Ab initio calculations of external-field shifts of the 661-nm quadrupolar clock transition in neutral Ag atoms

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Abstract
Frequency shifts of the Ag I 4d10s 2S1/2(F=0,MF=0) to 4d9s2 2D5/2(F[prime]=2, MF[prime]=0) electric-quadrupole transition at 330.6 nm due to external fields are calculated using multiconfigurational self-consistent field methods. As this forbidden transition is free from first order Doppler and Zeeman effects, it is under investigation for the realization of an atomic optical clock. The calculated perturbations are the light shift, the blackbody frequency shift, and the quadratic Zeeman shift. Results show that a total uncertainty of 10^{-18} could be reached without confining the atoms in a Lamb-Dicke regime in an optical lattice.

Reference


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I. INTRODUCTION

An accurate measurement of time and frequency is a prerequisite not only for fundamental science, concerning for instance the changes in fundamental constants over time, measuring gravitational redshifts, and timing pulsars, but also for technologies that support broadband communication networks and navigation with global positioning systems (GPS or GALILEO). The stability and accuracy of an atomic clock is related to the quality factor $Q$ of the reference transition on which it is based. The quest for atomic clocks with higher levels of stability and reproducibility is therefore prompting a move from the microwave to the optical region of the spectrum. In practice, forbidden optical transitions with natural linewidths around 1 Hz or less, offer potential for the accurate calculation of external-field shifts of the 661-nm quadrupolar clock transition of the present caesium microwave standard as applied for the definition of the Systeme International (SI) second, such improvement could lead to a redefinition of the second in the future.

A number of different atoms are currently being investigated in various laboratories, based on forbidden transitions in cold trapped ions or neutral atoms, and over recent years there has been significant progress in both areas [1]. For the “ion” approach [2,3], for example, its a commonly shared opinion that it may lead to a better ultimate frequency accuracy while its stability will likely remain limited by the quantum projection noise. In contrast, the “atomic” approach [4] should lead to a better frequency stability thanks to the numerous quantum absorbers contributing to the signal but with an accuracy which will be limited by the Doppler shift. Recently Katori [5] proposed and demonstrated a scheme that combines the advantages of both approaches. The idea is to trap Sr neutral atoms in the Lamb-Dicke regime in a three-dimensional (3D) optical lattice operating at a “magic” wavelength where the light shift of the clock transition vanishes. Thanks to this subwavelength confinement, the first-order Doppler shift as well as the photon recoil shift disappear. The Sr optical lattice clock demonstrated a linewidth two orders of magnitude narrower than that observed for neutral-atom optical clocks and a stability better than that of single-ion clocks [6].

Another strategy has been chosen by groups at Garching [7] and at CNAM in Paris [8] in closed collaboration with two of us, in that the quadrupolar transition $4\,^{10}\!S_{3/2} - 4\,^{10}\!P_{9/2} - 2\,^{10}\!D_{5/2}$ in neutral Ag atoms is applied. The use of neutral silver atoms as a candidates for a future optical clock has been first proposed by Bender and Hall in 1976 [9]. This transition presents numerous advantages. Although accurate calculation has never been published, the $5\,^{2}\!D_{5/2}$ metastable level has an estimated natural linewidth of about 1 Hz. This long-lived state is accessible from the ground state $5\,^{3}\!S_{1/2}$ with a two-photon transition at 661.2 nm, providing a first-order Doppler-free interaction with atoms of all velocities [9,10]. Furthermore, the nuclear spin $I = 1/2$ of the two stable isotopes $^{107,109}\!\text{Ag}$ induces a hyperfine structure which allows transitions between levels with $M_F = 0$ and thus are insensitive to the first order Zeeman effect. This also permits a sub-Doppler cooling mechanism that may lead to low temperatures and narrow transverse velocity distributions. Finally, as an important technical aspect, the frequencies needed to drive the clock transition and the cooling transition $(4\,^{10}\!S_{3/2} - 4\,^{10}\!P_{9/2} - 2\,^{10}\!D_{5/2}, \lambda = 328.126 \text{ nm})$ can be provided by solid state lasers based on a Nd:YLF crystal [11].

