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# A theoretical study of the $g$ -factor and lifetime of the $6s6p\ ^3P_0$ state of mercury

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We calculate the  $g$ -factor of the  $6s6p\ ^3P_0$  state of 199 and 201 mercury isotopes using a relativistic high-precision all-order method that combines the configuration interaction and the coupled-cluster approaches. Our values  $g(^{199}\text{Hg}) = -0.9485(49) \times 10^{-3}$  and  $g(^{201}\text{Hg}) = 0.3504(18) \times 10^{-3}$  are in agreement with the experimental measurements within the 0.5% theoretical uncertainty. We also calculate the hyperfine quenching rate of the  $6s6p\ ^3P_0$  state in  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$  and determine its lifetime to be 1.3 and 1.9 s, respectively.

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## I. INTRODUCTION

Mercury is one of a most promising candidates for a frequency standard due to its low susceptibility to the blackbody radiation (BBR). Recently, an optical lattice clock based on the clock transition between the  $^1S_0$  and  $^3P_0$  states of  $^{199}\text{Hg}$  has achieved the uncertainty at the level of  $8 \times 10^{-17}$ , with the dominating uncertainty being from a frequency shift introduced by the trapping lattice light [1]. To reduce this uncertainty further, thorough understanding of the mercury atomic structure is crucial. This work provides a benchmark test of theoretical accuracy in evaluating Hg atomic properties, an important step towards understanding the Hg complicated electronic structure. Accurate theoretical calculations of Hg properties, including the BBR and various sources of AC Stark shifts will be needed to further reduce the uncertainty of Hg atomic clock. For such calculations reliable estimates of the theoretical uncertainties are required.

An atomic response to externally applied magnetic field is characterized by a dimensionless number called the  $g$ -factor. For the  $^1S_0$  ground state of  $^{199}\text{Hg}$ , the  $g$ -factor was measured with a relative uncertainty at the  $8 \times 10^{-7}$  level [2, 3]. For the  $^3P_0$  state of  $^{199}\text{Hg}$ , which is of our interest because of its importance for Hg frequency standard, the  $g$ -factor was calculated and measured in Ref. [4]. The authors used a semi-empirical method of calculation and estimated the theoretical accuracy at the level of 1%, while the experimental precision was considerably greater.

A precise knowledge of the  $g$ -factor of the clock states is crucial in suppressing frequency shifts from magnetic field to the level of  $10^{-19}$  in a recent microwave-dressing scheme proposed by Zanon-Willette *et. al.* [5]. Since the calculation of the  $g$ -factor involves the same matrix elements as those used in the calculation of the lifetime of the  $^3P_0$  state of  $^{199}\text{Hg}$ , it is important to revisit the problem of an accurate and reliable calculation of this quantity.

We carried out the calculation of the  $g$ -factor of the

$6s6p\ ^3P_0$  state in the framework of a pure *ab initio* relativistic hybrid method combining the configuration interaction (CI) with the single-double coupled cluster approach [CI+all-order method, see Refs. [6, 7]] and found an excellent agreement with available experimental results. We have also calculated hyperfine structure (HFS) constants of the low-lying odd-parity states and the lifetime of the  $^3P_0$  state for  $^{199}\text{Hg}$ , resolving the discrepancy of theory and experiment for the latter.

## II. CALCULATION OF THE $6s6p\ ^3P_0$ $g$ -FACTOR

### A. Formulation of the problem

If an atom is placed in an external magnetic field  $\mathbf{B}$ , the interaction of the atomic magnetic moment  $\boldsymbol{\mu}$  with  $\mathbf{B}$  is described by the Hamiltonian

$$H = -\boldsymbol{\mu} \cdot \mathbf{B}. \quad (1)$$

The atomic magnetic moment  $\boldsymbol{\mu}$  is a sum of the electronic magnetic moment  $\boldsymbol{\mu}_e$  and the nuclear magnetic moment  $\boldsymbol{\mu}_I$ .

