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Fock space multireference coupled cluster theory: noniterative inclusion of triples for excitation energies

Nayana Vaval[1], **Sourav Pal**[1], **Debashis Mukherjee**[2,3]

[1] Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India
[2] Theory Group, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India
[3] S. N. Bose National Centre for Basic Sciences, Salt Lake, Calcutta 700 064, India

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Abstract. In this paper we propose and numerically implement a specific scheme for calculating the excitation energies (EEs) within the Fock space multireference coupled cluster framework, which includes the contributions from noniterative triples cluster amplitudes. These contribute to the EEs at the third order. We present results for CH^+ and N2, and study the effects of these noniterative triples on EEs.

Key words: Excitation energies – Fock space – Multireference coupled cluster theory – Triply excited amplitudes – Noniterative

1 Introduction

The single reference coupled cluster (SRCC) [1–4] method has already been established as a compact and efficient formulation for incorporating the dynamical correlation in electronic structure calculations for non-degenerate or closed-shell systems, where a single determinant can be an appropriate starting point for the cluster expansion. Different versions of the SRCC method with increasing precision have been developed [5]. Further recent technical innovations, viz. more efficient solution algorithm [6] and analytic derivative formulation [7], have made the SRCC method a powerful technique for the calculation of electronic energies and other properties [8–12] in the region around the equilibrium of closed-shell systems. The SRCC method with appropriate single-determinant model spaces can even be used for some limited open-shell cases like high-spin open-shell systems.

However, there are many situations which demand a multideterminant description of the model space, either as a consequence of symmetry or due to strong mixing, stemming from quasi-degeneracy. Typical examples are the excited states, bond-breaking situations and, in general, potential energy surface (PES) of even closed-shell systems away from equilibrium. In these cases the SRCC method suffers from the necessity to include high-rank cluster operators and also from what is known as the "intruder state" problem. To take care of such situations, it is necessary to start with a reference model space consisting of several determinants. The consequent coupled cluster (CC) developments, known as multireference coupled cluster (MRCC) theories, have appeared in the literature over the last two decades and mostly use the concept of an effective Hamiltonian and generalized Bloch equation. Extensive discussion of MRCC theories will be found in the review by Mukherjee and Pal [13]. The effective Hamiltonian-based MRCC theories can describe several states in a single calculation. These are primarily divided into valence-specific [14–16] and valence-universal (VU) [13, 17–29] varieties. While the former type is well-suited for the description of a specific state, the VUCC theories use a VU wave operator and a common vacuum description. Using a subset of holes and particles as active orbitals, the model-space determinants are classified into different active hole-particle sectors. While there are some advantages in a common vacuum description, it also contributes to the practical disadvantages of having to find states with lower hole-particle sectors when they are of no interest to us. There have been some recent attempts at removing these difficulties even within the common vacuum framework [24]. The VUCC method can be used to study the PES of systems which can be described by a low hole-particle sector with respect to an appropriate vacuum, but it can still suffer from the intruder state. The VUCC theories, however, are the methods of choice in the study of ions or low-lying excited states of closed-shell systems.

With the N-electron restricted Hartree-Fock (RHF) state as vacuum, the VUCC methods have been used for the description of the ionization potential (IP) [25, 26, 29] and low-lying ecitation energies (EEs) [27, 28] of closed-shell N-electron systems in a direct manner using

