

Some non-relativistic many electron theories: single reference case

Review Article

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Abstract: There has been substantial progress in the development of electron correlation methods with some benefits and drawbacks. In this paper, we give a review of electron correlation effects on many body particles system. We focus more on atoms and molecules rather than solid state and take into account single reference case only. We mainly discuss perturbation theory, coupled electron many electron theory and a few versions of coupled electron pair approximations with comparison configuration interaction and some coupled cluster methods in which coupled cluster method is crucially important for the crystalline solids, the electron gas and the heat of the reaction. We also show some results, reported by several authors, to fairly compare and judge the methods' feasibility mentioned above.

Keywords: *Many Body Particles • Davidson Type Corrections • Many Body Perturbation Theory and Coupled Electron Many Electron Theory • Coupled Electron Pair Approximations • Coupled Cluster*

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1. Introduction

It is well known that there have been many intensive studies conducted on the single configuration Hartree-Fock (HF) method. The suitability of the HF method has been proven for many applications to various problems in chemical interest [1]. On the other hand, the HF theory does not take into account the correlation between electron motions. Due to this deficiency of the HF method, it does not provide well degeneracy near equilibrium geometry nor does it provide dissociation energy for the molecules.

To be satisfactory as a general computational technique, the method should be size consistent, which is the most desirable property of molecules. The size consistency signifies that the total energy of the molecule system is expected to be rational with the number of electrons that the molecule has. In this article, we attempt to explain this issue in more detail in the next section. Another inevitable property is that the method should have the variation property of giving an upper bound to the energy. Lastly, the proposed method should provide invariant property under transformations

within a set of degenerate molecular orbital (MO). We mainly concentrate on the size consistency property here.

There are a variety of methods which try to calculate the correlation energy for molecules. One of the most commonly used methods is the configuration interaction (CI) method, which is exact and size consistent if one includes all excitations from reference determinant to the wave function, usually the HF determinant in the ground state. However, calculation of all configurations is too expensive for large molecules. On the other hand, CI method is not a size consistent method when one truncates it at the limited (*i.e.*, including a single and double (SD)) excitation. The method is then denoted as CI-SD. Thus, the lack of size consistency of limited CI method can be surpassed by the direct inclusion of corresponding higher excitations. However, the inclusion of higher excitations is unusual because of the computational difficulties. Nevertheless, there are a few methods that attempt to approximate those excitations. One of them is called Davidson correction [2,3], to which some variations exist. Davidson correction simply consists of a posteriori correction of size consistency

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error in double excitation CI energies by taking into account the effects of the unlinked cluster quadruple excitations (four-electron correlations) from coupled cluster (CC) expansion. However, the Davidson correction fails to give correct answers for the two electron system. Various other methods have attempted to modify Davidson correction by considering non-interacting systems [2-8]. Of the above-mentioned, some methods are related to the nondegenerate case and some of them are limited to the number of electron (moderate numbers of electron) which the system has.

Although CI has the important advantage that it is variational, it does not offer size consistency. In this case, we have another systematic procedure, which is not variational but is size consistent at each order of level, for finding the correlation energy, which can be achieved by using many body perturbation theory (MBPT) [9,10] (or often pronounced as a Møller-Plesset (MP) perturbation theory when using the HF reference function). This method is to be presented as two-partitioned of the Hamiltonian ($\hat{H} = \hat{H}_0 + \hat{V}$). Of these, first one is a zeroth-order part (\hat{H}_0), which are known as eigen functions and eigen values, the other one presents the perturbation part (\hat{V}). In this approach, substantial progress has been achieved, such as, the effect of doubly excited configurations in the second, third, fourth and even in higher orders of perturbation expansion, MP2, MP3, MP4 and MPn (n=5, 6,...) [11-13], respectively. In these levels, the important and dominant contribution comes from MP2 level. Nonetheless, quadruple excitation from fourth order of MP-PT plays an important role when we try to correct the size consistency in CISD. On the other hand, we do not neglect the effect of single and triply excited configurations; even if their contribution to the total correlation energy is small. They become important excitations when molecules dissociate. The theory is fully practical to fourth order (MP4) and it includes the effects of single, double, triple, and quadruple substitutions. A major advantage of MP (or MBPT) methods is that they are not iterative, but CC is. Their principal drawback is that they suffer from convergence problem which occurs when higher order MPn (n=5, 6,...) is studied in large molecules where the electron correlation effects are large [44].

