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Many Body Perturbation Methods in a Discrete Orbital Basis: Application to CH_4 and Ne

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Discrete basis many body perturbation calculations have been performed on Ne and CH_4 in a basis which mimics Boys' oscillator orbitals. The L-shell correlation energy obtained for Ne was -0.347 which is to be compared with the best numerical basis many body perturbation result of -0.336 ± 0.01 obtained by Lee, Dutta and Das and the best variational result of -0.322 obtained by Sasaki and Yoshimine. An analysis of 3- and 4-body corrections (pair-pair repulsions) and the effects of many body EPV renormalization for both localized and canonical SCF orbitals is presented.

Key words: Ne - CH_4 - Many body perturbation theory

1. Introduction

In the present communication we report correlation energy calculations for CH_4 and Ne computed within a theoretical framework that resembles the many body perturbation theory (MBPT) methods of Kelly [1]. However, in the present work the method has been formulated in such a manner (via the use of a discrete orbital basis; the use of infinite order diagram summation by solution of non-linear inhomogeneous equations; and the use of spin coupled pair functions and localized orbitals) that it is directly applicable to general molecular systems.

Our motivation for performing the present computations was to permit a detailed comparison with the results of Lee, Dutta and Das [2] on Ne, obtained using numerical basis MBPT methods, and the results of Ahlrichs *et al.* [3] on CH_4 using the related coupled electron pair and independent electron pair approximations (CEPA/IEPA). In particular we hoped to determine:

a) suitable Gaussian basis sets,
b) the importance of "many-body effects" (EPV-renormalization), and
c) the importance of 3- and 4-body diagrams (pair–pair repulsion corrections).

2. IEPA/CEPA versus MBPT in a Discrete Orbital Basis

The relationship between the IEPA/CEPA and MBPT methods in the special case [4] when IEPA/CEPA is formulated in terms of spin-orbital pairs has been clearly established in the work of Freed [5], Čížek [6], and by one of the present authors [7]. Many body effects only enter the theory at fourth order and a complete treatment of these has been published by the present authors [8]. The relationships (for spin orbital pairs) may be summarized as follows:

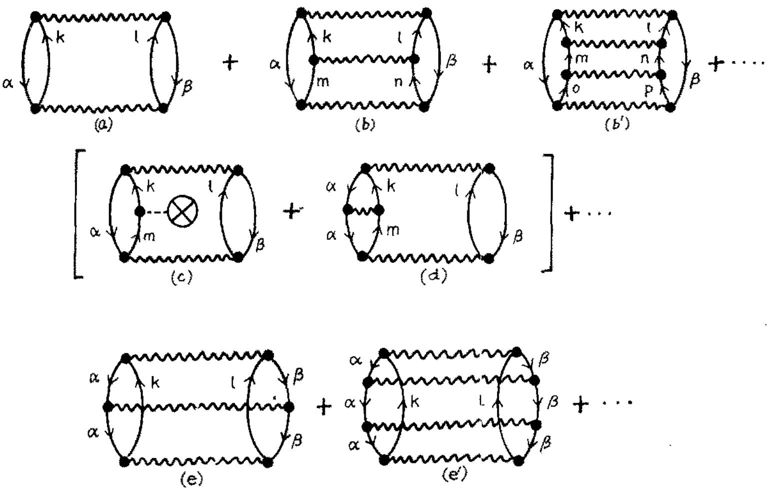

Fig. 1. Diagonal hole-line diagrams of the IEPA approximation

1) The infinite order summation of the diagrams[1] shown in Fig. 1 with no non-diagonal hole line interactions plus those EPV (1) rearrangement diagrams of Fig. 2 where $\gamma = \alpha$ and $\delta = \beta$ gives the IEPA.
2) The CEPA includes the diagrams of the IEPA plus the 3- and 4-body diagrams from the pair–pair repulsions shown in Fig. 3.
3) The coupled pair many electron theory (CPMET) of Čížek [6] includes [8] all the diagrams of Figs. 1, 2 and 3 summed to infinite order.
4) The MBPT methods of Kelly [1] as implemeted by Das *et al.* [2] in their Ne calculations include all the diagrams of the IEPA as discussed above plus *all* the EPV diagrams of Fig. 2. To this result were added all the third-order diagrams of Fig. 3 to give the final result.

