

On certain correspondences among various coupled-cluster theories for closed-shell systems

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Abstract. In this paper certain correspondences have been shown among various formulations of coupled-cluster theories for many electron closed-shell systems. Specifically it is shown that (i) the energy functional using unitary ansatz of the form $\exp(T-T^+)$ is exactly same order by order in T with the size-consistent energy functional $\langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle$ recently obtained by us in coupled-cluster framework; (ii) in the framework of unitary ansatz of the form $\exp(T-T^+)$, both non-variational and variational approaches lead to identical equations upto any given order in T and T^+ in $T \sim T_2$ approximation; (iii) variational procedure using our size-consistent energy functional or using the functional obtained in the framework of unitary ansatz (as envisaged by Kutzelnigg) leads to energy in both cases, in $T \sim T_2$ approximation, for a total of quadratic powers in T and T^+ , same as Cizek's linearised coupled pair many electron theory energy; (iv) in case of practical calculation of the energy through the variational procedures using our size-consistent energy functional and the functional in unitary ansatz framework, there is a loss of upper bound.

Keywords. Coupled-cluster theories; many body theory; size-consistency; atoms; molecules.

1. Introduction

The variational principle has, for a long time, been a key method for finding the approximate solutions to the eigenfunctions for a many-electron system. In its simplest application, for a form of the single-determinantal trial wavefunction, we get the Hartree-Fock (H-F) wavefunction. The H-F function, as is well-known, does not describe the electronic correlation. There have been many independent developments, either in the variational or other frameworks, of various post H-F methods to take account of the correlation effects. Configuration interaction (CI) procedure in the variational approach is one of the simplest methods to achieve this goal. An approximate CI function, however, lacks 'size-consistency'—an important desirable property of the wavefunction which shows additivity of energy for non-interacting fragments. A very appealing approach preserving size-consistency for even an approximate function is the coupled-cluster (C-C) formalism, first adapted in nuclear physics by Coester and Kummel (Coester 1958; Coester and Kummel 1960; Kummel 1962) and then in atomic and molecular physics by Cizek (1966, 1969) in which the correlated wavefunction $|\psi_{gr}\rangle$ is described as an action of an exponential operator $\exp(T)$ on the Hartree-Fock function $|\phi_{HF}\rangle$,

$$T = \sum_{i=1}^N T_i \quad (1)$$

for an N -electron system. T_i acting on the Hartree-Fock wavefunction generates i -fold linked excitations. Taking cue from 'the dominance of pair-correlation' idea of the 'many electron theory' of Sinanoğlu (Sinanoğlu 1962, 1964) T is approximated as T_2 and the quadruple excitation amplitudes are simulated as $T_2^2 |\phi_{\text{HF}}\rangle$. The cluster components of T_2 were obtained first by Cizek in the atomic and molecular physics for closed-shell systems in the non-variational framework using the method of moments (Cizek 1966, 1969). This has been known as the coupled pair many electron theory (CPMET). This non-variational theory yields a size-consistent energy expression automatically for truncation of the energy series in T .

For a variational adaptation of the c-c ansatz involving the energy functional $\langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$, size-consistency is not automatically guaranteed for a truncation of the series in T . Only certain specific ways of handling the functional preserve the size-consistency. The crux of the problem lies in the proper treatment of the norm $\langle \psi | \psi \rangle$. Unless the full expansion $\exp(T)$ is used *both* for the numerator and denominator, the energy functional, just as in a 'less than full' CI approach, would lack size-consistency. Following Primas (Primas 1961) and Van Vleck (Van Vleck 1929), Kutzelnigg cast the c-c theory in a variational framework using a unitary exponential wave operator $\exp(\sigma)$, where σ is anti-hermitian (Kutzelnigg 1977) satisfying size-consistency. In this case the norm $\langle \psi | \psi \rangle$ is unity. A parallel non-variational treatment using unitary ansatz to the theory of Cizek (Cizek 1966, 1969) has also been envisaged (Westhaus 1973; Mukherjee *et al* 1975, 1977).

