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Applications of core-valence extensive multi-reference coupled cluster theory and core-extensive coupled cluster-based linear response theory

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Abstract

The single reference coupled cluster based linear response theory (CCLRT) and valence-universal multi-reference coupled cluster (VU-MRCC) theory for direct difference energy calculations have been presented. The similarities and differences in the structure of these two formalisms have also been addressed. The core-extensive CCLRT is applied to compute the ionization potentials (IPs) of HCl and excitation energies of CuH using Hartree–Fock (HF) orbitals. We further report the relativistic applications of the VU-MRCC theory through the computation of the ground and excited/ionized state energies and related properties of Ag and Hg atoms using Dirac–Hartree–Fock (DHF) orbitals. The IPs, excitation energies, and the spectroscopic constants reported here are in favorable agreement with experiment and with other correlated calculations.

Keywords: CCSD; CCLRT; VU-MRCC

1. Introduction

The strong interplay of dynamical and non-dynamical correlation effects intertwined with the effect of orbital relaxation shapes the accuracy of the theoretical studies on the ground and excited state properties of atomic and molecular systems. A balanced treatment of the twin effects leads to an accurate prediction of the transition energies, potential energy surfaces/curves, and related properties. The single reference coupled cluster (SRCC) [1] method, developed by the cluster expansion of a single determinant reference function, is one of the most sophisticated, elegant and well established methods among the vast plethora of correlated many-body theories for treating dynamical correlation effects in a size-extensive manner in situations where the non-dynamical correlation effects can be sidelined, for example, the closed-shell states around the equilibrium internuclear configurations. The incorporation of the singly and doubly excited cluster operators (SD) only within the SRCC framework provides an accurate and reliable description of the electron correlation for non-degenerate states, and is one of the most extensively used class of SRCC approaches.

Motivated by the initial success of the SRCC method, several endeavors have come to force during the past couple of decades to generalize the SRCC method and make it suitable to encompass open-shell and/or quasi-degenerate states. The non-uniqueness of the exponential nature of the wave operator diversifies the methods to a host of MRCC strategies. The traditional MRCC methods hinge on the effective Hamiltonian approach and work within the complete model space (CMS), though they are rather more varied in their scope of applications [2]. The effective Hamiltonian based MRCC strategies fall within two broad classes: (i) state-universal (SU), a Hilbert-space approach [3] and (ii) valence-universal (VU), a Fock-space approach [4–7,10,11]. The SU-MRCC method highlights on only one valence sector at a time, with the cluster operators being defined with respect to each reference function. The VU-MRCC approach, on the contrary, uses a single wave operator that not only correlates the reference functions of interest, but also all the lower valence (or the so called *subdued*) sectors, obtained by deleting the occupancies systematically. At this juncture, we recall that the cluster amplitudes in Fock-space VU-MRCC are generated hierarchically through the *subsystem embedding condition* (SEC) [5,8], which is equivalent to the *valence universality* condition used by Lindgren [7] in his formulation.

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The linear response theory (LRT) or equation of motion (EOM) method [12–16] is another possible alternative which is used to compute the spectroscopic energies. The EOM–CC and SR–CCLRT methods are identical for the ionized/excited states energies, but the approximations used in these two methods differ for transition properties. The underlying physics is the same, in particular, state properties defined as energy derivatives are clearly identical since the state energies themselves are identical. Several models, iterative and non-iterative, have also been developed which partially include the effects of triple excitations [17]. Recently, Nooijen and Bartlett have developed a new method for calculating excited state energies and properties, the similarity transformed EOM–CC (STEOM–CC) method [18]. For singly excited states, the STEOM–CC is closely related to the Fock space CC method [18], but conceptually they are very different. In STEOM–CC, the ground state CC calculation describes the ground state dynamic correlation very well, whereas the differential correlation is handled through the second similarity transformation, which is built from an active space of ionized and electron-attached states.

The main advantage of the VU-MRCC theory is that its working equation is fully connected and hence size-extensive in nature in contrast to the LRT or EOM method which is core extensive and not core-valence extensive due to the presence of the disconnected diagrams while considering the charge-transfer excitations. Although, the LRT or EOM method is not fully extensive in nature, the method is *intruder free* [19] in contrast to the traditional VU-MRCC theory due to the CI-like structure of the working equation of the former. It should be noted that for the same truncation scheme of the operator manifold, VU-MRCC is equivalent to the LR-based CC methods [12,16] for one-valence problem.

In spite of formal rigor, the VU-MRCC equations are often plagued by the *intruder state problem*. This was circumvented in an elegant way by Mukherjee et al. [20] via ‘eigenvalue independent partitioning technique’ (EIP). The EIP technique converts the non-linear VU-MRCC equations for any model space into a set of non-hermitian eigenvalue equations (CCLRT like structure). Later, Mukherjee and co-workers [21] studied the IP and DIP related to the Auger electron spectroscopy of some interesting systems using the EIP method.