The basic difference then, between MBPT methods and IEPA/CEPA methods, arises in the treatment of the rearrangement diagrams of Fig. 2 and the level of approximation at which the diagrams of Fig. 3 are included.

3. Spin Coupled Pairs

In many of the calculations[2] that have been carried out using the IEPA/CEPA, the simple relationships just discussed in terms of spin orbital pairs, become obscured through the use of spin coupled pairs. In general, four spin coupling schemes are possible:

1) spin orbital pairs (no spin coupling) [4],
2) pairs coupled to form two electron spin eigenfunctions (such functions would carry a direct product representation of symmetric groups of order 2) (see Table 1, Ref. [11]),

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[1] The diagrams are evaluated with antisymmetrized vertices using the rules of Brandow [9] (see also Ref. [7]).

[2] In the IEPA/CEPA calculations of Meyer [10] and Ahlrichs *et al.* [3], a very efficient basis of non-orthogonal pseudo-natural orbitals was used. However, this technical innovation does not affect the theoretical interpretation of the method in any way whatsoever.

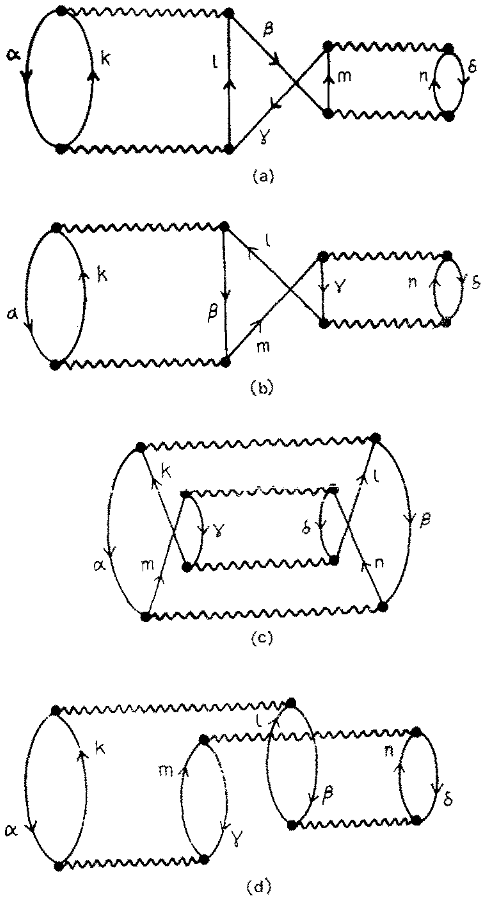

Fig. 2. Rearrangement diagrams (unlinked cluster corrections). The "exclusion principle violating" EPV renormalization diagrams are those for which one has two holes or particles excited with the same label (e.g. diagram a with $\gamma = \beta$, diagram b with $l = m$). The EPV diagrams with $(\gamma, \delta) = (\alpha, \beta)$ are included in the IEPA while our DB-MBPT + EPV result includes all EPV diagrams

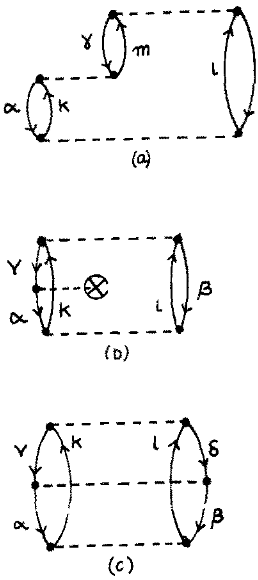

Fig. 3. The diagrams giving rise to the pair–pair repulsion corrections. Diagram a is a 3-body ring diagram – there are seven others related via exchange in one or more elements. Diagram b involves the off-diagonal matrix elements of the HF operator and vanishes for CMO. Diagram c is a 4-body diagram involving a non-diagonal hole line intermediate interaction

3) spin irreducible pairs [3] (such a coupling scheme is not unique and a wide variety is possible), and
4) spatial orbital pairs [10].

