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Use of a Size-consistent Energy Functional in Many Electron Theory for Closed Shells

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If the ground state wave-function ψ_{gr} is written as $\psi_{gr} = \Phi_0 + \chi$, with χ as the correlation part satisfying $\langle\Phi_0|\chi\rangle = 0$, and χ expressed as an expansion in terms of pair, pair-pair etc. cluster functions, then the expectation value of the energy $E = \langle\psi_{gr}|H|\psi_{gr}\rangle/\langle\psi_{gr}|\psi_{gr}\rangle$ has the property that the normalization term in the denominator completely cancels the unlinked part of the numerator, as noted by Sinanoglu. We use Cizek's coupled-pair ansatz $\psi_{gr} = \exp(T_2)\Phi_0$ for transcribing Sinanoglu's expansion in a many-body language to study the behaviour of the size-consistent (linked) energy functional thus generated. For calculating the matrix-elements of the cluster components of T, we use two recipes: (1) a variational determination of the cluster components using Euler's principle for the energy functional akin in spirit to the Varied Portion Approach (VPA) of Sinanoglu and (ii) a nonvariational determination of the cluster components using the conventional coupled-cluster theory. Results are presented for model test systems and are compared with variational CI and nonvariational coupled-cluster values. It has been observed that the values obtained from the size-consistent energy functional from the cluster components obtained from methods (i) and (ii) are quite close and both compare well with the nonvariational coupled-cluster results. Some useful simplifications afforded by the VPA are also indicated. A brief perspective of the method vis-a-vis other related theories is also given.

Key words: Many body theory—Size consistency—Coupled cluster theory.

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1. Introduction

The many electron correlation problem has remained for a long time a field of major interest in Quantum Chemistry. Historically, the Configuration Interaction (CI) procedure is the oldest and is also the most widely used technique – presumably because of its simple algebraic structure. This has also a serious drawback, however. The CI gives no clue to the expected physically dominant configurations that need enter the CI expansion. Without such a physical recipe, the CI calculations can not take into account the most important aspects of electron correlations in a compact CI expansion and thus becomes rapidly prohibitive for an accurate calculation of even modest sized systems. Sinanoglu [1] first pointed out that pair correlations and pair–pair correlations are the dominant modes of correlation in a closed-shell electronic system provided one starts out with Hartree–Fock (HF) orbitals, and developed a Many Electron Theory (MET) building on this idea. According to Sinanoglu, the pair correlation effects are adequately taken care of by including doubly excited configurations. The pair–pair correlations enter through the quadruply excited configurations but an essential simplification brought out by the MET is that the coefficients of the quadruply excited configurations can be well approximated as sum of products of coefficients for the various appropriate doubly excited configurations. MET emphasises this dominance of the pair cluster and its unlinked product counterparts and asserts that orbital polarization (entering through single excitations), three-body correlation (through triple excitations) and their unlinked cluster contributions are not significant. Sinanoglu [1] advocated a variational recipe to calculate the pair cluster functions under various decoupling approximations starting from the full variational energy functional. Writing the exact ground state function ψ_{gr} as a sum of H-F component Φ_0 and the correlation part χ, the exact energy E is formally given by

$$E=\frac{\langle\psi_{gr}|H|\psi_{gr}\rangle}{\langle\psi_{gr}|\psi_{gr}\rangle}=E_{\mathrm{HF}}+\frac{2\langle\Phi_0|H|\chi\rangle+\langle\chi|H-E_{HF}|\chi\rangle}{1+\langle\chi|\chi\rangle} \tag{1}$$

using the convention for intermediate normalization. In MET, the function χ is written as [1]

$$\chi=A\left[\frac{1}{\sqrt{2}}(123\cdots N)\sum_{i>j}^{N}\frac{\hat{U}_{ij}}{(ij)}+\tfrac{1}{2}(123\cdots N)\sum_{\substack{i>j\\k>l\\(ij)\neq(kl)}}^{N}\frac{\hat{U}_{ij}}{(ij)}\frac{\hat{U}_{kl}}{(kl)}+\cdots\right] \tag{2}$$