The effectiveness of quadruple excitation can be seen in the coupled pair many electron theory (CP-MET), which was initially investigated by Cizek [14,15] and applied to some small molecule systems [14,15]. This method, which is also called CC double (CCD) [16-20], based on earlier work of Coester and Kümmel [21,22] in nuclear theory, has been implemented to

large scale *ab initio* quantum chemical calculations [16,20]. The CP-MET method consists of the so-called connected clusters and disconnected clusters of quadruple excitations and neglects all single excitations. A variety of articles and derivations of equations of this approach and their applications are available [23-29]. We emphasize that these types of quadruple excitations are closely related with those that appear in the fourth order MBPT. One may want to neglect the quadruple excitation in CPMET, and adopt just the linear terms which were left out in equations. This method is called linear CPMET (L-CPMET) [25,27]. The L-CPMET approach is also pronounced as coupled electron pair approximation (CEPA(0)) [25,27]. It is also equivalent to LCCD [18,26,30] and D-MBPT(¥) [31]. Of all methods cited above, CEPA(0) is the most frequently used name in literature. Other versions of CEPA(n) (n=1,2,3,) type approaches are generated by modifying the CPMET equations. The CPMET and all versions of CEPA type approaches yield correlation energies unless the studied ground state is quasi-degenerate. Thus, one should use multi-reference (MR) approximation for high degenerate and quasi-degenerate groundstate.

The CC methods have been widely implemented due to its accurate technique for treatment of electronic correlation effects [14,15,32] and they behave very successfully particularly in the ground states of closed shell systems near equilibrium geometries [33-39]. Although it has the size consistency property, it does not provide variational energy and required iterative solutions for the energy. The CC methods depend on a set of projection equations, one for the correlation energy by projecting zero order wave function and one for the unknown amplitudes equations by projecting each excitation (single, double, triple, quadruple and higher). The most commonly used scheme of CC methods is the CCSD method, which neglects all important three electron correlations (triple excitations) for investigating further properties, and exact for two electron systems within the basis set space. General applications and programs were originally developed in 1978 [17,18,26,33-35]. Because of the difficulties of adding the triples excitations to the CCSD, a non-iterative scheme as shown CCSD(T) [40] was proposed, and it was applied to a variety of quantum chemistry packages [41]. Many improvements have been made to extend the CC expansion to the higher one and other approaches to the CCSD. The reader is encouraged to see more detailed information in [42-46].

As mentioned above, there are some inadequacies in the aforesaid methods, with respect to a single reference (SR) case. In the SR case, they are not able to describe

bond breaking process with dissociation channels, especially in open shell cases. There are basically three ways to prevent these difficulties: unrestricted HF wave function as a reference, nondynamical correlations, MR formalism. The latter option is the most preferable one. We do not propose to explain these approaches here. We rather attempt to compare the SR approaches and show the superiority of one over the other.

2. Discussion

In the variational CI method, the exact wave function $|\Psi\rangle$ is expanded over the reference function $|\phi_0\rangle$ by removing one, two, three, etc. electrons from the spin orbitals settled in the $|\phi_0\rangle$. Then, intermediately normalized full SRCI wave function can be written as follows,

$$|\Psi_{FCI}\rangle = |\phi_0\rangle + \sum_{i,a} c_i^a |\phi_i^a\rangle + \sum_{i>j, a>b} c_{ij}^{ab} |\phi_{ij}^{ab}\rangle + \sum_{i>j>k, a>b>c} c_{ijk}^{abc} |\phi_{ijk}^{abc}\rangle + \dots \quad (1)$$

or shortly

$$|\Psi_{FCI}\rangle = (1 + \hat{C}) |\phi_0\rangle, \quad (2)$$

where \hat{C} sum of excitation operators \hat{c}_i

$$\hat{C} = \sum_i \hat{c}_i. \quad (3)$$

Here \hat{c}_i stands for excitation of the electrons from occupied orbitals to unoccupied ones and i, j, k, \dots and a, b, c, \dots refer to occupied orbitals and unoccupied (virtual) orbitals in the reference determinant. Here, we have to already mention that by using Eqs. 2 and 3 we can compare CI coefficients with CC cluster operator, Eqs. 29, 30,

$$\begin{aligned} c_1 &= T_1 \\ c_2 &= T_2 + \frac{1}{2} T_1^2 \\ c_3 &= T_3 + T_1 T_2 + \frac{1}{3!} T_1^3 \\ c_4 &= T_4 + \frac{1}{2} T_2^2 + T_1 T_3 + \frac{1}{2} T_1^2 T_2 + \frac{1}{4!} T_1^4 \end{aligned} \quad (4)$$

and so on.