Recently we have attempted to develop an alternative rigorous treatment for the closed-shell system using the original non-unitary c-c ansatz $\exp(T)$ which also preserves size-consistency (Pal *et al* 1982). Unlike that in a unitary ansatz, the denominator in this case is not identically equal to unity and as such in a general coupled-cluster framework the denominator has to be explicitly cancelled to give the functional $\langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$ a linked and size-consistent property. We have been able to show the cancellation of such a denominator and thus give the energy functional the desirable linked property. Thus we could establish a rigorous treatment of the coupled-cluster ansatz in the variational form.

The purpose of this paper is to lay down certain correspondences we have noted during the development of the above theory among the following energy functionals for closed-shell systems. They are (a) the energy functional obtained in the unitary ansatz framework (b) the energy functional obtained by us and (c) energy obtained by Cizek in the non-variational framework. Specifically, we want to show the following interesting features obtained as a result of our studies:

- (i) The energy functional using a unitary ansatz of the form $\exp(T - T^+)$ is exactly same *order by order* in T with the size-consistent energy functional obtained by us, with T chosen as hole-particle excitation operators.
- (ii) In the framework of unitary coupled-cluster ansatz of the form $\exp(T - T^+)$ with T approximated as T_2 , if a non-variational procedure is used to solve the T -matrix elements upto any total power in T and T^+ ,* the equations are identical to the equations upto the same order obtained by the Euler variation of the energy functional and hence as such the energies obtained by both these

*From now on, we shall, for brevity, write ' m th power in T ' when we want to mean m th total power of T and T^+ .

procedures in the unitary cluster framework are the same upto any given order in T .

- (iii) In a variational procedure for the solution of T -matrix elements from the size-consistent energy functional (using a non-unitary C-C ansatz) in $T \sim T_2$ approximation, truncated to a quadratic power in T_2 (Pal *et al* 1982), the energy calculated upto quadratic approximation is the same as the linearised CPMET (L-CPMET) energy of Cizek (Cizek 1966, 1969). Hence such an energy has a lower bound property, as proved recently (Mukherjee 1981). Similarly if a variation is done on the functional in the unitary ansatz (Kutzelnigg 1977), truncated to quadratic power in T_2 , the energy obtained is again the same as the L-CPMET energy of Cizek and hence possesses a lower-bound property.
- (iv) For practical calculation of T -matrix elements in the variational procedure using either a unitary ansatz or a general non-unitary ansatz, truncation of the linked functional is necessary and the energy thus calculated in either of these frameworks lacks a strict upper bound property. This is known as the 'Emery difficulty' (Emery 1958; Bell and Squires 1962) in nuclear physics literature.

In § 2 we briefly review the three kinds of coupled-cluster approaches we want to see correspondence between. In § 3, we show the explicit correspondences as mentioned in (i) to (iii) above.

2. Brief review of the C-C approaches

The most widely known solution of the coupled-cluster matrix elements was done by Cizek using method of moments in the non-variational procedure (Cizek 1966, 1969). The ground state of the closed-shell wavefunction is written as

$$|\psi_{gr}\rangle = \exp(T) |\phi_{HF}\rangle, \quad (2)$$

with T involving hole-particle excitations only. The solution of the T -matrix elements were obtained by projecting $\exp(-T) H \exp(T) |\phi_{HF}\rangle$ on to the various excited states reached by T . In $T \sim T_2$ approximation only the doubly excited states are sufficient for projection to get the necessary equations. Energy can then be written as

$$E = \langle \phi_{HF} | \exp(-T) H \exp(T) | \phi_{HF} \rangle. \quad (3)$$

In the approximation $T \sim T_2$ if the energy is solved upto linear approximation, the energy thus obtained is L-CPMET energy.

