Effects of partial triple excitations in atomic coupled cluster calculations

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Abstract

In this article we study the effects of higher body excitations in the relativistic CC calculations for atoms and ions with one valence electron using Fock-space CCSD, CCSD(T) and its unitary variants. The present study demonstrates that CCSD(T) estimates the ionization potentials (IPs) and the valence electron removal energies quite accurately for alkali atoms and singly ionized alkaline earth ions, but yields unphysical energy levels for atoms and/or ions with partially filled sub-shell like C II. We further demonstrate that the higher body excitation effects can be incorporated more effectively through the unitary coupled cluster theory (UCC) compared to the CCSD(T) method.

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1 Introduction

The relativistic coupled cluster (CC) method has emerged as one of the most powerful and effective tool for accurate treatment of electron correlation and relativistic effects in many-electron systems [1]. The CC is an all-order non-perturbative scheme, and therefore, the higher order electron correlation effects can be incorporated more efficiently than using the order-by-order diagrammatic many-body perturbation theory (MBPT) [2]. The method is also size-extensive [3], a property which has been found to be crucial for accurate determination of state energies of atoms and related spectroscopic constants. The incorporation of the singly and doubly excited cluster operators (SD) within the single reference (SR) CC framework provides a reasonably accurate and reliable description of the electron correlation for non-degenerate states, and is one of the most extensively used class of CC approaches.

The CCSD scheme often fails to provide results of sufficient accuracy and even breaks down for highly correlated systems [4]. In recent years, considerable progress has been made in pushing the boundaries of its applicability through the inclusion of higher order clusters in CC methodology both in the singles [5] as well as in the multi-reference formulations [6, 7, 8]. In this regard, the non-iterative approaches like CCSD(T) [9] offer substantial time savings compared to their full CC counterparts, namely, CCSDT (CC with singles, doubles and triples) [10] and CCSDTQ (CC with singles, doubles, triples and quadruples) [11]. In this letter, we demonstrate that a unitary form of the wave operator for the closed shell component of the CC-ansatz can incorporate the effects of partial triples more efficiently than the non-iterative perturbative connected triples corrections, CCSD(T).

To illustrate our findings we compute the ionization potentials (IPs) and valence electron removal energies of C II and Rb I using the Fock-space multi-reference coupled cluster (FSMRCC) method for one electron attachment process (M^{+n}+e→$\mathrm{M}^{+(n-1)} + \Delta E$). The ground state electronic configurations of these two systems reveal that C II has an unfilled L-shell whereas Rb I has a completely filled N-shell followed by one electron ($5s$) in the O shell. In this article we demonstrate that partial triple excitation affects the determination of the ionization potential (IP), the valence electron removal energies and therefore the excitation energies (EEs) of the excited states depending on the vacancies in the principal shell. The behavior of partial triple excitations through CCSD(T) and UCCSD (UCC with singles and doubles excitations) for these kind of systems is also addressed. To our knowledge, this work is the first attempt to establish the effects of partial triple excitations through the core and valence excitations for determining the state energies for single valence atoms having a filled or unfilled sub-shell.

The structure of this article is as follows : Section 2 provides a brief outline of the Fock-space CC theory followed by the higher body effects in section 3. Subsections 3.1 and 3.2 presents the unitary coupled cluster theory and the results are discussed in the subsequent section.

2 Fock-space multi-reference coupled cluster theory for one-electron attachment process

Relativistic extension of coupled cluster (CC) theory is based on the no-virtual-pair approximation (NVPA) along with appropriate modification of orbital form and potential terms [12]. Relativistic CC theory begins with Dirac-Coulomb Hamiltonian (H) for an N electron atom which is expressed as

$$\mathrm{H} = \sum_{i=1}^{N} \left[c\vec{\alpha_i} \cdot \vec{p}_i + \beta mc^2 + V_{\mathrm{Nuc}}(r_i) \right] + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} \tag{1}$$

with all the standard notations often used. The normal ordered form of the above Hamiltonian is given by

$$\mathcal{H} = \mathrm{H} - \langle \Phi | \mathrm{H} | \Phi \rangle = \mathrm{H} - \mathrm{E}_{\mathrm{DF}} = \sum_{ij} \langle i | f | j \rangle \left\{ a_i^\dagger a_j \right\} + \frac{1}{4} \sum_{i,j,k,l} \langle ij || kl \rangle \left\{ a_i^\dagger a_j^\dagger a_l a_k \right\}. \tag{2}$$

where

$$\langle ij || kl \rangle = \langle ij | \frac{1}{r_{12}} | kl \rangle - \langle ij | \frac{1}{r_{12}} | lk \rangle. \tag{3}$$