and this expansion substituted into the Eq. (1) gives the starting master equation for MET. We have used Sinanoglu's standard notation for expressing χ. If χ is truncated after the first-term, and the approximate functional is varied, then we have precisely a "doubles CI" theory for correlation – now a routine technique. A more useful variant of this full (Raleigh–Ritz) variational principle has been extensively discussed by Sinanoglu which he has termed as the "Varied Portion Approach (VPA)" [2]. This is a variational principle for a principal component of the functional in Eq. (1) (thus also termed a "subvariational principle") which leads to Euler's equations of simpler structure. Thus, by varying contributions from each $\hat{U}_{ij}$ at a time, one generates equations for each $\hat{U}_{ij}$ and consequently gets a decoupled pair MET. Sinanoglu and Goscinski also demonstrated that the use of VPA to the numerator only of Eq. (1) leads to a lower bound equation for pair correlations [3]. One conspicuous feature of the functional (1) is the coupling of various clusters $\hat{U}_{ij}$ in the denominator through the normalisation term $(1+\langle\chi|\chi\rangle)$. It was emphasised by Sinanoglu [2] that this coupling is not physical but is merely an artifact originating through truncation of Eq. (2) after a finite product (usually after the first term, as in a CI). If all unlinked clusters are kept in χ, then the denominator gets completely cancelled with a factor originating from the numerator. It is now widely accepted that the chief trouble with a CI type of approach including fixed degree of excitation is the lack of size consistency (as manifested in the incomplete cancellation of the denominator) [4, 5]. Only the full cluster expansion leads to a size-consistent result through complete cancellation of the denominator.

We explore in this paper the property of the energy functional Eq. (1) where the unphysical coupling through the denominator is eliminated by utilising the full unlinked cluster expansion (Eq. (2)).

It is well known that ψ_{gr} in MET may be compactly written in the occupation number representation as

$$\psi_{gr} = \exp(T)\Phi_0 \tag{3}$$

with T approximated as T_2. This kind of exponential ansatz was first used in nuclear physics [6] and its potential importance in atomic and molecular physics was also soon noted [4, 5, 7]. Subsequently there has been a wide spread use of this "coupled cluster" ansatz [5–13]. The major thrusts in the various developments have been (a) a nonvariational approach using the method of moments and (b) use of a variational principle to the functional Eq. (1) where the complete cancellation of the denominator is not attempted [12]. The non-variational approach has no denominators and is consequently size consistent and is the natural extension and generalisation of the manybody perturbation theories developed somewhat earlier [15]. The methods (b) are size inconsistent for an approximate ψ_{gr} due to incomplete cancellation of the denominator. Taking cue from Sinanoglu's theory, we substitute the expression Eq. (3) in Eq. (1) and generate the size consistent energy functional through the cancellation of the denominator. Although this formal cancellation of the denominator for a general T has been known for some years [1, 7, 10, 14], the behaviour of the size-consistent energy functional under various choices for the cluster-components of T and truncation schemes have not been explored so far. We want to keep on record a preliminary study in that direction using some model test problems. Specifically we shall show the following: (a) Euler's principle to the size-consistent energy functional for the ground state can be used to determine the cluster components and hence a size-consistent energy for the ground state in excellent agreement with the coupled-cluster nonvariational results of Cizek; (b) if the energy functional is truncated after mth total power of T and T^+ and the resulting expression varied to solve for T, then the calculation of the terms involving mth total power of T and T^+ can be avoided altogether in the subsequent energy calculation. Thus, for an energy functional retaining up to quadratic power of T and T^+, the variational result contains up to linear terms only and is identical with the result from the linearised nonvariational theory, (c) substitution of the values of cluster components obtained from non-variational theory in the size-consistent energy functional leads to a similar value for energy but the advantage for the variational method under (b) above does not exist; (d) there is a loss of upper bound property of the energy functional for a truncated calculation which is, however, not very serious. The variational principle for the truncated size-consistent energy functional is thus more in the spirit of VPA [1] than the Raleigh-Ritz principle.

2. Calculation of the Energy Functional

We write the ground state using the coupled cluster ansatz:

$$\psi_{gr} = \exp(T)\Phi_0, \tag{4}$$

with T involving hole-particle excitations only, Φ_0, is the Hartree–Fock function. It may be noted that for closed shell systems, the operator $\exp(T)$ is in normal order: $N[\exp(T)] = \exp(T)$, and thus a simple $\exp(T)$ wave-operator suffices. It would, however, be useful to keep in mind that the $\exp(T)$ is a normally ordered operator. The linked nature of the energy functional

$$E = \frac{\langle\Phi_0|\exp(T^+)H\exp(T)|\Phi_0\rangle}{\langle\Phi_0|\exp(T^+)\exp(T)|\Phi_0\rangle} \tag{5}$$

has been noted earlier by several workers in various context [1, 7, 10, 14]. The proof becomes rather simple if both the numerator and the denominator in (5) are expanded in the usual way using the generalised Wick's theorem (GWT) [5], and the set of closed connected diagrams containing the hamiltonian vertex is factored out from the closed normalisation diagrams containing T and T^+ vertices contracted together. The normalisation diagrams, *taken to all orders*, cancel the denominator making the resultant expression linked and, therefore, size-consistent.