First of all, we want to present the importance of size consistency in terms of electron correlation. Initially, we have two identical molecules A and B and they constitute an AB molecule. We expect that their individual calculated energies should have the property of additive,

$$E(AB) = E(A) + E(B). \quad (5)$$

and wave functions have the property of multiplicative,

$$\Phi(AB) = \Phi(A)\Phi(B). \quad (6)$$

Here, to show the lack of size consistency in the CI, we truncated it at the double excitation for simplicity. For the separated molecule, we can write [48]

$$\Phi_{CID} = \Phi_{HF} + \Phi_D, \quad (7)$$

and we have

$$\Phi_{CID}(AB) = \Phi_{CID}(A)\Phi_{CID}(B) \quad (8)$$

$$\begin{aligned} &= \Phi_{HF}(A)\Phi_{HF}(B) + \Phi_{HF}(A)\Phi_D(B) + \Phi_{HF}(B)\Phi_D(A) + \Phi_D(A)\Phi_D(B) \\ &\quad + \Phi_{HF}(A)\Phi_D(A) + \Phi_{HF}(B)\Phi_D(B) \end{aligned} \quad (9)$$

$$= \Phi_{HF} + \Phi_D + \Phi_D(A)\Phi_D(B). \quad (10)$$

When we compare Eqs. 7 and 10, we immediately realize that they differ from quadruple excitations as can be seen from the last term in Eq. 10. Therefore, it is expected that these two functions will give different energies. Due to this deficiency, truncated CI wave function cannot be treated as an exact wave function for the accurate result. These deficiencies can be removed by replacing the CI wave function by CC exponential wave function [42]. Before considering the CC approaches, we should introduce methods that either modifies the original CI equations, which is called CEPA type method, or corrects the CI energy, which is called Davidson type method with its moderate versions.

A very semi empirical formula, which is based on assumptions that quadruple excitations are missing in CID wave function Eq. 7, for the correlation energy to correct the CISD proposed by Davidson [2,3]

$$\Delta E_{DC} = \Delta E_D (1 - c_0^2) \quad (11)$$

where ΔE_D is the correlation energy obtained from CISD calculations. Actually, Davidson correction presents the unlinked fourth order contribution of double excitations. Davidson correction has been proven as algebraic several times in different ways [4,6,7,48,49]. An intriguing formula can be derived by the assumption that wave function is truncated at double level while neglecting the single excitations in the Eq. 1. This correction can be justified by MBPT. When we use the

first order PT as a wave function [47]

$$\Psi = (1+S)^{-1/2}(\phi_0 + \phi_1), \quad (12)$$

Here, $S = \langle \phi_1 | \phi_1 \rangle$, $\phi_1 = R_0 V \phi_0$. Then, we can write [19,26],

$$R_0 V \phi_0 = \sum_{i>j, a>b} \frac{\langle ab || ij \rangle}{\varepsilon_{ij}^{ab}} |\phi_{ij}^{ab}\rangle, \quad (13)$$

and

$$\langle \Psi | \Psi \rangle = c_0^2 + \sum_{i>j, a>b} (c_{ij}^{ab})^2. \quad (14)$$

