A relativistic unitary coupled-cluster study of electric quadrupole moment and magnetic dipole hyperfine constants of $^{199}Hg^+$

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Searching for an accurate optical clock which can serve as a better time standard than the present day atomic clock is highly demanding from several areas of science and technology. Several attempts have been made to built more accurate clocks with different ion species. In this article we discuss the electric quadrupole and hyperfine shifts in the $5d^9 6s^2\,{}^2D_{5/2}\,(F=0, m_F=0) \leftrightarrow 5d^{10}6s\,{}^2S_{1/2}\,(F=2, m_F=0)$ clock transition in $^{199}Hg^+$, one of the most promising candidates for next generation optical clocks. We have applied Fock-space unitary coupled-cluster (FSUCC) theory to study the electric quadrupole moment of the $5d^9 6s^2\,{}^2D_{5/2}$ state and magnetic dipole hyperfine constants of $5d^9 6s^2\,{}^2D_{3/2,5/2}$ and $5d^{10}6s^1\,{}^2S_{1/2}$ states respectively of $^{199}Hg^+$. We have also compared our results with available data. To the best of our knowledge, this is the first time a variant of coupled-cluster (CC) theories has been applied to study these kinds of properties of $Hg^+$and is the most accurate estimate of these quantities to date.

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I. INTRODUCTION

The frequencies at which atoms emit or absorb electro-magnetic radiation during a transition can be used for defining the basic unit of time. The transitions that are extremely stable, accurately measurable and reproducible can serve as excellent frequency standards. Present frequency standard is based on the transition between the two hyperfine levels of a cesium atom ($[Xe]6s\left({}^2S_{1/2}, F=3, m_F=0\right) \leftrightarrow [Xe]6s\left({}^2S_{1/2}, F=4, m_F=0\right)$) with an accuracy of 1 part in 10^{15}. However, there is an ongoing search for even more accurate clocks in the optical regime. Recent day progress in technologies makes it feasible to built more accurate clocks with higher precision. Moreover this kind of study not only provides the foundation for a wide range of experiments and precision measurements but also can be used for stringent tests of our fundamental concepts and theories. Some recent studies of frequency standards have yielded sensitive probes of possible temporal variation of the fundamental constants [1, 2, 3]. Atomic frequency standards based on a single trapped ion has been established to provide more stability and accuracy than those of present-day time standards [4]. Among all the ionic candidates for frequency standards, $^{199}Hg^+$ [5] is believed to be the most reliable one. Recent progress on $^{199}Hg^+$ frequency standards [5, 6, 7] have revealed the feasibility of achieving an accuracy of 1 part in 10^{18} as compared to 1 part in 10^{15} which is the present day standard. In particular, the 282 nm transition ($5d^9 6s^2\,{}^2D_{5/2}\,(F=0, m_F=0) \leftrightarrow 5d^{10}6s\,{}^2S_{1/2}\,(F=2, m_F=0)$) is of interest in $^{199}Hg^+$. A schematic diagram of the energy levels and the clock transition is given in Fig. (1). The electronic structure of $^{199}Hg^+$ reveals that the excited (metastable) states which are interesting from the point of view of frequency standards, involve open d-shells and are very difficult to evaluate using any theoretical methods. Therefore, any kind of property calculation of $^{199}Hg^+$ involving an open d- shell is very complex and challenging.

To measure the transition frequency accurately one needs to determine the corresponding states (energy levels) with a high precision. When an atom interacts with an external field, the standard frequency may be shifted from the resonant frequency. The quality of the frequency standard depends upon the accurate and precise measurement of this shift. To minimize or maintain any shift of the clock frequency, the interaction of the atom with it's surroundings must be controlled. Hence, it is important to have a good knowledge of

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these shifts so as to minimize them while setting up the frequency standard. Some of these shifts are the linear and quadratic Zeeman shift, second-order Stark shift, hyperfine shift and electric quadrupole shift. The largest source of uncertainty in frequency shift arises from the electric quadrupole shift and the hyperfine shift of the clock transition. Departure of the spherical symmetries in the D states of $^{199}Hg^{+}$ gives rise to an electric quadrupole moment and in the presence of external electric field gradient the atomic electric quadrupole moment will cause a shift in the energy levels of the D states. On the other hand, the non-zero nuclear spin of $^{199}Hg^{+}$ produces nuclear multipole moments which interacts with the electron moments at the site of the nucleus which is caused by the nuclear spin. This interaction will lead to a hyperfine effect and the corresponding shift in the upper and lower levels are known as hyperfine shifts.

