

**PROBING ATOMIC CLOCK CANDIDATES
USING RELATIVISTIC COUPLED-CLUSTER
THEORY CALCULATIONS**

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**DEPARTMENT OF PHYSICS
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PROBING ATOMIC CLOCK CANDIDATES USING RELATIVISTIC COUPLED-CLUSTER THEORY CALCULATIONS

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy
to the



DEPARTMENT OF PHYSICS
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Dedicated to

**My parents and my family for their love,
care and affection**

CERTIFICATE

This is to certify that the thesis entitled **Probing Atomic Clock Candidates Using Relativistic Coupled-cluster Theory Calculations** submitted by **Ravi Kumar** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics is a record of bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard.

The material contained in the thesis has not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

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ABSTRACT

Atomic clocks are the most accurate time measurement device till date. Due to their unprecedented accuracy, they are important for several fundamental cause as well as technological applications – such as navigation devices, variation of fundamental constants, to study the physics beyond the standard model of particle physics, to maintain the international atomic time and coordinated universal time, and many more. Among the atomic clocks considered so far, the optical clocks, referred to as the next generation clocks, are reported to be most accurate, due to their high transition frequency. And in this context, group-13 ions based optical clocks, which are also an interest of the present thesis, are reported to be one of the best optical clocks. For example, the hyperfine induced $^1S_0 \rightarrow ^3P_0^o$ clock transition in Al^+ is reported to have a low fractional frequency shift of 9.4×10^{-19} [1, 2], which is, perhaps, the most accurate clock in existence today.

While we work and strive everyday to build an improved clock, the accuracy of atomic clocks is hindered by the environmental perturbations. The environmental perturbations lead to shifts in the clock transition frequency, and hence, contribute to the error of the clock. Among all, the blackbody radiation (BBR) shift is one of the dominant environment-induced shifts and contributes heavily to the inaccuracy of atomic clocks at room temperature. Since the BBR shift depends on the dipole polarizabilities, α , of the clock transition states of the atom, and the experimental measurements of BBR shift is nontrivial, one of the main aims of the present thesis is to compute the accurate values of α for clocks states which can be useful in estimating the BBR frequency shift. The calculation of accurate value of α is however a challenging task. The reason for this is attributed to the many-body interacting nature of the atoms and ions. To obtain a reliable value of α , the electron correlation effects, relativistic effects and quantum electrodynamical corrections must be included in the many-body calculations to the highest level of accuracy. The Relativistic Coupled-Cluster (RCC) theory is one of the most accurate

many-body theories for the atomic structure calculations [3]. It accounts for the electron-electron interaction to all orders of perturbation and has been used to calculate several atomic properties.

In the present thesis, we have developed a series of RCC methods and codes to calculate the properties of closed-shell, one-valence and two-valence atomic systems. We have employed these methods to compute electric dipole polarizability and other properties relevant to optical atomic clocks. In a first such calculation, we have employed nonlinear Perturbed Relativistic Coupled-Cluster (PRCC) theory to calculate α for ground state of group-13 ions B^+ , Al^+ , Ga^+ , In^+ and Tl^+ . The contribution from perturbative triples, relativistic effects and quantum electrodynamical corrections were also incorporated to get accurate results for dipole polarizability. From our calculations, we find that the linearized-PRCC value of α are on average $\approx 24\%$ larger than the previous theoretical results for all the ions. The reason for this could be attributed to the strong correlation effects due to divalent nature of these systems. We find that, it is essential to include nonlinear terms in the PRCC to get an accurate values of α for group-13 ions. From the analysis of virtual contributions, we find that the d -virtual electrons contribute significantly to α for Al^+ , whereas the dominant contribution comes from f virtual for Ga^+ , In^+ and Tl^+ . We find the combined contributions from Breit+QED as $\approx 2.1\%$, 1.7% , 1.6% and 1.1% , respectively for Al^+ , Ga^+ , In^+ and Tl^+ ions. This suggests that it is essential to include these interactions in RCC calculations to obtain the accurate value of α for group-13 ions

