Eur. Phys. J. D **37**, 171–176 (2006)
DOI: 10.1140/epjd/e2005-00279-1

THE EUROPEAN
PHYSICAL JOURNAL D

Relativistic coupled cluster method

Excitation and ionization energies of Sr and Yb atom

Malaya K. Nayak and Rajat K. Chaudhuri[a]

Indian Institute of Astrophysics, Bangalore-560034, India

Received 22 March 2005 / Received in final form 17 July 2005

Abstract. Relativistic coupled cluster method (CCM) is applied to compute the low lying excited and ion states of strontium and ytterbium atom. The resulting excitation and ionization energies are in excellent agreement with experimental data and with other correlated calculations. The nuclear magnetic dipole hyperfine constants (A) and electric quadrupole hyperfine constants (B) of excited states are also evaluated and are in accord with experiment. We further address the basis set dependency of the computed properties.

PACS. 31.25.Jf Electron correlation calculations for atoms and ions: excited states

1 Introduction

The accurate estimation of transition energies and nuclear magnetic dipole hyperfine constants for singly ionized metal ions, such as Sr^+ and Yb^+ is important because these atoms can be used in cold traps as possible frequency standards. For instance, an optical frequency standard based on Sr^+ has recently been developed at the National Physical Laboratory [1,2]. In addition, calculations of the hyperfine coupling constant are relevant to studies of parity non-conservation in atoms because the electroweak interaction is also a short range force like those determining the hyperfine coupling constant. However, the theoretical determination of the hyperfine coupling constant is, probably, one of the most non-trivial problems in atomic physics because an accurate prediction requires precise incorporation of the strongly entangled relativistic and higher order correlation and relaxation effects.

A variety of many-body methods (perturbative and non-perturbative) are available for incorporating relativistic and dynamical electron correlation contributions into descriptions of many-electron systems. Among the non-perturbative varieties, the coupled cluster (CC) method, has been demonstrated in extensive non-relativistic and relativistic studies to be capable of providing accurate predictions of transition energies and related properties for complex atomic and molecular systems. This article describes computations for excitation and ionization energies, magnetic dipole hyperfine constants, and other related properties of Sr and Yb atom using relativistic CC method. While the properties of Sr^+ have been studied using relativistic single reference second order many-body perturbation theory (SR-MBPT) [3] and coupled cluster methods [4], relativistic calculations for the corresponding neutral states are not available, in part, because of the greater complexity involved in the calculation of excited states for the neutral systems.

The open-shell CC (OSCC) [5–11] computation for the excitation energies of a closed shell neutral systems M can be carried out either via double electron attachment process to its doubly positive ion (M^{++}) [12] or through electron attachment and detachment processes [9,10] to the neutral systems M. The determination of excitation energies via double electron attachment process is computationally simple provided the doubly positive ion is closed shell or dominated by single reference function. In the present work, the excited state energies of Sr and Yb atom are computed using double electron attachment OSCC method as the ground state of Sr^{++} and Yb^{++} is closed shell.

2 Coupled cluster method

Since the Coupled Cluster method used in this work is discussed elsewhere [9,10,13], we only outline the essential features of the method here.

Here, we employ the straight forward extension of non-relativistic coupled cluster theory to the relativistic regime by adopting the no-virtual-pair approximation (NVPA) along with appropriate modification of orbital form and potential terms [12]. We begin with Dirac-Coulomb Hamiltonian (H) expressed in normal order

$$\begin{aligned} H_N &= H - \langle 0|H|0\rangle \\ &= \sum_{ij}\langle i|f|j\rangle\{a_i^\dagger a_j\} + \frac{1}{4}\sum_{i,j,k,l}\langle ij||kl\rangle\{a_i^\dagger a_j^\dagger a_l a_k\}, \quad (1) \end{aligned}$$

---

[a] e-mail: `rkchaudh@kffl.uchicago.edu`

where

$$\langle ij||kl\rangle = \langle ij|\frac{1}{r_{12}}|kl\rangle - \langle ij|\frac{1}{r_{12}}|lk\rangle. \tag{2}$$