In this article, we employ the CCLRT and VU-MRCC to compute the ground and excited/ionized state energies and relevant properties of HCl, CuH, Ag and Hg. The ground and excited/ionized state properties of HCl and CuH are computed using CCLRT while the VU-MRCC theory is employed for Ag and Hg atom. Because of low Z value, we employ the Hartree–Fock orbitals in the computation of the ground and excited/ionized state properties for HCl and CuH. On the other hand, four-component Dirac–Fock orbitals are used for Ag and Hg atom.

The paper is organized as follows. We briefly outline the CCLRT and VU-MRCC methods in Section 2. The computational details and results are discussed in the subsequent sections.

2. Methodology

2.1. Valence universal multi-reference coupled cluster theory: a core-valence extensive theory

Since the basic formalism of VU-MRCC theory for the energy difference is available elsewhere [4,6], we provide a brief overview of this method for general model space. We choose the Hartree–Fock (HF) (Dirac–HF in relativistic regime) solution for the closed-shell N-electron ground state Φ_{HF} as the vacuum to define holes and particles with the respect to Φ_{HF}. The holes and particles are further subdivided to introduce multi-reference aspect. We define a *model* space (P) which has all possible electron occupancies in the active orbitals to be *complete*, while others are said to be *incomplete*. In general, any second-quantized operator has k-hole and l-particle destruction operators for the active holes and particles and m-particle and n-hole excitation operators involving both active and inactive holes and particles. We define an operator A of valence rank (k,l) by $A^{(k,l)}$ where A contains exactly k-hole and l-particle destruction operators.

Using the ‘valence-universal’[4,6–11] ansatz for the wave operator Ω, the Fock-space Bloch equation for the CC-theory may be written as

$$H\Omega P^{(k,l)} = \Omega P^{(k,l)} H_{\mathrm{eff}} P^{(k,l)} \quad \forall\,(k,l) \tag{1}$$

where H is the N-electron Hamiltonian and:

$$H_{\mathrm{eff}} = P^{(k,l)} H \Omega P^{(k,l)}. \tag{2}$$

Here, the equation is taken to be 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. We express Ω in *normal* order as

$$\Omega = \{\exp(\tilde{S})\} \tag{3}$$

with $\tilde{S}$ containing only *external* operators (operators that connect the model space with the complementary space Q) of various valence ranks:

$$\tilde{S} = \sum_{k,l=0,0}^{m,n} S^{(k,l)}. \tag{4}$$

In second quantized notation, operator S for (0,0), (0,1) and (1,0) valence rank can be written as

$$S^{(0,0)} = \sum_{p}^{unocc} \sum_{\alpha}^{occ} \langle p | s_1^{(0,0)} | \alpha \rangle \{a_p^{\dagger} a_{\alpha}\} + \frac{1}{4} \times \sum_{p,q}^{uocc} \sum_{\alpha,\beta}^{occ} \langle pq | s_2^{(0,0)} | \alpha\beta \rangle \{a_p^{\dagger} a_q^{\dagger} a_{\beta} a_{\alpha}\} + \cdots, \tag{5}$$

$$S^{(0,1)} = \frac{1}{2} \sum_{p,q,r}^{uocc} \sum_{\alpha}^{occ} \langle pr | s_2^{(0,1)} | q\alpha \rangle \{a_p^{\dagger} a_r^{\dagger} a_{\alpha} a_q\} + \cdots \tag{6}$$

(for all active particles),

and

$$S^{(1,0)} = \frac{1}{2}\sum_{p}^{uocc}\sum_{\beta,\gamma,\alpha}^{occ}\langle p\alpha|s_2^{(1,0)}|\gamma\beta\rangle\{a_p^{\dagger}a_{\alpha}^{\dagger}a_{\beta}a_{\gamma}\} + \cdots, \tag{7}$$

(for all active holes),

respectively. At this juncture, it is convenient to single out the core-cluster amplitudes $S^{(0,0)}$ 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. (3) as:

$$\Omega = \exp(T)\{\exp(S)\} \tag{8}$$

Premultiplying Eq. (1) by $\exp(-T)$ and using Eq. (8), we get [22]

$$\bar{H}\Omega_v P^{(k,l)} = \Omega_v P^{(k,l)}\bar{H}_{\mathrm{eff}}P^{(k,l)} \quad \forall\,(k,l) \neq (0,0) \tag{9}$$

where

$$\bar{H} = \exp(-T)H\exp(T) \tag{10}$$

and:

$$\Omega_v = \{\exp(S)\} \tag{11}$$

Here, the core-cluster amplitudes T are assumed as solved at the lowest level of hierarchy of $(k,l)\equiv(0,0)$. Expressing the Hamiltonian H in normal order ($H = H_{\mathrm{N}} + E_{\mathrm{HF}}$), we rewrite Eq. (10) as:

$$\bar{H} = \exp(-T)H_{\mathrm{N}}\exp(T) + E_{\mathrm{HF}} = \tilde{H} + E_{\mathrm{HF}}. \tag{12}$$