In the subsequent work, we used PRCC theory to calculate the α of superheavy elements (SHEs) No, Cn, Nh⁺ and Og [4, 5]. To assess the trend of electron correlation as a function of Z , we also calculated the electron correlation and excitation energy and the corrections from the Breit and QED corrections for lighter homolog elements Yb for No; Zn, Cd, and Hg for Cn; Ga⁺, In⁺, and Tl⁺ for Nh⁺; and Kr, Xe, and Rn for Og. We find that, the dominant contribution to α comes from the valence electrons – $7s_{1/2}$ for No, Cn and Nh⁺, and $7p_{3/2}$ for Og. More than 50% of the total contribution is observed from the $7s_{1/2}$ for Cn and Nh⁺, whereas, more than 90% of contribution is observed from $7s_{1/2}$ and $7p_{3/2}$ orbitals for No and Og, respectively. From the analysis of the electron correlation effects, we find that the core polarization effects decrease as function of Z for the lighter homologs, whereas for SHEs it shows an opposite trend. Except for Cn and Og, we observed a trend of decreasing contributions as function of Z from the Breit interaction. The largest contribution of about 1.7% is observed in the case of Ga⁺. On the contrary, the Uehling potential and self-energy corrections have increasing contributions from lighter homologs to SHEs.

Next, we employ PRCC theory for one-valence to compute the α for ground state, $p_{1/2}$, and the spin-orbit (SO)-splitted excited state, $p_{3/2}$, of Al and In. In addition, to test the quality of many-body wavefunctions, we have also calculated the excitation energies of some lying states $3p_{1/2}$, $3p_{3/2}$, $4s_{1/2}$, $4p_{1/2}$ and $4p_{3/2}$ of Al and $5p_{3/2}$, $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$, $5d_{3/2}$ and $5d_{5/2}$ of In. Our computed excitation energies match very well with the experimental data from NIST [6]. Our recommended α for ground state $^2P_{1/2}$ is well within the experimental error bar for both the atoms [7, 8]. Comparing with other theory calculations, our recommended value is in the range of the reported data. On examining the correlation effects embedded in α , we find that for both the atoms, *valence-valence* (VC) contribution is larger than the core polarization (CP) contribution. From Al to In, the core polarization effect is observed to decrease, whereas the valence-valence contributions are found to increase.

In the last project of the thesis, we employ a Fock-space RCC theory for two-valence to compute the clock transition properties of Al^+ ion. We have computed the electric dipole transition amplitude, hyperfine matrix elements, excitation energies, and the life time of the clock state, 3P_0 , associated with the hyperfine induced $^1S_0 \rightarrow ^3P_0$ clock transition. Our computed excitation energies for low lying states $^3P_0^o$, $^3P_1^o$, $^3P_2^o$ and $^1P_1^o$, oscillator strengths for $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^1P_1$ transitions, magnetic dipole $A(^3P_1^o)$, $A(^3P_2^o)$, $A(^1P_1^o)$ and electric quadrupole $B(^3P_1^o)$, $B(^3P_2^o)$, $B(^1P_1^o)$ hyperfine structure constants agree well with the experimental results. Using these results, we estimate the lifetime of $^3P_0^o$ state, 20.20 ± 0.91 s, which is in excellent agreement with the experimental value 20.60 ± 1.4 s [9]. From the detailed analysis of results, we find that the contribution from the perturbative triples is essential to include in RCC calculations to get an accurate value of the life time of $^3P_0^o$. It contributes $\approx -6.4\%$ of the total value. The combined contribution from the Breit interaction and QED corrections is $\approx 0.8\%$ of the total value.