The unitary coupled-cluster ansatz can be used to describe the exact correlated wavefunction

$$|\psi_{gr}\rangle = \exp(\sigma) |\phi_{HF}\rangle, \quad (4)$$

σ being anti-hermitian. The idea of using a unitary ansatz was first conceived by Van Vleck and then by Primas (Van Vleck 1929; Primas 1961). A special choice of σ may be of the form $\sigma = T - T^+$. One can adopt a non-variational procedure, akin

to Cizek's theory, to solve for the T -matrix elements (Westhaus 1973; Mukherjee *et al* 1977; Van Vleck 1929). We then get the following system of equations

$$\begin{aligned} & \langle \phi_{\text{ex}} | \exp(-\sigma) H \exp(\sigma) | \phi_{\text{HF}} \rangle \\ & = \langle \phi_{\text{ex}} | \exp(T^+ - T) H \exp(T - T^+) | \phi_{\text{HF}} \rangle = 0, \end{aligned} \quad (5)$$

for a set of ϕ_{ex} which are generated by all possible excitations from the Hartree-Fock determinant. In the $T \sim T_2$ approximation, we again need to consider projections on to the doubly excited determinants only. Energy can then be found upto any given order from the expression

$$E = \langle \phi_{\text{HF}} | \exp(T^+ - T) H \exp(T - T^+) | \phi_{\text{HF}} \rangle. \quad (6)$$

On the other hand, a variational procedure using the unitary ansatz can also be applied as suggested by Kutzelnigg (Kutzelnigg 1977). The Euler functional in this framework is given by

$$E = \frac{\langle \phi_{\text{HF}} | \exp(-\sigma) H \exp(\sigma) | \phi_{\text{HF}} \rangle}{\langle \phi_{\text{HF}} | \exp(-\sigma) \exp(\sigma) | \phi_{\text{HF}} \rangle}, \quad (7)$$

for the wavefunction described by (4). The denominator *taken to all orders* is identically equal to 1. Hence the denominator is automatically cancelled, leaving the energy functional as just

$$E = \langle \phi_{\text{HF}} | \exp(-\sigma) H \exp(\sigma) | \phi_{\text{HF}} \rangle. \quad (8)$$

By Hausdorff's expansion such a functional is automatically linked and hence size-consistent. The linked cluster nature of the energy functional using the unitary cluster ansatz has been indicated earlier (Westhaus 1973; da Providencia 1963, 1965; Westhaus *et al* 1975; Yaris 1964, 1965). Just as in the non-variational theory, one can again choose σ as $\sigma = T - T^+$ such that the energy functional (8) becomes

$$E = \langle \phi_{\text{HF}} | \exp(T^+ - T) H \exp(T - T^+) | \phi_{\text{HF}} \rangle. \quad (9)$$

Kutzelnigg suggested a variational procedure to solve the T -matrix elements by invoking the Euler variation principle to the functional (9).

Recently we established another form of the size-consistent energy functional in the general coupled-cluster framework (not using an explicit unitary ansatz) which can be used for Euler variation (Pal *et al* 1982). We used an exponential ansatz such that

$$| \psi_{\text{gr}} \rangle = \exp(T) | \phi_{\text{HF}} \rangle. \quad (10)$$

T again involving hole-particle excitations of different ranks. Euler energy functional can be written as

$$E = \frac{\langle \phi_{\text{HF}} | \exp(T^+) H \exp(T) | \phi_{\text{HF}} \rangle}{\langle \phi_{\text{HF}} | \exp(T^+) \exp(T) | \phi_{\text{HF}} \rangle}. \quad (11)$$

Unlike in the case of unitary cluster the denominator cancellation is not automatic here. The norm correction term in the denominator is not trivially equal to unity. Thus the linked cluster nature of the functional (11) has to be explicitly proved. Only such a linked functional could then be useful. In what follows we shall show the functional (11) to be linked leading to

$$E = \langle \phi_{\text{HF}} | N [\exp(T^+) H \exp(T)] | \phi_{\text{HF}} \rangle_{\text{L, CI}} \quad (12)$$

where L, CI denotes linked and closed diagrams. N denotes normal ordering. The proof is reminiscent of the proof of the linked cluster theorem of the many body perturbation theory (Goldstone 1957). The linked nature of this kind of functional in a perturbative framework has also been indicated by Thouless (1961). We now show the linked nature of the energy functional (11). We first take the numerator and expand it using the generalised Wick's theorem (GWT) so that the numerator becomes the sum of all contractions between all possible powers of T^+ and T and H vertices.