Since, $\tilde{H}$ can be split into an operator part $\tilde{H}$ and the ground state energy E_{gr}, we likewise define $\tilde{H}_{\mathrm{eff}}$, generating the energy differences, and write

$$\bar{H}_{\mathrm{eff}} = \tilde{H}_{\mathrm{eff}} + E_{\mathrm{gr}} \tag{13}$$

and thus get the Fock-space Bloch equation for energy differences as:

$$\tilde{H}\Omega_v P^{(k,l)} = \Omega_v P^{(k,l)}\tilde{H}_{\mathrm{eff}}P^{(k,l)} \quad \forall\,(k,l) \neq (0,0) \tag{14}$$

Proceeding hierarchically from the lowest nontrivial valence ranks (1,0) and (0,1), we get

$$\tilde{H}\Omega_v P^{(1,0)} = \Omega_v P^{(1,0)}\tilde{H}_{\mathrm{eff}}P^{(1,0)} \tag{15}$$

and

$$\tilde{H}\Omega_v P^{(0,1)} = \Omega_v P^{(0,1)}\tilde{H}_{\mathrm{eff}}P^{(0,1)} \tag{16}$$

for the one-hole and one-particle model space, which correspond to the IP and EA problems.

The scheme of generating the elementary excitations (IP, EA, EE, etc.) proceed hierarchically. We first solve the ground state problem to determine the T amplitudes. The $S^{(1,0)}$ and $S^{(0,1)}$ are solved in the next level of hierarchy which are *decoupled* from each other. The $S^{(1,1)}$ are solved next in which all the cluster amplitudes of lower valence ranks, i.e. T, $S^{(1,0)}$, and $S^{(0,1)}$ *rigorously remain frozen*. At this juncture, we emphasize that it is possible to choose an 'incomplete' model space for (2,0)/(0,2) valence sector (related to double IP/EA) and yet continue to use the CC-equations for 'complete' model space.

2.2. *Single-reference coupled cluster based linear response theory: a core extensive theory*

In CC based LRT methods, the ground state CC operator is used to perform a similarity transformation of the Hamiltonian, which is then diagonalized within the space of excited determinants. SR–CCLRT is nowadays routinely used for the investigation of excited states of closed-shell molecules. A major theoretical advantage of the response based method lies in the representation of the excited state in terms of the ground state. This description thus automatically includes the correlation contribution from the ground state that remains more or less unchanged and which largely dominates in the low-lying excited state correlation. The additional differential correlations accompanying excitation can then be incorporated in a systematic manner in the dynamic linear response function. As a consequence, the response approach offers the flexibility of including the differential correlation and the additional correlation effects on top of the ground state correlation components. The common correlation terms then drop out in the energy differences, and the excitation energies obtained are thus described in a more balanced manner. It is thus not surprising that the pre-eminent success of the SRCC theory for the ground state has produced in turn a very successful linear response theory based on the SRCC wavefunction, and is widely accepted as a major method of choice for the excited states whose ground state is predominantly SR in character.

The CCLRT method for energy difference was first put forward by Mukherjee et al. [13]. In their formulation, the atom/molecule in its ground state is subjected to a photon field and the linear response of the ground state function described by the CC-ansatz is computed where the poles of the response functions are the elementary excitations. Depending on the nature of perturbation, one may obtain IP, EA, EE, DIP, etc. of the ground state. Mukherjee and co-workers [23] have also shown an equivalent but simpler derivation of this scheme.

In CCLRT approach, the wave operator Ω in Eq. (8) is expressed as

$$\Omega = \exp(T)W_k^{\dagger} \tag{17}$$

where the cluster operators $W_k^{\dagger}$ are expressed as

$$W_k^{\dagger} = \sum_{\alpha}^{occ}x_{\alpha}\{a_{\alpha}\} + \sum_{\alpha,\beta}^{occ}\sum_{p=1}^{unocc}x_{\alpha\beta}^{p}\{a_p^{\dagger}a_{\beta}a_{\alpha}i\} + \cdots \tag{18}$$

(for IP),

$$W_k^{\dagger} = \sum_{p}^{unocc}x_p\{a_p^{\dagger}\} + \sum_{p,q}^{uocc}\sum_{\alpha}^{occ}x_{\alpha}^{pq}\{a_p^{\dagger}a_q^{\dagger}a_{\alpha}\} + \cdots \tag{19}$$