सार

परमाणु घड़ियां अब तक का सबसे सटीक समय मापने वाला उपकरण है। उनकी अभूतपूर्व सटीकता के कारण, वे कई मूलभूत कारणों के साथ-साथ तकनीकी अनुप्रयोगों के लिए महत्वपूर्ण हैं - जैसे कि दिक्सूचक उपकरण, मौलिक स्थिरांक की भिन्नता, कण भौतिकी के मानक मॉडल से परे भौतिकी का अध्ययन करने के लिए, अंतरराष्ट्रीय परमाणु समय और समन्वित सार्वभौमिक समय को बनाए रखने के लिए, और भी बहुत कुछ। अब तक मानी जाने वाली परमाणु घड़ियों में प्रकाशिक घड़ियों को, जिन्हें अगली पीढ़ी की घड़ियों के रूप में संदर्भित किया जाता है, उनकी उच्च संक्रमण आवृत्ति के कारण सबसे सटीक बताया जाता है। इस सन्दर्भ में समूह-13 आयन आधारित प्रकाशिक घड़ियों को, जो कि वर्तमान शोध-प्रबन्ध की रुचि भी हैं, सर्वश्रेष्ठ प्रकाशिक घड़ियों में से एक बताया गया है। उदाहरण के लिए, Al^+ में अति सूक्ष्म प्रेरित $^1S_0 \rightarrow ^3P_0$ घड़ी संक्रमण में भिन्नात्मक आवृत्ति बदलाव के कम होने की सूचना है जो कि 9.4×10^{-19} [1,2] है, और ये शायद आज तक की सबसे सटीक घड़ी है।

जबकि हम एक बेहतर घड़ी बनाने के लिए हर रोज काम करते हैं और प्रयास करते हैं, पर पर्यावरणीय गड़बड़ी परमाणु घड़ियों की सटीकता को बाधित करती है। पर्यावरणीय गड़बड़ी घड़ी संक्रमण आवृत्ति में बदलाव की ओर ले जाती है और इसलिए घड़ी की त्रुटि में योगदान देती है। इन सब में, कृष्णिका विकिरण (बीबीआर) बदलाव प्रमुख पर्यावरण-प्रेरित बदलावों में से एक है और कमरे के तापमान पर परमाणु घड़ियों की अशुद्धि में भारी योगदान देता है। क्योंकि बीबीआर बदलाव परमाणु के घड़ी संक्रमण अवस्था के द्विध्रुवीय ध्रुवीकरण (α) पर निर्भर करता है, बीबीआर बदलाव का प्रायोगिक माप गैर-तुच्छ है, और वर्तमान शोध-प्रबन्ध के मुख्य उद्देश्यों में से एक घड़ियों के अवस्थाओं के लिए α के सटीक मूल्यों की गणना करना है, जो बीबीआर आवृत्ति बदलाव के अनुमान लगाने में उपयोगी हो सकता है। हालांकि α के सटीक मान की गणना एक चुनौतीपूर्ण कार्य है। इसका कारण परमाणुओं और आयनों की कई-शरीर परस्पर क्रिया करने वाली प्रकृति को जिम्मेदार ठहराया जाता है। α का एक विश्वसनीय मान प्राप्त करने के लिए, इलेक्ट्रॉन सहसंबंध प्रभाव, सापेक्ष प्रभाव और क्वांटम विद्युत-गतिकीय सुधारों को कई-शरीर गणनाओं में उच्चतम सटीकता का स्तर तक शामिल किया जाना चाहिए। सापेक्षिक युग्मित-समूह (आरसीसी) सिद्धांत परमाणु संरचना गणना के लिए सबसे सटीक कई-शरीर सिद्धांतों में से एक है [3]। यह विक्षुब्धता के सभी अनुक्रमों के लिए इलेक्ट्रॉन-इलेक्ट्रॉन परस्पर क्रिया को ध्यान में रखता है और कई परमाण्विक गुणों की गणना के लिए इस्तेमाल किया गया है।