$$E = \langle\Phi_0|N[\exp(T^+)H\exp(T)]|\Phi_0\rangle_{\text{"Linked"}} \tag{6}$$

where N denotes normal ordering, and "Linked" stands for linked closed diagrams. The proof is reminiscent of the linked-cluster theorem for closed-shell many-body perturbation theory [15]. Fig. 1 depicts the factorisation schematically and a set of typical diagrams appearing in Fig. 1 is displayed in Fig. 2.

We want to study the property of the energy functional (6) along two lines. The first of these would be to make Eq. (6) stationary with respect to the cluster components and then calculate the energy from Eq. (6). E is, however, an infinite degree polynormal in T and T^+ and thus would require truncation at a finite order for any practicable calculation. In the spirit of the analysis made by

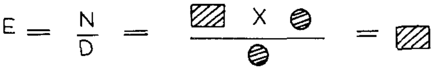

Fig. 1. Schematic representations of LCT. Square hatched box represents linked part of energy functional. Circular hatched box represents the normalization term. The disconnected top portion of the diagram of Fig. 1 is a member of the normalization term, and the bottom portion goes into the linked part of E

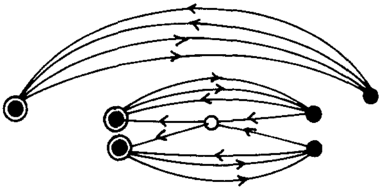

Fig. 2. Some representative diagrams of energy functional. The successive three vertices from the left are from T^+. The open circle is V. The rest are T vertices

Sinanoglu [1] we approximate T as T_2 [7, 8], and truncate the energy functional (Eq. 6) after cubic total power of T and T^+. This implies that pair, pair–pair and a large part of pair-triple correlations are taken into account. These are expected to be by far the most dominant terms of pair-correlation theories. We construct the equations diagrammatically: all the linked topologically distinct closed diagrams are considered which have at most three T and T^+ vertices. The spin integration is carried out graphically by the graphical Clebsch–Gordan coupling method [16–18]. We write a matrix-element of the form $\left\langle \begin{matrix} p & q \\ \sigma_1 & \sigma_2 \end{matrix} \middle| t_2 \middle| \begin{matrix} \alpha & \beta \\ \sigma_3 & \sigma_4 \end{matrix} \right\rangle_a$ as follows:

$$\left\langle \begin{matrix} p & q \\ \sigma_1 & \sigma_2 \end{matrix} \middle| t_2 \middle| \begin{matrix} \alpha & \beta \\ \sigma_3 & \sigma_4 \end{matrix} \right\rangle_a = \sum_{S,M} \{pq|t_2|\alpha\beta\}_s \left\langle \begin{matrix} \frac{1}{2} & \frac{1}{2} \\ \sigma_1 & \sigma_2 \end{matrix} \middle| \begin{matrix} S \\ M \end{matrix} \right\rangle \left\langle \begin{matrix} S \\ M \end{matrix} \middle| \begin{matrix} \frac{1}{2} & \frac{1}{2} \\ \sigma_3 & \sigma_4 \end{matrix} \right\rangle \tag{7}$$

where σ_i's are the spin-indices. Using the inverse transformation of Eq. (7), we can show that, for the spin-adapted matrix-elements $\{pq|t_2|\alpha\beta\}_s$, we have the relation

$$\{pq|t_2|\alpha\beta\}_s = \langle pq|t_2|\alpha\beta\rangle + (-1)^s \langle pq|t_2|\beta\alpha\rangle \tag{8}$$

for p, q particles and α, β holes, with $S = 0$ and 1. $\langle pq|t_2|\alpha\beta\rangle$ etc. are the spin-free Goldstone T_2 matrix-elements.