Here E_{DF} is the Dirac-Fock energy, f is the one-electron Fock operator, $a_i(a_i^\dagger)$ is the annihilation (creation) operator (with respect to the Dirac-Fock state as the vacuum) for the ith electron and $\{\cdots\}$ denotes the normal ordering of the creation/annihilation operators.

Since the FSMRCC theory has been described elsewhere [6, 7, 13], we provide a brief review of this method. The FSMRCC theory is based on the concept of common vacuum for both the N and N±m electron systems, which allows us to formulate a direct method for energy differences. In this method the holes and particles are defined with respect to the common vacuum for both the N and N±m electron systems. Model space of a (m,n) Fock-space contains determinants with m holes and n particles distributed within a set of what are termed as *active* orbitals. For example, in this present article, we are dealing with (0,1) Fock-space which is a complete model space (CMS) by construction and is given by

$$|\Psi_\mu^{(0,1)}\rangle = \sum_i \mathrm{C}_{i\mu} |\Phi_i^{(0,1)}\rangle \tag{4}$$

where $\mathrm{C}_{i\mu}$'s are the coefficients of $\Psi_\mu^{(0,1)}$ and $\Phi_i^{(0,1)}$'s are the model space configurations. The dynamical electron correlation effects are introduced through the *valence-universal* wave-operator Ω [6, 7]

$$\Omega = \{\exp(\tilde{\mathrm{S}})\} \tag{5}$$

where

$$\tilde{\mathrm{S}} = \sum_{k=0}^{m} \sum_{l=0}^{n} \mathrm{S}^{(k,l)} = \mathrm{S}^{(0,0)} + \mathrm{S}^{(0,1)} + \mathrm{S}^{(1,0)} + \cdots \tag{6}$$

At this juncture, it is convenient to single out the core-cluster amplitudes $\mathrm{S}^{(0,0)}$ and call them T. The rest of the cluster amplitudes will henceforth be called S. Since Ω is in normal order, we can rewrite Eq.(5) as

$$\Omega = \exp(\mathrm{T}) \{\exp(\mathrm{S})\} \tag{7}$$

The “valence-universal” wave-operator Ω in Eq.(7) is parametrized in such a way that the states generated by its action on the reference space satisfy the Fock-space Bloch equation

$$\mathrm{H}\Omega\mathrm{P}^{(\mathrm{k,l})} = \Omega\mathrm{P}^{(\mathrm{k,l})}\mathrm{H}_{\mathrm{eff}}\mathrm{P}^{(\mathrm{k,l})} \tag{8}$$

where

$$\mathrm{H}_{\mathrm{eff}} = \mathrm{P}^{(\mathrm{k,l})}\mathrm{H}\Omega\mathrm{P}^{(\mathrm{k,l})}. \tag{9}$$

Eq.(8) is valid for all (k,l) starting from k=l=0, the *core* problem to some desired *parent* model space, with k=m, l=n, say. In this present calculation, we truncate Eq.(6) at $m = 0$ and $n = 1$. The operator $\mathrm{P}^{(\mathrm{k,l})}$ in Eqs. (8) and (9) is the model space projector for k-hole and l-particle model space which satisfies

$$\mathrm{P}^{(\mathrm{k,l})}\Omega\mathrm{P}^{(\mathrm{k,l})} = \mathrm{P}^{(\mathrm{k,l})}. \tag{10}$$