वर्तमान शोध-प्रबन्ध में, हमने पूर्ण पूरित कोश, एक संयोजक और द्विसंयोजक परमाणु प्रणालियों के गुणों की गणना करने के लिए आरसीसी विधियों और कोडों की एक श्रृंखला विकसित की है। हमने ये तरीके विद्युत द्विध्रुव ध्रुवीकरण और प्रकाशिक परमाणु घड़ियाँ के लिए प्रासंगिक अन्य गुणों की गणना करने के लिए नियोजित किया है। इस तरह की पहली गणना में, हमने अरेखीय विक्षुब्धित सापेक्षिक युग्मित-समूह (पीआरसीसी) को B^+ , Al^+ , Ga^+ , In^+ और Tl^+ समूह-13 आयनों की निम्नतम अवस्था के लिए α की गणना करने के लिए नियोजित किया है। विक्षुब्धित टिस्पल्स, सापेक्षिक प्रभाव और क्वांटम विद्युत-गतिकीय सुधारों को द्विध्रुवीय ध्रुवीकरण के लिए सटीक परिणाम प्राप्त करने के लिए शामिल किया गया था। हमारी गणना से, हम पाते हैं कि α का रैखिककृत-पीआरसीसी मान सभी आयनों के लिए पिछले सैद्धांतिक परिणामों की तुलना में औसतन 24% बड़ा है। इसका कारण इन प्रणालियों की द्विसंयोजक प्रकृति के कारण मजबूत सहसंबंध प्रभाव माना जा सकता है। हम पाते हैं कि समूह-13 के लिए α का सटीक मान प्राप्त करने के लिए पीआरसीसी में अरेखीय पदों को शामिल करना आवश्यक है। आयन आभासी योगदान के विश्लेषण से, हम पाते हैं कि d-आभासी इलेक्ट्रॉन Al^+ के α के लिए महत्वपूर्ण रूप से योगदान करते हैं, जबकि Ga^+ , In^+ , Tl^+ के लिए प्रमुख योगदान f-आभासी इलेक्ट्रॉन से आता है। हम ब्रेइट और क्यूईडी के संयुक्त योगदान को 2.1%, 1.7%, 1.6%

और 1.1% के रूप में क्रमशः Al^+ , Ga^+ , In^+ और Tl^+ आयनों के लिए पाते हैं। इससे पता चलता है कि इसे समूह-13 आयनों के लिए α का सटीक मान प्राप्त करने के लिए आरसीसी गणना में ये परस्पर क्रिया शामिल करना आवश्यक है।

बाद के काम में, हमने अतिभारी तत्वों (एसएचई), No, Cn, Nh^+ और Og [4,5], के α की गणना करने के लिए पीआरसीसी सिद्धांत का उपयोग किया है। Z के फलन के रूप में इलेक्ट्रॉन सहसंबंध की प्रवृत्ति का आकलन करने के लिए हमने, No के लिए Yb; Cn के लिए Zn, Cd, और Hg; Nh^+ के लिए Ga^+ , In^+ , और Tl^+ ; और Og के लिए Kr, Xe, और Rn, इलेक्ट्रॉन सहसंबंध और उत्तेजना ऊर्जा और हल्के समजातीय तत्वों के लिए बरेइट और क्यूईडी सुधारों की भी गणना की। हम पाते हैं कि, α के लिए प्रमुख योगदान No, Cn और Nh^+ के लिए $7s_{1/2}$, और Og के लिए $7p_{3/2}$ संयोजी इलेक्ट्रॉनों से आता है। Cn और Nh^+ के लिए कुल योगदान का 50% से अधिक $7s_{1/2}$ से देखा जाता है, जबकि, 90% से अधिक योगदान $7s_{1/2}$ और $7p_{3/2}$ ऑर्बिटल्स से क्रमशः No और Og के लिए देखा जाता है। इलेक्ट्रॉन सहसंबंध प्रभावों के विश्लेषण से हम पाते हैं कि मुख्य ध्रुवीकरण प्रभाव हल्के समजातीय के लिए Z के सापेक्ष घटती प्रवृत्ति, जबकि एसएचई के लिए यह एक विपरीत प्रवृत्ति को दर्शाता है। Cn और Og को छोड़कर, हमने बरेइट परस्पर क्रिया से Z के फलन के रूप में योगदान में कमी की प्रवृत्ति देखी है। लगभग 1.7% का सबसे बड़ा योगदान Ga^+ के मामले में देखा गया है। इसके विपरीत, उहलिंग क्षमता और आत्म-ऊर्जा सुधारों में हल्के समजातीय से लेकर एसएचई तक योगदान बढ़ रहा है।