The various possible spin coupling schemes may be the source of some confusion in the interpretation of pair function theories of electron correlation. Thus a brief review in the case of a closed shell SCF function Ψ_0 may be helpful.

Let us consider the component of a pair function formed by excitation from SCF orbitals (with $\alpha(\beta)$ spin), $i(\bar{i})$ and $j(\bar{j})$ into virtual orbitals $r(\bar{r})$ and $s(\bar{s})$. We could define *two electron spin eigenfunctions* in terms of singlet and triplet particle-hole creation-annihilation operators, $C_{ir}^{\overset{S}{T_0}} = (2)^{-1/2}(\eta_r^\dagger \eta_i \pm \eta_{\bar{r}}^\dagger \eta_{\bar{i}})$, $C_{ir}^{T_+} = \eta_r^\dagger \eta_{\bar{i}}$, $C_{ir}^{T_-} = \eta_{\bar{r}}^\dagger \eta_i$, which give pair function $C_{ir}^S C_{js}^S \Psi_0$, $C_{ir}^{T_0} C_{js}^{T_0} \Psi_0$, $C_{ir}^{T_+} C_{js}^{T_-} \Psi_0$, and $C_{ir}^{T_-} C_{js}^{T_+} \Psi_0$. Alternatively, we could define *two electron spin eigenfunctions* in terms of hole-pair annihilators, $Q_{ij}^{\overset{S}{T_0}} = (2)^{-1/2}(\eta_i \eta_{\bar{j}} \mp \eta_{\bar{i}} \eta_j)$, $Q_{ij}^{T_+} = \eta_{\bar{i}} \eta_{\bar{j}}$ and particle-pair creators $Q_{rs}^{\dagger \overset{S}{T_0}} = (2)^{-1/2}(\eta_r^\dagger \eta_{\bar{s}}^\dagger \mp \eta_{\bar{r}}^\dagger \eta_s^\dagger)$, $Q_{rs}^{\dagger T_+} = \eta_r^\dagger \eta_s^\dagger$, $Q_{rs}^{\dagger T_-} = \eta_{\bar{r}}^\dagger \eta_{\bar{s}}^\dagger$. These operators give rise to pair functions, $Q_{rs}^{\dagger S} Q_{ij}^S \Psi_0$, $Q_{rs}^{\dagger T_0} Q_{ij}^{T_0} \Psi_0$, $Q_{rs}^{\dagger T_+} Q_{ij}^{T_+} \Psi_0$ and $Q_{rs}^{\dagger T_-} Q_{ij}^{T_-} \Psi_0$. In each case the triplets may be vector coupled to a singlet and this defines *spin irreducible pairs.* Of course any unitary transformation of the spin irreducible pairs yields an equally acceptable spin eigenfunction. Thus neither the two electron spin eigenfunctions nor the spin irreducible pairs are unique in any way and one's choice of function depends upon the expediency of the particular situation. An even greater variety is possible for open shell systems. Finally one defines spatial orbital pairs within the IEPA scheme by allowing full coupling between the two vector spin singlets.

In the CEPA method (aside from small EPV renormalization effects) the result is not dependent on the coupling scheme chosen. However, in the IEPA and related methods, the result of each spin coupling scheme is to include the effects of *some* of the diagrams of Fig. 3 but *not to infinite order.* The proper spin coupling will always be correctly accounted for by including the diagrams of the type shown in Fig. 3 to a sufficiently high order of perturbation theory.