$$\text{Numerator} = \sum_{m,n}^{\infty} \frac{1}{m!} \frac{1}{n!} \langle \phi_{\text{HF}} | N [T^{+m} H T^n] | \phi_{\text{HF}} \rangle_{\text{L, CI}} \quad (13)$$

For choosing all possible contractions for any terms corresponding to m number of T^+ - vertices and n number of T -vertices we first take out k -number of T^+ vertices, and l - number of T vertices in all possible manner and contract them with the hamiltonian vertex. T operators cannot contract among themselves as they are all of hole-particle excitation types. Similarly T^+ 's cannot contract among themselves. The rest of the $(m-k)$ number of T^+ vertices and $(n-l)$ number of T vertices are contracted together so that the numerator becomes

$$\begin{aligned} \text{Numerator} = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{k=0}^m \sum_{l=0}^n \frac{1}{m!} \frac{1}{n!} {}^m C_k {}^n C_l \langle \phi_{\text{HF}} | \overbrace{T^{+k} H T^l} | \phi_{\text{HF}} \rangle_{\text{Linked, closed}} \times \\ \langle \phi_{\text{HF}} | \overbrace{T^{+m-k} T^{n-l}} | \phi_{\text{HF}} \rangle. \end{aligned} \quad (14)$$

This can be written as,

$$\begin{aligned} \text{Numerator} = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{k=0}^m \sum_{l=0}^n \frac{1}{k!} \frac{1}{l!} \frac{1}{(m-k)!} \frac{1}{(n-l)!} \langle \phi_{\text{HF}} | \overbrace{T^{+k} H T^l} | \phi_{\text{HF}} \rangle_{\text{Linked, closed}} \\ \times \langle \phi_{\text{HF}} | \overbrace{T^{+m-k} T^{n-l}} | \phi_{\text{HF}} \rangle, \end{aligned} \quad (15)$$

Since,

$$\frac{1}{(m-k)!} = 0 \quad \text{for } k > m, \quad (16)$$

and,

$$\frac{1}{(n-l)!} = 0 \quad \text{for } l > n. \quad (17)$$

We can rewrite the series as

$$\begin{aligned} \text{Numerator} = & \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{1}{k!} \frac{1}{l!} \frac{1}{r!} \frac{1}{s!} \langle \phi_{\text{HF}} | \overbrace{T^{+k} H T^l} | \phi_{\text{HF}} \rangle_{\text{Linked, closed}} \\ & \times \langle \phi_{\text{HF}} | \overbrace{T^{+r} T^s} | \phi_{\text{HF}} \rangle, \end{aligned} \tag{18}$$

[defining $(m - k)$ as r and $(n - l)$ as s .]

The factor $\sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \frac{1}{r!} \frac{1}{s!} \langle \phi_{\text{HF}} | \overbrace{T^{+r} T^s} | \phi_{\text{HF}} \rangle$ is the same as the denominator if the denominator is similarly expanded using GWT. Hence the denominator is cancelled leaving the energy functional as that in (12).

3. Correspondences

First we show that our size-consistent energy functional (12) is exactly same *order by order in T* as the energy functional (6) or (9). The functional (12) when expanded is merely

$$E = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m!} \frac{1}{n!} \langle \phi_{\text{HF}} | \overbrace{T^{+m} H T^n} | \phi_{\text{HF}} \rangle_{\text{Linked, closed}} \tag{19}$$