The valence universal Fock space open-shell coupled cluster method is employed which begins with the decomposition of the full many-electron Hilbert space of dimension N into a reference space $\mathcal{M}_0$ of dimension $M \ll N$, defined by the projector P, and its orthogonal complement $\mathcal{M}_0^{\perp}$ associated with the projector $Q = 1 - P$. A valence universal wave operator Ω is then introduced which satisfies

$$|\Psi_i\rangle = \Omega|\Psi_i^{(0)}\rangle, \quad i = 1, \ldots, M \tag{3}$$

where $|\Psi_i^{(0)}\rangle$ and $|\Psi_i\rangle$ are the *unperturbed* and the *exact* wave functions of the ith eigenstate of the Hamiltonian, respectively. The wave operator Ω, which formally represents the mapping of the reference space $\mathcal{M}_0$ onto the target space $\mathcal{M}$ spanned by the M eigenstates $|\Psi_i\rangle$, has the properties

$$\Omega P = \Omega, \;\; P\Omega = P, \;\; \Omega^2 = \Omega. \tag{4}$$

With the aid of the wave operator Ω, the Schrödinger equation for the M eigenstates of the Hamiltonian correlating with the M-dimensional reference space, i.e.,

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle, \quad i = 1, \ldots, M, \tag{5}$$

is transformed into a generalized Bloch equation,

$$H\Omega P = \Omega H \Omega P = \Omega P H_{\rm eff} P, \tag{6}$$

where $H_{\rm eff} \equiv PH\Omega P$ is the effective Hamiltonian. Once equation (6) is solved for the wave operator Ω, the energies E_i, $i = 1, \ldots, M$, are computed by diagonalizing the effective Hamiltonian $H_{\rm eff}$ in the M-dimensional reference space $\mathcal{M}_0$.

The Dirac-Fock equations are first solved for M^{++} which defines the (0-hole, 0-particle) sector of the Fock space. Following Lindgren's formulation [9], we express the Schrödinger equation for the (0-hole, 0-particle) correlated reference space state as

$$\begin{aligned} H|\Psi_{\rm ref}^{(0,0)}\rangle &= E_{\rm ref}\Omega^{(0,0)}|\Phi_{\rm ref}\rangle \\ &= E_{\rm ref}\left\{\exp(S^{(0,0)})\right\}|\Phi_{\rm ref}^{(0,0)}\rangle, \end{aligned} \tag{7}$$

where $|\Phi_{\rm ref}^{(0,0)}\rangle$ is the *unperturbed* closed shell reference space state, $\Omega^{(0,0)}$ is the *valence universal* wave operator and $E_{\rm ref}$ is the *exact* reference state energy. The curly brackets in equation (7) denote normal ordering. The 0-hole, 0-particle cluster operator $S^{(0,0)}$ is defined with respect to $\Phi_{\rm ref}^{(0,0)}$ as

$$\begin{aligned} S^{(0,0)} = &\sum_{p,\alpha}\left\langle p|s_1^{(0,0)}|\alpha\right\rangle\{a_p^{\dagger}a_{\alpha}\} \\ &+ \frac{1}{4}\sum_{p,q,\alpha,\beta}\left\langle pq|s_2^{(0,0)}|\alpha\beta\right\rangle\{a_p^{\dagger}a_q^{\dagger}a_{\beta}a_{\alpha}\} + \cdots \end{aligned} \tag{8}$$

where the hole and particle orbitals are labeled by $\alpha, \beta, \ldots$, and $p, q, \ldots$, respectively. The cluster amplitudes $S^{(0,0)}$ are determined by pre-multiplying equation (7) with $[\Omega^{(0,0)}]^{-1}$ and projecting the resulting equation onto the virtual space states Q, i.e., by setting

$$Q^{(0,0)}\mathcal{H}P^{(0,0)} = 0 \tag{9}$$

where the operator $\mathcal{H}$ is defined as

$$\mathcal{H} = \left[\Omega^{(0,0)}\right]^{-1} H\Omega^{(0,0)}. \tag{10}$$

One-electron is then added to the correlated reference space state following the Fock-space strategy

$$\begin{aligned} M^{++} + e &\rightarrow M^{+} \\ M^{+} + e &\rightarrow M. \end{aligned}$$

