Investigations of Ra^+ properties to test possibilities of new optical frequency standards

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The present work tests the suitability of the narrow transitions $7s\ ^2S_{1/2} \rightarrow 6d\ ^2D_{3/2}$ and $7s\ ^2S_{1/2} \rightarrow 6d\ ^2D_{5/2}$ in Ra^+ for optical frequency standard studies. Our calculations of the lifetimes of the metastable $6d$ states using the relativistic coupled-cluster theory suggest that they are sufficiently long for Ra^+ to be considered as a potential candidate for an atomic clock. This is further corroborated by our studies of the hyperfine interactions, dipole and quadrupole polarizabilities and quadrupole moments of the appropriate states of this system.

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Accurate time and frequency measurement is crucial for the advance of science and technology in many fields. This leads to a number of searches to find candidates for optical frequency standards. The current frequency standard is based on the ground state hyperfine transition in atomic cesium and has a quality factor (Q) of 10^{15} [1]. Atomic spectral lines with high Q are generally interesting for standards, however good control over systematic line shifts will be essential. As a result of the remarkable advances in the field of ion trapping and laser cooling, single ions like Hg^+ [2], In^+ [3], Ca^+ [4], Sr^+ [5], Yb^+ [6], Cd^+ [7] and Ba^+ [8] are particularly interesting as they can be localized using their electric charge rather than light forces, which is necessary for atom trapping. Very accurate measurements have been performed on Hg^+ and Sr^+, where Q exceeds 10^{17}. Some of the major systematic errors associated with the clock frequency are the Stark effect, Zeeman effect and quadrupole shifts due to stray electric fields in the ion trap [9]. These errors can be estimated from high precision theoretical studies of hyperfine structure constants, polarizabilities and quadrupole moments of the appropriate atomic states. Indeed, studies of these quantities are also essential for parity non-conservation (PNC) studies [10, 11]. Some of the above mentioned errors can be eliminated by considering the clock transition between suitable hyperfine states [2].

An experiment is in progress at KVI to search for an suitable optical frequency standard by measuring the frequency of either $7s\ ^2S_{1/2} \rightarrow 6d\ ^2D_{3/2}$ or $7s\ ^2S_{1/2} \rightarrow 6d\ ^2D_{5/2}$ transitions in Ra^+. A similar experiment is also being planned at IACS [12]. In this paper, we report our theoretical studies on the feasibility of these transitions for the optical frequency studies in Ra^+. In the case of Ba^+ it has been pointed out that PNC and optical frequency standards experiments share many features in common [8]. The techniques used in the Ba^+ experiments can be extended to Ra^+ as the electronic structures of the two ions are similar. However, Ra^+ has one important advantage: the low lying transition wavelengths (see Fig. 1(a)) of this ion are in the optical regime making them more easily accessible than their counterparts in Ba^+. Although, it appears that these wavelengths can be measured very precisely using modern spectroscopic techniques, it is however necessary to

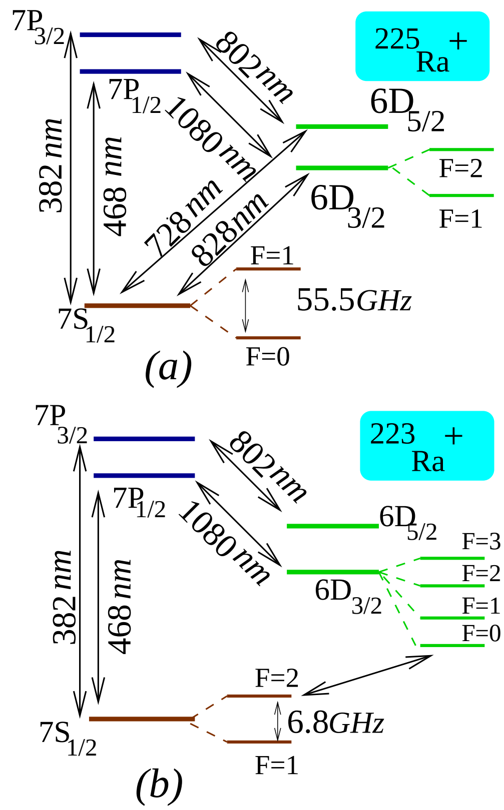

FIG. 1: (color online) Schematic diagram of energy levels of Ra^+ with transitions for possible optical frequency standards.