We describe an atomic state  $|\psi\rangle = |FM\rangle$  in the basis of its total angular momentum  $\mathbf{F} = \mathbf{J} + \mathbf{I}$ , where  $\mathbf{J}$  and  $\mathbf{I}$  are the total electronic and nuclear angular momenta, respectively, and  $M$  is the magnetic quantum number.

Below we follow an approach of Ref. [4]. Assuming that  $\boldsymbol{\mu} = -\mu_0 g \mathbf{F}$ , directing the external magnetic field  $\mathbf{B}$  along the  $z$ -axis, and using Eq. (1), we easily obtain for the energy shift of the atomic state  $|\psi\rangle$ :

$$\Delta E = \langle \psi | H | \psi \rangle = g \mu_0 M B, \quad (2)$$

where  $\mu_0$  is the Bohr magneton and  $g$  is a dimensionless  $g$ -factor.

We focus our analysis on the odd  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$  isotopes of mercury with the 1/2 and 3/2 nuclear spin  $I$ , respectively. Due to the non-zero nuclear spin there is the hyperfine structure interaction  $H_{\text{hfs}}$  between the

atomic electrons and the nucleus. As a result, an eigenfunction  $|\psi\rangle$  of the Hamiltonian  $H$ , differs from the bare atomic state wave function  $|\psi^{(0)}\rangle = |{}^3P_0, IM\rangle$  (we take into account that  $J = 0$  and  $F = I$ ). Treating the hyperfine structure interaction as a perturbation, we can write the resulting  ${}^3P_0$  state wave function  $|\psi\rangle$  in the first order of the perturbation theory as

$$|\psi\rangle = |\psi^{(0)}\rangle + \sum_n \frac{|\psi_n^{(0)}\rangle \langle \psi_n^{(0)} | H_{\text{hfs}} | \psi^{(0)} \rangle}{E_{3P_0} - E_n}, \quad (3)$$

where the summation goes over all bare atomic state wave functions  $|\psi_n^{(0)}\rangle = |\gamma_n I J_n; F_n M_n\rangle$  allowed by the selection rules of the operator  $H_{\text{hfs}}$ ;  $J_n$  is the total angular momentum of the electrons and  $\gamma_n$  encapsulates all other electronic quantum numbers.

Substituting the wave function  $|\psi\rangle$ , given by Eq. (3), into Eq. (2), we have

$$g\mu_0 MB \approx \langle {}^3P_0, IM | H | {}^3P_0, IM \rangle + 2 \sum_n \frac{\langle {}^3P_0, IM | H | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | H_{\text{hfs}} | {}^3P_0, IM \rangle}{E_{3P_0} - E_n}, \quad (4)$$

where we keep the terms up to the first order in  $H_{\text{hfs}}$  and use the fact that both  $H$  and  $H_{\text{hfs}}$  operators are real. Therefore, the calculation of the  $g$ -factor involves evaluation of the matrix elements of two operators:  $H$  and  $H_{\text{hfs}}$ .

### B. Matrix elements of the $H_{\text{hfs}}$ operator

The hyperfine structure coupling due to nuclear multiple moments may be represented as a scalar product of two tensors of rank  $k$ ,

$$H_{\text{hfs}} = \sum_k \mathbf{N}^{(k)} \cdot \mathbf{T}^{(k)},$$

where  $\mathbf{N}^{(k)}$  and  $\mathbf{T}^{(k)}$  act in the space of nuclear and electronic coordinates, respectively.

In our case, only the interaction of magnetic dipole nuclear moment with the electrons (the first term in the sum over  $k$ ) gives a non-zero contribution to the second term of Eq. (4). The contribution of the quadrupole term is zero for both considered isotopes. If  $J = 0$  and  $J_n = k = 2$ , the second term in Eq. (4) turns to zero because  $\mu_e$  is a vector operator and  $J_n$  can only be equal to 1.