Each term in the series expansion gives contribution for $(m + n)$ th power of T . The functional (8) in the unitary ansatz when expanded by Hausdorff's formulae gives

$$\begin{aligned} E = & \langle \phi_{\text{HF}} | H | \phi_{\text{HF}} \rangle + \langle \phi_{\text{HF}} | [H, \sigma] | \phi_{\text{HF}} \rangle \\ & + \frac{1}{2!} \langle \phi_{\text{HF}} | [[H, \sigma], \sigma] | \phi_{\text{HF}} \rangle + \dots \end{aligned} \tag{20}$$

If we substitute σ as $T - T^+$ in (20) we get the corresponding expansion for the functional (6) or (9). We note that because of (20) the energy functional (6) or (9), as in the case of (12), leads only to linked, closed contribution of T^+, H, T vertices. Because of the multicommutator expansion, for each term we must evaluate the innermost commutator first and then the commutator of the resultant operator with the next σ and so on. Since T^+ cannot contract with anything to its left and T cannot contract with anything to its right each commutator would ensure that there is no T vertex to the left of H and no T^+ vertex to the right of H such that when term by term we go on evaluating higher order commutator only linked terms of the nature of $\overbrace{T^{+m} H T^n}$ would survive for $(m + n)$ number of σ 's appearing in a multicommutator term. Let us now investigate the factor for such an expression.

As is evident in the Hausdorff's formulae if we have a total of $(m + n)$ number of σ 's or $(m + n)$ total number of T and T^+ vertices appearing in any term of the multi-commutator expansion, the factor for the Housdorff's formulae is $1/(m + n)!$. Out of these total of $(m + n)$ number of T^+ and T vertices if we choose m number of T^+ vertices and n number of T vertices for contraction, the number of ways we can choose is $(m + n)C_m$. Hence the total factor corresponding to such a term which can arise out of contributions from linked terms of $T^{+m} H T^n$ is $1/m!n!$. Hence order by order in T the size-consistent energy functional (12) is identical to the functional (6) or (9) in unitary ansatz framework.

We now go ahead to show the correspondence (ii) as mentioned in § 1. We have already mentioned that in the framework of unitary ansatz the energy functional in the non-variational procedure as given in (6) is identical to the Euler functional used for variation as given in (9). In the non-variational procedure the T -matrix elements are obtained by the system of equations given by (5). In $T \sim T_2$ approximation diagrams representing the non-variational equations which arise out of projection of $\exp(T^+ - T) H \exp(T - T^+)$ on to the doubly excited states, are linked and have two hole and two particle lines left open. On the other hand variation of the functional (9) with respect to T_2 or T_2^+ matrix elements may be looked upon as a deletion of T_2 or T_2^+ vertex leading to diagrams with two-hole and two-particle lines left open and the same factor arising out of the functional (9). We note here that since the set of T_2 and T_2^+ matrix elements are hermitian conjugates to each other, the variation with respect to one set of elements (say T_2^+) is sufficient. Figure 1 shows a typical term of the closed-linked functional (9) and figure 2 shows the effect of the variation with respect to a T_2^+ vertex. If rank of T is same, (i.e. say, if only T_2 vertices and T_2^+ vertices are used) there are no T^+ vertices joined entirely to T vertices or vice-versa in the functional (9). Otherwise we will have unlinked terms. Figure 1 shows a term showing T_2^+ vertices joined to T_2 vertices through the linkage of H . In such a case as in $T \sim T_2$ approximation, variation or deletion of a T^+ or T vertex leaves the rest of the diagram open but still linked such that the total contribution through variation of (9) upto any order in T is same as the non-variational eq. (5) upto the same order in T . Hence the subsequent energies calculated by (6) and (9) upto a given order in T

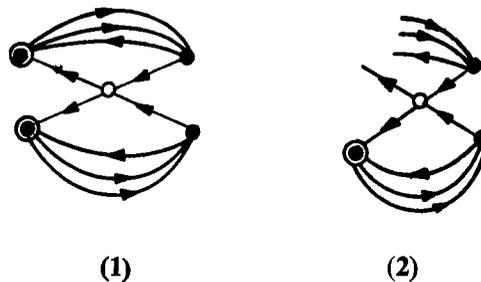


Figure 1. A representative diagram of the energy functional (9). The two vertices from left are T^+ vertices, the open circle is V . The rest two shaded circles at the right are T vertices. Arrows pointing to the left represent particle lines, arrows to the right represent hole lines.