To formulate the theory for direct energy differences, we pre-multiply Eq.(8) by exp(-T) (i.e., Ω_c^{-1}) and get

$$\overline{\mathrm{H}}\Omega_v\mathrm{P}^{(\mathrm{k,l})} = \Omega_v\mathrm{P}^{(\mathrm{k,l})}\mathrm{H}_{\mathrm{eff}}\mathrm{P}^{(\mathrm{k,l})} \qquad \forall(k,l) \neq (0,0) \tag{11}$$

where $\overline{\mathrm{H}}$=$\mathrm{e}^{-\mathrm{T}}$ H e^{T}. Since $\overline{\mathrm{H}}$ can be partitioned into a connected operator $\tilde{\mathrm{H}}$ and $\mathrm{E}_{\mathrm{ref/gr}}$ (N-electron closed-shell reference or ground state energy), we likewise define $\tilde{\mathrm{H}}_{\mathrm{eff}}$ as

$$\mathrm{H}_{\mathrm{eff}} = \tilde{\mathrm{H}}_{\mathrm{eff}} + \mathrm{E}_{\mathrm{ref/gr}}. \tag{12}$$

Substituting Eq.(12) in Eq.(11) we obtain the Fock-space Bloch equation for energy differences:

$$\tilde{\mathrm{H}}\Omega_v\mathrm{P}^{(\mathrm{k,l})} = \Omega_v\mathrm{P}^{(\mathrm{k,l})}\tilde{\mathrm{H}}_{\mathrm{eff}}\mathrm{P}^{(\mathrm{k,l})}. \tag{13}$$

Eqs. (8) and (13) are solved by Bloch projection method, involving the left projection of the equation with $\mathrm{P}^{(\mathrm{k,l})}$ and its orthogonal complement $\mathrm{Q}^{(\mathrm{k,l})}$ to obtain the effective Hamiltonian and the cluster amplitudes, respectively. At this juncture, we recall that the cluster amplitudes in FSMRCC are generated hierarchically through the *subsystem embedding condition* (SEC) [13, 14] which is equivalent to the *valence universality* condition used by Lindgren[6] in his formulation. For example, in the present application, we first solve the Fock-space CC for k=l=0 to obtain the core-cluster amplitudes T. The operator $\tilde{\mathrm{H}}$ and $\tilde{\mathrm{H}}_{\mathrm{eff}}$ are then constructed from this core-cluster amplitudes T to solve the Eq. (13) for k=0, l=1 to determine $\mathrm{S}^{(0,1)}$ amplitudes. The effective Hamiltonian constructed from H, T, and $\mathrm{S}^{(0,1)}$ is then diagonalized within the model space to obtained the desired eigenvalues and eigenvectors

$$\tilde{\mathrm{H}}_{\mathrm{eff}}\mathrm{C}^{(0,1)} = \mathrm{C}^{(0,1)}\mathrm{E}. \tag{14}$$

3 Higher order excitations

It is now widely recognized that the effects of higher body clusters must be included in CC calculations to improve the accuracy of the predicted/computed quantities. Here by the term ‘higher body effects’, we mean effects from triple, quadruple excitations etc. In this letter, we shall restrict ourselves only to triple excitations for the time being and will comment on other higher excitations later. The most straightforward approach is to include the full three body excitation operators T_3 and S_3 in the CC ansatz via $\mathrm{T}=\mathrm{T}_1+\mathrm{T}_2+\mathrm{T}_3$ and $\mathrm{S}=\mathrm{S}_1+\mathrm{S}_2+\mathrm{S}_3$. This direct approach, known as CCSDT, is computationally very expensive.

In this article we have used the unitary ansatz to simulate the effects of triples and some other higher body excitations, *e.g.*, quadruples etc. in the core sector. In addition, we have also considered the effects of partial triple excitations in a perturbative way for the (0,1) valence sector known as CCSD(T). These are discussed in the next two subsections.

3.1 Higher body excitations through unitary ansatz

Unitary coupled-cluster (UCC) theory was first proposed by Kutzelnigg [15]. In this theory, the effective Hamiltonian is Hermitian by construction and the energy which is the expectation value of this operator in the reference state is an upper bound to the ground state energy [16].