In IEPA calculations [3] the hole-pair, particle-pair scheme has been used with vector coupling of the triplets. In the present work we use the same scheme *without* vector coupling to facilitate diagrammatic analysis and because of computational convenience. Finally, it must be pointed out that the EPV renormalization is transferred from a spin orbital pair basis to the spin-irreducible pair basis in an *ad hoc* fashion in the IEPA/CEPA methods [10]. In the present work we are able to treat these many-body effects rigorously.

4. Computational Methods

4.1. The Discrete Basis Many Body Perturbation Theory Method (DB-MBPT)

The method used in the present calculations may now be summarized as follows:

1. The IEPA diagrams are summed to infinite order using the appropriate set of nonlinear inhomogeneous equations. The equations are solved in a basis of two electron spin eigenfunctions (scheme 2 above).

2. The *full* EPV renormalization is then computed [1, 8]. (We shall denote this step as DB-MBPT + EPV.)
3. The resulting correlation energies are then "corrected to first order" in the pair-pair repulsions [5] (diagrams of Fig. 3).

Thus the essential difference between our DB-MBPT + EPV calculations and the numerical basis MBPT calculations of Das *et al.* is that we have used two electron spin eigenfunctions rather than spin orbital pairs.

4.2. Basis Sets

In the MBPT methods used by Das *et al.* [2] and Kelly [1] it was possible to use numerical atomic orbitals (up to $l = 6$) including all continuum contributions. However, in using this method it is necessary to make certain numerical approximations (e.g. the geometric approximation) in summing the diagrams. The resulting loss in accuracy is quite serious. (Das *et al.* quote an accuracy of only ± 0.01 for their Ne calculation.) In a discrete basis calculation one is attempting to make an accurate point-wise approximation to the complete basis of Das *et al.* [2], while at the same time keeping the dimension of the non-linear equations to be solved small enough for diagrams to be summed to infinite order. Because our basis is rather unconventional it deserves some comment at this point.

Some time ago, Boys [12, 13] defined a basis of oscillator orbitals which was ideally suited for the computation of correlation effects. Oscillator orbitals were defined in terms of localized molecular orbitals (LMO) as

$$\eta_a^{lmn} = \bar{X}_a^l \bar{Y}_a^m \bar{Z}_a^n \Phi_a \tag{1}$$

where Φ_a is an LMO and $\bar{X}_a$, $\bar{Y}_a$ and $\bar{Z}_a$ are defined relative to the principle axis system of the second moment tensor associated with the electron density in LMO Φ_a. We have found it possible to use the following approximate form:

$$\eta_a^{lmn} = (X - R_{ax})^l (Y - R_{ay})^m (Z - R_{az})^n \exp \alpha(r - R_a)^2 \tag{2}$$

where R_a is the centroid of the charge density of LMO Φ_a. This function is merely a floating Gaussian and would resemble Boys oscillator orbitals (Eq. (1)) if the charge distribution in LMO Φ_a were approximately spherical. The exponent α remains to be optimized, however, we have found that the optimum value lies very close to one which reproduces the average spherical quadratic moment of the LMO Φ_a. Further, we have found that the use of functions of degree 0 (degree $= l + m + n$) leads to near linear dependencies while functions of degree 2 have almost no effect if the basis is complete with respect to s and p functions centred on the heavy atom. (In preliminary test calculations on H_2O the addition of a set of oscillator orbitals of degree 2 to a basis consisting of a double zeta plus oscillator orbitals of degree 1 increased the correlation energy by less than 0.5%.) Thus our basis was the standard Gaussian 10*s* 6*p* basis [14] in the contraction (61111/411) for the Ne and C plus a 4*s* basis [14] on H contracted (31). This set was then augmented by a single set of oscillator orbitals of degree 1. The oscillator orbitals were arranged tetrahedrally at distances 0.376 and 1.26 with exponents (α) 2.247 and 0.546 for Ne and CH_4 respectively.