(for EA),

and

$$W_k^{\dagger} = \sum_{p}^{unocc}\sum_{\alpha}^{occ}x_{\alpha}^{p}\{a_p^{\dagger}a_{\alpha}\} + \frac{1}{2}\sum_{p,q}^{uocc}\sum_{\alpha,\beta}^{occ}x_{\alpha\beta}^{pq}\{a_p^{\dagger}a_q^{\dagger}a_{\beta}a_{\alpha}\} + \cdots \quad \text{(for EE).} \tag{20}$$

The ionized/excited state Ψ_k are generated from the ground state by the action of ionization/excitation operator $W_k^\dagger$, and the corresponding energy ω_k are obtained from an equation of the form [13,23–27]:

$$[H, W_k^\dagger]|\Psi_0\rangle = E_k W_k^\dagger |\Psi_0\rangle \tag{21}$$

Since T and $W_k^\dagger$ commute, premultiplying Eq. (21) by $\exp(-T)$ we get the following equation of motion

$$[\tilde{H}, W_k^\dagger]|\phi_0\rangle = (E_k - E_{gr}) W_k^\dagger |\phi_0\rangle \equiv \omega_k W_k^\dagger |\phi_0\rangle \tag{22}$$

where $\bar{H} = \tilde{H} + E_{gr}$. Projecting Eq. (22) on to the bi-orthogonal space, we get an eigenvalue equation of the form:

$$AX_k = \Lambda X_k. \tag{23}$$

It is evident from above that CCLRT has altogether a much simpler structure compared to core-valence extensive VU-MRCC theory. There is no hierarchical generation of the cluster amplitudes except for the ground state (which is common to both), neither there is any special consideration for the appropriate choice of normalization. From the very mode of derivation it is quite clear that the energies computed via CCLRT method are core-extensive in nature. For the valence component, CCLRT behaves like a truncated CI which destroys its extensive nature. As a result of this, the method is not core-valence extensive.

3. Results and discussions

3.1. HCl system

The valence and satellite lines of HCl [28–32] have been studied experimentally by Adam [30,31] and by Svensson et al. [32] who have recorded the HCl valence ionization spectrum up to 52 eV using XPS and SRPS [32]. So far, 11 satellite lines have been observed of which seven peaks are found to lie below the continuum for doubly ionized states. The HCl satellite peaks [33] have been studied theoretically by the Green's function (GF) method, ADC(3) (algebraic diagrammatic construction accurate to 3rd order), approximate ADC(4) (algebraic diagrammatic construction accurate to 4th order) [34,35], symmetry-adapted-cluster configuration interaction general-R (SAC-CI-general-R) [36–40], and the SAC-CI-SD-R (single double-R) methods. While the previous theoretical studies are quite successful in assigning some satellite peaks, the computed first valence ionization potentials for the $^2\Pi$ state deviates significantly (by 0.3–0.4 eV) from the experiment.

Compared to the singly ionized photo-electron spectrum, the doubly ionized photo-electron spectrum of HCl is not so well probed. The Auger spectrum of HCl has been measured by Svensson et al. [41] and Aksela et al. [42]. Subsequent independent theoretical interpretations of the high kinetic energy region of HCl by Aksela [42] and Kvalheim [43] use direct CI and semi-internal CI. However, the CI (both direct and semi-internal) estimate is not so accurate for the Auger energies relative to the lowest lying doubly ionized $(2\pi)^{-2\,3}\Sigma^-$ state. Except for the first excited doubly ionized state $(2\pi)^{-2\,3}\Sigma^-$, the computed CI Auger energies deviate substantially (by 0.3 eV or more) from the experiment.

An aug-CC-PVTZ basis comprising 84 GTOs is employed for the computations of IPs and DIPs of HCl. The Cl basis is constructed from the (15s9p2d1f)/[5s4p2d1f] GTOs of Woon and Dunning [44] augmented with one $s(\zeta_s = 0.0591)$, one $p(\zeta_p = 0.0419)$, one $d(\zeta_d = 0.135)$, and one $f(\zeta_f = 0.312)$ diffuse function. For the H atom, the (5s2p1d)/[3s2p1d] GTO basis of Dunning [45] is augmented by one $s(\zeta_s = 0.02526)$, one $p(\zeta_p = 0.102)$, and one $d(\zeta_d = 0.247)$ diffuse function. The ADC [33] and SAC-CI calculations [46] employ a smaller basis of 67 GTOs constructed from a (14s11p4d/5s2p)/[10s8p4d/3s2p] set.