The normal ordered dressed Hamiltonian is expressed by the Baker-Hausdorff-Campbell expansion in CC theory as

$$\begin{aligned}\overline{\mathcal{H}} &= e^{-\mathrm{T}}\mathcal{H}e^{\mathrm{T}} \\ &= \mathcal{H} + [\mathcal{H},\mathrm{T}] + \frac{1}{2!}[[\mathcal{H},\mathrm{T}],\mathrm{T}] \\ &+ \frac{1}{3!}[[[\mathcal{H},\mathrm{T}],\mathrm{T}],\mathrm{T}] + \frac{1}{4!}[[[[\mathcal{H},\mathrm{T}],\mathrm{T}],\mathrm{T}],\mathrm{T}]. \end{aligned} \tag{15}$$

In UCC, the operator T is replaced by $\sigma_c = \mathrm{T} - \mathrm{T}^\dagger$ in the above equation. As a result, $\overline{\mathcal{H}}$ is expressed in terms of a non-terminating series of commutators. For practical reasons, one truncates the series after some finite order. Truncation at the n-th order commutator leads to the nomenclature UCC(n).

Using UCC(*3*) approximation and without modifying the last term of the above expression, one can show that the dressed Hamiltonian takes the form

$$\overline{\mathcal{H}} = \mathcal{H} + \overline{\mathcal{H}\mathrm{T}} + \frac{1}{2!}(\overline{\overline{\mathcal{H}\mathrm{T}}\mathrm{T}} + 2\overline{\overline{\mathrm{T}^\dagger\mathcal{H}}\mathrm{T}}) + \frac{1}{3!}(\overline{\overline{\overline{\mathcal{H}\mathrm{T}}\mathrm{T}}\mathrm{T}} + 3\overline{\mathrm{T}^\dagger\overline{\mathrm{T}^\dagger\overline{\mathcal{H}\mathrm{T}}}} + 3\overline{\mathrm{T}^\dagger\overline{\overline{\mathcal{H}\mathrm{T}}\mathrm{T}}}) + \frac{1}{4!}\overline{\overline{\overline{\overline{\mathcal{H}\mathrm{T}}\mathrm{T}}\mathrm{T}}\mathrm{T}} \tag{16}$$

Here 'overline' denotes the contraction between two sets of operators. For example, the term $\overline{\mathcal{H}\mathrm{T}}$ corresponds to the contraction between the operators $\mathcal{H}$ and T. A typical contribution to the term $\overline{\overline{\mathcal{H}\mathrm{T}_2}\mathrm{T}_2}$ is given by

$$B_{ab}^{pq} = \frac{1}{2}\sum_{dgrs} V_{dgrs} t_{ad}^{pr} t_{gb}^{sq}. \tag{17}$$

Here V_{dgrs} is the two-electron Coulomb integral and t_{ad}^{pr} is the cluster amplitude corresponding to a simultaneous excitation of two electrons from orbital $a \rightarrow p$ and $d \rightarrow r$, respectively. This term is common both to CCSD and UCCSD whereas the latter contains some higher order terms containing $\mathrm{T}^\dagger$ which are not present in the CCSD expansion of $\overline{\mathcal{H}}$ [17]. Diagrammatic techniques are used to obtain all the terms which contribute to this specific contribution. Fig. 1 shows two typical diagrams arises from UCC(3) which correspond to a subset of effective triple (1a) and quadruple excitation (1b) effects respectively.

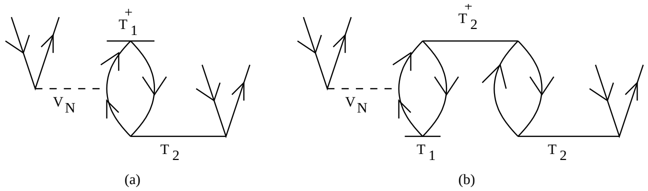

Figure 1: Typical effective triples and quadruples diagrams arising from UCC(*3*). V_N represents the Coulomb vertex.