The added oscillator orbitals have almost no effect on the SCF result (our SCF result for Ne is still 0.01 from the HF limit). However, "the computed correlation energy" (defined as the difference between the SCF result and the correlation energy calculation) should not

Table 1. IEPA-MBPT Correlation energies of Ne and CH_4 (Canonical MO)

	Ne			CH_4		
	Present Work[a]		Ref.[b][2]	Present Work[c]		
Pairs	DB-MBPT[d]	DB-MBPT + EPV[e]	MBPT-EPV[f]	Pairs	DB-MBPT[d]	DB-MBPT + EPV[e]
$2p$–$2p$	−0.28786	−0.28128	−0.25082	t_1–t_1	−0.19785	−0.18879
$2p$–$2s$	−0.08332	−0.08152	−0.09491	$2a_1$–t_1	−0.06822	−0.06532
$2s$–$2s$	−0.01255	−0.01251	−0.01268	$2a_1$–$2a_1$	−0.01354	−0.01342
Sum of pairs	−0.38374	−0.37532	−0.35841		−0.27961	−0.26753
Pair–Pair Repulsions	First-Order Correction	First-Order Correction with EPV Renormalization	Third-Order Diag. 3	Pair–Pair Repulsions	First-Order Correction	First-Order Correction with EPV Renormalization
$(2p\ 2p)$–$(2p\ 2p)$	0.02382	0.02213	0.02109	(t_1t_1)–(t_1t_1)	0.01185	0.00991
$(2s\ 2p)$–$(2s\ 2p)$	0.00509	0.00488	0.00622	$(2a_1t_1)$–$(2a_1t_1)$	0.00498	0.00441
$(2s\ 2s)$–$(2p\ 2p)$	0.00161	0.00157	0.00165	$(2a_12a_1)$–(t_1t_2)	0.00301	0.00288
$(2s\ 2p)$–$(2p\ 2p)$	−0.00056	−0.00053	−0.00522	$(2a_1t_1)$–(t_1t_1)	−0.00095	−0.00148
$(2s\ 2s)$–$(2s\ 2p)$	−0.00015	−0.00015	−0.00130	$(2a_12a_1)$–$(2a_1t_1)$	−0.00018	−0.00018
Total pair-pair Repulsions	0.02981	0.02790	0.02244		0.01871	0.01554
Total computed correlation energy	−0.35393	−0.34742[g]	−0.33597		−0.26090	−0.25199

[a] SCF Energy −128.53629.

[b] SCF Energy −128.54829.

[c] SCF Energy −40.18949.

[d] Diagrams of Fig. 1 plus EPV terms of Fig. 2 with $\gamma = \alpha$ and $\delta = \beta$.

[e] As with (d) but with all EPV terms of Fig. 2 included.

[f] As with (e) but no spin coupling.

[g] Ref. [3] obtains −0.31233 and −0.27495 with IEPA and CEPA giving a pair–pair repulsion correction of 0.03738.

be strongly dependent on the SCF result. One may always improve the SCF accuracy by adding atom centred polarization functions in the usual manner.

5. Results and Discussion

The results of our calculations of the correlation energies of Ne and CH_4 are summarized in Tables 1, 2 and 3, along with the results of Das *et al.* [2] and Ahlrichs *et al.* [3] for comparison. In Tables 1 and 2 we display the pair correlation energies and pair-pair repulsion corrections for canonical molecular orbitals (CMO) and LMO. In Table 3 the pair-pair repulsion corrections are analysed in terms of contributions from the diagrams of Fig. 3.