The singly ionized (M^{+}) correlated state is expressed as

$$\begin{aligned} H|\Psi_i^{(0,1)}\rangle &= E_i\Omega^{(0,1)}|\Phi_{\rm ref}^{(0,1)}\rangle \\ &= E_i\{\exp(S^{(0,0)} + S^{(0,1)})\}|\Phi_{\rm ref}^{(0,1)}\rangle, \end{aligned} \tag{11}$$

where E_i is the energy of the ith singly ionized state and $\Phi_{\rm ref}^{(0,1)}$ is the reference space for (0-hole, 1-particle) valence sector

$$|\Phi_{\rm ref}^{(0,1)}\rangle = \sum_p C_p a_p^{\dagger}|\Phi_{\rm ref}^{(0,0)}\rangle \tag{12}$$

where $a_p^{\dagger}$'s are particle creation operators. Pre-multiplying equation (11) by $\left[\Omega^{(0,0)}\right]^{-1}$ we get

$$\mathcal{H}\left\{1 + S^{(0,1)}\right\}|\Phi_{\rm ref}^{(0,1)}\rangle = H_{\rm eff}^{(0,1)}\{1 + S^{(0,1)}\}|\Phi_{\rm ref}^{(0,1)}\rangle, \tag{13}$$

where

$$\begin{aligned} S^{(0,1)} = &\sum_{p\neq v}\left\langle p|s_1^{(0,1)}|v\right\rangle\{a_p^{\dagger}a_v\} \\ &+ \frac{1}{2}\sum_{p,q,v,\alpha}\left\langle pq|s_2^{(0,1)}|v\alpha\right\rangle\{a_p^{\dagger}a_q^{\dagger}a_{\alpha}a_v\} + \cdots \end{aligned} \tag{14}$$

in which v refers to valence orbital (unoccupied at DF level). $H_{\rm eff}^{(0,1)}$ is the effective Hamiltonian for the (0, 1) valence sector which on diagonalization yields electron affinity or valence electron removal energy. The cluster amplitudes $S^{(0,1)}$ are determined by projecting equation (13) on the virtual space states which are orthogonal to $\Phi_{\rm ref}^{(0,1)}$ reference space space. The operator $\{\exp(S^{(0,1)}\}$ reduces to $(1 + S^{(0,1)})$ because

$$S^{(0,1)}S^{(0,1)}|\Phi_{\rm ref}^{(0,1)}\rangle = 0. \tag{15}$$

[$S^{(0,1)} - S^{(0,1)}$ contraction is not allowed due to normal ordering.] Once $S^{(0,0)}$ and $S^{(0,1)}$ are known, the correlated reference space states for the neutral species (M) can be expressed as

$$\begin{aligned}|\Psi^{(0,2)}\rangle &= \Omega|\Phi^{(0,2)}_{\rm ref}\rangle \\ &= \left\{\exp\left(S^{(0,0)} + S^{(0,1)} + \frac{1}{2}S^{(0,1)}S^{(0,1)}\right.\right. \\ &\quad \left.\left. + S^{(0,2)}\right)\right\}|\Phi^{(0,2)}_{\rm ref}\rangle \end{aligned} \quad (16)$$

where $S^{(0,2)}$ are cluster operators for double electron attachment process. The unperturbed function $\Phi^{(0,2)}_{\rm ref}$ is defined as

$$|\Phi^{(0,2)}_{\rm ref}\rangle = \sum_{p,q} C_{pq} a^\dagger_p a^\dagger_q |\Phi^{(0,0)}_{\rm ref}\rangle. \quad (17)$$

The excited state energies are then computed by diagonalizing the effective Hamiltonian $H^{(0,2)}_{\rm eff}$, where

$$H^{(0,2)}_{\rm eff} = \langle\Phi^{(0,2)}_{\rm ref}|\hat{H}_D\{S^{(0,1)} + \frac{1}{2}S^{(0,1)}S^{(0,1)} + S^{(0,2)})\}|\Phi^{(0,2)}_{\rm ref}\rangle, \quad (18)$$

where

$$S^{(0,2)} = \frac{1}{4}\sum_{p,q,v_1,v_2}\left\langle pq|s^{(0,2)}_2|v_1v_2\right\rangle \{a^\dagger_p a^\dagger_q a_{v_2} a_{v_1}\} + \cdots \quad (19)$$