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find out which transition is the most suitable for optical frequency standard. This can be decided by the experimentalists from the knowledge of different physical quantities of the involved states that can be used to control the sources of error.

First of all, one must determine which of the isotopes of Ra^+ merit consideration for optical clock studies. In this context, it is worthwhile to note that only ^{223}Ra and ^{225}Ra have half-lives of a few days ($\sim$ 10days) and these isotopes are therefore obvious choices. However, they have different nuclear spins (Is); the former has $I = 3/2$ whereas the latter has $I = 1/2$ and this results in different hyperfine splittings. One has to take into account the various systematic errors while considering both these isotopes. It is possible to eliminate the quadrupole Stark shift by considering the transition between the hyperfine (F) states such as $|6s(J = 1/2), I = 3/2; F = 2\rangle \rightarrow |5d(J = 3/2), I = 3/2; F = 0\rangle$ transition (see Fig. 1(b)) for the frequency standard although knowledge of the hyperfine structure constants and the polarizabilities are still required for these experiments. It is necessary to study the hyperfine structure constants, lifetimes and a few other spectroscopic quantities for the $7s$ and $6d$ states of this system in order to assess the suitability of the proposed clock transitions.

Electron correlation and relativistic effects must be treated accurately for Ra^+. Relativistic coupled-cluster (RCC) theory; a size-consistent, size-extensive and an all order perturbation method is well suited for this purpose [13]. It has been successfully applied to determine accurately certain ground and excited states properties of Sr^+ [14] and Ba^+ [15]. We employ the same method in the present study to obtain accurate results for Ra^+. The presence of the non-linear terms in this method makes it challenging to obtain the ground and excited state wave functions for a large system like Ra^+. We had observed earlier that these effects are important for accurate studies [16] in other heavy systems. In order to obtain the wave functions for Ra^+, we solve the RCC equations considering single, double and leading triple excitations (CCSD(T) method). This involves the determination of 10^7 cluster amplitudes self-consistently. This is one of the largest computations to date for obtaining the wave functions of an atomic system.

The starting point of our work is the relativistic generalization of the valence universal coupled-cluster (CC) theory introduced by Mukherjee et al. [17] which was put later in a more compact form by Lindgren [18]. In this approach, the atomic wave function $|\Psi_v\rangle$ for a single valence (v) open-shell system is expressed as

$$|\Psi_v\rangle = e^T\{1 + S_v\}|\Phi_v\rangle, \tag{0.1}$$

where $|\Phi_v\rangle$ is the reference state constructed out of the Dirac-Fock (DF) orbitals of the closed-shell system ($|\Phi_0\rangle$) by appending the valence electron orbital. Here T and S_v are the excitation operators from the core and valence-core sectors (for example see [14, 16] for the second quantization representations of these operators and equations to obtain their amplitudes). The single particle orbitals in the present calculations are linear combinations of Gaussian type functions [19].

The transition matrix element of a hermitian operator (O) corresponding to the initial state $|\Psi_i\rangle$ and the final state $|\Psi_f\rangle$ can be expressed using the RCC method as

$$\begin{aligned}\langle O\rangle_{if} &= \frac{\langle\Psi_i|O|\Psi_f\rangle}{\sqrt{\langle\Psi_i|\Psi_i\rangle\langle\Psi_f|\Psi_f\rangle}} \\ &= \frac{\langle\Phi_i|\{1+S_i^\dagger\}\overline{O}\{1+S_f\}|\Phi_f\rangle}{\sqrt{N_i N_f}},\end{aligned} \tag{0.2}$$

where we define $\overline{O} = e^{T^\dagger}Oe^T$ and $N_v = \langle\Phi_v|e^{T^\dagger}e^T + S_v^\dagger e^{T^\dagger}e^T S_v|\Phi_v\rangle$ for the valence electron v. We calculate the above expression using the procedure followed in the earlier works [14, 15, 16]. The expectation values are determined by considering the special condition $i = f$.