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Correspondence to: S. Pal

only one- and two-body cluster operators. Terms coming from the triply excited amplitudes are completely missing in this initial development. From a perturbative point of view, some of these terms contribute first at the third order and their neglect entails errors of at least the third order. The full inclusion of the triple excitations resulting in the infinite partial summation of these terms is, however, computationally expensive at this stage. On the other hand, it is computationally feasible to include the triply excited amplitudes in an approximate way which takes care of the leading-order corrections. For IP calculations, approximate inclusion of triples in the calculations correcting the IP values to at least third [28] and fourth order in perturbation [29] were achieved, and these were found to be quite significant. From these considerations the contributions of similar low-order triply excited amplitudes are likely to be important in the computational scheme for calculating EEs. The objective of this paper is to present the inclusion of these triply excited amplitudes using an incomplete one-hole one-particle model space, which contributes to the EEs at least up to the third order. There are several ways one can achieve this we implement a specific version which we denote as the multireference coupled cluster singles doubles which we denote as $(\mathrm{MRCCSD}) + \mathrm{T}^{\mathrm{m}}(3)$ scheme. We will show that this can be done by a noniterative inclusion of the triples, which is computationally simple.

In Sect. 2 we briefly summarize the VUCC theory. This will help us to introduce the notations and present the background for Sect. 3, where we present the equations for the inclusion of the triply excited amplitudes to generate EEs correct upto the third order. We will note that these are essentially noniterative triples. In Sect. 4 we present some model results for N_2 and CH^+, and compare these with earlier results using singles and doubles amplitudes only and experimental values.

2 VUCC theory: a résumé

In the VUCC-based theories a convenient vacuum (usually a RHF wave function of a neutral N-electron closed-shell system) is chosen with respect to which holes and particles are defined. The set of holes and particles is subdivided into active and inactive subsets depending on the problem of interest. With the definition of a common vacuum, any general model space may consist of determinants with, say, m number of active particles and n number of active holes. In the conventional notation, this model space is said to belong to the (m,n) sector, where the first index refers to the number of active particles and the second index refers to the number of active holes in the model space. The set of correlated wave functions, Ψ_μ, corresponding to the model space $\Psi_\mu^{(0)}$ is generated by the action of a normal-ordered exponential wave operator on the model space. Thus one may write

$$|\Psi_\mu^{(0)(m,n)}\rangle = \sum_i C_{\mu i}|\Phi_i\rangle \ , \tag{1}$$

$$|\Psi_\mu\rangle = \{\exp(\overline{\mathrm{T}}^{[\mathrm{m,n}]})\}|\Psi_\mu^{(0)}\rangle \ . \tag{2}$$

Superscripts (m,n) refer to the Fock-space sector, and the braces denote the normal ordering of the wave operator. $\overline{T}^{[m,n]}$ is an operator which can destroy any number of active particles and holes among the subset of m active particles and n active holes and can be written as

$$\overline{T}^{[m,n]} = \sum_{k=1}^{m}\sum_{l=0}^{n} T^{(k,l)} \tag{3}$$

where $T^{(k,l)}$ destroys exactly k active particles and l active holes. The wave operator Ω thus correlates all lower-valence sectors. This is the reason for valence universality. The energies are obtained as eigenvalues of an effective Hamiltonian within the model space. Thus the energies of multiple states are obtained at one time. The effective Hamiltonian and the cluster operators for different valence sectors are obtained from the Bloch equation which is given by

$$[H\Omega - \Omega H_{\mathrm{eff}}]P = 0 \ , \tag{4}$$

where P is the model-space projector. The projection of the above equations to the model space defines the effective Hamiltonian. The projection of Eq. (4) to the virtual-space determinants yields the cluster amplitudes. A subsystem embedding condition (SEC) is prescribed to solve the equations of different valence sectors starting from the lowest sector upwards. The normal ordering of the formulation ensures that in the equations of a specific valence sector, the amplitudes of higher sectors do not appear. Equations of different valence sectors are thus hierarchically decoupled. The following equations are solved hierarchically upwards:

$$P^{(k,l)}[H\Omega - \Omega H_{\mathrm{eff}}]P^{(k,l)} = 0 \ , \tag{5}$$

for $k = 0, 1, \ldots m$ and $l = 0, 1, \ldots n$;