In this article we have used the relativistic Fock-space unitary coupled cluster (FSUCC) method, one of the most accurate theories to describe the electron correlation effects in many-electron atoms, to calculate electric quadrupole moment and hyperfine constants of $^{199}Hg^{+}$. The excited states which are of interests in $^{199}Hg^{+}$involve open d- shells which make the calculation very complex and challenging. Unlike ordinary Fock-space coupled-cluster (FSCC) theory, FSUCC is based on unitary groups and contains much more physical effects in the same level of approximation. Although the electric quadrupole moment (EQM) has been determined by the experimentalists and the theoreticians, to the best of our knowledge, this is the first time a theory of this kind is being applied to study the properties of a complicated system like $^{199}Hg^{+}$**.** The precise determination of the hyperfine constants using FSUCC theory can be considered as benchmarking of the determination of atomic states. Therefore, the accuracy obtained for the EQMusing this approach can help us to determine the uncertainty (which is $\sim 3.5\%$for the experiment) of the same which will be very useful in the frequency standard studies.

The structure of the paper is as follows : Section I gives a brief introduction about the importance of using $^{199}Hg^{+}$ in frequency standards. It also introduces the importance of applying FSUCC theory in this problem. This is followed by Sec. II which deals with a short theoretical description of FSUCC theory, electric quadrupole moment and hyperfine structure. We present the results and the relevant discussions in the next two Sec. III. Finally, in Sec. IV we conclude and highlight the important findings of our work.

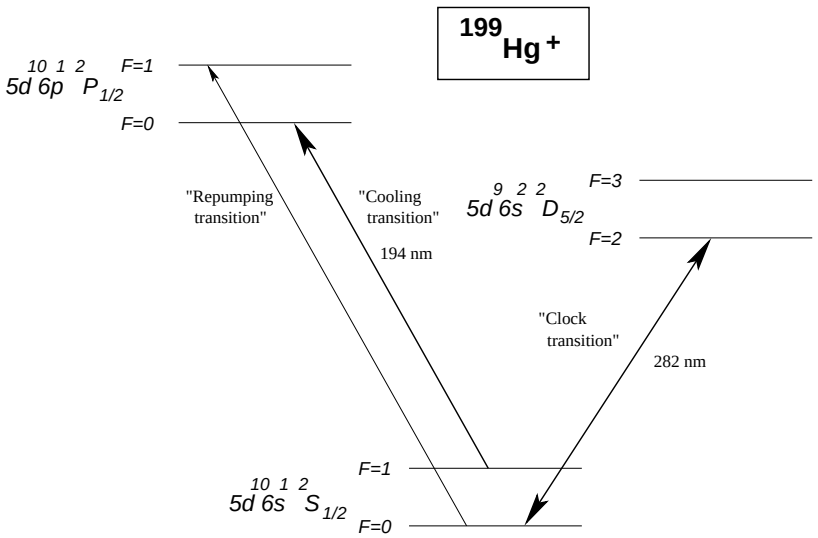

Figure 1: Partial energy level diagram (including hyperfine levels) of the $^{199}Hg^{+}$ion. The 'clock-transition' $(5d^{9}6s^{2}\,{}^{2}D_{5/2}\,(F=0,m_F=0) \;\leftrightarrow\; 5d^{10}6s^{2}\,{}^{2}S_{1/2}\,(F=2,m_F=0))$ which is of interest, is a forbidden electric quadrupole ($E2$) type at 282 nm.

II. THEORETICAL DETAILS

In this section we describe the theoretical formulation of our work. Relativistic Fock-space unitary coupled-cluster (FSUCC) theory is a variant of well known Fock-space coupled-cluster (FSCC) theory in the relativistic regime which is based on an unitary ansatz. More details about UCC theory for atoms can be found in Ref. [8] which is referred as I in the following sections. Therefore, we have just outlined the FSUCC

theory here. We obtain the open shell $5d^9 6s^2\,{}^2D_{5/2}$ and $5d^9 6s^2\,{}^2D_{3/2}$ states of $^{199}Hg^+$ using core ionization technique. In one of our earlier papers, we have outlined the treatment of open-shell coupled-cluster core ionization potential (OSCC-IP) [9] which is referred as II in this manuscript. For determining the $5d^{10}6s\,{}^2S_{1/2}$ state of $^{199}Hg^+$ we have used the open-shell coupled-cluster with electron attachment (OSCC-EA) method [10]. For more details we refer to the original article by Lindgren and Mukherjee [10].

A. Fock-space unitary coupled cluster theory

Relativistic coupled-cluster (RCC) theory is based on the no-virtual-pair approximation along with the appropriate modification of the orbital form and potential terms [11]. One begins with the Dirac-Coulomb Hamiltonian (H) for an N-electron atom which is expressed as

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

with all the standard notations often used. In FSCC/FSUCC method, the self-consistent field solution of the Hartree-Fock (Dirac-Fock in relativistic regime) for the N-electron closed shell ground state Φ is chosen as the vacuum (for labeling purpose only) to define holes and particles with respect to Φ. The multi-reference aspect is then introduced by subdividing the hole and particle orbitals into active and inactive categories, where different occupations of the active orbitals will define a multi-reference *model* space for our problem. We call a model space to be *complete* if it has all possible electron occupancies in the active orbitals, otherwise incomplete. The classification of orbitals into active and inactive groups is, *in principle*, arbitrary and is at our disposal. However, for the sake of computational convenience, we treat only a few hole and particle orbitals as active, namely those are close to the Fermi level.