Up to the cubic powers of T, the spin-reduction scheme gives rise mostly to triads, and, in the most involved cases (i.e. those involving T^{+2} and T and its hermitian conjugate) products of two $9-j$'s. The non-linear equations may thus be formed directly in terms of the spin-adapted T_2 matrix-elements $\{pq|t_2|\alpha\beta\}_s$. Collecting all the T matrix elements in a column $\boldsymbol{T}$ and T^+'s in a row $\boldsymbol{T}^+$, E may be compactly written as

$$\begin{aligned} E = E_{\mathrm{HF}} + [&\boldsymbol{T}^+\boldsymbol{A}^{1,0} + \boldsymbol{A}^{0,1}\boldsymbol{T} + \boldsymbol{T}^+\boldsymbol{A}^{1,1}\boldsymbol{T} \\ &+ \boldsymbol{T}^+ \otimes \boldsymbol{T}^+\boldsymbol{A}^{2,1}\boldsymbol{T} + \boldsymbol{T}^+\boldsymbol{A}^{1,2}\boldsymbol{T} \otimes \boldsymbol{T}] \end{aligned} \tag{9}$$

where $\boldsymbol{A}^{m,n}$ is the matrix of coefficients associated with mth and nth power of T^+ and T respectively. For the approximation $T \approx T_2$, the coefficients $\boldsymbol{A}^{2,0}$ and $\boldsymbol{A}^{0,2}$ are zero as it is not possible to draw linked closed diagrams with a hamiltonian vertex and two T^+ or two T on either side of H. The energy E being a number, each term in the square bracket of Eq. (9) contains a complete sum over all the indices. To be specific, and to give a more elaborate illustration of the matrix elements of $\boldsymbol{A}^{m,n}$, we write out in long hand the $\boldsymbol{T}^+ \otimes \boldsymbol{T}^+ \boldsymbol{A}^{2,1} \boldsymbol{T}$ term below:

$$\boldsymbol{T}^+ \otimes \boldsymbol{T}^+ \boldsymbol{A}^{2,1} \boldsymbol{T} = \sum_{ijk} T_i^+ T_j^+ A^{2,1}_{ij,k} T_k \tag{10}$$

T_i is the ith element of the row matrix $\boldsymbol{T}^+$ and $T_i^+ T_j^+$ should be interpreted as the (i, j) element of a row matrix $\boldsymbol{T}^+ \otimes \boldsymbol{T}^+$. Indices i, j, k etc. are the composite indices for possible combinations of $\{pq|t_2|\alpha\beta\}_s$, with p, q particles and α, β as holes; $S = 0, 1$. From the hermitian nature of the energy expression (6), it follows that $(\boldsymbol{A}^{m,n})^+ = \boldsymbol{A}^{n,m}$. The detailed expression for Eq. (9) is given in Appendix 1. In Appendix 2, we show using one of the more involved cases, how the spin-reduction is effected.

The equations determining T's are obtained by differentiating E in Eq. (9) with respect to all the distinct $\{pq|t_2|\alpha\beta\}_s$ matrix-elements:

$$\frac{\partial E}{\partial\{pq|t_2|\alpha\beta\}_s} = 0 \tag{11a}$$

and

$$\frac{\partial E}{\partial\{\alpha\beta|t_2^+|pq\}_s} = 0 \quad \text{for all}\, p \geq q,\, \alpha \geq \beta\,;\, s = 0, 1. \tag{11b}$$

The Eqs. (11) are coupled simultaneous quadratic equations in the matrix-elements $\{pq|t_2|\alpha\beta\}_s$ and $\{\alpha\beta|t_2^+|pq\}_s$. As $\{pq|t_2|\alpha\beta\}_s = \{\alpha\beta|t_2^+|pq\}_s$, it is evident that the sets (11a) and (11b) are hermitian conjugates of each other and only one set needs to be solved with matrix-elements $\{\alpha\beta|t_2^+|pq\}_s$ equated as $\{pq|t_2|\alpha\beta\}_s$.

We now demonstrate an interesting property of the variational energy functional: if E is truncated after Kth power of T and T^+ and T's are determined variationally, then one may avoid calculation of the Kth power terms in E to get the energy. This seems to be computationally advantageous, for the number of terms tend to increase rapidly with powers of T.