$$Q^{(k,l)}[H\Omega - \Omega H_{\mathrm{eff}}]P^{(k,l)} = 0 \ , \tag{6}$$

for $k = 0, 1, \ldots m$ and $l = 0, 1, \ldots n$. For the specific case of low-lying excited states, we have started from the N-electron RHF as a vacuum. The active-inactive subdivision of holes and particles is usually done on the basis of energies of the orbitals. The model space consists of one active hole and one active particle and is thus a $(1,1)$ valence-sector model space. The vacuum or the N-electron RHF is outside the model space. The correlated wave function $\Psi_\mu^{(1,1)}$ is obtained by the action of the $\{\exp(\overline{T}^{[1,1]}\}$ wave operator. $\overline{T}^{[1,1]}$ may be decomposed as

$$\overline{T}^{[1,1]} = T^{(0,0)} + T^{(0,1)} + T^{(1,0)} + T^{(1,1)} \ , \tag{7}$$

where $T^{(0,0)}$ is, by definition, the cluster operator that acts on a single determinantal RHF. Each of these T-operators can again be decomposed into one, two and three, etc. body components. For example, at the MRCCSD level, $T^{(0,1)}, T^{(1,0)}$ and $T^{(1,1)}$ may be written in a singles and doubles approximation as

$$
\begin{aligned}
T^{(0,1)} &= \sum_{i\in a_h,k\notin a_h} \langle i|T_1^{(0,1)}|k\rangle i^+k \\
&\quad + 1/2! \sum_{k,l,a,i\in a_h} \langle ia|T_2^{(0,1)}|kl\rangle i^+a^+lk + \cdots \\
T^{(1,0)} &= \sum_{a\in a_p,c\notin a_p} \langle c|T_1^{(1,0)}|a\rangle c^+a \\
&\quad + 1/2! \sum_{k,d,c,a\in a_p} \langle cd|T_2^{(1,0)}|ak\rangle c^+d^+ka + \cdots \\
T^{(1,1)} &= \sum_{i\in a_h,a\in a_p} \langle i|T_1^{(1,1)}|a\rangle i^+a \\
&\quad + 1/2! \sum_{k,c,a\in a_p,i\in a_h} \langle ic|T_2^{(1,1)}|ak\rangle i^+c^+ka + \cdots
\end{aligned}
\tag{8}
$$

$T_1^{(1,1)}$ is a deexcitation operator, which acting on this model space generates the Hartree-Fock determinant. It has been shown [28–30] that for obtaining EEs using the hole-particle model space, these operators are not required. The wave function, however, contains these operators and thus, for example, the amplitudes of these operators will be required for obtaining the transition amplitudes. Since our current interest is only computation of EEs, we have ignored the $T_1^{(1,1)}$ operators in the present scheme. It may also be noted that the $(1,1)$ model space is an incomplete model space and intermediate normalization (IN) has to be abandoned for the proof of linked-cluster theorem in the Bloch equation. However, for this special $(1,1)$ problem, it has been pointed out that the [26–31] expression for the $H_{\text{eff}}^{(1,1)}$ is similar in structure to the one obtained by using IN, i.e. $P\Omega P = P$. We solve Eqs. (5) and (6) progressively from the $(0,0)$ sector for $m = 1$ and $n = 1$. In the evaluation of $(H\Omega)_c$ in Eqs. (5) and (6), it is computationally convenient to construct an intermediate operator $\overline{H}$ obtained by connecting H with powers of $T^{(0,0)}$ in all possible manners:

$$
\overline{H} = (He^{T^{(0,0)}})_C \ . \tag{9}
$$

Two separate forms of $\overline{H}$ have been used before, one which contains only $T_2^{(0,0)}$ amplitudes. This may be referred to as the CCD form of $\overline{H}$. The other contains both $T_1^{(0,0)}$ and $T_2^{(0,0)}$ amplitudes. For the third-order corrections due to the triples, which is the objective of this paper, it is sufficient to use the CCD form of $\overline{H}$. We will use this form in our present scheme. In general, $\overline{H}$ will have a closed and an open part. The closed part of $\overline{H}$ is the ground-state energy itself. If we drop this term from H_{eff}, we will get the EEs directly on diagonalization of H_{eff}. We thus consider only the open part of $\overline{H}$. In earlier applications of MRCCSD we considered only one- and two-body parts of the operator. However, for including noniterative triples, we will need approximate three-body parts, too. We represent one-, two- and three- body parts of $\overline{H}$ as $\overline{F}, \overline{V}$ and $\overline{W}$, respectively. To evaluate the singlet and triplet excited states dominated by single-hole particle excitations with the active orbitals, one diagonalizes the following spin-integrated form of matrices H_{EE}^S and H_{EE}^T, respectively

$$
\begin{aligned}
(H_{EE}^S)_{\alpha p,\beta q} &= (H_{\text{eff}}^{(0,1)})_{\alpha\beta}\delta_{pq} + (H_{\text{eff}}^{(1,0)})_{qp}\delta_{\alpha\beta} \\
&\quad - 2\langle \alpha q|H_{\text{eff}}^{D(1,1)}|p\beta\rangle + \langle \alpha q|H_{\text{eff}}^{E(1,1)}|\beta p\rangle,
\end{aligned}
\tag{10}
$$

$$
\begin{aligned}
(H_{EE}^T)_{\alpha p,\beta q} &= (H_{\text{eff}}^{(0,1)})_{\alpha\beta}\delta_{pq} + (H_{\text{eff}}^{(1,0)})_{qp}\delta_{\alpha\beta} \\
&\quad + \langle \alpha q|H_{\text{eff}}^{E(1,1)}|\beta p\rangle
\end{aligned}
\tag{11}
$$

where α, β are active-hole orbitals (spatial) and p, q are active-particle orbitals (spatial). $H_{\text{eff}}^{[D(1,1)]}$ is the direct block of the $(1,1)$ effective Hamiltonian and $H_{\text{eff}}^{[E(1,1)]}$ is the corresponding exchange block. The diagrammatic representation of these blocks is shown in Fig. 1a and b, respectively. In the next section we present the perturbative analysis of the triply excited amplitudes and a computational scheme to include the amplitudes so that the EEs are correct through to the third order.

3 Perturbative analysis

In this section we will derive the equations for the inclusion of the triply excited amplitudes which contribute to EE at the third order. The calculation of the lowest-order triples in our scheme is along the lines of the MRCCSD + $T^*(3)$ scheme for the calculation of the lowest-order T_3 amplitudes for IPs [28]. This requires the solution of a set of simple equations for the triple amplitudes which are decoupled from each other as well as from the existing singles and doubles equation.

As seen from Eqs. (10) and (11) we would like to include the triples in such a way that $H_{\text{eff}}^{(0,1)}$, $H_{\text{eff}}^{(1,0)}$ as well as the direct and exchange blocks of $H_{\text{eff}}^{(1,1)}$ are correct through to the third order. This scheme for correcting $H_{\text{eff}}^{(0,1)}$ to the third order has already been implemented in the MRCCSD + T^{*3} scheme for IPs [28]. We note that the $T_3^{(0,0)}$ amplitudes do not contribute to any of the above H_{eff} at the third order. The leading contribution of $T_3^{(0,1)}$ to $H_{\text{eff}}^{(0,1)}$ comes from the term $\overline{V}T_3^{(0,1)}$. This appears to be the only $T_3^{(0,1)}$ containing term in $H_{\text{eff}}^{(0,1)}$, which can contribute at the third order. Thus, taking care of full singly and doubly excited amplitudes of the $(0,1)$ sector, one can write the effective Hamiltonian for the $(0,1)$ sector as