5.1. Efficiency of Basis Sets

The numerical basis MBPT results of Das *et al.* [2] are directly comparable with our DB-MBPT + EPV results. Comparison of our results in column 3 of Table 1 and column 3 of Table 3 with the corresponding results of Das *et al.* in column 4 of Table 1 and column 6 of Table 3 shows good agreement with respect to total correlation energy and the magnitude and sign of the various possible pair-pair repulsion corrections. In making this comparison it must be recognized that our SCF result is 0.012 above that of Das *et al.* and that they estimate an overall error of ±0.01 through approximate[3] methods used in diagram summation. It is not possible to make similar comparisons with our CH_4 results. However, the difference between the empirical correlation energy of CH_4 [10] (–0.295) and the $C(^3P)K$ shell correlation energy obtained by Kelly [15] (–0.042) gives an estimate of –0.253 for the valence shell correlation energy which agrees very well with our CMO result of –0.252. Our SCF result in this case is 0.031 above the HF limit, but despite this our basis appears to be highly efficient for the calculation of correlation effects for both Ne and CH_4. Thus we have some confidence that any conclusions drawn from a more detailed analysis of the results (particularly LMO basis calculations) will have some validity.

5.2. Importance of EPV *Renormalization*

The EPV renormalization is always included in the numerical basis MBPT calculations of the type pioneered by Kelly [1]. However, the CEPA calculations of Meyer on CH_4 [10] and those of the present author [16] on BH are the only previous examples where EPV renormalization effects have been included in a discrete basis calculation. In Meyer's calculations this renormalization (the hole line rearrangement effects only) was included in a rather *ad hoc* manner due to the use of spin irreducible pairs. In the present work we include the full EPV renormalization in a basis of two electron spin eigenfunctions.

The effect of EPV renormalization on the total correlation energies (see Tables 1 and 2) is small (less than 3%). But the effect in the pair-pair repulsion energies in Ne is about 7%, so the low overall correction results from a cancellation of effects. Meyer [10] computes an overall error due to EPV renormalization in CH_4 of the order of 1%. This rather low

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[3] Das *et al.* [2] approximate the sum of diagrams beyond third order using a geometric approximation. In our calculations we routinely start from a geometric approximation. For Ne our DB-MBPT result obtained from a geometric approximation is –0.38266 which is very close to the infinite order result of –0.38374. However, this does reflect a considerable cancellation of errors since a typical pair correlation energy is in error by about 2% using the geometric approximation.

Table 2. IEPA-MBPT Correlation energies of Ne and CH_4 (Localized MO)

	Ne			CH_4		
	Present Work		Ref.[a] [3]	Present Work		Ref.[b] [3]
Pairs	DB-MBPT	DB-MBPT + EPV	Diagonal CEPA Contributions	DB-MBPT	DB-MBPT + EPV	Diagonal CEPA Contributions
ii	−0.12191	−0.12141	−0.1032	−0.15525	−0.15599	−0.1320
ij	−0.23634	−0.23123	−0.2010	−0.13601	−0.12773	−0.1086
Sum of pairs	−0.35825	−0.35264	−0.3042	−0.29126	−0.28372	−0.2406
Pair–Pair Repulsions	First-Order Correction	First-Order Correction with EPV Renormalization	Off-Diagonal CEPA Contributions	First-Order Correction	First-Order Correction with EPV Renormalization	Off-Diagonal CEPA Contributions
ij/*ij*	0.02485	0.02357	0.00492	0.02172	0.01889	0.00366
ii/*ij*	−0.00374	−0.00372	0.00936	−0.00102	−0.00099	0.00912
ij/*ik*	−0.01167	−0.01114	0.02484	−0.00379	−0.00334	0.00840
ii/*jj*	0.00097	0.00096	0.00108	0.00068	0.00063	0.00048
ii/*jk*	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
ij/*kl*	0.00022	0.00021	0.00021	0.00014	0.00013	0.00006
Total pair–pair Repulsions	0.01066	0.00988	0.04041	0.01772	0.01532	0.02172
Total Correlation Energies	−0.34760	−0.34277	−0.26338	−0.27354	−0.26842	−0.2189

[a] SCF Energy −128.52734. [b] SCF Energy −40.21147.