We designate by $\Psi_i^{0(k,l)}$ a model space of k-hole and l-particle determinants, where in the present instance ($\mathrm{Hg} - e \longrightarrow \mathrm{Hg}^+$), $l = 0$ and k ranges from 0 to 1. Generally, any second quantized operator has k-hole and l-particle annihilation operators for the active holes and particles. For convenience, we indicate the "hole-particle valence rank" of an operator by a superscript (k,l) on the operator. Thus, according to our notation, an operator $A^{(k,l)}$ will have exactly k-hole and l-particle annihilation operators.

We now describe the type of ansatz used to derive the FSUCC equations for direct energy difference calculations in one-electron detachment processes. The Hartree-Fock/Dirac-Fock function Φ is denoted by $\Psi^{(0,0)}$ and the inactive hole and particle orbitals (defined with respect to Φ) are labeled by the indices $a, b, c, \cdots$ and $p, q, r, \cdots$, respectively. The corresponding active holes and particles are labeled by the indices $\alpha, \beta, \gamma \cdots$ and $u, v, w \cdots$, respectively. Note that there will be *no active* particles for electron detachment processes. The cluster operator correlating the N-electron ground/reference state is denoted in our notation by $S^{(0,0)}$ which can be split into various n-body components depending upon the various hole-particle excitation ranks. The cluster operator $S^{(0,0)}$ upto two-body can be written in second quantized notation as,

$$S^{(0,0)} = S_1^{(0,0)} + S_2^{(0,0)} + \cdots = \sum_{p,a} \langle p|s_1^{(0,0)}|a\rangle \{a_p^\dagger a_a\} + \frac{1}{4} \sum_{a,b,p,q} \langle pq|s_2^{(0,0)}|ab\rangle \{a_p^\dagger a_q^\dagger a_b a_a\} + \cdots \tag{2}$$

where $a^\dagger$ (a) denotes creation (annihilation) operator with respect to $\Phi_{\rm HF/DF}$ and $\{\cdots\}$ denotes *normal* ordering. It should be noted that $S^{(0,0)}$ cannot destroy any holes or particles; acting on Φ, it can only create them.

For $(N-1)$ electron states the model space consists of one active hole and zero active particle $(k = 1, l = 0)$ and hence according to our notation the valence sector for $(N-1)$ electron states can be written as (1,0) sector. We introduce an wave operator Ω which generates all valid excitation from the model space function for $(N-1)$ electron states. The wave operator Ω for the (1,0) valence problem is given by

$$\Omega = \{\exp(S^{(0,0)} + S^{(1,0)})\}. \tag{3}$$

In this case the additional cluster operator $S^{(1,0)}$ must be able to destroy the active particle present in the (1,0) valence space. Like $S^{(0,0)}$, the cluster operator $S^{(1,0)}$ can also be split into various n-body components

depending upon hole-particle excitation ranks. The one- and two-body $S^{(1,0)}$ (depicted in Fig.(2)) can be written in the second quantized notation as

$$S^{(1,0)} = S_1^{(1,0)} + S_2^{(1,0)} + \cdots = \sum_{\alpha \neq b} \langle \alpha | s_1^{(1,0)} | b \rangle \{ a_\alpha^\dagger a_b \} + \frac{1}{2} \sum_{p,b,c} \langle p\alpha | s_2^{(1,0)} | cb \rangle \{ a_p^\dagger a_\alpha^\dagger a_b a_c \} + \cdots \tag{4}$$

where α denotes the active particle which is destroyed.

In general, for a (k,l) valence problem, the cluster operator must be able to destroy any subset of k- active holes and l- active particles. Hence, the wave operator Ω for (k,l) valence sector may be written as

$$\Omega = \{ \exp(\tilde{S}^{(k,l)}) \}. \tag{5}$$

where

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

We define the exact wave function $\Psi_i^{(k,l)}$ for (k,l) valence sector as

$$\Psi_i^{(k,l)} = \Omega \Psi_i^{0(k,l)} \tag{7}$$

where

$$\Psi_i^{0(k,l)} = \sum_i C_i^{(k,l)} \Phi_i^{(k,l)}. \tag{8}$$

The functions $\Phi_i^{(k,l)}$ in Eq.(8) are the determinants included in the model space $\Psi_i^{0(k,l)}$ and $C^{(k,l)}$ are the corresponding coefficients. Substituting the above form of the wave-function (given in Eqs. (7) and (8)) in the Schrödinger equation for a manifold of states $H|\Psi_i^{(k,l)}\rangle = E_i |\Psi_i^{(k,l)}\rangle$, we get

$$H\Omega \left(\sum_i C_i |\Phi_i^{(k,l)}\rangle \right) = E_i \Omega \left(\sum_i C_i |\Phi_i^{(k,l)}\rangle \right), \tag{9}$$

where E_i is the i-th state energy.