The proof is straightfoward. We write the correlation energy E_c as

$$E_c = E - E_{\mathrm{HF}} = \sum_{\substack{m,n \\ m+n=1,K}} \boldsymbol{T}^+ \otimes \boldsymbol{T}^+ \otimes \cdots m \text{ times } \boldsymbol{A}^{m,n}$$

$$\boldsymbol{T} \otimes \boldsymbol{T} \otimes \cdots n \text{ times} = \sum_{\substack{m,n \\ m+n=1,K}} X^{m,n} \tag{12}$$

The quantity $X^{m,n}$ is a homogeneous polynomial of the matrix-elements of T^+ and T of degree m and n respectively. The variational equations for T and T^+ are of the form:

$$\frac{\partial E_c}{\partial T_i^+} = \sum_{\substack{m,n \\ m+n=1,K}} \frac{\partial X^{m,n}}{\partial T_i^+} = 0 \tag{13a}$$

$$\frac{\partial E_c}{\partial T_i} = \sum_{\substack{m,n \\ m+n=1,K}} \frac{\partial X^{m,n}}{\partial T_i} = 0 \tag{13b}$$

The set (13b) is hermitian conjugate of the set (13a). Multiplying Eq. (13a) by T_i^+, Eq. (13b) by T_i and summing over i, we obtain

$$\sum_{\substack{m,n \\ m+n=1,K}} \sum_i T_i^+ \frac{\partial X^{m,n}}{\partial T_i^+} = 0 \tag{14a}$$

$$\sum_{\substack{m,n \\ m+n=1,K}} \sum_i \frac{\partial X^{m,n}}{\partial T_i} T_i = 0 \tag{14b}$$

Using Euler's theorem for homogeneous polynomials:

$$\sum_i T_i^+ \frac{\partial X^{m,n}}{\partial T_i^+} = m \cdot X^{m,n} \tag{15a}$$

$$\sum_i \frac{X^{m,n}}{T_i} \cdot T_i = n \cdot X^{m,n} \tag{15b}$$

in Eqs. (14a) and (14b), and adding them together, we have

$$\sum_{\substack{m,n \\ m+n=1,K}} (m+n) X^{m,n} = 0 \tag{16}$$

which may be rewritten as

$$\sum_{\substack{m,n \\ m+n=1,K-1}} (m+n) X^{m,n} + K \sum_{m=0,K} X^{K-m,m} = 0 \tag{17}$$

Using Eq. (17), we may eliminate the $(m+n)=K$ terms in Eq. (12) in favour of the lower order quantities:

$$E_c = \sum_{r=1,K-1} \frac{K-r}{K} \sum_{m=0,r} X^{r-m,m} \tag{18}$$

An interesting side-line of the above observation is that, up to quadratic terms in E, E_c would be given by

$$E_c^{(2)} = \tfrac{1}{2}[\boldsymbol{A}^{0,1}\boldsymbol{T} + \boldsymbol{T}^+\boldsymbol{A}^{1,0}] = \boldsymbol{A}^{0,1}\boldsymbol{T} \tag{19}$$

where $(\boldsymbol{A}^{1,0})^+ = \boldsymbol{A}^{0,1}$ has been used. This is essentially the result of the linearised nonvariational coupled-cluster theory of Cizek [7]. Recently it has been shown to possess an interesting bound property [19]. No such simple correspondence with the nonvariational coupled-cluster theory could be discerned, however, after the cubic terms are brought in.

As the second line of development, we have also evaluated the energy functional by substituting the value of T matrix-elements obtained from the nonvariational coupled-cluster theory in Eq. (6) to get an idea regarding how close the correspondence is between the variational and the nonvariational results. As for the nonvariational T's and Eqs. (13a) and (13b) do not hold, we no longer have the simpler results, Eq. 18. Thus, the use of VPA simplifies the resulting expression for the size-consistent energy functional.

3. Results and Discussion

The formalisms presented here have been applied to a set of heterocyclic compounds in a PPP framework. The results for the correlation energy up to cubic total power of T^+ and T are shown in Table 1. The Table contains (1) variational results retaining up to cubic and quadratic total power of T^+ and T (the latter is equivalent to the linearised non-variational coupled-cluster method) (2) results from a calculation in which non-linear nonvariational T matrix elements from Cizek's C-C theory are simply substituted in the energy functional (Eq. (6)) (3) results from nonlinear non-variational coupled-cluster method for comparison (4) results from a CI containing all double excitation (these essentially involve the same number of variable parameters as in (1) and (2); and (5) full CI results for comparison. A perusal of the Table shows that the variational C-C theory up to cubic terms provides results near the values generated by (2) and also both are rather close to the non-variational non-linear results (3). Computationally, the variational method and the approach (2) are rather comparable: The equations determining T would have some additional terms in variational method, but in energy the third order terms would not have to be explicitly computed – as implied by Eq. (18), a simplification not possible for (2) where T's have been computed by a non-variational procedure. All the results are substantially different from the size-inconsistent "doubles only" CI involving the same number of parameters. The results are often slightly lower than the full CI values indicating that truncation of the linked energy functional leads to a loss of upper bound property. This was first observed in nuclear calculations using the cluster expansion method using Jastrow function and is known as the "Energy difficulty" [20]. The results indicate that this, however, may not be serious. Formally speaking, the loss of the bound property stems essentially from the fact that the truncated series for E, written as a single power series of T, does not correspond to an expectation value like quantity *having polynomials of some fixed finite degree appearing in numerator and denominator.* If, however, the dominant terms contributing to the energy functional are retained in the truncated series, the energy thus calculated would be very close to the exact energy and thus would very nearly be stationary. It is thus meaningful to postulate an Euler principle for the truncated functional. Sinanoglu has also advocated