Table 3. Analysis of pair–pair repulsion corrections in Ne and CH_4

	Ne					CH_4			
	Present Work				Ref. [2]	Present Work			
	CMO		LMO			CMO		LMO	
	DB-MBPT	DB-MBPT + EPV	DB-MBPT	DB-MBPT + EPV	MBPT + EPV	DB-MBPT	DB-MBPT + EPV	DB-MBPT	DB-MBPT + EPV
3-Body (Diagram 3a)	0.02784	0.02598	0.02366	0.02237	0.02079	0.01262	0.00981	0.02274	0.01994
4-Body (Diagram 3c)	0.00197	0.00192	0.00198	0.00187	0.00165	0.00609	0.00573	0.00107	0.00094
Off-diagonal HF (Diagram 3b)			−0.01498	−0.01437				−0.00609	−0.00557
Total	0.02981	0.02791	0.01066	0.00987	0.02244	0.01871	0.01554	0.01772	0.01531

estimate is due to his neglect of particle line rearrangement diagrams (Fig. 2b) which become important as one uses more complete basis sets.

While the EPV renormalization effects are small in the present example one expects that they will become very important as the number of electrons increases and as one goes to larger basis sets. A brief consideration of the EPV hole-line and EPV particle-line diagrams of Figs. 3a and 3b with $\beta = \gamma$ and $m = l$ illustrates this point. The hole-line rearrangement diagram represents the simultaneous correlation of two semi-disjoint pairs while the particle-line rearrangement diagram represents the simultaneous correlation of two disjoint pairs via a common particle. As the number of holes or particles states accessible to the system increases the "probability of this event occurring" increases and so does the importance of the corresponding diagram. Future calculations on Ne–Ne would illustrate this conjecture.

The neglect of the non-EPV rearrangement diagrams (off-diagonal matrix elements) leads to the loss of invariance of the unlinked cluster effects (see Ref. [8] for a full discussion) to a unitary transformation among either the occupied or virtual orbitals. However, inspection of Tables 1–3 shows that the EPV renormalization corrections differ very little between CMO and LMO and this observation lends some validity to the approximation of neglecting the non-EPV terms.

5.3. Analysis of the Pair–Pair Repulsion Corrections

The previous discussion gives us some confidence that our results are reliable and we can now discuss the importance of the pair–pair repulsions in both the CMO and LMO bases. Before attempting this however it is relevant to make a brief comment on our localized orbitals.

In all our calculations we have limited ourselves to valence shell correlation only. However, in the construction of our LMO we included the 1*s* core and since this mixed slightly with the 2*s* orbital, the computed valence shell correlation energy will not be equal for CMO and LMO. The difference is most apparent for CH_4 where the LMO correlation energy lies 3% below the CMO result. However, since the pair-pair repulsion correction is of the order of 10% of the overall correlation energy it is still meaningful to compare the CMO and LMO results in detail.

The most important result concerning pair-pair repulsions relates to the use of spin coupled pairs. The good agreement between our results and those of Das *et al.* (Tables 1 and 3) which has already been discussed, shows that the use of two electron spin eigenfunctions has almost no effect on the interpretation of the results. This is to be expected since the dominant effect of coupling the pairs in this way is to include the effect of diagram 3c with $\gamma = \bar{\alpha}$ and $\delta = \bar{\beta}$ to infinite order.

Inspection of our results obtained for LMO in a basis of two electron spin eigenfunctions with those of Ahlrichs *et al.* [3] obtained in a basis of spin irreducible pairs as presented in Table 2 allows a comparison of the effects arising from the different spin coupling schemes. For the disjoint pair-pair corrections (*ii*/*jj*, *ii*/*jk*, *ij*/*kl*) the matrix elements are identical and it can be seen that our results are in satisfactory agreement with respect to sign and magnitude. However, for the joint (*ij*/*ij*) and semi-disjoint (*ii*/*ij*, *ij*/*ik*) pair-pair corrections, the results are very different in the two approaches. For example the *ij*/*ij* corrections in the present calculations are an order of magnitude larger than those of

Ahlrichs *et al.* In addition our correction for semi-disjoint pairs is large and negative while that of Ahlrichs *et al.* is large and positive. Thus we observe a partial cancellation of effects that does not occur in a basis of spin irreducible pairs. Clearly, the pairs involving the same spatial orbitals are strongly coupled and since the choice of coupling to spin irreducible pairs is not unique anyway (particularly for open shell systems) it may be more efficient to allow the diagrams of Fig. 3 to couple the pairs rather than imposing this from the outset.