Figure 2. Effect of variation with respect to a T^+ vertex to the diagram represented by figure 1. This generates the corresponding term arising out of the variation of the energy functional (9) with respect to a T^+ vertex. The left vertex is T^+ vertex, the open circle is V . The last two shaded vertices at the right are T -vertices. Again the arrows pointing to the left represent particle lines, the arrows pointing to the right represent hole lines.

in the non-variational and variational procedures respectively in the framework of unitary ansatz are same. This simple correspondence breaks down when T_1 or T_3 terms also are brought in. If T_1 or T_3 terms are used along with T_2 , the rank of T is no longer same and hence the above arguments will not hold.

Now we show an interesting correspondence of the size-consistent energy functional (12) with L-CPMET energy of Cizek. If we truncate the functional upto a total of quadratic powers in T^+ in $T \sim T_2$ approximation and solve for the matrix elements of T_2 by employing an Euler variation and then substitute the T_2 -matrix elements in the functional, the energy thus obtained upto quadratic powers in T_2 is identically equal to Cizek's L-CPMET energy. For showing this, we write the expansion of E in (12) upto quadratic powers in T in $T \sim T_2$ approximation as

$$E = E_{\text{HF}} + \underline{\underline{T_2^+}} A^{1,0} + \underline{\underline{A^{0,1}}} T_2 + \underline{\underline{T_2^+}} \underline{\underline{A^{1,1}}} T_2 \quad (21)$$

where $\underline{\underline{T_2}}$ and $\underline{\underline{T_2^+}}$ are matrices containing various hole-particle excitation amplitudes like $\langle pq | t_2 | \alpha \beta \rangle$ and $\langle \alpha \beta | t_2^+ | pq \rangle$ for p, q particles, α, β holes. and $\underline{\underline{A^{m,n}}}$ is the matrix of coefficients associated with m number of T^+ vertices and n number of T -vertices when linked expectation value is evaluated. From the hermitian nature of (11) it follows that $(A^{m,n})^+ = A^{n,m}$. Differentiating E in (21) with respect to T_2^+ matrix elements and equating it to zero we get the following system of equations,

$$\frac{\partial E}{\partial \langle \alpha \beta | t_2^+ | pq \rangle} = 0, \quad (22)$$

for p, q particles and α, β holes.

or,

$$\underline{\underline{A^{1,0}}} + \underline{\underline{A^{1,1}}} T_2 = 0 \quad (23a)$$

The number of such equations is exactly equal to the total number of matrix elements of T_2 . Similarly we get another set of equations by differentiating with respect to T_2 matrix elements

$$\underline{\underline{A^{0,1}}} + \underline{\underline{T_2^+}} \underline{\underline{A^{1,1}}} = 0. \quad (23b)$$

The set (23a) is hermitian conjugate of (23b). Premultiplying (23a) by the matrix $\underline{\underline{T_2^+}}$, we get

$$\underline{\underline{T_2^+}} \underline{\underline{A^{1,0}}} + \underline{\underline{T_2^+}} \underline{\underline{A^{1,1}}} T_2 = 0. \quad (24)$$

Equation (24) can be used in (21) so that E in this approximation can be written as

$$E = E_{\text{HF}} + \underline{\underline{A^{0,1}}} T_2. \quad (25)$$

Hence upto quadratic powers the correlation energy

$$E_c^{(2)} = \underline{\underline{A^{0,1}}} T_2. \quad (26)$$

This is essentially the result of the linearised coupled-cluster theory of Cizek in the non-variational framework. No such simple correspondence exists when cubic terms are brought in. Since the L-CPMET energy has been shown to possess a lower bound nature (Mukherjee 1981), the energy obtained from variation of the size-consistent energy functional (12) under approximations (truncations upto quadratic powers in T_2) also has a lower bound property.