The vertical ionization potentials (valence as well as satellite) of HCl obtained from CCLRT compared with experiment [32] and with other correlated calculations [33,46] have been presented in Table 1. The two $^2\Pi$ and $^2\Sigma$ main peaks at 12.8 and 16.6 eV, respectively, in the experimental ionization spectrum are more accurately reproduced in our calculation than the other theoretical approaches. The CCLRT estimates the $(2\pi)^{-1}$ and $(5\sigma)^{-1}$ states to be at 12.54 and 16.61 eV while they are predicted to lie at 12.50 and 16.56 eV by the SAC-CI-SD-R method. The shake-up states are mainly described as two-electron processes (often called 2h–1p process). Theoretical investigations suggest that the 4σ orbital plays a significant role in characterizing the shake-up states. On the other hand, the contribution of the 4σ orbital to $^2\Pi$ valence ionization potentials (VIP) is not so important.

The Auger energies of HCl relative to its lowest lying doubly ionized state $(2\pi)^{-2\,3}\Sigma^-$ state are shown in Table 2. The CC Auger energies are computed using VU-MRCC method via eigenvalue independent partitioning technique [20]. The CCLRT for IP problem is first solved followed by the generation of $S^{(1,0)}$ cluster amplitudes from CCLRT-IP eigenvectors via EIP procedure. The effective Hamiltonian H_{eff} for (2,0) valence sector is then constructed (using the $S^{(1,0)}$ cluster amplitudes) and diagonalized to get the desired roots. The CC calculations for the $(5\sigma)^{-2\,1}\Sigma^+$ transition energy (with respect to the lowest lying $(2\pi)^{-2\,3}\Sigma^-$ state) is, however, not as accurate as the rest of the states, but this deficiency is also present for semi-internal CI calculations.

Table 1
Comparison of valence and shake-up ionization potentials (eV) of HCl obtained via CCLRT with experiment and other correlated calculations

State	ADC(4) [33]	SAC-CI-R [46]	This method	Expt. [32]
$^2\Sigma$	16.45	16.46	16.61	16.6
	25.88	26.38	25.60	25.85
	27.94	28.78	28.64	28.5
	31.91	32.43	32.21	32
	34.90	34.65	34.60	34.65
	36.61		36.44	35.5–41
$^2\Pi$	12.43	12.41	12.54	12.8

All theoretical calculations are performed at $R_{\mathrm{HCL}} = 1.2746$ Å.

Table 2
Comparison of relative Auger energies (with respect to the lowest lying doubly ionized $(2\pi)^{-2}\,{}^3\Sigma^-$ state, eV) of HCl obtained via CC calculations with experiment and other correlated calculations

Assignment	SDCI [43]	This method	Expt. [41,42]
$(2\pi)^{-2}(^3\Sigma^-)$	0.0	0.0	0.0
$(2\pi)^{-2}(^1\Delta)$	1.6	1.54	1.48
$(2\pi)^{-2}(^1\Sigma^+)$	3.0	2.53	2.75
$(2\pi5\sigma)^{-1}(^3\Pi)$	3.9	3.67	3.29
$(2\pi5\sigma)^{-1}(^1\Pi)$	5.5	5.34	
$(5\sigma)^{-2}(^1\Sigma^+)$	10.6	10.25	9.7

Table 3
Comparison of the equilibrium bond length r_e (Å), harmonic vibrational frequency ω (cm^{-1}) and dissociation energy D_e (eV) of CuH

	r_e	ω	D_e
Experiment [52]	1.463	1941	2.75
SCF [49]	1.569	1642	1.42
DHF by Collins et al. [49]	1.541	1699	1.48
DHF by Nakajima et al. [53]	1.540	1715	1.45
DKS by Nakajima et al. [53]	1.460	1928	2.86
HF-CCSD [47]	1.501	1814	2.48
This work	1.492	1818	2.64

3.2. CuH system

The ground state properties of CuH have been studied extensively by several research groups. For instance, Hrusak et al. [47] have studied the ground state potential energy surface of CuH using various CC schemes with Hartree–Fock orbitals. Marian [48] and Collins [49], on the other hand, employed spin-free Douglas–Kroll transformed Dirac Hamiltonian [50] and its variants in their calculations. Here, we investigate the ground state properties of CuH using CC method with Hartree–Fock orbitals. We also report the excited state energies computed with Hartree–Fock orbitals using CCLRT-EE method at the singles-doubles level. The basis set employed in this calculation is constructed from Roos's [51] (7s3p)/[3s2p] (for H) and (17s12p9d4f)/[7s7p4d2f] (for Cu) contraction scheme.

Fig. 1 depicts the ground and excited state potential curves of CuH as computed using CC method. We emphasize that the potential energy estimated from CC with perturbative triples CCSD(T) fails badly upon dissociation (not shown here). However, this type of behavior of the CCSD(T) potential energy curves near the bond breaking region is commonly observed and appears even in the bond fragmentation of simple diatomic molecules. The spectroscopic constants for the ground state of CuH computed using the CC method are compared with experiment [52] and with other calculations [49,53] in Table 3 which shows that the spectroscopic constants estimated through Douglas–Kohn–Sham approximation [54,55] match well with experiment. The present calculation produces quite accurate ground state dissociation energy but the equilibrium bond length and harmonic vibrational frequency deviates from the experiment by 0.03 Å and 123 cm^{-1}, respectively (see Table 3).