Thus, we can write in the spherical basis

$$H_{\text{hfs}} = \mathbf{N}^{(1)} \cdot \mathbf{T}^{(1)} = \sum_{q=-1}^1 (-1)^q N_{-q}^{(1)} T_q^{(1)}. \quad (5)$$

It is convenient to define  $\mathbf{N}^{(1)}$  in a dimensionless form as

$$\mathbf{N}^{(1)} = \boldsymbol{\mu}_I / \mu_N,$$

where  $\mu_N$  is the nuclear magneton and  $\boldsymbol{\mu}_I$  is the nuclear magnetic dipole moment.

The operator  $T_q^{(1)}$  can be presented as the sum of the one-particle operators

$$T_q^{(1)} = \sum_{i=1}^{N_e} \left( T_q^{(1)} \right)_i,$$

where  $N_e$  is the number of the electrons in the atom and the one-particle operator  $\left( T_q^{(1)} \right)_i$  is given by (see, e.g., [8]):

$$\left( T_q^{(1)} \right)_i = |e| \frac{[\mathbf{r}_i \times \boldsymbol{\alpha}_i]_q}{r_i^3} \mu_N.$$

Here  $e$  is the electron charge,  $[\mathbf{a} \times \mathbf{b}]$  is the vector product of the vectors  $\mathbf{a}$  and  $\mathbf{b}$ ,  $r_i$  is the radial position of the  $i$ -th electron, and  $\boldsymbol{\alpha}_i$  is the Dirac matrix.

The wave function  $|\gamma I J; F M\rangle$  can be written in a form

$$|\gamma I J; F M\rangle = \sum_{m, \lambda} C_{Jm, I\lambda}^{FM} |\gamma J m\rangle |I \lambda\rangle, \quad (6)$$

where  $C_{Jm, I\lambda}^{FM}$  is the Clebsch-Gordan coefficient,  $|\gamma J m\rangle$  and  $|I \lambda\rangle$  are the electronic and nuclear components of the wave function, and  $m$  and  $\lambda$  are the projections of  $J$  and  $I$ , correspondingly.

To find the matrix element of  $H_{\text{hfs}}$ , we use Eqs. (5) and (6), apply the Wigner-Eckart theorem to the electronic and nuclear components of the matrix element, and sum up analytically the Clebsch-Gordan coefficients over all magnetic quantum numbers (see for details, e.g., [8]). Finally, we arrive at the following expression [8, 9]:

$$\begin{aligned} & \langle \gamma' I J'; F' M' | H_{\text{hfs}} | \gamma I J; F M \rangle = (-1)^{I+J'+F} \\ & \times \langle I || N^{(1)} || I \rangle \langle \gamma' J' || T^{(1)} || \gamma J \rangle \begin{Bmatrix} I & I & 1 \\ J & J' & F \end{Bmatrix} \delta_{F'F} \delta_{M'M}. \end{aligned}$$

For the nuclear component, we express the matrix elements  $\langle I || N^{(1)} || I \rangle$  through magnetic dipole moment  $\mu_I$ , defined as

$$\begin{aligned} \mu_I &= \langle I, M_I = I | (\boldsymbol{\mu}_I)_z | I, M_I = I \rangle \\ &= \sqrt{\frac{I}{(2I+1)(I+1)}} \langle I || \mu_I || I \rangle. \end{aligned}$$

Then, we obtain the respective reduced matrix element

$$\langle I || N^{(1)} || I \rangle = \sqrt{\frac{(2I+1)(I+1)}{I}} \frac{\mu_I}{\mu_N}.$$

### C. Magnetic-dipole hyperfine structure constants

Magnetic dipole HFS constant  $A$  of an atomic state  $|\gamma J\rangle$  is expressed via the matrix element  $\langle \gamma J || T^{(1)} || \gamma J \rangle$  of the electronic tensor  $\mathbf{T}^{(1)}$  as

$$A = \frac{\mu_I}{I \mu_N} \frac{\langle \gamma J || T^{(1)} || \gamma J \rangle}{\sqrt{J(J+1)(2J+1)}}.$$

To test the quality of our wave functions near the nucleus, we calculated the magnetic-dipole HFS constants  $A$  for the low-lying odd-parity states  $6s6p^{1,3}P_J$  and compared them with the experimental results.