While the clock transition has no linear Zeeman shift, it does have a quadratic Zeeman shift and an ac Stark shift.
Since none of these shifts have been measured yet, it is useful to have calculated values. In this paper, we report accurate calculations of the systematic shifts of the clock transition due to external fields as well as good estimates of the lifetime of the \( 5^2D_{5/2} \) state. The oscillator strengths, transition-matrix elements, lifetimes, and polarizabilities for several low-lying levels have been calculated. It is pointed out that this approach would allow one to reach an equivalent level of total uncertainty as the scheme proposed by Katori. All the calculations were carried out using two multiconfiguration self-consistent field (MCSCF) methods based on the Hartree-Fock (HF) and Dirac-Fock (FD) equations combined with a configuration-interaction (CI) for taking into account the core-core and core-valence correlation effects. Unless specified otherwise, we use atomic units \((|e| = \hbar = m_e = 1)\) throughout the paper.

II. THEORY

A. Transition properties

Let \( \mathbf{D} \) be the dipole-moment operator for the interaction of the atomic electrons with the radiation field. Making use of the Wigner-Eckart theorem, the line strength of an electric dipole transition between a ground state \( |\gamma J\rangle \) and an excited state \( |\gamma' J'\rangle \) is linked to the reduced matrix element by

\[
S_{\gamma\gamma'} = |\langle \gamma' | \mathbf{D} | \gamma J \rangle|^2.
\]

Of special importance is the oscillator strength, the so-called \( f \) value, which is linked to the line strength by

\[
f(\gamma J, \gamma' J') = \frac{2}{3(2J+1)} \omega_{\gamma'\gamma} S_{\gamma\gamma'}
\]

where \( \omega_{\gamma'\gamma} = E_{\gamma' J'} - E_{\gamma J} \) is expressed in hartrees and \( S \) in atomic units of \( e^2 a_0^2 \).

The lifetime \( \tau_{\gamma' J'} \) of the level \( |\gamma' J'\rangle \) is

\[
\tau_{\gamma' J'} = \frac{1}{\sum_{\gamma' J'} A(\gamma' J', \gamma J)},
\]

where \( A \) is the transition rate for emission given by

\[
A(\gamma' J', \gamma J) = \frac{4}{3c^3} \omega_{\gamma'\gamma} S_{\gamma\gamma'}.
\]

B. Computational details

In the MCHF method [12], the wave function \( \Phi \) of an LS term labeled \( \gamma LS \), is expanded in terms of configuration state functions (CSFs) with the same LS term

\[
\Psi(\gamma LS) = \sum_n c_n(\gamma) \Phi(\gamma'\gamma LS),
\]

where \( \gamma \) represents all further quantum numbers necessary for the unique specification of the quantum state. The CSFs are antisymmetrized products of spinorbitals

\[
\phi_{nlm_p}(\mathbf{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi) \xi_m(\sigma).
\]

In the multiconfigurational self-consistent field (MCSF) calculations, the radial functions \( P_{nl}(r) \) and the expansion coefficients \( c_n(\gamma) \) are simultaneously optimized to self-consistency. Once the spinorbitals are known, relativistic effects can be taken into account by performing CI calculations within the Breit-Pauli (BP) approximation. In this framework, the atomic state functions (ASFs) are expanded over CSFs which are now eigenfunctions of the total angular momentum \( \mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2 \),

\[
\Psi(\gamma LSJM) = \sum_n c_n(\gamma) \Phi(\gamma'\gamma LSJM).
\]

The combination of the MCDF and relativistic CI methods allows a more accurate treatment of the relativistic many body problem. In this context, the function of an atomic state of parity \( P \) labeled \( \gamma PJM \) is expanded in terms of \( jj \)-coupled CSFs of the same parity and of same \( J \) and \( M \) quantum numbers according to

\[
\Psi(\gamma PJM) = \sum_n c_n(\gamma) \Phi(\gamma'\gamma PJM).
\]

The CSFs are built from antisymmetrized product of relativistics spinorbitals

\[
\phi_{nlm_p}(\mathbf{r}) = \frac{1}{r} \left( P_{nl}(r) X_{\kappa m}(\hat{\mathbf{r}}) \right).
\]