It is evident from equation (19) that under two-body truncation scheme, $S^{(0,2)} = 0$ for *complete model space* (CMS) [10,14]. Thus, for CMS, the excited energies for the neutral species can be determined with aid of $S^{(0,0)}$ and $S^{(0,1)}$ cluster amplitudes. We emphasize that in the procedure, valence electron removal energies are the by-products of this scheme with *no extra* cost. [Representative Goldstone diagrams for $H^{(0,2)}_{\rm eff}$ and $H^{(0,1)}_{\rm eff}$ are depicted in Fig. 1.]

3 Computational details

The large and small component relativistic radial wave functions are expressed as linear combinations of basis functions,

$$P_{n\kappa}(r) = \sum_{p=1}^{N} C^L_{\kappa p} g^L_{\kappa p}(r); \qquad Q_{n\kappa}(r) = \sum_{p=1}^{N} C^S_{\kappa p} g^S_{\kappa p}(r), \quad (20)$$

where the summation index p runs over the number of basis functions N and $g^L_{\kappa p}$ ($g^S_{\kappa p}$) and $C^L_{\kappa p}$ ($C^S_{\kappa p}$) are the basis functions and expansion coefficients for the large (small) components, respectively. The basis functions employed in these calculations are Gaussian type orbitals (GTOs) of the form,

$$g^L_{\kappa p}(r) = N^L_p r^{n_\kappa} e^{-\alpha_p r^2}, \quad (21)$$

with

$$\alpha_p = \alpha_0 \beta^{p-1}, \quad (22)$$

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

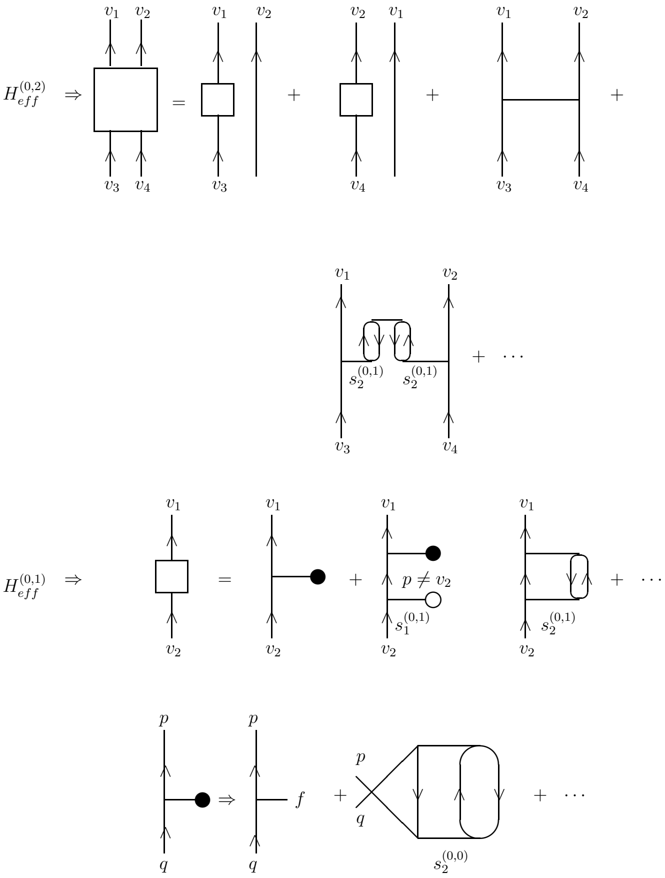

Fig. 1. Representative $H_{\rm eff}$ diagrams for (0, 1) and (0, 2) valence sector.

$$g^S_{\kappa p}(r) = N^S_p\left(\frac{d}{dr} + \frac{\kappa}{r}\right) g^L_{\kappa p}(r), \quad (23)$$

where

$$N^S_p = \sqrt{\frac{\alpha_p}{2n_\kappa - 1}[4(\kappa^2 + \kappa - n_\kappa) - 1]}. \quad (24)$$

The ground and excited state properties of Sr, Yb and their positive ions are computed using $37s33p28d12f5g$ GTOs with $\alpha_0 = 0.00525$ and $\beta = 2.73$. [High lying unoccupied orbitals are kept frozen in CC calculations.]