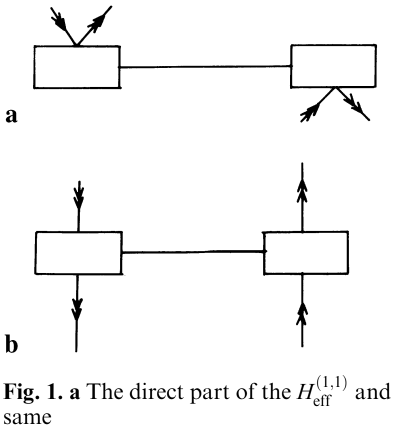

Fig. 1. **a** The direct part of the $H_{\text{eff}}^{(1,1)}$ and **b** the exchange part for the same

$$P^{(0,1)}H_{\mathrm{eff}}^{(0,1)}P^{(0,1)} = P^{(0,1)}[\overline{H}\mathrm{e}^{T_1^{(0,1)}+T_2^{(0,1)}} + \overline{V}T_3^{(0,1)}]P^{(0,1)} \ . \tag{12}$$

Similarly in this scheme the effective Hamiltonian for the (1,0) sector may be written as

$$P^{(1,0)}H_{\mathrm{eff}}^{(1,0)}P^{(1,0)} = P^{(1,0)}[\overline{H}\mathrm{e}^{T_1^{(1,0)}+T_2^{(1,0)}} + \overline{V}T_3^{(1,0)}]P^{(1,0)} \ . \tag{13}$$

To evaluate the triply excited amplitudes of the (0,1) and (1,0) sectors we have to consider the projection of the Bloch equation to the $Q_3^{(0,1)}$ and $Q_3^{(1,0)}$ sectors, respectively.

$$Q_3^{(0,1)}[H\Omega - \Omega H_{\mathrm{eff}}]P_3^{(0,1)} = 0 \ , \tag{14}$$

$$Q_3^{(1,0)}[H\Omega - \Omega H_{\mathrm{eff}}]P_3^{(1,0)} = 0 \ . \tag{15}$$

For evaluating these amplitudes to the lowest order, we need the following terms in each of Eqs. (14) and (15)

$$Q_3^{(0,1)}[\overline{F}T_3^{(0,1)} + \overline{W} - T_3^{(0,1)}\overline{F}]P_3^{(0,1)} = 0 \ , \tag{16}$$

$$Q_3^{(1,0)}[\overline{F}T_3^{(1,0)} + \overline{W} - T_3^{(1,0)}\overline{F}]P_3^{(1,0)} = 0 \ , \tag{17}$$

where $\overline{W}$ is the three-body part of the operator $\overline{H}$.

Let us now examine the terms in $H_{\mathrm{eff}}^{(1,1)}$, which derive contributions from the three-body cluster amplitudes. As we have discussed for the special (1,1) sector, despite our abandoning the IN, that the expression for $H_{\mathrm{eff}}^{(1,1)}$ is similar in structure to the one obtained in the case of IN. This point has been discussed in detail in the Ref. [27]. We present the terms upto the triply excited level.

$$\begin{aligned} H_{\mathrm{eff}}^{(1,1)} = P^{(1,1)}[&\overline{H}\mathrm{e}^{T_1^{(0,1)}+T_2^{(0,1)}+T_1^{(1,0)}+T_2^{(1,0)}+T_2^{(1,1)}} \\ &+ \overline{H}T_3^{(0,1)} + \overline{H}T_3^{(1,0)} + \overline{H}T_3^{(1,1)} \\ &+ \overline{H}T_1^{(1,0)}T_3^{(0,1)} + \overline{H}T_1^{(0,1)}T_3^{(1,0)}]P^{(1,1)} \ . \end{aligned} \tag{18}$$