3.2 Higher order excitations in the valence sector

Triple excitations are included in the open shell CC amplitude which correspond to the correlation to the valence orbitals, by an approximation that is similar in spirit to CCSD(T) [9]. The approximate valence triple excitation amplitude is given by

$$\mathrm{S}_{abk}^{pqr} = \frac{\{\overline{V\mathrm{T}_2}\}_{abk}^{pqr} + \{\overline{V\mathrm{S}_2}\}_{abk}^{pqr}}{\varepsilon_a + \varepsilon_b + \varepsilon_k - \varepsilon_p - \varepsilon_q - \varepsilon_r}, \tag{18}$$

where S_{abk}^{pqr} are the amplitudes corresponding to the simultaneous excitation of orbitals a, b, k to p, q, r, respectively; $\overline{V\mathrm{T}_2}$ and $\overline{V\mathrm{S}_2}$ are the correlated composites involving V and T, and V and S respectively

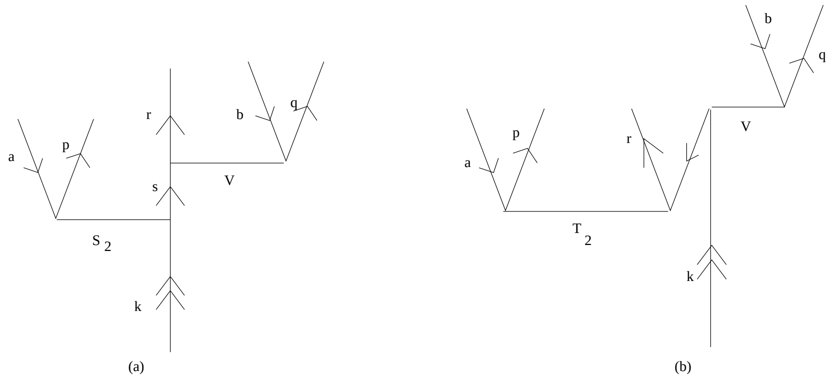

Figure 2: Some typical important diagrams which arise due to the inclusion of triple excitations through Eq.(21). In this diagram V denotes the Coulomb vertex.

where V is the two electron Coulomb integral and ε's are the orbital energies. The above amplitudes (some representative diagrams are given in Fig. 2) are added appropriately to the singles and doubles S amplitude determining equations and these equations are then solved iteratively.

4 Results - CC calculations for atoms with single valence electron

In this article we have considered two systems C II and Rb I. C II is the singly ionized C atom and the ground state has an atomic structure like Boron (B I) : $1s^2 2s^2 2p_{1/2}$ where as the electronic structure of Rb I ground state is [Kr]$5s$ *i.e.* $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s$. As because the ground state of C II and Rb I is an open-shell doublet, we begin with C III and Rb II which defines the (0h,0p) valence sector. We then employ the open-shell Fock space CC theory for one electron attachment process to compute the ionization potentials (IPs) of the ground state and excitation energies (EEs) of the the first few excited states of C II and Rb I, which are given in tables 2 and 3 respectively. We have also calculated those quantities taking into account the effect of partial triple excitations for the valence electron and are listed as CCSD(T)/UCCSD(T) in the corresponding tables.

The Dirac-Fock equations are first solved for closed shell ions (C III and Rb II), which defines the (0,0) sector of the Fock space. The ion is then correlated using the closed shell CCSD/UCCSD, after which one-electron is added following the Fock-space strategy:

$$\mathrm{M}^{+\mathrm{n}}(0,0) + e \longrightarrow \mathrm{M}^{+(\mathrm{n}-1)}(0,1). \tag{19}$$

Both the DF and relativistic CC programs utilize the angular momentum decomposition of the wave-functions and CC equations. Using the Jucys- Levinson-Vanagas (JLV) theorem [18], the Goldstone diagrams are expressed as a products of angular momentum diagrams and reduced matrix element. This procedure simplifies the computational complexity of the DF and CC equations. We use the kinetic balance condition to avoid the “variational collapse” [19].