4 Results and discussions

Table 1 compares the calculated first ionization potential (FIP) and low lying excitation energies (EE) of Sr and Yb with the experimental data [15–17]. As can be seen from Table 1, the CC ionization potentials for Sr and Yb atoms are in excellent with the experiment (off by 28 cm^{-1} for Sr and 111 cm^{-1} for Yb).

The reference space for excitation energy calculations is constructed by allocating $5s$ ($6s$) valence electrons of

Table 1. First ionization potential (FIP) and low lying excitation energies (EE) and fine structure splittings (FS) of Sr and Yb atoms. All entrees are in cm^{-1}.

Atoms		State	This work	CC [18]	Expt. [15,17]
Sr	FIP		45954		45926
	EE				
		[Kr]5s^2(^{1}S$_0$)	0		0
		[Kr]5s5p(^{3}P$_0$)	14333		14327
		[Kr]5s5p(^{3}P$_1$)	14547		14514
	FS		214		187
		[Kr]5s5p(^{3}P$_2$)	14969		14898
	FS		422		384
		[Kr]5s4d(^{3}D$_1$)	17839		18159
		[Kr]5s4d(^{3}D$_2$)	17879		18219
	FS		40		60
		[Kr]5s4d(^{3}D$_3$)	17957		18319
	FS		78		100
		[Kr]5s5p(^{1}P$_1$)	22634		21698
		[Kr]5s6s(^{3}S$_1$)	28978		29038
		[Kr]5s6s(^{1}S$_1$)	30522		30592
Yb	FIP		50552	51142	50441
	EE				
		4f^{14}6s^2(^{1}S$_0$)	0		0
		4f^{14}6s6p(^{3}P$_0$)	17576	17346	17288
		4f^{14}6s6p(^{3}P$_1$)	18424	18082	17992
	FS		848	736	704
		4f^{14}6s6p(^{3}P$_2$)	20218	19847	19710
	FS		1794	1765	1718
		4f^{14}5d6s(^{3}D$_1$)	25865	24981	24489
		4f^{14}5d6s(^{3}D$_2$)	25966	25229	24751
		4f^{14}5d6s(^{3}D$_3$)	26125	25735	25270
		4f^{14}6s7s(^{3}S$_1$)	32967		32695
		4f^{14}6s7s(^{1}S$_0$)	34932		34351

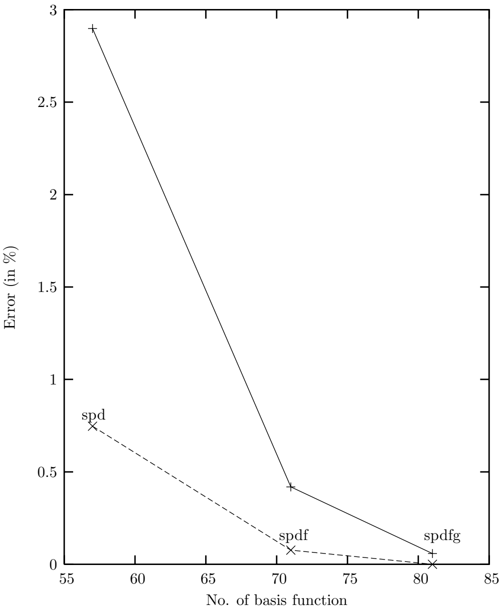

Fig. 2. Abs. error (in %) in the computed valence electron removal energy (×) and magnetic hyperfine constant (+) for ^{2}S$_{1/2}$(5s) state vs. number of basis functions.