The calculation was carried out for  $^{201}\text{Hg}$  ( $I = 3/2$  and  $\mu_I/\mu_N = -0.560225$  [10]) in the CI+all-order approximation, including the Breit interaction. We also calculated the random-phase approximation (RPA) and other, generally smaller, core-Brueckner ( $\sigma$ ), structural-radiation (SR), two particle (2P), and normalization (Norm)) corrections. These corrections are described in detail in Refs. [11, 12].

The results are presented in Table I. We find significant cancellations between the RPA and sum of the other corrections ( $\sigma$ +SR+2P+Norm) for the HFS constants. While the calculations of the wave functions and the RPA corrections are carried out to all orders in our present method, the smaller core-Brueckner, two-particle, structural-radiation, and normalization corrections are treated in the second-order of the many-body perturbation theory (MBPT). This difference in their treatment results in an additional uncertainty due to a cancellation of these effects. The  $A(^3P_1)$  and  $A(^3P_2)$  HFS constants obtained at the CI+all-order stage of the calculation are very close to the experimental values and we expect that the CI+all-order approximation will produce the most reliable results for the nondiagonal matrix elements of the  $T^{(1)}$  operator needed for the calculation of the  $^3P_0$   $g$ -factor.

A larger difference with the experiment for the  $^1P_1$  HFS constant, 7.5%, is likely caused by the presence of the core-excited  $5d^96s^26p$   $J = 1$  states in the Hg spectrum which mix with the  $5d^{10}6s6p$   $^1P_1$  state. A similar problem is well known in Yb, where the  $4f^{14}6s6p$   $^1P_1$  state is separated from the core excited  $4f^{13}5d6s^2$   $J = 1$  state by only  $3789\text{ cm}^{-1}$ , leading to a severe, by a factor of 3.8, discrepancy of the theoretical hyperfine constant value [16] with the experiment. In Hg, the energy separation of the  $5d^{10}6s6p$   $^1P_1$  and the nearest  $5d^96s^26p$   $J = 1$  state is much larger,  $24744\text{ cm}^{-1}$ . While our agreement with experimental hyperfine constant is worse for the  $^1P_1$  state than for the  $^3P_{1,2}$  states, it is by far better than a similar calculation gives in Yb, clearly demonstrating that the problem of admixture of the core-excited states, that is a reason for the Yb discrepancy, is less pronounced for Hg.

#### D. The $^3P_0$ $g$ -factor

From Eq. (4), the  $g$ -factor of the  $^3P_0$  state can be expressed as

$$\begin{aligned} g(^3P_0) &\approx \frac{\langle ^3P_0, IM | H | ^3P_0, IM \rangle}{\mu_0 MB} \\ &+ 2 \sum_n \frac{\langle ^3P_0, IM | H | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | H_{\text{hfs}} | ^3P_0, IM \rangle}{\mu_0 MB (E_{^3P_0} - E_n)} \\ &\equiv \delta g_I + \delta g_{\text{hfs}}. \end{aligned} \quad (7)$$

The first term can be approximated by [17]:

$$\delta g_I \approx -\frac{m}{m_p} \frac{\mu_I}{I \mu_N}, \quad (8)$$

where  $m$  and  $m_p$  are the electron and proton masses, respectively. For 201 isotope we find  $\delta g_I \approx 0.203 \times 10^{-3}$  in a good agreement with an accurate value  $\delta g_I = 0.200183(4) \times 10^{-3}$  obtained in [4].

The second term is simplified using the Wigner-Eckart theorem:

$$\delta g_{\text{hfs}} = \frac{2}{3} \frac{\mu_I}{I \mu_N} \sum_n \frac{\langle ^3P_0 || \mu_e || \gamma_n J_n \rangle \langle \gamma_n J_n || T^{(1)} || ^3P_0 \rangle}{\mu_0 (E_n - E_{^3P_0})}. \quad (9)$$

If we keep only one term ( $6s6p^3P_1$ ) in the summation over  $|\gamma_n J_n\rangle$  and take into account that  $\langle ^3P_0 || \mu_e || ^3P_1 \rangle = \sqrt{2}\mu_0$  in the  $LS$ -coupling approximation, we arrive at the formula for  $\delta g_{\text{hfs}}$  given in Ref. [17].