Since the energy functional (9) in unitary ansatz framework is identical to the functional (12) *order by order* in T , a similar variation of the functional (9) in unitary ansatz framework truncated to quadratic powers in T in $T \sim T_2$ approximation leads to L-CPMET energy and hence has a lower bound property.

We now illuminate on the point (iv) mentioned in §1. For practical evaluation of the T -matrix elements by Euler variation to the size-consistent energy functional (12) in the framework of general non-unitary ansatz the truncation upto some finite powers in T and T^+ has to be done. This kind of variation leads to the energy which does not retain the upper bound property. This loss of upper bound property was first observed in nuclear structure calculations using cluster expansion method using Jastrow function and is known as the 'Emery difficulty' (Emery 1958; Bell and Squires 1962). The loss of the upper bound property is due to the fact that the truncated power series for E , written as a simple power series, does not correspond to an expectation-value like quantity having polynomials of some *fixed finite degree* appearing both in the numerator and denominator. While the denominator has been cancelled exactly with the implicit assumption of infinite degree expansion, the numerator, as a result of truncation contains only upto finite degree in T . If however, the dominant terms contributing to the energy are retained in the functional, the loss of the upper bound is not very serious. This is quite akin to the Sinanoğlu's method of 'varied portion approach' (Sinanoğlu and Bruckner 1970).

The same loss in upper bound property can be expected if Euler variation is done for the energy functional (9) in the framework of unitary coupled-cluster ansatz. The denominator being automatically cancelled because it is equal to unity essentially means that the denominator has been expanded upto infinite order in T while again for practicable calculation, the numerator has to be truncated to some finite power in T . Hence the functional (9) truncated to a finite power does not correspond to an expectation-value like quantity having some fixed finite degree appearing in the numerator and denominator. But again with the inclusion of enough terms, effect of this loss may be obviated.

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References

- Bell J S and Squires E J 1962 *Adv. Phys.* **10** 21
- Cizek J 1966 *J. Chem. Phys.* **45** 4256
- Cizek J 1969 *Adv. Chem. Phys.* **14** 35

- Coester F 1958 *Nucl. Phys.* **22** 179
Coester F and Kummel H 1960 *Nucl. Phys.* **17** 477
da Providencia J 1963 *Nucl. Phys.* **46** 401
da Providencia J 1965 *Nucl. Phys.* **61** 87
Emery V J 1958 *Nucl. Phys.* **6** 585
Goldstone J 1957 *Proc. R. Soc. (London)* **A239** 267
Kummel H 1962 *Nucl. Phys.* **22** 179
Kulzetnigg W 1977 in *Method of electronic structure theory* (ed) H F Schaeffer III (New York : Plenum)
Mukherjee D 1981 *Chem. Phys. Lett.* **79** 559
Mukherjee D, Moitra R K and Mukhopadhyay A 1975 *Molec. Phys.* **30** 1861
Mukherjee D, Moitra R K and Mukhopadhyay A 1977 *Pramana* **2** 545
Pal S, Durga Prasad M and Mukherjee D 1982 (to be published)
Primas H 1961 *Helv. Phys. Acta* **34** 331
Sinanoğlu O 1962 *J. Chem. Phys.* **36** 706
Sinanoğlu O 1964 *Adv. Chem. Phys.* **6** 315
Sinanoğlu O and Bruckner K 1970 *Three approaches to electronic correlation in atoms* (Yale University Press)
Thouless D J 1961 *The quantum mechanics of many body systems* (New York: Academic Press)
VanVleck J H 1929 *Phys. Rev.* **33** 467
Westhaus P 1973 *Int. J. Quantum Chem.* **7** 463
Westhaus P, Bradford E G and Hall D 1975 *J. Chem. Phys.* **62** 1607
Yaris R J 1964 *J. Chem. Phys.* **41** 2419
Yaris R J 1965 *J. Chem. Phys.* **42** 3019