Table 1. Correlation energy in ev of some heterocyclic compounds in PPP framework

Molecule	Variation results up to cubic terms	Variational results up to quadratic terms[a]	Results with non-linear non-variational T's substituted into the energy expression	Non-linear non-variational coupled-cluster results	"Double only CI"	Full CI
Pyridazine	1.20071	1.28450	1.19669	1.23962	0.96035	1.13562
Pyrazine	1.15116	1.22511	1.14790	1.18568	1.03623	1.08354
Pyridine	1.13718	1.20960	1.13389	1.17100	1.02236	1.06990
Pyrimidine	1.13595	1.20762	1.13276	1.16951	0.80539	1.07645
Tetrazine	1.29028	1.38870	1.28462	1.33535	1.16426	1.23236

[a] This is equivalent to the linearised non-variational coupled-cluster results.

the same recipe in connection with a variational determination of the pair-function appearing in the theory of electron correlation which he has termed the "varied portion approach" [2]. Closeness of our results with the full CI values indicates that the dominant terms have been included in our truncated energy functional. As the terms which would have restored the upper bound property appear in fourth order and beyond in perturbation theory, the discrepancy should not be very serious [23].

In view of the lack of a consistent wave-function for a truncated energy series of Eq. (6), it is not immediately apparent that the resulting one particle density preserves the particle number. This, however, may be proved in the following manner. From Eq. (6), it follows that the one particle density is of the form

$$\rho_1 = \rho_{1\mathrm{HF}} + \rho_{1corr}$$

where $\rho_{1\mathrm{corr}}$ is the correlation component coming from T^+/T containing terms. Noting that $tr\rho_{1\mathrm{HF}} = N$, the particle number, we have to show that $tr\rho_{1corr} = 0$. The component $\sum_\alpha [\rho_{1corr}]_{\alpha\alpha}$ for the holes in the trace are the coefficients of the terms containing T^+/T vertices sandwiching the bare one-body operators $h_{\alpha\alpha}$. Its value is numerically equal to all closed connected diagrams containing T^+/T vertices, but with an additional negative sign, because insertion of an $h_{\alpha\alpha}$ vertex increases hole lines by one. The component $\sum_p [\rho_{1corr}]_{pp}$, however, has exactly the value of the T^+/T closed diagrams, because insertion of a h_{pp} vertex leaves number of hole lines unaltered. The total trace of ρ_{1corr} thus becomes zero due to mutual cancellation.

To study the effect of truncation of the rank of T we have done another set of calculations including T_1 operators as well on some of the systems. These results are summarised in Table 2. As may be seen that, as expected, while the correction is in the proper direction the effect of T_1 is not significant.

We conclude the paper with a brief discussion concerning the relation of the variational formalism with other works. Kutzelnigg [21] has suggested the use of a unitary wave-operator of the form exp $(T - T^+)$. Such a waveoperator would, by Housdorff formula lead to a linked cluster expansion automatically [22]. If his T is chosen to be only of hole-particle excitation type, then his multi-commutator expansion would be structurally similar to ours, though the wavefunction and the consequent interpretations would be very different. Kutzelnigg's wave-function has a normalisation correction to the coefficient of Φ_0 while

Table 2. Effect of truncation in the rank of T on correlation energy on same heterocyclic compounds in PPP framework