The terms in the bracket are the only possible terms which can have nonvanishing contributions from the $P^{(1,1)}$ model space to the $P^{(1,1)}$ model space. However, since our objective is to include only those triply excited amplitudes which correct the EEs at the MRCCSD level to the third order, we need the matrix of H_{eff} to be correct through to the third order. Since, the leading contributions to the $T_3^{(0,1)}, T_3^{(1,0)}$ or $T_1^{(1,0)}$ and $T_1^{(0,1)}$ amplitudes are at the second order, the last two terms in the bracket need not be considered. For the same reason, $\overline{H}$ at the second order onwards need not be considered. So, for example, $\overline{F}T_3^{(1,1)}$ can have a nonvanishing contribution, but the part of $\overline{F}$ that can contract with $T_3^{(1,1)}$ to give a nonvanishing $P^{(1,1)}$ to $P^{(1,1)}$ contribution, is a hole-particle $\overline{F}$. The dominant part of *h-p* $\overline{F}$ comes from the connected products of $VT_2^{(0,0)}$, and thus *h-p* $\overline{F}$ starts to contribute at the second order onwards. Hence these $\overline{F}T_3^{(1,1)}$ terms can only contribute to $H_{\mathrm{eff}}^{(1,1)}$ from the fourth order onwards. $\overline{V}T_3^{(1,1)}$, on the other hand, does not have any nonvanishing $P^{(1,1)}$ to $P^{(1,1)}$ projections. The same is true for the $\overline{F}T_3^{(0,1)}$ and $\overline{F}T_3^{(1,0)}$ terms. Thus, we are left with the following terms coming from the triply excited cluster amplitudes which can contribute at the third order onwards.

$$H_{\mathrm{eff}}^{(1,1)} = P^{(1,1)}[\overline{V}T_3^{(0,1)} + \overline{V}T_3^{(1,0)} + \overline{V}T_3^{(1,1)}]P^{(1,1)} \ . \tag{19}$$

Figure 2 diagrammatically depicts the above terms contributing to $H_{\mathrm{eff}}^{(1,1)}$. We can now consider various approximate versions to include these terms. For example, we may consider terms which have only third-order contributions from the above terms. We can, for example, devise schemes which differ in the inclusion of various infinite partial summations, the contributions of all of which will be from the third order onwards. In this paper, we present a scheme which uses $\overline{V}$ in Eq. (19) with the cluster amplitudes of $T_3^{(0,1)}, T_3^{(1,0)}$ and $T_3^{(1,1)}$ operators calculated at their lowest, i.e. second order. These will also be obtained by using $\overline{F}$ and $\overline{V}$. This was the scheme used for the MRCCSD + $T^*(3)$ calculation of IP by Pal et al. in Ref. [28]. As it turns out, this ensures that the triply excited amplitudes have to be calculated in a noniterative manner. In this particular application, $\overline{V}$ in Eq. (19) contains $(He^{T_2^{(0,0)}})_c$ with the fully converged and $T_2^{(0,0)}$ amplitudes. It does not contain the $T_1^{(0,0)}$ and $T_3^{(0,0)}$ amplitudes. The minimum contribution from $T_1^{(0,0)}$ and $T_3^{(0,0)}$ amplitudes to $\overline{V}$ is at the third order onwards and hence the inclusion of these in $\overline{V}$ is not required for correction of the triples to $H_{\mathrm{eff}}^{(1,1)}$ at the third order. To evaluate the triply excited amplitudes of the (1,1) sector, we have to consider the projection of the Bloch equation to $Q_3^{(1,1)}$. To evaluate these amplitudes to the lowest second order the following terms must be considered.

$$\begin{aligned} Q_3^{(1,1)}[&\overline{F}T_3^{(1,1)} + \overline{V}T_2^{(1,1)} + \overline{V}T_2^{(0,1)} \\ &+ \overline{W} - T_3^{(1,1)}\overline{F}]P_3^{(1,1)} = 0 \ . \end{aligned} \tag{20}$$

In Eq. (20) we need the three-body part of $\overline{H}$, i.e. $\overline{W}$, which should be correct through to at least the second