Following Lindgren [12], Mukherjee [13], Lindgren and Mukherjee [14], Sinha *et al.* [15] and Pal *et al.* [16], the Fock-space Bloch equation for the FSCC may be written as

$$H\Omega P^{(k,l)} = P^{(k,l)} H_{\text{eff}}^{(k,l)} \Omega P^{(k,l)} \qquad \forall (k,l) \tag{10}$$

where

$$H_{\text{eff}}^{(k,l)} = P^{(k,l)} \Omega^{-1} H \Omega P^{(k,l)} \tag{11}$$

and $P^{(k,l)}$ is the model space projection operator for the (k,l) valence sector (defined by $\sum_i C_i^{(k,l)} \Phi_i^{(k,l)}$). For complete model space, the model space projector $P^{(k,l)}$ satisfies the *intermediate* normalization condition

$$P^{(k,l)} \Omega P^{(k,l)} = P^{(k,l)}. \tag{12}$$

At this juncture, we single out the cluster amplitudes $S^{(0,0)}$ and call them T. The rest of the cluster amplitudes will henceforth be called S. The normal ordered definition of Ω enables us to rewrite Eq.(6) as

$$\Omega = \exp(T)\{\exp(S)\} = \exp(T)\Omega_v \tag{13}$$

where Ω_v represents the wave-operator for the valence sector.

To formulate the theory for direct energy differences, we pre-multiply Eq.(10) by $\exp(-T)$ and get

$$\overline{H} \Omega_v P^{(k,l)} = \Omega_v P^{(k,l)} H_{\text{eff}}^{(k,l)} P^{(k,l)} \ , \quad \forall (k,l) \neq (0,0) \tag{14}$$

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

$$\widetilde{H}_{\rm eff}^{(k,l)} = H_{\rm eff}^{(k,l)} - E_{\rm gr}, \quad \forall (k,l) \neq (0,0) \tag{15}$$

Substituting Eq.(15) in Eq.(14) we obtain the Fock-space Bloch equation for energy differences:

$$\widetilde{H}\Omega_v P^{(k,l)} = \Omega_v P^{(k,l)} \widetilde{H}_{\rm eff}^{(k,l)} P^{(k,l)}, \quad \forall (k,l) \neq (0,0) \tag{16}$$

Eqs. (10) and (16) are solved by the Bloch projection method for $k = l = 0$ and $k = 0, l \neq 0$, respectively, involving the left projection of the equations with $P^{(k,l)}$ and its orthogonal complement $Q^{(k,l)}$ ($P^{(k,l)} + Q^{(k,l)}$=1) to obtain the effective Hamiltonian and the cluster amplitudes, respectively. At this point, we recall that the cluster amplitudes in FSCC are solved hierarchically through the *subsystem embedding condition* [17, 18] which is equivalent to the *valence universality* condition used by Lindgren [12] in his formulation. For example, in the present application, we first solve the FSCC for $k = l = 0$ to obtain the cluster amplitudes T. The operator $\widetilde{H}$ and $\widetilde{H}_{\rm eff}^{(1,0)}$ are then constructed from this cluster amplitudes T to solve Eq. (16) for $k = 1$, $l = 0$ to determine $S^{(1,0)}$ amplitudes. $\widetilde{H}$ is then diagonalized within the model space to obtained the desired eigenvalues and eigenvectors. The diagonalization is followed from the eigenvalue equation

$$\widetilde{H}_{\rm eff}^{(1,0)} C^{(1,0)} = C^{(1,0)} E. \tag{17}$$

where

$$\widetilde{H}_{\rm eff}^{(1,0)} = P^{(1,0)}[\widetilde{H} + \overbrace{\widetilde{H}S^{(1,0)}}]P^{(1,0)}. \tag{18}$$

The expression $\overbrace{AB}$ in Eq.(18) indicates that operators A and B are connected by common orbital(s).

In FSUCC, the wave operator Ω in Eq.(13) is replaced by

$$\Omega = \exp(\sigma)\left\{\exp\left(S\right)\right\} = \Omega_c \Omega_v \tag{19}$$

with the cluster operator defined as $\sigma = T - T^\dagger$. In comparison to the ordinary coupled cluster (CC) theory the wave operator σ in UCC contains de-excitation operator ($T^\dagger$) as well and therefore UCC theory contains more higher order effects than the conventional CC theory in the same level of approximation. In this work we have used unitary coupled-cluster theory in the single and double excitation approximation to treat the closed shell correlation consistently. We refer to the article I for further details.