We calculate the non-diagonal reduced matrix elements of the  $\mathbf{T}^{(1)}$  operator using the same method as for the HFS constants and take the CI+all-order values as final.

The sum in Eq. (9) is strongly dominated by the first,  $6s6p^3P_1$  intermediate state, which has the smallest energy separation with the  $^3P_0$  state. The next contribution, from the  $6s6p^1P_1$  state, is less than 1%. The contribution of the subsequent intermediate state,  $6s7p^3P_1$ , is  $\sim 10^{-8}$ , which is negligible at the present level of accuracy.

We calculate the  $^{201}\text{Hg}$  matrix elements needed for the evaluation of  $\delta g_{\text{hfs}}$  to be

$$\begin{aligned} \langle ^3P_0 || \mu_e || ^3P_1 \rangle &= 1.390 \mu_0, \\ \langle ^3P_1 || T^{(1)} || ^3P_0 \rangle &= -23206 \text{ MHz} \approx -0.7741 \text{ cm}^{-1}, \\ \langle ^3P_0 || \mu_e || ^1P_1 \rangle &= -0.224 \mu_0 \\ \langle ^1P_1 || T^{(1)} || ^3P_0 \rangle &= -12035 \text{ MHz} \approx -0.4014 \text{ cm}^{-1} \end{aligned} \quad (10)$$

Combining these matrix elements with the experimental energy differences from the NIST database [18] we obtain

$$\begin{aligned} \delta g_{\text{hfs}}(^3P_0) &\approx \delta g_{\text{hfs}}(^3P_1) + \delta g_{\text{hfs}}(^1P_1) \\ &\approx (0.1516 - 0.0014) \times 10^{-3} = 0.1502 \times 10^{-3}. \end{aligned}$$

Because the contribution of the  $^3P_1$  state dominates, the uncertainty in our calculation of  $\delta g_{\text{hfs}}(^3P_0)$  is determined by the uncertainty in the value of *nondiagonal* matrix element  $\langle ^3P_1 || T^{(1)} || ^3P_0 \rangle$ . The magnetic-dipole HFS constants of the  $^3P_1$  and  $^3P_2$  states are smaller than the experimental values by 0.8% and 1.2%, respectively (see last column of Table I). Based on this comparison, and taking into account that  $A(^3P_J) \sim \langle ^3P_J || T^{(1)} || ^3P_J \rangle$ , we assume that the uncertainty in the diagonal matrix elements of the  $\mathbf{T}^{(1)}$  operator does not exceed 1.2%.

Our analysis shows that the  $6s6p_{1/2}$  configuration contributes to the  $^3P_0$  and  $^3P_1$  terms at the level of 99% and 81%, respectively. Therefore, we expect that the behavior of the wave functions of these two states near

TABLE I: Magnetic dipole HFS constants  $A$  (in MHz) for  $^{201}\text{Hg}$  are presented. In the 2nd column, labeled as “CI+All”, the results obtained in the CI+all-order approximation are listed. In the 3rd to 7th columns, we present different corrections to the “CI+All” values. The values in column labeled “Total” are obtained as (CI+All)+RPA+ $\sigma$ +SR+2P+Norm. Last column gives the differences (in %) between the CI+All and experimental results.

	CI+All	RPA	$\sigma$	SR	2P	Norm.	Total	Experiment	Diff.(%)
$A(6s6p\ ^3P_1)$	-5499	-560	283	-45	-82	252	-5651	-5454.569(3) [13]	0.8
$A(6s6p\ ^3P_2)$	-3391	-393	168	-18	-14	147	-3501	-3352.0292(8) [14]	1.15
$A(6s6p\ ^1P_1)$	1422	153	-69	30	-0.1	-74	1462	1316 [15]	7.45

the nucleus should be similar. As a result, we estimate the uncertainty of the *nondiagonal* matrix element  $\langle ^3P_1 || T^{(1)} || ^3P_0 \rangle$  to be also at the level of 1.2%.