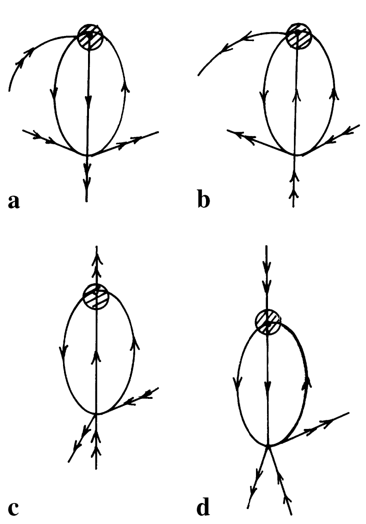

Fig. 2. **a** $\overline{V}T_3^{(0,1)}$ terms contributing to $H_{\mathrm{eff}}^{(1,1)}$; **b** the contribution of the $\overline{V}T_3^{(1,0)}$ term; **c** and **d** the contribution of $\overline{V}T_3^{(1,1)}$ terms of $H_{\mathrm{eff}}^{(1,1)}$

order. This is obtained by considering $VT_2^{(0,0)}$ with the converged values of the $T_2^{(0,0)}$ amplitudes. The converged $T_2^{(0,0)}$ amplitudes bring in higher-order terms through infinite order partial summation. The equations suggest that these triply excited amplitudes at the $(0,1), (1,0)$ and (1,1) sectors may be obtained by a single-shot non-iterative calculation. Thus corrections of the $H_{\text{eff}}^{(1,1)}$ at least upto the third order require a computationally simple prescription of the evaluation of triply excited cluster amplitudes.

4 Results and discussion

In this section we present some pilot applications of the $\text{MRCCSD} + T^*(3)$ model to EEs. As example systems we choose N_2 and CH^+ molecules for which earlier MRCCSD results of low-lying EE exist. For N_2, the Huzinaga-Dunning double-zeta basis augmented by a set of polarized *d*-functions on each *N* atoms (with exponent 0.0930) has been used. The calculations of the vertical EE have been performed at the near experimental bond distance of $R = 2.74$ a.u. We should point out that the earlier MRCCSD results of N_2 presented in Ref. [27] were obtained by freezing the two lowest occupied and the two highest virtual orbitals in the basis set right from the stage of the ground-state CC calculations. But we have done the present calculations without freezing these orbitals at the level of the ground-state CC calculation. Only at the state of the (0,1), (1,0) and (1,1) sector have the lowest two occupied and the highest two virtual orbitals been frozen. These MRCCSD results with the present freezing scheme have been presented under the MRCCSD heading. The T*(3) results in Table 1 have also been obtained at this level. MRCCSD as well as MRCCSD + T*(3) calculations have been performed using only one- and two-body parts of CCD $\overline{H}$. Two active-hole orbitals $3\sigma_g$ and $1\pi_u$ and one active particle $1\pi_g$ are employed in our calculations. Since we are interested in describing the low-lying states dominated by single excitations from $3\sigma_g$ and $1\pi_u$ to $1\pi_g$ orbitals, this model space is adequate. Even with a larger set of active orbitals, the VUCC method will produce the same results for these states. The experimental vertical EEs reported here are as quoted by Nielsen et al. [30] from a calculation of the numerical solution of the Schrodinger's equation using the rovibronic constants given by Huber and Herzberg [31]. We have tabulated the singlet and triplet EEs for transitions dominated by $3\sigma_g \to 1\pi_g$ and $1\pi_u \to 1\pi_g$. In the absence of full configuration interaction (FCI) results the experimental numbers are presented here only as indicative comparisons. We find that most of the results in the $T^*(3)$ scheme are less than the MRCCSD numbers. It is also observed that even in the $T^*(3)$ scheme the $3\sigma_g$ to $1\pi_g$ EEs are poorly obtained. On the other hand, it is encouraging to note that the EEs dominated by $1\pi_u$ to $1\pi_g$ improve in comparison to the experimental values in the $T^*(3)$ scheme. In this sense, the trend is not exactly the same as the one obtained by a similar scheme for IPs. However, since the basis set is not saturated, comparison with the experimental values may not be indicative of quality of the scheme.