इसके बाद, हम निम्नतम अवस्था के लिए Al और In की $p_{1/2}$, और प्रचक्रण-कक्षा (एसओ)-विभाजित उत्तेजित अवस्था $p_{3/2}$, की α की गणना करने के लिए एकल-संयोजी पीआरसीसी सिद्धांत को नियोजित करते हैं। इसके अलावा, कई-शरीर तरंग फलन की गुणवत्ता का परीक्षण करने के लिए, हमने कुछ निम्न परमाणु अवस्थाओं, Al के लिए $3p_{1/2}$, $3p_{3/2}$, $4s_{1/2}$, $4p_{1/2}$ और $4p_{3/2}$ और $5p_{3/2}$, $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$, $5d_{3/2}$ और In के लिए $5d_{5/2}$, की उत्तेजना ऊर्जा की गणना भी की है। हमारी गणना की गई उत्तेजना ऊर्जा एनआईएसटी [6] के प्रयोगात्मक डेटा से बहुत अच्छी तरह मेल खाती है। निम्नतम अवस्था $2p_{1/2}$ के लिए दोनों परमाणुओं के लिए हमारी अनुशंसित α प्रयोगात्मक त्रुटि बार के भीतर अच्छी तरह से है [7, 8]। अन्य सिद्धांत गणनाओं की तुलना में, हमारा अनुशंसित मान प्रकाशित किए गए डेटा के दायरे में है। α में सन्निहित सहसंबंध प्रभावों की जांच करने पर हम पाते हैं कि दोनों परमाणुओं के लिए, संयोजी-संयोजी (वीसी) का योगदान कोर ध्रुवीकरण (सीपी) से बड़ा है। Al से In तक, कोर ध्रुवीकरण प्रभाव के योगदान में कमी देखी गई है, जबकि संयोजी-संयोजी योगदान में वृद्धि पायी जाती है।

शोध-प्रबन्ध की अंतिम परियोजना में, हम Al^+ आयन के घड़ी संक्रमण गुणों की गणना करने के लिए द्विसंयोजी फॉक-स्पेस आरसीसी सिद्धांत को नियोजित करते हैं। हमने विद्युत द्विध्रुव संक्रमण आयाम, अति सूक्ष्म आव्यूह तत्व, उत्तेजना ऊर्जा, और घड़ी अवस्था 3P_0 के जीवन काल की गणना की है, जो अति सूक्ष्म प्रेरित $^1S_0 \rightarrow ^3P_0$ घड़ी संक्रमण से जुड़ा हुआ है। हमारी गणना निचले अवस्थाओं 3P_0 , 3P_1 , 3P_2 और 1P_1 के लिए उत्तेजना ऊर्जा, $^1S_0 \rightarrow ^3P_1$ और $^1S_0 \rightarrow ^1P_1$ संक्रमण के लिए दोलितर-सामर्थ्य, $A(^3P_1)$, $A(^3P_2)$, $A(^1P_1)$ चुंबकीय द्विध्रुवीय और $B(^3P_1)$, $B(^3P_2)$, $B(^1P_1)$ वैद्युत चतुर्ध्रुव अति सूक्ष्म संरचना स्थिरांक प्रयोगात्मक परिणामों से अच्छी तरह सहमत हैं। इन परिणामों का उपयोग करते हुए हम 3P_0 अवस्था के जीवनकाल $20.20 \pm 0.91s$ का अनुमान लगाते हैं, जो प्रयोगात्मक मूल्य $20.60 \pm 1.4s$ [9] के साथ उत्कृष्ट समझौता में है। परिणामों के विस्तृत विश्लेषण से, हम पता लगाते हैं कि 3P_0 के जीवन काल का सटीक मान प्राप्त करने के लिए आरसीसी गणना में विक्षुब्ध टिर्पल्स के योगदान को शामिल करना आवश्यक है। यह कुल मान का $\sim -6.4\%$ योगदान देता है। बरेइट परस्पर क्रिया और क्यूईडी सुधारों का संयुक्त योगदान कुल मान का 0.8% है।

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