The hyperfine structure anomaly, which results from the variation of the magnetic dipole density distribution over the nuclear volume from nucleus to nucleus [19] is already accounted for in our estimate since any uncertainties due to this effect are already included in the difference of our values for the hyperfine constants with the experiment.

We estimated the contribution of the second-order (in  $H_{\text{hfs}}$ ) corrections to the  $g(6s6p\ ^3P_0)$  to be negligible at the present level of accuracy, in agreement with [4]. Therefore, our uncertainty in the value of  $\delta g_{\text{hfs}}(^3P_0)$  is  $\sim 1.2\%$ .

Combining our result with  $\delta g_I = 0.200183(4) \times 10^{-3}$  from [4], we obtain for  $^{201}\text{Hg}$ :

$$g(6s6p\ ^3P_0) = 0.3504(18) \times 10^{-3}. \quad (11)$$

An accurate analysis of Lahaye and Margerie [4] gives the ratio of the  $g$ -factors for 201 and 199 isotopes of Hg to be

$$\frac{{}^{201}g(6s6p\ ^3P_0)}{{}^{199}g(6s6p\ ^3P_0)} = -0.369\,414(16). \quad (12)$$

Using Eqs. (11) and (12) we determine the  $g$ -factor of  $^{199}\text{Hg}$  ( $I = 1/2$  and  $\mu_I/\mu_N = 0.5058852$ ):

$$g(6s6p\ ^3P_0) = -0.9485(49) \times 10^{-3}. \quad (13)$$

A comparison of our results with most accurate experimental data and theoretical values obtained in Ref. [4] is given in Table II. Lahaye and Margerie [4] used a semi-empirical calculation method, following an approach of Lurio *et al.* [15, 20]. They expressed  $g(6s6p\ ^3P_0)$  through  $g(6s6p\ ^1S_0)$  and a combination of hyperfine parameters defined in [15]. Certain parameters were found from the experimental data on the  $A(^3P_{1,2})$  and  $A(^1P_1)$  HFS constants. Other parameters were assumed to be connected to each other by definite ratios. Lahaye and Margerie carried out two calculations. In the second calculation one of ratios between hyperfine parameters was slightly modified (see [4] for more details) what resulted in slightly different values of the  $g$ -factors. The theoretical values obtained in Ref. [4] in two these calculations are presented in the table. The difference between them was treated by the authors as an uncertainty of the result.

TABLE II: The theoretical and experimental values of  $g(6s6p\ ^3P_0) \times 10^3$  for  $^{201}\text{Hg}$  and  $^{199}\text{Hg}$ . The uncertainties are given in parentheses. Two theoretical results were obtained in Ref. [4] (see the text for details).

	Theory	Experiment
$^{201}\text{Hg}$	0.3504(18)(this work)	0.351058(16) [21]
	0.3524 [4]	0.35108(7) [4]
	0.3486 [4]	0.3509(4) [22]
$^{199}\text{Hg}$	-0.9485(49)(this work)	-0.950319(26) [21]
	-0.9541 [4]	-0.9504(4) [4]
	-0.9435 [4]	-0.9502(10) [22]

In the framework of the pure *ab initio* method, described above, we obtained the values of the  $g$ -factors with the 0.5% relative uncertainty, which is two times smaller than that in Ref. [4]. Within the theoretical uncertainty our results are in excellent agreement with all available experimental values.