The quantity \( \kappa \) is the relativistic angular momentum quantum number:

\[
\kappa = \pm (j + 1/2) \quad \text{for} \quad l = j \pm 1/2.
\]

\( P_{nl}(r) \) and \( X_{\kappa m}(\hat{\mathbf{r}}) \) are called the small and large component of the radial wave functions with \( X_{\kappa m}(\hat{\mathbf{r}}) \) being a spinor spherical harmonic in the \( lsj \) coupling scheme

\[
X_{\kappa m}(\hat{\mathbf{r}}) = \sum_{m_l m_s} \left( \frac{l^2 - m_l^2}{2} \right)^{1/2} Y_{lm}(\theta, \phi) \xi_m(\sigma).
\]

In the MCDF approach, the Dirac-Coulomb Hamiltonian

\[
H_{\text{DC}} = \sum_i \left[ c \alpha_i \cdot \mathbf{p}_i + (\beta_i - 1) c^2 \frac{Z}{r_i} \right] + \sum_{i < j} \frac{1}{r_{ij}}
\]

is used to perform the MCSCF calculations. The optimized spinorbitals can be used then to carry out relativistic CI calculations using a Hamiltonian that can include other interaction operators which have been omitted in Eq. (10). The most important is the transverse photon interaction operator

\[
H_{\text{trans}} = - \sum_{i < j} \left[ \frac{\alpha_i \cdot \alpha_j \cos(\alpha_i \cdot \alpha_j r_{ij})}{r_{ij}} + (\alpha_i \cdot \mathbf{v}_j) \times (\alpha_j \cdot \mathbf{v}_i) \cos(\alpha_i \cdot \alpha_j r_{ij}) - 1 \right] \frac{1}{\alpha_i^2 r_{ij}}
\]

which, in the low-frequency limit \( \omega_{ij} \to 0 \), is referred to as the Breit operator. The lowest-order nuclear motional corrections, the dominant quantum-electrodynamical corrections, that is, the self-energy and the vacuum polarization, may be included as well.
Below, we used the ATSP program [13] for the MCHF and the BP+CI calculations, while the GRASP92 program [14] was applied for the MCDF computations. The subsequent CI calculations were performed by means of the RELCI component of the RATIIP package [15]. In these computations, the Breit interaction along with the vacuum polarization were included in the CI calculations. We also used a semiempirical relativistic Hartree-Fock (RHF) approach described by Cowan [16]. Although, this method suffers from the drawback that the core-core and core-valence correlations are not taken into account, it has the great advantage of being simple to use and that it does not require high-performance computers.

It is difficult to say which method has the best accuracy without having reliable experimental data available. However, it is commonly shared that the MCSCF methods give better results than the RHF one. Furthermore, in this paper, very large scale multiconfigurational calculations have been performed only with the MCDF+CI. Hence, we expect that the values obtained by this method are the most reliable ones. The results of the two other methods are reported only for purpose of comparison.