	Variational results with		
Molecule	$T = T_2$	$T = T_1 + T_2$	FCI
Pyrazine	1.15116 ev	1.14389 ev	1.0835 ev
Tetrazine	1.29028 ev	1.27883 ev	1.2323 ev
Pyrimidine	1.13595 ev	1.11304 ev	1.0764 ev

our ansatz exp $(T)\phi_0$ implies an "intermediate normalization" convention:

$$\langle\Phi_0|\exp(T)|\Phi_0\rangle = 1 \tag{20}$$

reminiscent of perturbation theory. It is worth noting here that the unitary [21, 22] ansatz would also entail Emery difficulty due to truncation. Nakatsuji's [12] variational formalism within the coupled-cluster framework involves both the numerator and denominator and thus lacks size-consistency. Paldus et al. [10] have developed a mixed variational procedure to study the energy differences. Starting from an exact wavefunction obtained from non-variational coupled-cluster theory, they introduce a composite operator $S \exp(T)$ to create the ion from ϕ_0 and vary the energy functional with respect to the S matrix elements. Paldus et al. have proved a linked cluster theorem containing both numerator and denominator and it thus has a totally different algebraic structure.

Generalization of the linked-cluster theorem for open-shells using an operator of the form $N[\exp(T)]$ acting on a set of degenerate reference functions is under way [24]. These will be communicated in due course.

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Appendix 1

The energy expression given in Eq. (15) symbolically in matrix form may be written as follows:

$$\begin{aligned}
E = E_{\mathrm{HF}} &+ \tfrac{1}{2} \sum_{\substack{\alpha,\beta,p,q\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{\alpha\beta|v|pq\}_\sigma (2\sigma+1)\\
&+ \tfrac{1}{2} \sum_{\substack{\alpha,\beta,p,q,\gamma\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{rq|t_2|\alpha\beta\}_\sigma \langle r|f|p\rangle (2\sigma+1)\\
&- \tfrac{1}{2} \sum_{\substack{\alpha,\beta,\gamma,p,q\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{pq|t_2|\alpha\gamma\}_\sigma < \beta|f|\gamma\rangle (2\sigma+1)\\
&+ \tfrac{1}{8} \sum_{\substack{\alpha,\beta,p,q,r,s\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{rs|t_2|\alpha\beta\}_\sigma \{pq|v|rs\}_\sigma (2\sigma+1)\\
&+ \tfrac{1}{8} \sum_{\substack{\alpha,\beta,\gamma,\sigma,p,q\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{pq|t_2|\gamma\delta\}_\sigma \{\alpha\beta|v|\gamma\delta\}_\sigma (2\sigma+1)\\
&+ \tfrac{1}{16} \sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{rs|t_2|\gamma\delta\}_\sigma \{rs|t_2|\alpha\beta\}_\sigma \{\gamma\delta|v|pq\}_\sigma (2\sigma+1)\\
&+ \tfrac{1}{16} \sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s\\ \sigma}} \{pq|t_2|\alpha\beta\}_\sigma \{rs|t_2|\gamma\delta\}_\sigma \{pq|t_2|\gamma\delta\}_\sigma \{rs|v|\alpha\beta\}_\sigma (2\sigma+1)
\end{aligned}$$

$$-\tfrac{1}{8}\sum_{\substack{\alpha,\beta,\gamma,\delta\\ p,q,r,s\\ \sigma_i,\sigma_j}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{ps|t_2|\gamma\delta\}_{\sigma_j}\{rq|t_2|\alpha\beta\}_{\sigma_i}\{rs|v|\gamma\delta\}_{\sigma_j}(2\sigma_i+1)(2\sigma_j+1)$$

$$-\tfrac{1}{8}\sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s,\\ \sigma_i,\sigma_j}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{rs|t_2|\beta\delta\}_{\sigma_j}\{pq|t_2|\alpha\gamma\}_{\sigma_i}\{\gamma\delta|v|rs\}_{\sigma_j}(2\sigma_i+1)(2\sigma_j+1)$$

$$-\tfrac{1}{8}\sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s,\\ \sigma_i,\sigma_j}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{rs|t_2|\gamma\delta\}_{\sigma_j}\{rq|t_2|\alpha\beta\}_{\sigma_i}\{ps|v|\gamma\delta\}_{\sigma_j}(2\sigma_i+1)(2\sigma_j+1)$$

$$-\tfrac{1}{8}\sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s,\\ \sigma_i,\sigma_j}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{rs|t_2|\gamma\delta\}_{\sigma_j}\{pq|t_2|\alpha\gamma\}_{\sigma_i}|\beta\delta|v|rs\}_{\sigma_j}(2\sigma_i+1)(2\sigma_j+1)$$