In the actual computation, the DF ground state and excited state properties are computed using the finite basis set expansion method (FBSE) [20] with a large basis set of Gaussian type functions (GFs) of the form

$$F_{i,k}(r) = r^k \cdot e^{-\alpha_i r^2} \tag{20}$$

with $k = 0, 1, \ldots$ for $s, p, \ldots$ type functions, respectively. For the exponents, the even tempering condition

$$\alpha_i = \alpha_0 \beta^{i-1} \tag{21}$$

is applied. The nucleus has a finite structure and is described by the two parameter Fermi nuclear distribution

$$\rho = \frac{\rho_0}{1 + \exp((r-c)/a)}\,, \tag{22}$$

Table 1: Total number of the basis functions and the even tempering parameters (α_0 and β) used in the calculations. GTOs stand for the Gaussian type orbitals used to generate the DF wave-functions. 'Active orbitals' refer to the number of orbitals used in the CC/UCC calculations. The parameters α_0 and β for C II (Rb I) are 0.005 (0.00523) and 2.25 (2.09) respectively which are used in Eq. (21) to generate the DF orbitals.

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	$g_{7/2}$	$g_{9/2}$
C II									
No. of GTOs	35	32	32	25	25	25	25	20	20
Active orbitals	14	13	13	11	11	9	9	6	6
Rb I									
No. of GTOs	38	35	35	25	25	25	25	20	20
Active orbitals	14	12	12	10	10	9	9	6	6

Table 2: Ionization potential (IP) and the excitation energies (EEs) (in cm^{-1}) for C II. The column 'Koopman' contains the Dirac-Fock energies and the columns designated as (T) contain the effects of partial triple excitations in the valence sector. Observed values of IP and EEs are taken from the NIST table [21] unless mentioned otherwise.

	State	Koopman	CCSD	CCSD(T)	UCCSD	UCCSD(T)	Observed
IP	$2p\,^2P_{1/2}$	189794.81	196575.36	197825.00	196739.57	197988.30	196592.44 [22]
EE	$2p\,^2P_{3/2}$	73.28	73.44	-17.22	45.37	44.67	63.42
	$3s\,^2S_{1/2}$	110674.88	109729.32	108025.07	108203.18	105768.50	116537.65
	$3p\,^2P_{1/2}$	127422.46	131623.85	132703.83	131766.92	132838.66	131724.37
	$3p\,^2P_{3/2}$	127433.78	131636.80	132726.16	131780.30	132860.20	131735.52

where the parameter c is the half charge radius and a is related to skin thickness, defined as the interval of the nuclear thickness in which the nuclear charge density falls from near one to near zero. We have taken a large basis set to check the convergence of the results on the number of basis functions used. Excitations from all the core electrons have been considered for all the cases. The details of the basis sets used in the calculations presented here are given in table 1.

5 Analysis and discussions

Tables 2 and 3 present the ionization potential (IP) for the ground state and the excitation energies (EEs) for the few low lying excited states for C II and Rb I, respectively. From the calculations and the tabulated results we have observed a nice feature about the usage of perturbative triple excitations often used in the

Table 3: Ionization potential (IP) and the excitation energies (EEs) (in cm^{-1}) for Rb I. Observed values given in the last column are taken from the NIST table [21].

	State	Koopman	CCSD	CCSD(T)	UCCSD	UCCSD(T)	Observed
IP	$5s\,^2S_{1/2}$	30592.05	33690.23	33694.39	33691.16	33694.91	33690.57
EE	$5p\,^2P_{1/2}$	10660.57	12610.94	12594.57	12611.16	12594.81	12578.95
	$5p\,^2P_{3/2}$	10898.41	12850.35	12849.30	12850.59	12849.54	12816.54
	$4d\,^2D_{5/2}$	17494.13	19484.27	19444.28	19483.57	19430.27	19355.20
	$4d\,^2D_{3/2}$	17481.27	19482.91	19434.31	19482.19	19435.20	19355.65