Table 2 presents the EEs for CH^+ at an equilibrium distance ($R = 2.13713$ a.u.). The basis set used contains 5*S* type and 3*P* type functions contracted from a primitive set of 9*S* and 5*P* Gaussian functions augmented by a set of *d* functions having 0.75 as an exponent [32]. Similarly, for hydrogen a 3*S* set contracted from primitive 5*S* type functions is used with a set of *P*-functions having an exponent of 1.0. One- and two-body parts of CCD $\overline{H}$ have been used. A 3σ active hole and a 1π active

Table 1. Vertical excitation energies (EEs) for N_2 in a double-zeta polarized basis ($R = 2.074$ a.u.) All energies are in eV: TDA, Tamm Dancoff Approximation; RPA, Random phase approximation; MRCCSD, Multireference coupled cluster singles doubles

State	TDA	RPA	MRCCSD	T*(3)	Expt.
$B^3\Pi_g(3\sigma_g - \Pi_g)$	7.94	7.58	8.03	7.09	8.1
$\alpha^1\Pi_g(3\sigma_g - \Pi_g)$	9.94	9.27	9.37	8.92	9.3
$A^3\Sigma_u^+(1\Pi_u - 1\Pi_g)$	3.45	7.60	7.93	7.51	7.8
$B^3\Sigma_u^-(1\Pi_u - 1\Pi_g)$	7.93	9.92	10.03	9.63	9.7
$W^3\Delta_u(1\Pi_u - 1\Pi_g)$	7.35	5.92	9.12	8.70	8.9
$\alpha'^1\Sigma_u(1\Pi_u - 1\Pi_g)$	8.51	7.93	10.17	9.76	9.9
$\omega'^1\Delta_u(1\Pi_u - 1\Pi_g)$	9.09	8.81	10.65	10.24	10.3
$b'^1\Sigma_u^+(1\Pi_u - 1\Pi_g)$			16.27	15.54	14.4

Table 2. Vertical EE for CH^+ at ($R = 2.13713$ a.u.). FCI, full configuration interaction; C, 5S3P1D $\alpha_d = 0.75$; H, 3S1P $\alpha_p = 1.0$

State	With freezing[b]		Without freezing[b]		FCI[a,b]
	MRCCSD	T*(3)	MRCCSD	T*(3)	
$\Delta E_S(X^1\Sigma^+ - A^1\Pi)$	3.18	3.11	3.16	3.09	3.23 (3.07)
$\Delta E_T(X^1\Sigma^+ - {}^3\Pi)$	1.05	0.83	1.03	0.80	—

[a] See Ref. [35]; experimental values are quoted in parentheses

[b] All energies are in eV

particle have been chosen in this calculation. We have reported the EEs for two cases: (1) without any freezing (2) with freezing of the lowest-occupied and the highest virtual orbital only from the $(0,1)$, $(1,0)$ and $(1,1)$ sector calculation. We compare our results with experimental as well as FCI values. The values in parentheses correspond to the experimental values. It can be seen that with freezing, the MRCC as well as $\mathrm{MRCC} + T^*(3)$ values are 0.02 eV higher than the values without freezing for the single state. However, for the triplet this difference is nearly 0.22 eV. For triplet states, the FCI as well as the experimental values are not available, but for the singlet it can be seen that the values in $\mathrm{MRCCSD} + T^*(3)$ scheme are going in the right direction compared to the experimental numbers. However, when benchmarked against the FCI values one notices that the $\mathrm{MRCCSD} + T^*(3)$ results correct the MRCCSD values in the wrong direction.

Even in the $\mathrm{MRCCSD} + T^*(3)$ scheme to obtain IPs, we observed [28] that the third-order triples often made the IP values go in the wrong direction. This, was rooted to the general problem of convergence in the perturbation series. For IPs, a further inclusion of triples to the fourth order as shown by Vaval et al. [29] corrected the IPs significantly. Such effort for EEs are worth undertaking.

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