B. Electric quadrupole shift

The interaction of the atomic quadrupole moment with the external electric-field gradient is similar to the interaction of a nuclear quadrupole moment with the electric fields generated by the atomic electrons inside the nucleus. In the presence of the electric field, this interaction gives rise to an energy shift by coupling with the gradient of the electric field. The quadrupole moment $\mathbf{\Theta}$ of an atomic state $|\Psi(\gamma JFM_F)\rangle$ is defined as the diagonal matrix element of the quadrupole operator with the maximum value M_J and is expressed as

$$\mathbf{\Theta} = \langle \Psi(\gamma JFM_F)| \, \Theta_{zz} \, |\Psi(\gamma JFM_F)\rangle \ . \tag{20}$$

Here γ specifies the electronic configuration of the atoms which distinguishes the initial and final states; J is the total angular momentum of the atom and F is the summation of nuclear and atomic angular momentum with M_F its projection. The electric quadrupole operator in terms of the electronic coordinates is given by

$$\Theta_{zz} = -\frac{e}{2} \sum_j \left(3z_j^2 - r_j^2\right), \tag{21}$$

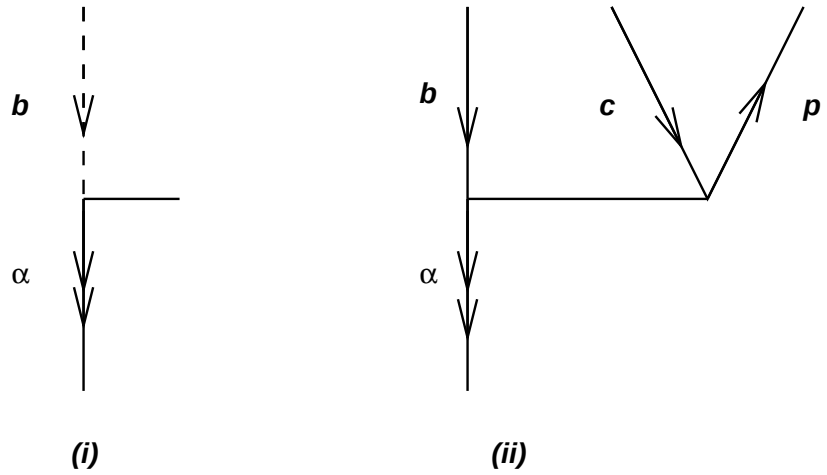

Figure 2: Diagrammatic representation of the open-shell cluster operators in the single and double excitation (SD) approximation. Fig (i) and (ii) corresponds to single and double excitations amplitudes respectively as given in Eq. (4). The lines represented by double arrow stand for occupied valence orbital and the downward single arrows are occupied orbitals (including the valence) ; the line with an upward arrow corresponds to particle. The dashed lines represent inactive orbitals.

where the sum is over all the electrons and z is the coordinate of the jth electron. To calculate the quantity we express the quadrupole operator in its single particle form as

$$\Theta_m^{(2)} = \sum_m q_m^{(2)}. \tag{22}$$

The single particle reduced matrix element of the electric quadrupole operator is expressed as [19]

$$\langle j_f \| \, q_m^{(2)} \, \| j_i \rangle = \langle j_f \| \, C_m^{(2)} \, \| j_i \rangle \int dr \, r^2 \left(\mathcal{P}_f \mathcal{P}_i + \mathcal{Q}_f \mathcal{Q}_i \right). \tag{23}$$

In Eq.(23), the subscripts f and i correspond to the final and initial states respectively; $\mathcal{P}$ and $\mathcal{Q}$ are the radial part of the large and small components of the single particle Dirac-Fock wavefunctions respectively and j_i is the total angular momentum for the ith electron. The angular factor is given in by

$$\begin{aligned} \langle j_f \| \, C_m^{(k)} \, \| j_i \rangle = \quad & (-1)^{(j_f+1/2)} \sqrt{(2j_f+1)} \sqrt{(2j_i+1)} \\ & \times \begin{pmatrix} j_f & 2 & j_i \\ -1/2 & 0 & 1/2 \end{pmatrix} \pi(l,k,l') \end{aligned} \tag{24}$$

where

$$\pi(l,k,l') = \begin{cases} 1 & \text{if } l+k+l' \text{ even} \\ 0 & \text{otherwise ;} \end{cases}$$

l and k being the orbital angular momentum and the rank of the interaction respectively.