Sr (Yb) among 5s6s7s5p6p4d5d (6s7s8s6p7p5d6d for Yb) valence orbitals in all possible way. The computed CC excitation energies for the low lying states of Sr atom are in accord with the experiment except for the ^{1}P$_1$ state of Sr. The maximum error in the estimated excitation energy for Sr is only 71 cm^{-1} (or 0.47%) for the ^{3}P$_2$(5s5p) state. The CC method also provides a fairly accurate estimate of the ^{1}S$_0$(5s^2) → ^{3}P$_0$(5s5p), ^{1}S$_0$(5s^2) → ^{3}P$_1$(5s5p), ^{1}S$_0$(5s^2) → ^{1}S$_0$(5s6s), and ^{1}S$_0$(5s^2) → ^{3}S$_1$(5s6s) transition energies, which deviate by 6, 31, 60, and 70 cm^{-1}, respectively, from the experiment. Compared to S and P states, our computed excitation energies for ^{1}P$_1$ state and $s \rightarrow d$ transition and are not so accurate for Sr atom. The errors in our estimated transition energies for Sr D states are off by 1.8%. It is evident from Table 1 (also from Tabs. 3 and 4 of Ref. [18]) that accurate estimate of $s \rightarrow p$(^{1}P$_1$) transition energy is quite problematic. Inclusion of low lying f orbitals in the reference space is probably necessary to improve the accuracy of ^{1}P$_1$ (also D) state energies. However, this is not considered here because of computational complexity.

The ionization and low excitation energies of Yb are also reasonably close to the experiment but are not as accurate as those obtained for Sr atom from CCM. The earlier CC calculation by Eliav et al. [18] estimates the FIP of Yb to be 51142 cm^{-1}, which is off by 732 cm^{-1} from the experiment. Like Sr, the transition energies of Yb for ^{3}S and ^{3}P states are more accurately reproduced by CC than the D states. At this juncture, we emphasize that similar trend is also observed by Eliav et al. in their CC calculations for Yb, Ba and Ra atom [12,18].

Based on our Sr calculations (see Fig. 2), we feel that the correlation contribution to the transition energies from orbitals with $l \geq 5$ will be non-negligible for Yb (l is the orbital angular momentum). Thus, we believe that the inaccuracy in our computed transition energies of Yb mainly arises due to the basis set inadequacy. The absence of Breit interaction in our calculations is also partly responsible for the inaccuracy and efforts are underway to enable including these effects.

Table 2 compares the CC calculations for low lying valence electron ionization energies of Sr$^+$ and Yb$^+$ with other correlated calculations [3,4,18,19] and with experiment [15]. As can be seen in Table 2, the valence electron removal energies and associated fine structure splitting (labeled as FS in Tab. 2) for Sr and Yb are well reproduced in the present calculations. A careful analysis indicates that, for Sr atom, only the [Kr]5p CC valence electron removal energy is slightly poor (off by 129 cm^{-1}) compared to the Martensson's [4] estimate (off by 60 cm^{-1}), while the [Kr]5s valence electron removal

Table 2. Theoretical and experimental valence electron ionization energies and fine structure splittings (FS) of Sr^+ and Yb^+ ions. All entrees are in cm^{-1}.

State	MBPT	CC	This work	Experiment [15,17]
Sr^+				
$5s(^2\mathrm{S}_{1/2})$	89631 [3]	89126 [4]	88965	88964
$5p(^2\mathrm{P}_{1/2})$	65487 [3]	65309 [4]	65120	65249
$5p(^2\mathrm{P}_{3/2})$	64663 [3]	64499 [4]	64315	64448
FS	824 [3]	810	805	801
$6s(^2\mathrm{S}_{1/2})$			41079	41228
$6p(^2\mathrm{P}_{1/2})$			33096	33194
$6p(^2\mathrm{P}_{3/2})$			32801	32906
FS			295	288
Yb^+				
$6s(^2\mathrm{S}_{1/2})$	0		0	0
$5d(^2\mathrm{D}_{3/2})$	22888 [19]	23770 [18]	23179	23285
$5d(^2\mathrm{D}_{5/2})$	23549 [19]	25072 [18]	24342	24333
	661 [19]	1302	1253	1372
$6p(^2\mathrm{P}_{1/2})$	26000 [19]	27868 [18]	27664	27062
$6p(^2\mathrm{P}_{3/2})$	29005 [19]	31324 [18]	31037	30392
FS	3005 [19]	3456	3373	3330

Table 3. Magnetic dipole (A) and electric quadrupole hyperfine (B) constant (in MHz) of the ground and low lying excited states Sr^+ and Yb^+.