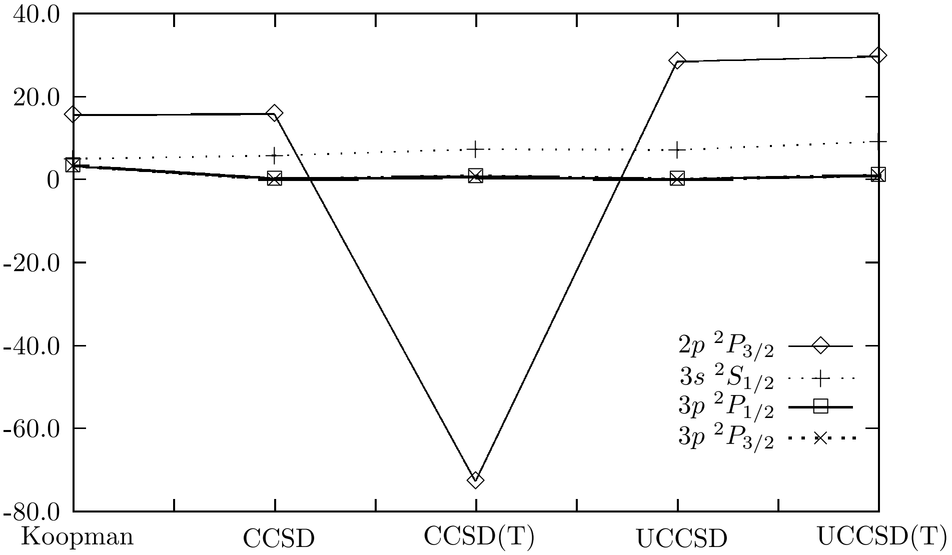

Figure 3: Relative error (in %) in estimation of EEs for different states of C II. The acronyms for the different methods are discussed in the text and in the tables.

CC calculations. From Table 2 we have observed that for singly ionized C I *i.e.* C II (an element in the group IV in the periodic table), CCSD method works reasonably well to estimate the IP of the ground state and EE for the first excited state, whereas the UCCSD method performs better for estimating the EEs of the excited states like $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$. When we consider the effect of perturbative partial triple excitations for the valence electron, namely CCSD(T), the method fails miserably to estimate the IP and the EE's. Moreover CCSD(T) even fails to determine the ground state of C II. This is reflected in the value of the EE of the $2p\,^2P_{3/2}$ state which has a negative sign. That indicates CCSD(T) determines $2p\,^2P_{3/2}$ to be the ground state of C I instead of $2p\,^2P_{1/2}$. On the other hand, when we apply UCCSD(T) to estimate IP and EEs for C II it performs better than CCSD(T) but still is not good enough to calculate them accurately as compared to CCSD and UCCSD. Moreover UCCSD(T) is also capable of determining $2p\,^2P_{1/2}$ as the ground state of C II.

Table 3 contains the IP of the ground state and EEs for the first few excited states of the alkali atom Rb which is positioned in the Gr-I in the periodic table. We have observed that both CCSD/UCCSD perform better to determine the IP of the ground state and the EE for the first excited states. Whereas, to determine the EEs of the second excited state and onwards, the partial triple excitations from the valence sector contribute quite significantly. If we do a close comparison to the effects of partial triple excitations in the CCSD and UCCSD level, denoted by CCSD(T) and UCCSD(T) respectively we can find out that UCCSD(T) even performs better to determine the EE's of the high lying excited states.

We have shown earlier [17] that unlike CCSD, UCCSD can contains more effects from higher order excitations in the same level of excitation because of the structure of the core excitation operator. Consideration of higher order excitation is the key point to understand the improved performance of UCCSD for the high lying excited states. This has been discussed in section 3.1. In CCSD(T) and UCCSD(T) we have considered the effect of partial triples denoted by (T) in the valence sector. If we take a close look at the electronic structure of the atoms considered in the calculations we will find that for C II, the core is defined as $1s^2 2s^2$ and the L-shell (with principal quantum number 2) is not completely filled. On the other hand for Rb I the core is defined as [Kr] which has a completely filled N-shell (principal quantum number 4). When we apply CCSD(T) or UCCSD(T) for C II, because of the unfilled L-shell, the correlation effect, the most important many-body effects in multi-electron atoms, between the valence electron and the electrons from the unfilled L-shell (in this case the $2s$ electrons) turns out to be very important. This is reflected in the Koopman energies listed in the table. More explicitly, although the $2s$ sub-shell (L_1 shell) is fully occupied in the ground state of C II, but the vacancy in the rest of the L shell makes the case a little different than Rb I. In figure 3 and 4 we have graphically shown our findings. In fig 4 the figure given in the inside box contains