Lifetimes of the $6d$ *states*: It is necessary to know the lifetimes of the $6d$ metastable states to understand how reliably the proposed experiments can be performed in that time period. The lifetimes (in second (s)) of these states can be determined from the inverse of the total transition probabilities (A). The net transition probabilities (in s^{-1}) of the $6d$ states are given by

$$\begin{aligned}A_{6d5/2} &= A^{\mathrm{E2}}_{6d5/2\rightarrow 7s1/2} + A^{\mathrm{E2}}_{6d5/2\rightarrow 6d3/2} + A^{\mathrm{M1}}_{6d5/2\rightarrow 6d3/2}, \\ A_{6d3/2} &= A^{\mathrm{E2}}_{6d3/2\rightarrow 7s1/2} + A^{\mathrm{M1}}_{6d3/2\rightarrow 7s1/2},\end{aligned} \tag{0.3}$$

where

$$A^{\mathrm{E2}}_{f\rightarrow i} = \frac{1.11995\times 10^{18}}{(2j_f+1)\lambda^5} S^{\mathrm{E2}}_{f\rightarrow i} \tag{0.4}$$

$$A^{\mathrm{M1}}_{f\rightarrow i} = \frac{2.69735\times 10^{13}}{(2j_f+1)\lambda^3} S^{\mathrm{M1}}_{f\rightarrow i}, \tag{0.5}$$

where $S_{f\rightarrow i} = |O_{fi}|^2$ and λ (in Å) are the transition line strength for the operator O (in atomic unit (au)) and wavelength, respectively. These quantities depend on both the transition amplitudes and wavelengths, and they can be calculated using a single *ab initio* method. However, we use experimental wavelengths [20] to reduce the errors in the determination of the lifetimes.

Since there are no experimental or theoretical predictions of the lifetimes of the $6d$ states, we calculate the E2 transition amplitudes using both the length and velocity gauges in order to assess the numerical accuracies of the results. These results are given in Table I along with the M1 transition amplitudes and the lifetimes of the $6d$ states. We have used the E2 amplitudes in the length gauge as it converges faster than the corresponding values in the velocity gauge. The errors are estimated from the discrepancies of the results obtained with different choices of bases.

Transition states $f \to i$	$O^{\rm E2}_{f\to i}$ (au) *Length*	*Velocity*	$O^{\rm M1}_{f\to i}$ (au)	Lifetime (s)
$\vert 6d_{3/2}\rangle \to \vert 7s_{1/2}\rangle$	14.87(7)	14.77(22)	0.0024(2)	0.893(4)
$\vert 6d_{5/2}\rangle \to \vert 7s_{1/2}\rangle$	19.04(5)	19.87(1.0)		0.301(3)
$+\vert 6d_{5/2}\rangle \to \vert 6d_{3/2}\rangle$	8.80(4)	10.5(2.5)	1.546(1)	0.297(4)

TABLE I: Transition amplitudes (in au) due to M1 and E2 transitions in both length and velocity gauges. Length gauge results of the E2 amplitudes along with M1 amplitudes are considered for the determination of lifetimes.

Using the RCC method, we find that due to the enhanced role of electron correlation, core polarization effects in particular, the M1 transition amplitude for the $|6d_{3/2}\rangle \to |7s_{1/2}\rangle$ transition is $0.0024(2)ea_0$ where the DF value is $\sim 10^{-5}ea_0$. From the calculated E2 amplitudes of this transition, we obtain the lifetime of the $6d_{3/2}$ state as 0.627(4)s. Inclusion of the above M1 transition probability changes its value to 0.893(4)s; this change is around 30% of the total result and this finding is different from our earlier studies on similar states of other alkaline earth metal ions [22]. However, like the other $d_{5/2}$ states in those systems, the lifetime of the $6d_{5/2}$ state reduces from 0.301s to 0.297s after including the contribution of the M1 transition probability in the $|6d_{5/2}\rangle \to |6d_{3/2}\rangle$ transition.