Ions		Ref. [4]	This work	Experiment
Sr^+				
	$A_{5s}(^2\mathrm{S}_{1/2})$	1000.0	999.89	1000.47 [20]
	$A_{5p}(^2\mathrm{P}_{1/2})$	177.0	175.12	
	$A_{5p}(^2\mathrm{P}_{3/2})$	35.3	35.60	36.8 [21]
	$A_{4d}(^2\mathrm{D}_{5/2})$	1.0	1.87	2.17 [20]
	$B_{4d}(^2\mathrm{D}_{5/2})$	52.0	51.12	49.11 [20]
Yb^+				
	$A_{6s}(^2\mathrm{S}_{1/2})$		12386.20	
	$A_{6p}(^2\mathrm{P}_{1/2})$		2179.94	
	$A_{6p}(^2\mathrm{P}_{3/2})$		322.60	

Table 4. Electric dipole matrix elements of low lying excited states of Sr^+ and Yb^+. Entrees with parentheses are semi-empirically adjusted values.

Ion	Transition	Guet et al. [3]	This work
Sr+			
	$5p_{1/2} \rightarrow 5s_{1/2}$	3.052 (3.060)	3.107
	$5p_{3/2} \rightarrow 5s_{1/2}$	4.313 (4.325)	4.392
Yb+			
	$6p_{1/2} \rightarrow 6s_{1/2}$		2.781
	$6p_{3/2} \rightarrow 6s_{1/2}$		3.914

energy and fine structure splittings (FS) are better reproduced in the present calculations. The FS reported in this work are off by 4 and 7 cm^{-1} for $^2\mathrm{P}_{1/2}(5p) \rightarrow {}^2\mathrm{P}_{3/2}(5p)$ and $^2\mathrm{P}_{1/2}(6p) \rightarrow {}^2\mathrm{P}_{3/2}(6p)$ states, respectively.

We now compare the excitation energies of Yb and its positive ion reported by Eliav et al. [18] with the present calculations. As can be seen in Tables 1 and 2 that the excitation energies (also FS) of Yb are better reproduced than its positive ion in Eliav et al. calculations whereas the positive ion state energies of Yb are in better agreement in our calculations. The EEs of Yb and Yb^+ in the present calculations are off by $\sim$2.75% and $\sim$1.3%, respectively. On the other hand, EEs reported in reference [18] are off by $\sim$1.1% (for Yb) and $\sim$3.2% (for Yb^+) from the experiment. This is quite interesting but is beyond the scope of the present approach to pinpoint the underlying reason of this trend.

The theoretically determined nuclear magnetic dipole and electric quadrupole hyperfine constants for the excited states of Sr^+ and Yb^+ are presented in Table 3. Table 3 indicates that our predicted nuclear magnetic dipole and electric quadrupole hyperfine constants are in general agreement with experiments. The nuclear magnetic dipole hyperfine constants reported here for $^2\mathrm{S}_{1/2}$, $^2\mathrm{P}_{3/2}$, and $^2\mathrm{D}_{5/2}$ states are off by 0.58, 1.20, and 0.5 MHz and are more accurate (on an average) than the previously reported A value [4]. Similar trend is also observed in our predicted B value for $^2\mathrm{D}_{5/2}(4d)$ state, which is off by 2.0 MHz from the experiment. We emphasize that unlike transition energies, accuracy of one-electron properties such as nuclear magnetic dipole hyperfine constants strongly depends on the basis set. Figure 2 depicts the accuracy of A_{5s} and $^2\mathrm{S}_{1/2}(5s)$ valence electron removal energies against the basis set. As can be seen in Figure 2 that the error in the computed A_{5s} value sharply drops from 3% to 0.5% when f orbitals are included in the basis set. The computed error decreases further (from 0.5% to 0.05%) when g orbitals are included in the calculations. Since our computed transition energies and related properties (for Sr) are quite accurate, we strongly feel that our predicted A and B constants for Yb^+ will also be in accord with the experiment.

