W. Smith, J. Chem. Phys. 52, 67 (1970).

[33] J. S. Sims and S. A. Hagstrom, Phys. Rev. A 4, 908 (1971).

[34] U. Kaldor, Phys. Rev. A 7, 427 (1973).

[35] C. F. Bunge, Theor. Chim. Acta 16, 126 (1970).

[36] B. G. Adams, K. Jankowski, and J. Paldus, Phys. Rev. A 24, 2330 (1981) (paper III of this series).

[37] B. G. Adams, K. Jankowski, and J. Paldus, Chem. Phys. Lett. 67, 144 (1979).

[38] J. Paldus, K. Jankowski, B. G. Adams, and J. Čížek, in *Correlation Problem: Daresbury Study, November 1979*, edited by M. F. Guest and S. Wilson (Science Research Council, Daresbury Laboratory, Warrington, England, 1980), p. 92.

[39] K. Jankowski and J. Paldus, Int. J. Quantum Chem. 18, 1243 (1980).

[40] J. Paldus, B. G. Adams, and J. Čížek, Int. J. Quantum Chem. 11, 813 (1977).

[41] B. G. Adams, Ph.D. thesis, University of Waterloo, Ontario, Canada, 1978 (unpublished).

[42] I. Shavitt (private communication).

[43] We have found that the matrices $[b_{ij}]$ at each iteration are diagonally dominant so the Gaussian elimination algorithm can be effectively implemented without partial pivoting.

[44] This was accomplished by branching around the nonlinear part of the CPMET program using the matrix $[b_{ij}]$ to construct the CI matrix and inserting a diagonalization routine kindly supplied by Prof. I. Shavitt (Ref. 41).

[45] C. Schwartz, Phys. Rev. 126, 1015 (1962).

[46] Note that the Hartree-Fock energy for the Bunge's basis Ref. 30 used here is −14.572 986 a.u. The Hartree-Fock limit is −14.573 023 20(4) given by R. C. Raffenetti, J. Chem. Phys. 59, 5936 (1973).

[47] S. Salomonson, I. Lindgren, and A.-M. Mårtensson, Phys. Scr. 21, 351 (1980).

[48] D. L. Freeman, Phys. Rev. B 15, 5512 (1977).

[49] R. F. Bishop and K. H. Lührmann, Phys. Rev. B 17, 3757 (1978).

[50] See References 37 and 38 for preliminary results.

[51] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 128, 2675 (1962).

[52] J. Paldus and J. Čížek, in *Energy, Structure, and Reactivity*, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973), p. 198.

[53] J. Paldus, J. Čížek, M. Saute, and A. Laforgue, Phys. Rev. A 17, 805 (1978).

[54] B. G. Adams and J. Paldus (unpublished).

[55] J. Paldus, in *Post Hartree-Fock: Configuration, Report on Workshop, August, 1978*, edited by C. F. Bender (NRCC, Lawrence Berkeley Laboratory, University of California), p. 242.