### III. CALCULATION OF THE LIFETIME OF THE $6s6p\ ^3P_0$ STATE OF $^{199}\text{Hg}$ AND $^{201}\text{Hg}$

The hyperfine quenching rate of the  $^3P_0$  state can be represented (in a.u.) by [23]:

$$A_{\text{HFS}}(^3P_0 \rightarrow ^1S_0) = \frac{4\alpha^3\omega_0^3}{27} \left( \frac{\mu_I}{\mu_N} \right)^2 \frac{I+1}{I} |X|^2, \quad (14)$$

where  $\alpha \approx 1/137$  is the fine-structure constant,  $\omega_0 \equiv E(^3P_0) - E(^1S_0)$ , and

$$X \equiv \sum_n \frac{\langle ^1S_0 || D || \gamma_n J_n \rangle \langle \gamma_n J_n || T^{(1)} || ^3P_0 \rangle}{E(n) - E(^3P_0)} + \sum_m \frac{\langle ^1S_0 || T^{(1)} || \gamma_m J_m \rangle \langle \gamma_m J_m || D || ^3P_0 \rangle}{E(m) - E(^1S_0)}, \quad (15)$$

where  $\mathbf{D}$  is the electric dipole moment operator.

Restricting the sum over  $|\gamma_n J_n\rangle$  to the first two terms,  $6s6p\ ^3P_1$  and  $6s6p\ ^1P_1$ , and the sum over  $|\gamma_m J_m\rangle$  to one term,  $6s7s\ ^3S_1$ , we obtain

$$A_{\text{HFS}}(^3P_0 \rightarrow ^1S_0) \approx \frac{4\alpha^3\omega_0^3}{27} \left(\frac{\mu_I}{\mu_N}\right)^2 \frac{I+1}{I} \times \left| \frac{\langle ^1S_0 || D || ^3P_1 \rangle \langle ^3P_1 || T^{(1)} || ^3P_0 \rangle}{E(^3P_1) - E(^3P_0)} + \frac{\langle ^1S_0 || D || ^1P_1 \rangle \langle ^1P_1 || T^{(1)} || ^3P_0 \rangle}{E(^1P_1) - E(^3P_0)} + \frac{\langle ^1S_0 || T^{(1)} || ^3S_1 \rangle \langle ^3S_1 || D || ^3P_0 \rangle}{E(^3S_1) - E(^1S_0)} \right|^2. \quad (16)$$

The matrix elements  $\langle ^1S_0 || D || ^3P_1 \rangle = 0.4831(8)$  a.u. and  $\langle ^1S_0 || D || ^1P_1 \rangle = 2.64(3)$  a.u., needed for the calculation, were obtained from the experimentally known weighted average lifetimes of the  $^3P_1$  and  $^1P_1$  states,  $\tau(^3P_1) = 118.9(4)$  ns and  $\tau(^1P_1) = 1.34(3)$  ns [24].

Taking into account the CI+all-order matrix elements given in (10) and using

$$\begin{aligned} \langle ^1S_0 || T^{(1)} || ^3S_1 \rangle &= 14610 \text{ MHz} \approx 0.4873 \text{ cm}^{-1}, \\ \langle ^3S_1 || D || ^3P_0 \rangle &= -1.36 \text{ a.u.} \end{aligned}$$

and the energy differences from the energy level NIST database [18], we find

$$A_{\text{HFS}}(^3P_0 \rightarrow ^1S_0) \approx \frac{4\alpha^3\omega_0^3}{27} \left(\frac{\mu_I}{\mu_N}\right)^2 \frac{I+1}{I} \times |(-2.12 - 0.64 - 0.11) \cdot 10^{-4}|^2 \text{ a.u.},$$

where the three terms in  $|...|^2$  are the contributions from the  $^3P_1$ ,  $^1P_1$ , and  $^3S_1$  states, respectively. Taking into account that  $1 \text{ a.u.} \approx 2\pi \times 6.5797 \cdot 10^{15} \text{ s}^{-1}$ , we arrive at

$$A_{\text{HFS}}(^3P_0 \rightarrow ^1S_0) \approx \left(\frac{\mu_I}{\mu_N}\right)^2 \frac{I+1}{I} \times 0.99 \text{ s}^{-1}$$

and, finally,

$$A_{\text{HFS}}(^3P_0 \rightarrow ^1S_0) \approx \begin{cases} 0.52 \text{ s}^{-1}, & \text{for } ^{201}\text{Hg} \\ 0.76 \text{ s}^{-1}, & \text{for } ^{199}\text{Hg} \end{cases}.$$