Finally using the Wigner-Eckart theorem we define the electric quadrupole moment in terms of the reduced matrix elements as

$$\langle j_f | \, \Theta_m^{(2)} \, | j_i \rangle = (-1)^{j_f - m_f} \begin{pmatrix} j_f & 2 & j_i \\ -m_f & 0 & m_f \end{pmatrix} \langle j_f \| \, \Theta^{(2)} \, \| j_i \rangle \tag{25}$$

More details about the evaluation of the electric quadrupole moment using RCC theory is described in one of our recent papers [20]. The electric quadrupole shift is evaluated using the relation [21]

$$\langle \Psi(\gamma JFM_F)| \Theta |\Psi(\gamma JFM_F)\rangle = \frac{-2A\left[3M_F^2 - F(F+1)\right]\langle \Psi(\gamma JF)\| \Theta^{(2)} \|\Psi(\gamma JF)\rangle}{[(2F+3)(2F+2)(2F+1)2F(2F-1)]^{1/2}} \times \mathcal{O}(\alpha,\beta) \tag{26}$$

and

$$\mathcal{O}(\alpha,\beta) = \left[(3\cos^2\beta - 1) - \epsilon(\cos^2\alpha - \sin^2\alpha)\right]. \tag{27}$$

Here α and β are two of the three Euler angles that take the principal-axis frame of the electric field gradient to the quantization axis and ϵ is an asymmetry parameter of the electric potential function [21].

C. Magnetic dipole hyperfine shift

The non-zero nuclear spin gives rise to nuclear multipole moments which interact with the electric multipole moments generated by the atomic electrons at the site of the nucleus and this interaction is collectively known as hyperfine interaction [22]. Theoretical determination of hyperfine constants is one of the most stringent tests of accuracy of the atomic wave functions near the nucleus. Also accurate predictions of hyperfine coupling constants require a precise incorporation of relativistic and correlation effects. Like the $^{201}Hg^+$ isotope, $^{199}Hg^+$ also has a non zero nuclear spin ($I = \frac{1}{2}$) and the $m_F = 0$ levels for both the $^2S_{1/2}$ and $^2D_{5/2}$ states are independent of the first order Zeeman shift.

The hyperfine interaction is given by

$$H_{hfs} = \sum_k M^{(k)} \cdot \mathcal{T}^{(k)}, \tag{28}$$

where $M^{(k)}$ and $\mathcal{T}^{(k)}$ are spherical tensors of rank k, which corresponds to nuclear and electronic parts of the interaction respectively. The lowest $k = 0$ order represents the interaction of the electron with the spherical part of the nuclear charge distribution.

In the first order perturbation theory, the energy corresponding to the hyperfine interaction of the fine structure state are the expectation values of H_{hfs} such that

$$\begin{aligned} W(J) &= \langle IJFM_F| \sum_k M^{(k)} \cdot \mathcal{T}^{(k)} |IJFM_F\rangle \\ &= \sum_k (-1)^{I+J+F} \left\{ \begin{array}{ccc} I & J & F \\ J & I & k \end{array} \right\} \langle I\| M^{(k)} \|I\rangle \langle J\| \mathcal{T}^{(k)} \|J\rangle . \end{aligned} \tag{29}$$

Here $\mathbf{I}$ and $\mathbf{J}$ are the total angular angular momentum for the nucleus and the electron state, respectively, and $\mathbf{F} = \mathbf{I} + \mathbf{J}$ with the projection M_F.

The magnetic dipole hyperfine constant (A) comes from the magnetic dipole hyperfine operator $\mathcal{T}_q^{(1)}$ which is a tensor of rank 1. For an eigen state $|IJ\rangle$ of the Dirac-Coulomb Hamiltonian, A is defined as

$$A = \mu_N \left(\frac{\mu_I}{I}\right) \frac{\langle J\| \mathcal{T}^{(1)} \|J\rangle}{\sqrt{J(J+1)(2J+1)}}, \tag{30}$$

where μ_I is the nuclear dipole moment defined in units of Bohr magneton μ_N. The magnetic dipole hyperfine operator $\mathcal{T}_q^{(1)}$ can be expressed in terms of single particle rank 1 tensor operators and is given by the first order term of Eq. (29)

$$\mathcal{T}_q^{(1)} = \sum_q t_q^{(1)} = \sum_j -ie\sqrt{\frac{8\pi}{3}} r_j^{-2} \overrightarrow{\alpha_j} \cdot \mathbf{Y}_{1q}^{(0)}(\widehat{r_j}). \tag{31}$$

Table I: Electric quadrupole moment ($\mathbf{\Theta}$ in ea_0^2) of the $5d^9 6s^2\,{}^2D_{5/2}$ state of $^{199}Hg^+$. Entry within the parenthesis correspond to dressed one-body contribution. FSUCC stands for the present calculation. MCHF and MCDF correspond to multi-configuration Hartree-Fock and multi-configuration Dirac-Fock (relativistic MCHF) respectively and 'Expt.' is the experimental value.