$$+\tfrac{1}{2}\sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s,\\ \sigma_i,\sigma_j,\sigma_k,\sigma_l,\sigma_m}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{rq|t_2|\gamma\beta\}_{\sigma_j}\{ps|t_2|\alpha\delta\}_{\sigma_k}\{\delta\gamma|v|sr\}_{\sigma_l}(2\sigma_i+1)$$

$$\times(2\sigma_j+1)(2\sigma_k+1)(2\sigma_l+1)\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \sigma_i\\ \sigma_m & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \sigma_j & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \sigma_l\\ \sigma_m & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \sigma_k & \frac{1}{2}\end{Bmatrix}$$

$$+\tfrac{1}{2}\sum_{\substack{\alpha,\beta,\gamma,\delta,\\ p,q,r,s,\\ \sigma_i,\sigma_j,\sigma_k,\sigma_l,\sigma_m}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{rq|t_2|\gamma\beta\}_{\sigma_j}\{rs|t_2|\gamma\delta\}_{\sigma_k}\{\delta\alpha|v|sp\}_{\sigma_l}$$

$$\times(2\sigma_i+1)(2\sigma_j+1)(2\sigma_k+1)(2\sigma_l+1)\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \sigma_i\\ \sigma_m & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \sigma_j & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \sigma_l\\ \sigma_m & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \sigma_k & \frac{1}{2}\end{Bmatrix}$$

$$+\sum_{\substack{\alpha,\beta,\gamma,\\ p,q,r,\\ \sigma_i,\sigma_j,\sigma_k}}\{pq|t_2|\alpha\beta\}_{\sigma_i}\{pr|t_2|\alpha\gamma\}_{\sigma_k}\{q\gamma|v|\beta r\}_{\sigma_j}$$

$$\times(2\sigma_i+1)(2\sigma_j+1)(2\sigma_k+1)\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & \sigma_i\\ \sigma_k & \frac{1}{2} & \frac{1}{2}\\ \frac{1}{2} & \sigma_j & \frac{1}{2}\end{Bmatrix}.$$

The indices α, β etc. are hole orbitals, p, q etc. are particle orbitals; σ_i, σ_j are coupled spins and $\begin{Bmatrix}a & b & c\\ d & e & f\\ g & h & i\end{Bmatrix}$ are $g-j$ symbols, f is the $H-F$ operator and v is the two-body repulsion operator.

Appendix 2

We shall briefly indicate here the spin-adaption procedure of a rather involved third order term containing $\boldsymbol{T}^{+}\otimes\boldsymbol{T}^{+}\mathrm{A}^{2,1}\boldsymbol{T}$. We take both the T matrix-elements and the two-body matrix-elements of the Hamiltonian H to be antisymmetrized

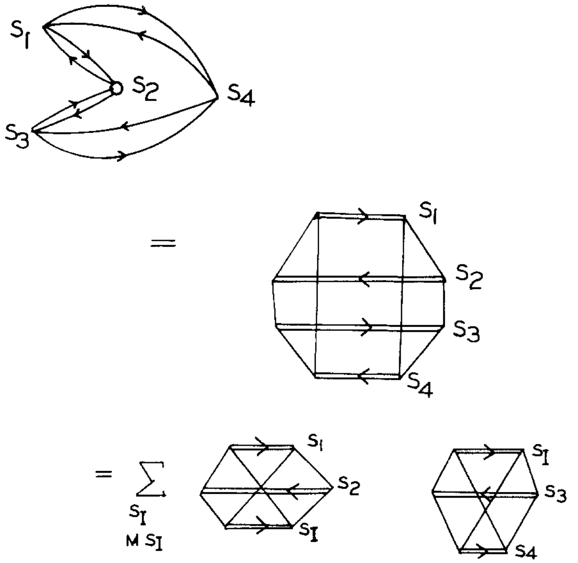

Fig. 3. Spin reduction of third order terms leading to two 9-J symbols

(i.e. of Hugenholtz-type), so that the so called "direct" and "exchange" terms are grouped together – leading to an effective reduction of the number of diagrams. The spin reduction procedure would, however, lead to a higher rank $n-j$ symbol in such a choice. It appears that a diagram of m total vertices may in the most involved case yield a $3m-j$ symbol. In the particular illustrative example, shown in Fig. 3 a 12-j symbol appears which we break down into a sum of products of two 9-j symbols for a convenient evaluation.

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