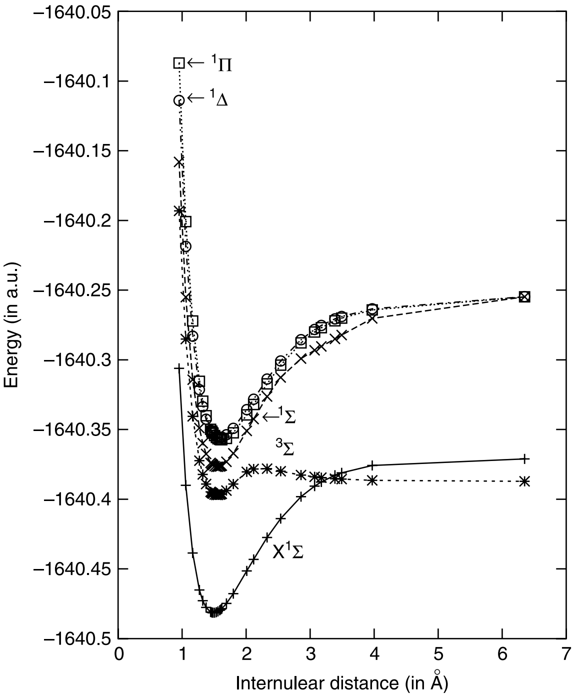

Fig. 1. Potential energy curves for the ground and excited states of CuH.

Though the CC calculations of the equilibrium bond length and the vibrational frequency are slightly deviated from the corresponding experimental values, they offer quite good estimates of excited state energies (see Table 4). The vertical excitation energies of CuH are computed at the experimental geometry using CCLRT-EE with HF orbitals. As can be seen in Table 4, CCLRT-EE provides a reasonably accurate estimate of low lying transition energies. The excitation energies computed using CCLRT-EE are off by 0.007 eV for $^1\Sigma$, 0.042 eV for $^3\Pi$ state. The experimental transition energy for $X^1\Sigma \rightarrow \Delta$ is -3.53 eV. According to present calculation, the observed Δ state lying 3.53 eV above the ground state is a singlet Δ state.

3.3. Ag atom

We use a 36s30p28d15f GTOs to compute the ionization potential and excited state energies of Ag using CC. The ground state configuration of Ag is [Kr]4d^{10}5s^1 ($^2S^{1/2}$). Because of its high Z value, Ag must be treated relativistically.

Here, we employ the straight forward extension of non-relativistic Fock-space coupled cluster theory to the relativistic regime by adopting the no-virtual-pair approximation (NVPA)

Table 4
Vertical excitation energies (eV) of CuH

State	This method	Expt. [52]
$1^3\Sigma$	2.338	
$1^1\Sigma$	2.899	2.905
$1^3\Pi$	3.207	3.275
$1^3\Delta$	3.315	
$1^1\Delta$	3.529	3.530
$1^1\Pi$	3.540	
$2^3\Sigma$	4.981	

Table 5
Ionization potential (IP) and excitation energies (EE) of Ag from relativistic CC calculations in per centimeter

	State	This method	MBPT(3) [57]	CCSD(T) [58]	Expt. [59]
IP	$5s_{1/2}(^2S_{1/2})$	60,823	58,369	60,423	61,106
EE	$6s_{1/2}(^2S_{1/2})$	42,329			42,556
	$6p_{1/2}(^2P_{1/2})$	29,757 (0.2467)	28,073 (0.2497)		29,552
	$6p_{3/2}(^2P_{3/2})$	30,639 (0.5024)	28,946 (0.5134)		30,472
Interval		882	873		920
	$5d_{3/2}(^2D_{3/2})$	48,512	46,082		48,744
	$5d_{5/2}(^2D_{5/2})$	48,533	46,104		48,764
Interval		21	22		20

Entries within parentheses are oscillator strengths.