We note that these hyperfine quenching rates are approximately 60 times greater than those published in Ref. [25],  $0.013 \text{ s}^{-1}$  for  $^{199}\text{Hg}$  and  $0.0088 \text{ s}^{-1}$  for  $^{201}\text{Hg}$ . Unfortunately, Ref. [25] does not contain any details on how these values were obtained or any intermediate results. We assume that a reason of this disagreement might be a calculation error made in [25]. Our present  $^{199}\text{Hg}$  quenching rate,  $0.76 \text{ s}^{-1}$ , is in a good agreement with the experimental value  $0.692(14) \text{ s}^{-1}$  [26]. The corresponding lifetimes of the  $^3P_0$  state in  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$  are 1.3 and 1.9 s, respectively.

#### IV. DISCUSSION AND SUMMARY

Our theoretical results agree with all the experimental values within the uncertainty of the calculations, providing excellent benchmarks of theoretical accuracy in Hg.

We identified several directions towards further improvement of Hg theory accuracy discussed below.

We find that an accurate calculation of the HFS constants requires accurate treatment of the corrections to the matrix elements of the HFS operator beyond the random-phase approximation, such as smaller core-Brueckner, structural-radiation, and normalization corrections. We treat these corrections in the second-order of MBPT, while the calculations of the wave functions and RPA corrections are done to all orders of MBPT. Since we find significant cancellations between the RPA and sum of the other corrections for the HFS constants, the difference in their treatment results in an additional uncertainty. Based on a comparison of the theoretical and experimental values of the HFS constants, we assume that if the corrections beyond RPA are included in all orders of the perturbation theory, the cancellation between different corrections will be even more pronounced.

Another improvement may stem from an inclusion of triple excitations into construction of the effective all-order Hamiltonian. The effect of the triple excitations is known to be significant for calculating HFS constants of alkali-metal atoms. All of these corrections are much smaller for the electric-dipole matrix elements and the HFS constants present excellent opportunity for benchmark testing. Both of the above method developments may be carried out by incorporating corresponding modified linearized coupled-cluster all-order codes into the CI+all-order approach.

Another effect that may affect the calculation accuracy of the Hg properties is the presence of the core-excited  $5d^9 6s^2 6p$  states in the Hg spectrum. Our CI+all-order value of  $^1P_1$  HFS constant differs by 7.5% from the experiment, i.e., the agreement with experiment is worse than for the  $^3P_{1,2}$  states. Future improvement of the  $^1P_1$  properties could require a consideration of the core-excited states on the same footing as the  $5d^{10} nln'l'$  states.

To summarize:

(i) Our calculation demonstrates theory ability to calculate such a complicated quantity as g-factor of the  $^3P_0$  state with a 0.5% accuracy from first principles rather than semi-empirical approaches.

(ii) It provides much needed benchmark test of theoretical accuracy in the first principles evaluation of Hg atomic properties, clearly demonstrating predictive capabilities of our method for the Hg clock development.

(iii) Previous calculations of the HFS constants for the multivalent atoms generally assumed cancellation of the various corrections to the HFS operator *beyond* RPA. Our

calculation clearly demonstrates that for Hg this is incorrect. In fact, we find that other corrections, such as the core Brueckner and structural radiation corrections, are large and nearly cancel the RPA corrections. This observation allowed us to calculate the values of the g-factors for 199 and 201 isotopes with a high accuracy. This also demonstrates a clear need for developing approaches to treat the corrections to all orders of the perturbation theory. Theoretical calculations of HFS constants are used to infer nuclear magnetic moment in systems where other methods are not available.

(iv) We have calculated the hyperfine quenching rate of the  $6s6p\ ^3P_0$  state resolving the discrepancy between the experiment and theoretical result obtained previously. An accurate knowledge of this quantity is very important for the experimentalists working with the Hg atomic

clock in the  $^1S_0 - ^3P_0$  transition. The lifetime of the excited clock state is a crucial factor in ultimate Hg clock uncertainty.

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