Hence, as we can see from Eq. 14

$$1 - c_0^2 = \sum_{i>j, a>b} (c_{ij}^{ab})^2 = \sum_{i>j, a>b} \frac{\langle ab || ij \rangle \langle ij || ab \rangle}{(1+S)(\varepsilon_{ij}^{ab})^2} = \frac{S}{1+S}, \quad (15)$$

and

$$E_2 S = (1 - c_0^2) \Delta E_D. \quad (16)$$

Renormalized Davidson correction is given [3] as,

$$\Delta E_{RDC} = \Delta E_{SD} \frac{(1 - c_0^2)}{c_0^2}. \quad (17)$$

The aforementioned formulas do not provide correlation energies for the two electrons system due to the fact that quadruple excitations do not exist and it is inconsistent for very large number of electrons. There have been attempts to derive energy equation for the large number of electrons [4,5] and correction is known as Davidson-Silver or Siegbahn

$$\Delta E_{DS} = \Delta E_{SD} \frac{(1 - c_0^2)}{2c_0^2 - 1}. \quad (18)$$

More complicated formulas were derived by Pople [6]. A more general equation was suggested by Meissner [7] considering the interacting pairs of electrons

$$\Delta E_{MC} = \Delta E_{SD} \frac{(1 - c_0^2)(N-2)(N-3)}{c_0^2 N(N-1)}, \quad (19)$$

This formula vanishes for $N=2,3$ and gives accurate results for small molecules [7]. The comparative results can be seen in Table 1.

Here, E_{ref} means that full CI calculation is considered. The PC and DD formulations can be found in [8].

All Davidson type corrections are over-estimated, since quadruple corrections, which are take into account the above corrections, cancels the entire $(-E_2 S)$ [42]. In this case, CEPA type corrections, which are based on pair energies, give a good estimate for the $(-E_2 S)$ term. CEPA takes into account higher substitutions neglected

in the CI(SD) approach in an approximate manner. In the CEPA method, correlation energy is given by the sum of pair energies:

$$\Delta E = \sum_{ij} \varepsilon_{ij} = \sum_{ij} (\sum_{ab} c_{ij}^{ab} \langle \phi_0 | \hat{H} | \phi_{ij}^{ab} \rangle). \quad (20)$$

Before we introduce other CEPA variations, we have to examine CI equations at the truncated level, usually doubles.

We can write CI equations for the double excited coefficient and neglect the triple excitations, as follows

$$\begin{aligned} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_0 \rangle + \sum_{k,c} c_k^c \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_k^c \rangle + \sum_{k>l, c>d} c_{kl}^{cd} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_{kl}^{cd} \rangle \\ + \sum_{k>l, c>d}^{*ij, ab} c_{ij}^{ab} c_{kl}^{cd} \langle \phi_0 | \hat{H}_N | \phi_{kl}^{cd} \rangle = c_{ij}^{ab} \Delta E, \quad (21) \end{aligned}$$

If we use small notation for the last term of l.h.s. of Eq. 21, we get

$$c_{ij}^{ab} K_{ij}^{ab} = \sum_{k>l, c>d}^{*ij, ab} c_{ij}^{ab} c_{kl}^{cd} \langle \phi_0 | \hat{H}_N | \phi_{kl}^{cd} \rangle, \quad (22)$$

$$\begin{aligned} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_0 \rangle + \sum_{k,c} c_k^c \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_k^c \rangle + \\ + \sum_{k>l, c>d} c_{kl}^{cd} \langle \phi_{ij}^{ab} | \hat{H}_N | \phi_{kl}^{cd} \rangle + c_{ij}^{ab} K_{ij}^{ab} = c_{ij}^{ab} \Delta E. \quad (23) \end{aligned}$$

An approximation for the coefficient is used in Eq. 21 and it appears on the l.h.s. of Eq. 22 and it is shown as,

$$c_{ijkl}^{abcd} \approx c_{ij}^{ab} c_{kl}^{cd}. \quad (24)$$

For the exact definition Eqs. 21 and 23, it is recommended to see Szalay [50], Koch *et al.* [51], and Aldrich's [27] works. First approximation is called CEPA(0) [25,27], which is obtained by completely cancelling all the Exclusion Principle Violation (EPV) terms in Eq. 23,

$$K_{ij}^{ab} = \Delta E, \quad (25)$$

It was Kelly [52,53] who first suggested the following approximations, as a CEPA(3),

$$c_{ij}^{ab} (\Delta E - K_{ij}^{ab}) = c_{ij}^{ab} (\varepsilon_{ij} + \sum_d (\varepsilon_{id} + \varepsilon_{dj})). \quad (26)$$

When only the diagonal part of EPV term is considered, then it is called CEPA(2) [54,55];

$$c_{ij}^{ab} (\Delta E - K_{ij}^{ab}) = c_{ij}^{ab} \varepsilon_{ij}, \quad (27)$$

and exact for the separated electron pairs if localized orbitals are used [50]. Another version is called CEPA(1) [54,55] and it uses non-localized orbitals as well,

Table 1. The comparison of size consistency corrections of some small molecules ^a. Correlation energy is given in mH.