FSUCC	HF	MCHF	MCDF	Expt.
-0.517 (-0.739)	-0.664 [26]	-0.544 [27, 28]	-0.56374 [25]	-0.510 (18) [28]

Here $\overrightarrow{\alpha}$ is the Dirac matrix and $\mathbf{Y}^{\lambda}_{kq}$ is the vector spherical harmonics. The index j refers to the jth electron of the atom with r_j as its radial distance and e as the magnitude of the electronic charge.

The corresponding shift in the energy level is known as magnetic dipole hyperfine shift and is expressed as

$$W_{M1} = A\frac{F(F+1) - I(I+1) - J(J+1)}{2}. \tag{32}$$

III. RESULTS AND DISCUSSIONS

The transition which can serve as a new frequency standard is the forbidden electric quadrupole ($E2$) transition $5d^9 6s^2\,{}^2D_{5/2} \longrightarrow 5d^{10}6s^1\,{}^2S_{1/2}$ in $^{199}Hg^+$. The possible shift which are crucial for accurate determination of the desired transition frequency are mainly of two kinds : electric quadrupole shifts of the $5d^9 6s^2\,{}^2D_{5/2}$ state and the magnetic dipole hyperfine shifts of both the $5d^9 6s^2\,{}^2D_{5/2}$ (upper) and the $5d^{10}6s^2\,{}^1S_0$ (lower) states. Departure of the charge distribution from spherical nature to non-spherical in the $5d^9 6s^2\,{}^2D_{5/2}$ state will give rise to an electric quadrupole moment which eventually will produce a shift in the energy level in the presence of an external electric field gradient. On the other hand, the non-zero nuclear spin of the $^{199}Hg^+$ which causes the non-zero nuclear dipole moment (multipole moment of the first kind) will give rise to the magnetic dipole hyperfine effect in the presence of the electron multipole moment at the site of the nucleus caused by the electron spin. This magnetic dipole hyperfine effect will produce a shift in the energy levels for both (upper and lower) states and are directly related to the magnetic dipole hyperfine constant (A) which is given by Eq. (32).

In this paper we have calculated electric quadrupole moment (Θ) of the $5d^9 6s^2\,{}^2D_{5/2}$ state and magnetic dipole hyperfine constant (A) of the $5d^9 6s^2\,{}^2D_{5/2}$, $5d^{10}6s^2\,{}^1S_0$ and $5d^9 6s^2\,{}^2D_{3/2}$ states of $^{199}Hg^+$ using relativistic Fock-space unitary coupled cluster theory. FSUCC theory, is much more rigorous than its ordinary counterpart (Fock-space coupled cluster theory, namely FSCC) and other atomic many-body theories like configuration interaction , many-body perturbation theory etc. The accuracy of our this calculation establishes the necessity of applying a theory of this kind to calculate properties for complicated D-states. In our calculation we have considered the ground state ($5d^{10}6s^2\,{}^1S_0$) of ^{199}Hg as the Dirac-Fock (DF) reference state. We then apply the closed shell unitary cluster operator to correlate the ground state which is followed by a core ionization calculation to produce the open shell states ($5d^9 6s^2\,{}^2D_{3/2}$ and $5d^9 6s^2\,{}^2D_{5/2}$) of $^{199}Hg^+$. The basis functions are constructed by using a large finite basis set expansion of Gaussian type orbitals [23] with s, p, d, f and g functions ($34s32p30d20f15g$). The nucleus is assumed to have a finite structure (Fermi type). This closed shell correlation calculation is followed by OSCC-IP [9] calculations to obtain the $5d^9 6s^2\,{}^2D_{5/2}$, $5d^9 6s^2\,{}^2D_{3/2}$ states and an OSCC-EA [10] calculation for obtaining the $5d^{10}6s^2\,{}^1S_0$ state of $^{199}Hg^+$. Excitations from all the core orbitals have been considered to do a complete correlation treatment. We have also studied the effects of higher angular momentum states and found that to be negligible. Therefore we have omitted the higher order symmetries to generate the basis functions. In an earlier paper by one of the authors [24], the FSCC method has been employed to estimate these quantities. In principal, FSUCC is more rigorous than FSCC and contains more higher order effects in the same level of approximation because of the unitary structure of the closed shell correlation operator.

This particular calculation with $^{199}Hg^+$ is much more challenging than the treatment of alkal-metal atoms and alkali like ions. The d-shell vacancies in the excited states of $^{199}Hg^+$ introduce additional complexities

Table II: Magnetic dipole hyperfine constant (A in MHz) of different states of $^{199}Hg^{+}$. Entry within the parenthesis correspond to dressed one body contribution. FSUCC stands for the present calculation. The $\mu_N \left(\frac{\mu_I}{I}\right)$ values used in the calculation is taken from Ref. [29].