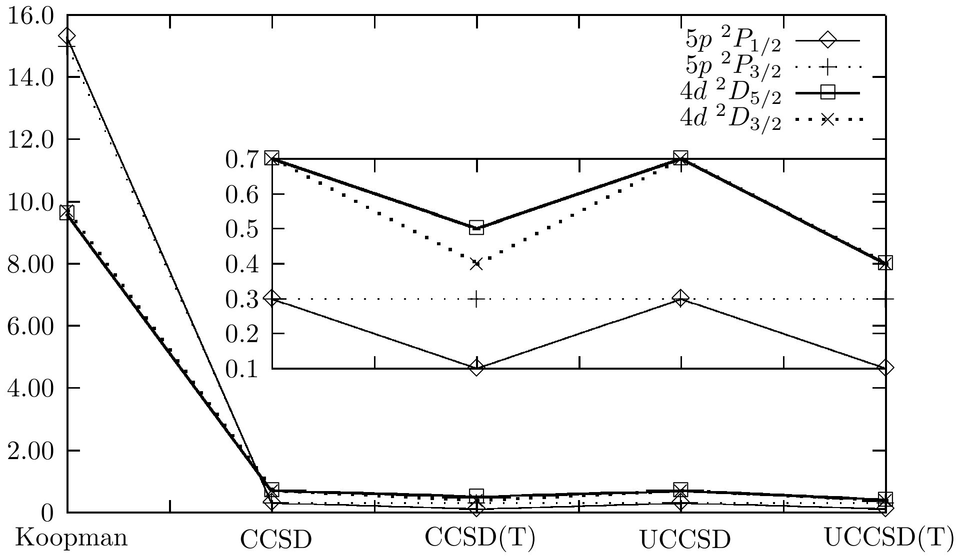

Figure 4: Relative error (in %) in estimation of EEs for different states of Rb I. The figure shown in the inside box is a magnification of the relative errors for different CC methods.

the relative errors (in %) in estimating the EEs of first few excited states using different CC methods. This inner figure helps us to see the relative errors for the different CC methods in a proper scaling.

To generalize our findings we have also studied two more systems, Li I, the alkali atom with filled K-shell but unfilled L-shell (Ground state of Li I : $1s^22s$) and Al I with the ground state configurations $1s^22s^22p^63s^23p$ (unfilled M shell). Both Li I and Al I have similarities with Rb I and C II respectively in terms of the vacancies in the principal shell. Earlier we have reported the determination of the IP and EEs for Al I using CCSD and UCCSD [23]. For the alkali atoms like Li I and Rb I, the valence electrons feel the potential of a core with a completely filled principal shell (K and M shell respectively). On the other hand for C II and Al I the core do not have a completely filled principal shell. For these two atoms the electron correlation between the electrons in the unfilled principal shell play important roles in determining the state energies. In this study we have found the similar pattern of performance of CCSD/UCCSD and CCSD(T)/UCCSD(T) for systems with filled/unfilled principal shell for the core state.

6 Conclusion

In conclusion, we want to focus on the findings of our work in the following way. The contribution of partial triples through CCSD(T)/UCCSD(T) method works well for atoms or ions with a filled principal shell in the core. On the other hand if there is a vacancy in the principal shell in the core the coupled cluster (CC) and the unitary coupled cluster (UCC) method with partial triple excitations in the valence sector fails miserably. In general CCSD method works well to determine the IP of the ground state and the EE of the first excited state. Whereas, the unitary counterpart of CCSD, namely UCCSD performs better to determine the EEs for the high lying excited states.

To our knowledge this is the first attempt to analyze the effects of partial triple excitation in atomic coupled cluster calculations in this manner. One can generalize our findings to estimate the state energies for atoms/ions with an unfilled principal shell in their configuration. The present study clearly demonstrates that CCSD(T) is, in general, not the best method for accurate determination of state energies for atoms with a single valence electron. This is important because CCSD(T) is used to estimate the error in the theoretical determination of state energies and atomic properties like transition probabilities and expectation values [24]. Our findings in this work will focus on the issue to search for a new method for estimating the error.

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