along with appropriate modification of orbital form and potential terms [56]. The four-component relativistic spinors are generated by solving the Dirac–Fock Hamiltonian. The large and small component relativistic radial wave functions are first expressed as linear combinations of basis functions

$$P_{n\kappa}(r) = \sum_{p=1}^{N} C_{\kappa p}^{L} g_{\kappa p}^{L}(r); \qquad Q_{n\kappa}(r) = \sum_{p=1}^{N} C_{\kappa p}^{S} g_{\kappa p}^{S}(r), \tag{24}$$

where the summation index p runs over the number of basis functions N and $g_{\kappa p}^{L}$ ($g_{\kappa p}^{S}$) and $C_{\kappa p}^{L}$ ($C_{\kappa p}^{S}$) are the basis functions and expansion coefficients for the large (small) components, respectively. The basis functions employed in these calculations are GTOs of the form

$$g_{\kappa p}^{L}(r) = N_{p}^{L} r^{n_\kappa} \mathrm{e}^{-\alpha_p r^2}, \tag{25}$$

with

$$\alpha_p = \alpha_0 \beta^{p-1}, \tag{26}$$

where α_0, β are user defined constants, n_κ specifies the orbital symmetries (1 for s, 2 for p, etc.) and N_p^L is the normalization factor for the large component. The small component normalization factor is obtained by imposing the *kinetic balance* condition.

As the ground state of Ag is open-shell doublet, we begin with Ag^+ which defines the (0h,0p) valence sector. The ground and excited state energies of Ag are computed through (0h,1p) VU-MRCC strategy:

$$\mathrm{Ag}^+ + \mathrm{e} \rightarrow \mathrm{Ag}$$

The ionization potential (IP) and excitation energies (EE) of Ag are compared with other correlated calculations [57,58] and with recommended data from National Institute of Standards and Technology (NIST) database [59] in Table 5. The IP of Ag was computed by Neogrady et al. [58] using the spin-free Douglas–Kroll [50] (DK) orbitals whereas Safronova et al. [57] employed relativistic spinors in their IP and EE calculations. As can be seen in Table 5, the ionization potential computed using the CCSD(T) method with DK orbitals is more accurate (off by 683 cm^{-1}) than that obtained from third order MBPT calculations with relativistic spinors (off by 2737 cm^{-1}). This effectively indicates that the higher order correlation contribution is quite significant in IP calculations for this system. That the relativistic effect is non-negligible for Ag is also evident from Table 5. The IP computed with the Dirac–Fock orbitals is off by only 283 cm^{-1} (or 0.4%) and is in much better agreement with the experiment than the other two calculations mentioned above. The present calculations also provide reasonably accurate estimate of EEs for Ag and fine-structure splittings than the MBPT(3) estimates.

The errors in our estimated excitation energies are 227 cm^{-1} (or 0.5%) for the $^2S_{1/2}$ state, 205 cm^{-1} (or 0.7%) for the $^2P_{1/2}$ state, 167 cm^{-1} (or 0.5%) for the $^2P_{3/2}$ state, 232 cm^{-1} for the $^2D_{3/2}$ state, and 231 cm^{-1} (or 0.5%) for the $^2D_{5/2}$ state. The oscillator strengths (f) for 5s → 5p transitions are also displayed in Table 5. Since, our estimated transitions energies are quite accurate, we believe that our predicted oscillator strengths will be in good agreement with the experiment.

3.4. Hg atom

In this section, we compute the ground and excited state properties of Hg using VU-MRCC method with four component Dirac–Fock orbitals. The accurate estimation of electric quadrupole moment (Θ) of Hg^+ is important as it can be used as possible frequency standards to test the stability of fundamental constants. In fact, the frequency ν_{Hg} of $^{199}\mathrm{Hg}^+$ $5d^{10}6s(^2S_{1/2}, F=0, m_F=0) \leftrightarrow 5d^9 6s^2(^2D_{5/2}, F=2, m_F=0)$ electric quadrupole transitions at 282 nm is now being compared [60] to the frequency ν_{Cs} of the ground state hyperfine transition $[\mathrm{Xe}]6s(^2S_{1/2}, F=3, m_F=0) \leftrightarrow [\mathrm{Xe}]6s(^2S_{1/2}, F=4, m_F=0)$ in neutral Cs to test the stability of the product of fundamental

Table 6
Ionization potential (IP) of ^{199}Hg and excitation energies (EE) of its positive ion

	Config.	State	This work		Eliav et al. [66]	Expt. [68]
			Basis I	Basis II		
IP	$5d^{10}6s$	$^2S_{1/2}$	83,895	83,894	84,237	84,184
EE	$5d^{10}6s$	$^2S_{1/2}$	0	0		0
	$5d^9 6s^2$	$^2D_{5/2}$	33,506	33,506	35,437	35,514
		$^2D_{3/2}$	48,622	48,622	50,785	50,552
		Interval	15,116	15,116	15,348	15,038
	$5d^{10}6p$	$^2P_{1/2}$	52,792	52,780	52,030	51,485
		$^2P_{3/2}$	61,607	61,594	61,269	60,608
		Interval	8814	8814	9239	9123

All entries are in per centimeter.

constants $g_{Cs}(m_e/m_p)\alpha$, where g is the nuclear g-factor (m_e/m_p), the electron-to-proton mass ratio and α is the fine-structure constant.