Finally, we should like to comment briefly on the decomposition of the pair–pair repulsions corrections into contributions (Table 3) arising from the diagrams of Fig. 3. For both CMO and LMO the 3-body correction (diagram 3a) dominates. In the LMO basis the contribution to the *ij*/*ij* correction arises almost entirely from this effect. On the other hand, for LMO this contribution is partially cancelled by the contribution from diagram 3b, and the correction for semi-disjoint pair-pair repulsions arises almost entirely from this diagram. The 4-body corrections (diagram 3c) are very small (especially for LMO) and contribute mainly to the corrections for *ii*/*jj* pair–pair repulsions.

In general the contributions from diagrams 3a and 3c do not change drastically on going from CMO to LMO and it is the large negative contribution from diagram 3b which is responsible for any large difference in the overall effect of pair-pair repulsions.

The results for CH_4 suggest that for well-localized systems the *ij*/*ij* (diagram 3a) corrections may dominate if one uses two electron spin eigenfunctions as a basis. This effect has also been observed in our calculations of CH_2F_2 reported elsewhere [7] and calculations on substituted ethanes and ethylenes are now in progress to verify this.

6. Conclusions

It is apparent that the basis of oscillator orbitals used in this work is adequate to reproduce numerical basis MBPT results. Calculations using this type of basis are certainly feasible for molecular systems containing up to four first-row atoms. While we have presented only isolated molecule results, there is no reason to expect that this approach will not remain suitable for all calculations where a pair function method is possible.

The EPV renormalization effects in these calculations are small, however this error will become more important (and perhaps dominant) as the number of electrons increases and when one considers distortions from equilibrium geometries.

The major conclusion of the present work concerns the simplicity of the pair–pair repulsion corrections for LMO in a basis of two electron spin eigenfunctions. It would appear that the major correction is the contribution of diagram 3a to the *ij*/*ij* pair–pair repulsions and diagram 3b to the semi-disjoint (*ii*/*ij*, *ij*/*ik*) pair–pair repulsions. These two types of contribution always have the opposite sign in the LMO basis and hence approximately cancel. This approximate cancellation is not observed in the CMO basis because diagram 3b vanishes identically. This observation is to be contrasted with the situation using spin irreducible pairs [3] where this partial cancellation does not occur. However, while this cancellation reduces the error due to pair–pair repulsions in the calculation of correlation energies this same cancellation of effects may not occur when calculating other properties.

Finally, one must be somewhat cautious regarding conclusions with respect to basis completeness. Considering the effort in basis optimization by Sasaki and Yoshimine [17] for Ne and by Meyer [10] for CH_4 who obtain valence shell correlation energies of −0.322 and

–0.241 respectively it may seem surprising that the present basis should come close to 100%. The basis of our conclusions is a detailed comparison with the numerical many body perturbation results of Lee Dutta and Das [2]. It should be noted that Das and co-workers quote an error of ±0.01; however, this represents the numerical precision of their calculations and not the error from a rigorous upper bound. This same error arising from the non-variational nature of the calculation must be present in our calculation as well. The major source of this type of error is the fact that the diagrams of Fig. 3 are not summed to infinite order and the fact that we have not included all non-EPV rearrangement diagrams. In addition, we have assumed that the correlation energy is not strongly dependent on the accuracy of the SCF starting point. Our SCF results are not particularly good and this may affect the accuracy of the correlation slightly.

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