The electric dipole (E1) transition matrix elements for excited states of Sr^+ and Yb^+ are displayed in Table 4. It is evident from Table 4 that the $\eta = \langle np_{3/2}|\mathrm{E1}|ns_{1/2}\rangle / \langle np_{1/2}|\mathrm{E1}|ns_{1/2}\rangle$ ($n = 5$ for Sr^+ and 6 for Yb^+) decreases as Z (nuclear charge) increases. [Note that for light atoms $\langle np_{3/2}|\mathrm{E1}|ns_{1/2}\rangle / \langle np_{1/2}|\mathrm{E1}|ns_{1/2}\rangle \approx \sqrt{2}$.] Table 4 further shows that our estimated transition matrix elements and η for Sr^+ are reasonably close to those reported by Guet et al. [3].

5 Concluding remarks

Relativistic open-shell coupled cluster method is described and applied to compute the low lying states of the Sr and Yb atom and to their positive ions. Satisfactory results are obtained for the transition energies, valence electron ionization potentials and other related properties. The present work clearly demonstrates that the accuracy of one-electron properties strongly depend upon the choice of basis set function. It further demonstrates that the contribution to the one-electron properties from orbital with higher angular momentum is non-negligible.

References

1. M.G. Boshier, G.P. Barwood, G. Huang, H.A. Klein, Appl. Phys. B **71**, 51(2000)
2. G. Barwood et al., IEEE Trans. Instrum. Meas. **50**, 543 (2001)
3. C. Guet, W.R. Johnson, Phys. Rev. A **44**, 1531 (1991)
4. A. Mårtensson-Pendrill, J. Phys. B **35**, 917 (2002)
5. F. Coester, Nucl. Phys. **7**, 421 (1958)
6. F. Coester, H. Kümmel, Nucl. Phys. **17**, 477 (1960)
7. J. Čížek, J. Chem. Phys. **45**, 4256 (1966)
8. J. Paldus, X. Li, Adv. Chem. Phys. **110**, 1 (1999), and references therein
9. I. Lindgren, Int. J. Quant. Chem. **S 12**, 33 (1978); I. Lindgren, Phys. Rev. A **31**, 1273 (1985)
10. D. Mukherjee, S. Pal, Adv. Quant. Chem. **20**, 281 (1989)
11. R.J. Bartlett, in *Modern Electronic Structure Theory*, edited by D.R. Yarkony (World Scientific, 1995), Vol. II, p. 1047, and references therin
12. E. Eliav, U. Kaldor, Phys. Rev. A **53**, 3050 (1996)
13. D. Mukherjee, R.K. Moitra, A. Mukhopadhyay, Mol. Phys. **33**, 955 (1977)
14. D. Sinha, S.K. Mukhopadhyay, R. Chaudhuri, D. Mukherjee, Chem. Phys. Lett. **154**, 544 (1989)
15. C.E. Moore, Atomic Energy Levels, Natl. Bur. Standard, Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 35 (U.S. GPO, Washington, D.C., 1971), Vol 1
16. G. Ferrari, P. Cancio, R. Drullinger, G. Giusfredi, M. Prevedelli, C. Toninelli, G.M. Tino, Phys. Rev. Lett. **91**, 243002 (2003)
17. W.C. Martin, R. Zalubas, L. Hagan, in *Atomic Energy Levels-The Rare-Earth Elements* (Natl. Bur. Standards, Washington, D.C., 1978)
18. E. Eliav, U. Kaldor, Phys. Rev. A **52**, 291 (1995)
19. V.A. Dzuba, V.V. Flambaum, M. V. Marchenko, Phys. Rev. A **68**, 022506 (2003)
20. G.P. Barwood, K. Gao, P. Gill, G. Huang, H.A. Klein, Phys. Rev. A **67**, 013402 (2003)
21. F. Buchinger et al., Phys. Rev. C **41**, 2883 (1990), F. Buchinger et al., Phys. Rev. C **42**, 2754 (1990)