State	FSUCC	FSCC [24]	MCDF [25]	Expt. [28]
$5d^9 6s^{2\,2}D_{5/2}$	995	972	963.5	986.19 (4)
	(865)			
$5d^9 6s^{2\,2}D_{3/2}$	2780	2713	2478.3	
	(2734)			
$5d^{10} 6s^{1\,2}S_{1/2}$	40487	40440		40507
	(32963)			

in the determination of atomic states and related properties. The core ionization technique has been used in connection with the FSUCC method for the first time to study the one-electron properties of ions of this kind.

The earlier calculation [24] by one of the authors using FSCC has estimated the electric quadrupole moment ($\mathbf{\Theta}$ in ea_0^2) of $5d^9 6s^{2\,2}D_{5/2}$ state of $^{199}Hg^{+}$ as 0.527 ea_0^2, which was off by $0.017\,ea_0^2$ from the experiment (neglecting the experimental uncertainty). The present estimate of $\mathbf{\Theta}$, on the other hand, is off by $0.007\,ea_0^2$ from the central experimental value. We observe that both the results (FSCC and FSUCC) are within the experimental uncertainty ($\sim 3.5\%$). However, it can be concluded that the accuracy obtained in the present case using FSUCC will help to reduce the experimental uncertainty. This can be understood by observing the fact that at a given level of approximation (for this case singles and doubles, namely SD) FSUCC theory contains much more correlation and higher order excitation effects compared to FSCC. Therefore applying an improved theory of this kind will give some valuable inputs to the frequency standard measurements using $^{199}Hg^{+}$.

In a recent calculation Itano [25] used the multi-configuration Dirac-Fock (MCDF) method to estimate $\mathbf{\Theta}$ (in ea_0^2) of the same state which gave the value to be 0.56374 (this disagrees with the experimental value by $\sim 10.5\%$). The numbers of the electric quadrupole moments $\mathbf{\Theta}$ (in ea_0^2) of the $5d^9 6s^{2\,2}D_{5/2}$ and $5d^9 6s^{2\,2}D_{3/2}$ states of $^{199}Hg^{+}$are given in table I.

We have also used FSUCC to determine the magnetic dipole hyperfine constants (A) of the $5d^9 6s^{2\,2}D_{5/2}$, $5d^9 6s^{2\,2}D_{53/2}$ and $5d^{10} 6s^{1\,2}S_{1/2}$ states of $^{199}Hg^{+}$. Precise calculations of A values are not only theoretical checks of the experimental determination but also provide information about the accuracies of the atomic wavefunctions which are used in this calculation. Table II contains the tabulated values of the A using different methods. The previous result obtained by FSCC [24] by one of the authors, reveals that the FSUCC is able to produce a significant improvement over all of the values calculated here and the theoretical accuracies have been reduced by significant amounts. Experimental value of A for the $5d^9 6s^{2\,2}D_{3/2}$ state is not available. The accuracies of the entire calculation ensure that the prediction of the A value of the $5d^9 6s^{2\,2}D_{3/2}$ state will be able to lead to a precise measurement of the same.

From the given results in table (I) and (II) the effects of electron correlation in determining electric quadrupole moment and hyperfine constants can be estimated easily. The numbers in the parentheses correspond to the effects of the dressed one-body operator and the difference between the two values turns out to be the contribution from electron correlation (many-body) effects. For the electric quadrupole moment the correlation effects turns out to be $\sim 43\%$ and for the hyperfine constants the correlation contributions range from $\sim 2\%$ to $\sim 19\%$. These effects clearly establish the power of the FSUCC method to very accurately determine the atomic properties, such as electric quadrupole moment and hyperfine constants.

IV. CONCLUSION

In summary, we have used the FSUCC method to determine the electric quadrupole moment of the $5d^9 6s^{2\,2}D_{5/2}$ state and magnetic dipole hyperfine constants of the $5d^9 6s^{2\,2}D_{5/2}$, $5d^9 6s^{2\,2}D_{3/2}$ and $5d^{10} 6s^{1\,2}S_{1/2}$ states of $^{199}Hg^{+}$. The calculation involving $^{199}Hg^{+}$ is very complex and challenging because the excited states which are of interests involve open d- shells. The calculated values of the hyperfine

constants can be considered as benchmarking of the determination of atomic states using FSUCC theory. Therefore, the accuracy obtained for the electric quadrupole moments using this approach can help us to determine the uncertainty which is very important to determine for the frequency standard studies. To our knowledge this is the most accurate theoretical determination of these quantities to date and are very important in the context of producing a next generation frequency standard. FSUCC along with the core ionization method has been applied to determine any atomic properties of these kinds. This calculation will serve not only as a supplement to the ongoing experiments but also to establish this theory in determining different problems with atoms and ions.

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