Species	1-C2	CISD	DC	RD	DS	PC	MC	DD	E ref.
BH3	0.030 329	47.15	48.58	48.62	48.67	48.27	47.94	48.28	48.05
CH+	0.061 549	68.58	72.80	73.08	73.39	71.64	70.38	71.72	70.31
BeH2	0.027 072	39.79	40.86	40.89	40.92	40.53	40.23	40.54	40.23
LiH(2.0 P)	0.027 800	21.19	21.78	21.80	21.82	21.50	21.30	21.50	21.20
BH(2.0 P)	0.100 712	78.31	86.19	87.08	88.18	84.36	81.82	84.63	82.01
CH2 (3B1)	0.042 835	151.69	158.18	158.47	158.79	156.89	155.32	156.95	155.80
HF	0.036 439	257.77	267.16	267.52	267.90	265.75	263.84	265.81	266.00
NH	0.038 663	165.96	172.38	172.64	172.92	171.07	169.54	171.12	170.00
H2O	0.047 594	255.23	267.38	267.99	268.66	265.75	263.107	265.86	265.50

^aFrom the work of W. Duch and G.H.F. Diercksen [8].

Table 2. BH at R=2.336 P (basis from [73]), negative valance shell correlation energies in mH ^a (canonical representation).

Methods	a	b
CID	68.3	69.4
CEPA(5)	68.5	69.7
CEPA(3)	69.7	70.9
CEPA(1)	70.9	72.0
CEPA(4)	71.0	72.2
CEPA(2)	72.0	73.3
CEPA(0)	74.0	75.5
CP-MET	70.0	70.8
CCSD	-	71.6
Full CI	-	72.7

^aOnly doubles [41]

^b[27] only singles and doubles

^cFrom the work of S. Koch and W. Kutzelnigg [51]

$$c_{ij}^{ab}(\Delta E - K_{ij}^{ab}) = c_{ij}^{ab}(\varepsilon_{ij} + \frac{1}{2} \sum_d (\varepsilon_{id} + \varepsilon_{dj})). \quad (28)$$

The CEPA(1) differs from CEPA(3) by just a factor of $\frac{1}{2}$, which is required for the desired orbital invariance property [48]. We have provided here results obtained from these methods to be compared in Table 2.

The CC method is basically based on the exponential form of the wave function,

$$\Psi = \exp(\hat{T})\phi_0. \quad (29)$$

In this method exponential *Ansätze* is given,

$$\exp(\hat{T}) = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots, \quad (30)$$

where $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots$ is excitation operator which accounts an efficient way of including the effects of higher excitations. General definition of excitation operator can be presented as follows,

$$\hat{T}_m = \frac{1}{(m!)^2} \sum_{\substack{ij\dots \\ ab\dots}} \{a^+ ib^+ j\dots\} t_{ij\dots}^{ab\dots}. \quad (31)$$

The exponential form of wave function ensures the size consistency property even truncated level of Eq. 29, which is the more desirable characteristic for calculation of molecules, even solid states and electron gas. First implementations started considering only doubly excitations in the wave function and were referred to as CCD [16-22] or CPMET [16-23]. We can get the CCD wave function by substituting Eqs. 30 and 31 into the Eq. 29, then we have

$$|\Psi_{CCD}\rangle = |\phi_0\rangle + \frac{1}{4} \sum_{ijab} t_{ij}^{ab} |\phi_{ij}^{ab}\rangle + \frac{1}{32} \sum_{ijab} \sum_{klcd} t_{ij}^{ab} t_{kl}^{cd} |\phi_{ijkl}^{abcd}\rangle. \quad (32)$$