Here, we employ (1h–0p) VU-MRCC to compute the quadrupole moment of Hg^+. Since, the quadrupole shift is zero in $5d^{10}6s(^2S_{1/2})$ level, the quadrupole shift of the $5d^96s^2(^2D_{5/2})$ state of Hg^+ alone determines the shift of the Hg^+ optical clock transition. To our knowledge, only two theoretical calculations on quadrupole moment of Hg^+ are available in the literature. The first one is the single reference Hartree–Fock (HF) calculation of Itano [61] and the other is multi-configuration Dirac–Hartree–Fock (MCDHF) calculation of Oskay et al. [62]. The HF calculation [61] estimates the quadrupole moment to be $-0.664ea_0^2$, whereas the MCDHF calculations predict $\Theta(D,5/2)=-0.5440ea_0^2$ (a_0 is the Bohr radius). Though MCDHF estimates Θ better than HF, it is still $\sim$7% larger than the experimental value a_0^2[62]. The accurate estimation of hyperfine matrix element (A) for $5d^96s^2(^2D_{5/2})$ state of Hg^+ is also a non-trivial problem. For instance, using MCDHF with limited configuration state functions, Brage et al. [63] obtained A to be 1315 MHz for this state. On the other hand, employing larger configuration space, Oskay et al. [62] obtained a value for A to be 963.5 MHz which is 22.5 MHz lower than the experimental value [61].

The ground and excited state properties of Hg and its positive ion are computed with two sets of basis functions to investigate the convergence of the computed properties. The first basis (Basis I) is constructed from 34s32p30d20f15g GTOs. To this set 10h GTOs are added to construct the second basis set (Basis II). Since the contribution from high lying unoccupied orbitals are not significant [64,65], these orbitals are kept frozen in CC calculations.

The IPs of Hg computed from VU-MRCC using Dirac–Coulomb–Hamiltonian are compared with the experiment values in Table 6. It is worth mentioning that the Breit interaction is not included in the present calculations. We have also quoted the results of Eliav et al. [66]. Eliav et al. have used the same method with Dirac–Coulomb–Breit Hamiltonian. As can be seen in Table 6, the IPs computed for $5d^{10}6s$ and $5d^96s^2$ states by Eliav et al. [66] are closer to experimental values than those obtained by us. Since the basic formalism and working equations of Eliav et al. [66] and ours are same, we feel that the difference in the estimated IPs may arise due to the absence of Breit interaction in our calculations. Although the ^2P fine structure splitting is better reproduced in their [66] calculations, our calculation presents a more accurate estimate of ^2D fine structure splitting.

We now discuss the quadrupole moment results for $^2D_{5/2}$ state (displayed in Table 7). The large deviation in Itano's predicted Θ value for Hg^+ primarily arises due to the neglect of electron correlation in the calculation. The importance of electron correlation is also evident from Oskay et al. [62] MCDHF calculations which show that the electron correlation contribution to Θ is $\sim$25%. It is well known that the incorporation of correlation effect in a compact manner is, however, difficult via MCDHF scheme or even through finite order many-body perturbation theory(MBPT) [67]. In fact, CC is the most suitable scheme for such a problem. Being an all-order approach, it can incorporate higher order electron correlation and relaxation effects more efficiently than the finite order MBPT method. Our calculation estimates the quadrupole moment for $^2D_{5/2}$ state of Hg^+ to be $-0.527ea_0^2$, which to our knowledge, is the most accurate estimate of Θ(D,5/2) for Hg^+. The magnetic hyperfine matrix elements (A) reported for Hg^+ are also in accordance with the experiment. The present calculations further show that contribution of h orbitals to IP, A and Θ for Hg is negligible.

Table 7
The $5d^96s^2(^2D_{5/2})$ state electric quadrupole moment (ea_0^2) and magnetic hyperfine matrix elements A (MHz) of $^{199}Hg^+$

	This method		HF [61]	MCHF [62]	Experiment
	Basis I	Basis II			
Θ	-0.527	-0.527	-0.664	-0.544	-0.510 [62]
$A^s_{1/2}$	40,440	40,464			40,507 [60]
$A^d_{3/2}$	2713	2720			
$A^d_{5/2}$	972	972		963.5	986.19 [61]

4. Conclusion

In this paper, we have presented the non-relativistic application of the CCLRT theory to the systems HCl and CuH, using Hartree–Fock orbitals. We also report here the relativistic calculation on Ag and Hg atoms using Dirac–Hartree–Fock orbitals via the VU-MRCC method. The results obtained via CCLRT and VU-MRCC methods have been compared to other available theoretical and experimental results from which it is clear that our results are quite encouraging and satisfactory for all the systems considered here. However, it is important to mention that we aim to investigate more complex systems in order to establish the generality of the methods mentioned here in the near future.

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