Quadrupole moments of the $6d$ *states:* In order to estimate the error in the frequency of the clock transition arising from quadratic Stark shifts, it is necessary to know the quadrupole moments of the relevant states. The quadrupole moment of a valence state (v) is given by

$$\Theta(v) = \langle \Psi_v | O^{\rm E2} | \Psi_v \rangle, \tag{0.6}$$

where $O^{\rm E2}$ is the E2 transition operator. We divide the the above expression into three parts as follows

$$\Theta(v) = \Theta_{DF}(v) + \Theta_{cv}(v) + \Theta_v(v). \tag{0.7}$$

Here Θ_{DF}, Θ_{cv} and Θ_v are the DF, core-valence and valence electron correlation effects. In Table II, we present these contributions for the $6d_{3/2}$ and $6d_{5/2}$ states. In this table, the difference between the total RCC result and the sum of all the above three contributions is due to the normalization of the wave functions. The quadrupole moment of the $7s$ state is clearly zero as the quadrupole moment operator is of rank two. Therefore, we determine these quantities only for the $6d$ states.

As given in Table II, the dominant contribution comes from Θ_{DF} followed by Θ_v, which contains core-polarization and pair-correlation effects to all orders, make significant contributions as in Sr^+ [14] and Ba^+ [15]. We have followed the same procedure as in the lifetime calculations to estimate errors in these results.

State	Θ_{DF}	Θ_{cv}	Θ_v	Θ
$6d_{3/2}$	3.48	−0.01	−0.51	2.90(2)
$6d_{5/2}$	5.19	−0.02	−0.65	4.45(9)

TABLE II: Quadrupole moments of atomic states in au.

Polarizabilities: We determine the dipole polarizabilities for $7s$ and $6d$ states and quadrupole polarizability of the $7s$ state for our study. The static ($\alpha_0^1(J_v)$) and tensor dipole ($\alpha_2^1(J_v)$) polarizabilities for the valence v state with angular momentum J_v are given by

$$\alpha_0^1(v) = -4 \sum_{k\neq v} \frac{|\langle J_v|D|J_k\rangle|^2}{E_v - E_k} \tag{0.8}$$

and

$$\alpha_2^1(v) = 4\sqrt{\frac{30 j_v(2j_v-1)(2j_v+1)}{(j_v+1)(2j_v+3)}} \sum_{k\neq v} (-1)^{J_v+J_k+1} \left\{ \begin{array}{ccc} J_v & 1 & J_k \\ 1 & J_v & 2 \end{array} \right\} \frac{|\langle J_v|D|J_k\rangle|^2}{E_v - E_k}, \tag{0.9}$$

respectively, where D is the E1 operator. Similarly, the static quadrupole polarizability ($\alpha_0^2(v)$) is given by

$$\alpha_0^2(v) = -4 \sum_{k\neq v} \frac{|\langle J_v|O^{\rm E2}|J_k\rangle|^2}{E_v - E_k}. \tag{0.10}$$

We have used the sum-over-states approach and experimental energies to reduce the errors in the calculations; the calculated energies were used obtained from the RCC method where the experimental energies were not available.

We express generally the polarizabilities as

$$\alpha(v) = \alpha_{DF}(v) + \alpha_c(v) + \alpha_{cv}(v) + \alpha_v(v), \tag{0.11}$$

where each term is defined similar to the corresponding terms of the quadrupole moment expression given in Eq. (0.7) except for α_c which is the pure core orbital contribution. We calculate α_v contributions from the calculated intermediate states using the RCC method. However, α_c and α_{cv} are calculated using the second order many-body perturbation theory (MBPT(2)), where the residual Coulomb interaction and E1/E2 operators are treated as perturbation. All these results are tabulated in Table III.

We have obtained up to $10s$, $10p$, $10d$, $9f$ and $9g$ low-lying states using the RCC method to calculate the above quantities. Contributions from other higher states are accounted for using MBPT(2). They are just given as

	State	α_{DF}	α_c	α_{cv}	α_v	α_t	αs
α_0^1	$7s_{1/2}$	99.39	14.57	−1.54	−4.34	−0.02	107.86
	$6d_{3/2}$	926.32	14.57	−1.31	39.05	0.03	978.66
	$6d_{5/2}$	1208.13	14.57	−7.53	77.18	0.03	1292.38
α_2^1	$6d_{3/2}$	−220.67	1.21	0.76	65.38	−0.01	−153.12
	$6d_{5/2}$	−168.53	1.21	1.27	16.78	−0.01	−149.28
α_0^2	$7s_{1/2}$	2920.83	56.57	0.34	−436.04	5.50	2547.20