The CC wave function includes all connected and disconnected clusters involving \hat{T}_2 only. The most widely used extension of CC approach which is obtained including the single excitations [30] to the Eq. 32, is the so called CCSD model, which is defined by

$$\hat{T}_{CCSD} = \hat{T}_1 + \hat{T}_2. \quad (33)$$

The CCSD method is exact for two electrons yet it needs to be included in the case of triple excitation to get excellent approximation, *i.e.*,

$$\hat{T}_{CCSDT} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3. \quad (34)$$

There have been some approximate schemes [56-60] for considering the triple excitations due to difficulties of direct calculations of \hat{T}_3 . However, all these attempts try to calculate in an iterative manner. This kind of calculations is not practical for computing even for small molecules. Not to mention, its complexity increases with increasing number of electrons. The

Table 3. Correlation corrections (in mH) with various coupled cluster methods relative to full configuration interaction ^a values.

Molecule	CCSD ^{b,d}	CCSDT ^{b,d}	CCSDTQ ^{b,d}	CCSDTQP ^{c,d}
BH (R)	1.790	0.068	0.001	0.000
HF (1.5R)	5.099	0.646	0.041	0.000
H₂O (2.0R)	21.404	-2.472	-0.015	0.026
SiH₂ (1.5R)	6.685	0.058	-0.015	0.001
CH₂ (2.0R)	14.648	-1.900	-0.050	0.000
N₂ (R)	13.465	1.626	0.192	0.016
C₂ (R)	29.597	3.273	0.622	0.103

^aBauchlicher and Taylor [74-76]; Bauchlicher et al. [77]; Kurcharski and Bartlett [78]; Christiansen et al. [79].^bKurcharski and Bartlett [80].^cMusial et al. [81]^dBartlett and Musial [43]

most efficient model was proposed by Raghavachari *et al.* [60] in a non-iterative manner (CCSD(T)) and has remained one of the most accurate schemes for correlation of energies [60]. Generalization of any desired order can be obtained with mathematical induction [42]. In addition, one may get confused generating higher order diagrams. Fortunately, there are some automatic computer programs available [61-64]. We can see the effectiveness of inclusion of these higher order contributions in Table 3.

The CCSD(T) has many feasibilities to perform, such as, finding equilibrium geometries, harmonic and fundamental vibrational frequencies, heats of formation, binding energies, dipole moments, polarizabilities and other properties [65-67]. Apart from CCSD(T), other non-iterative approximations, including quadruple excitations, have been suggested [68-71].

3. Conclusions

In conclusion, Davidson type corrections regard the major part of the differences between the CID and L-CPMET energies [72]. The simple formula proposed by Meissner [7], Eq. 19, has proper asymptotic behavior (for asymptotic behavior results see Fig. 2 in [8]) and more accurate [8] than the other Davidson type variants given in Eqs. 11, 17 and 18, in single reference case. Among Davidson type corrections, The MC, the Pople correction (PC) [6] and Duch and Diercksen (DD) [8] correction should be the preferred choice, but not more than 10 electrons.

All the afore mentioned approaches in the previous paragraph account only for double substitutions and neglect the singly and triply excited configurations

which become important when one wants to describe the reliable potential energy curves.

As we can see from Table 2, all the correlation energies obtained from CEPA variants, especially CEPA(1) and CEPA(4) [51] at the near equilibrium geometries, are closest to CP-MET one. If we consider physical properties and compare them, the CEPA(2) method presents better than other CEPA variants. The CEPA(2) variants become more important and reliable choice than the other variant and CP-MET method, if number of electrons increases [51].

To sum up, CP-MET and all the CEPA variants do not provide upper bonds to energy and they are limited to single reference configuration with double substitutions exclusively [51].

The MBPT mostly offers a finite order approximation to the correlation problem. On the one hand, CC theory allows us to work on an infinite order approximation in selected cluster operators which is convenient [43]. The CC theory combines the linked-diagram advantage of MBPT with finite order summations. Thus, it is expected to give the best convergence [42,43]. As we mentioned in the above discussion, superiority of CC approach is its size consistent property which facilitates its application to infinite systems such as crystalline solids and electron gas [43]. Another example for the use of CC approach is in determining heat of reactions [43]. In addition, some simple polymers have been investigated using CC scheme [82,83]. We have presented some illustration of higher excitations of CC approach in Table 3. As it can be seen from Table 3, the inclusion of higher excitations yields correct exact wave function relative to the full CI, the full CI wave function being exact.

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