TABLE III: Dipole and quadrupole polarizabilities in au.

tail contributions (α_t) in the table. Using the expression

$$\alpha^2_{0,6d}(7s) \;=\; - \sum_{k=6d_{3/2},6d_{5/2}} \frac{|\langle \Psi_{7s}|O^{\mathrm{E2}}|\Psi_k\rangle|^2}{E_{6s}-E_k}, \quad (0.12)$$

we obtain $\alpha_2^0(7s) = 1037(7)a_0^5$ along with the corresponding α_c contribution. This is usually necessary for the lifetime measurements of the $6d$ states.

	$7s_{1/2}$	$6d_{3/2}$	$6d_{5/2}$
$7p_{1/2}$	3.28	3.64	
$8p_{1/2}$	0.04	0.07	
$7p_{3/2}$	4.54	1.54	4.92
$8p_{3/2}$	0.50	0.15	0.40
$5f_{5/2}$		4.47	1.31
$6f_{5/2}$		0.86	0.21
$5f_{7/2}$			6.21
$6f_{7/2}$			1.08

TABLE IV: Important reduced E1 matrix elements in au used to determine the dipole polarizabilities.

In Table IV, we present the important reduced E1 matrix elements which are used in the determination of dipole polarizabilities. These results are in reasonable agreement with those of Dzuba et al. which are calculated using another many-body approach [21].

Hyperfine structure constants: Studies of these constants are important to investigate the underlying physics of the wave functions in the nuclear region, especially to estimate the errors of the PNC matrix elements [26]. The magnetic dipole (A_h) and electric quadrupole (B_h) hyperfine structure constants of the valence v state with angular momentum J_v are given by

$$A_h(v) = \frac{\mu_N g_I}{J_v}\langle \Psi_v|\mathrm{T}^{(1)}|\Psi_v\rangle \quad (0.13)$$

and

$$B_h(v) = 2eQ_N\langle \Psi_v|\mathrm{T}^{(2)}|\Psi_v\rangle, \quad (0.14)$$

respectively. In the above expressions, μ_N, g_I and Q_N are the nuclear magnetic moment, gyromagnetic ratio and quadrupole moment, respectively. Explicit expressions and the single particle matrix elements of $\mathrm{T}^{(1)}$ and $\mathrm{T}^{(2)}$ are given in [23]. We have used $g_I = 0.18067$ [24] and $Q_N = 1.254$ [25] for ^{223}Ra and $g_I = -1.4676$ [24] for ^{225}Ra in these calculations.

		$7s_{1/2}$	$6d_{3/2}$		$6d_{5/2}$	
		A_h	A_h	B_h	A_h	B_h
^{223}Ra$^+$						
	RCC	3567.26	77.08	383.88	−23.90	477.09
	Expt.	3404.0(1.9)				
^{225}Ra$^+$						
	RCC	−28977.76	−626.13		194.15	
	Expt.	−27731(13)				

TABLE V: Hyperfine structure constants in MHz.

The trends of the correlation effects in the hyperfine interactions of the $7s$ and $6d$ states in the present system are similar to the corresponding states in Ba$^+$ [15, 26]. We have found 23%, 31% and 181% correlation contributions with respect to the DF results of A_h in the $7s$, $6d_{3/2}$ and $6d_{5/2}$ states, respectively. The core-polarization (CP) effect in the $6d_{5/2}$ state is very strong and its contribution is larger than the DF result. This gives rise to the unusual behavior of the electron correlation effects.

Conclusion: We have successfully carried out accurate calculations of the lifetimes, polarizabilities, quadrupole moments and hyperfine structure constants in Ra$^+$ using the RCC theory. Our calculated values of the lifetimes of the $6d$ states which are 0.893s and 0.297s, respectively, suggest that Ra$^+$ could be a suitable candidate for an optical frequency standard with an accuracy better than 10^{-18}. The results of the different properties that we have calculated can serve as benchmarks to guide experimentalists. On the other hand, precise measurements of these quantities can also be used to test our method of calculation.

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