III. ENERGIES, LIFETIMES, AND SPECTROSCOPIC PROPERTIES OF THE LOW-LYING LEVELS

For the RHF approach, the configuration interaction integrals for all electron configurations were fixed at 0.08 of their HF values. The exchange integrals, spin-orbit integrals as well as the averaged energy of the relevant configurations were let to vary in the process of fitting the state energies. For energy fitting, we use experimental values of the excited state energies from Ref. [17]. The MCHF calculations were carried out for the ground $4d^{10}5s^2$ LS term and for the excited terms $4d^{10}5p^2P$ and $4d^{10}5s2D$. They led to the orbital set consisting of the $\{1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 5f, 5s, 5d\}$ orbitals which was then used to perform the BP+CI calculations for characterizing the $5S_{1/2}$ ground state and the four lowest-lying excited states $n=5^2P_{1/2}, 5^2P_{3/2}, 5^2D_{5/2}$, and $5^2D_{3/2}$. For both the MCHF and the BP+CI calculations, tens of CSFs were appropriately generated by single (S) and double (D) excitations from the reference configuration $4d^{10}5s^25p^6$, $4d^{10}5p^6$, and $4d^{10}5s^25p^6$. The MCDF calculations allowed to obtain a final orbital set which consists of the orbitals $\{1s_{1/2}, 2s_{1/2}, 2p_{1/2}, 2p_{3/2}, 3s_{1/2}, 3p_{1/2}, 3p_{3/2}, 3d_{5/2}, 3d_{3/2}, 4s_{1/2}, 4p_{1/2}, 4p_{3/2}, 4d_{5/2}, 4f_{7/2}, 5s_{1/2}, 5p_{1/2}, 5p_{3/2}, 5d_{5/2}, 5d_{3/2}, 6s_{1/2}, 6p_{1/2}, 6p_{3/2}, 6d_{5/2}, 6d_{3/2}, 7s_{1/2}, 7p_{1/2}, \text{ and } 7p_{3/2}\}$ orbitals. Using the extended optimal level EOL option of the GRASP92 code, these orbitals were optimized by minimizing the energy functional given by the average of the energies of the $5S_{1/2}$ ground state and the four lowest-lying excited states $2p_{1/2}^2, 2p_{3/2}^2, 2D_{5/2}^2, \text{ and } 2D_{3/2}^2$. The calculations were performed in several steps wherein the CSFs were generated by SD excitations from the relativistic reference configurations $4d^4A_d4d^55s_{1/2}, 4d^4A_d4d^55p_{1/2}, 4d^4A_d4d^55s^2$, and $4d^4A_d4d^55s^2\cdot J=1/2, 3/2, 5/2$. We considered first all orbitals up to the $n=4$ shell excepted the $4f_{5/2}$ and $4f_{7/2}$ ones. Thereafter, we systematically increased the size of the orbital set while keeping the $n=1–3$ and $4s_{1/2}, 4p_{1/2}, \text{ and } 4p_{3/2}$ orbitals fixed.

For most of the CI calculations following the MCDF ones, the CSFs were generated from the same reference configurations as for the MCDF calculations, by allowing SD and also triple ($T$) excitations of the valence electrons into the $n=5, n=6$, and $n=7$ shells. These excitation schemes will be referred to by the $nSD$ and $nSDT$ notations, and the sets of CSFs which they lead to by $\{nSD\}$ and $\{nSDT\}$. In these calculations, the core is defined by the filled $n\leq\{1–3\} \text{ and } 4s_{1/2}, 4p_{1/2}, \text{ and } 4p_{3/2} \text{ subshells.}$ In the other CI calculations that have been carried out, the core was defined by the filled $n=\{1–3\}$ shells in order to allow the polarization of the $4s_{1/2}, 4p_{1/2}, \text{ and } 4p_{3/2} \text{ "semicore" electrons by the valence electrons.}$ In this case, the CSFs were obtained from the same reference configurations by considering only SD excitations into the $n=7$ shell; this excitation scheme will be referred to as $7SD$. We estimated an accuracy of few percent for the electric dipole matrix elements. The difference in the calculated properties due to the mass shift between the two isotopes $^{107}Ag \text{ and } ^{109}Ag$ are less than the uncertainties. The data used for the numerical evaluations are from the $^{109}Ag$ isotope.

Table I gives the energies of the ground state $2S_{1/2}^0$ and the calculated values of the energy $\Delta E$ of the lowest-lying excited states $n=5^2P_{1/2}, 5^2P_{3/2}, 5^2D_{5/2}^1, \text{ and } 5^2D_{3/2}^1$ with regard to the energy of the ground state and as functions of the number $n_e$ of CSFs involved in the MCDF+CI calculations. When only valence correlations were considered, convergence of the energy of the five states is achieved by combining the $\{6SDT\}$ and $\{7SD\}$ CSF sets. No further improvement is achieved if triple excitations into the $n=7$ shell are included as seen from the results obtained for the $\{7SDT\}$ set. In fact, the incorporation of triple excitations by passing from the $\{5SD\}$ to the $\{6SD\}$ set or from a $\{nSD\} \cup \{(n+1)SD\}$ to a $\{nSD\} \cup \{(n+1)SD\}$ set. From the CI calculations performed with $\{7SD\}$ set, we found a quite large decrease of the energies of the states which shows that the polarization of the electrons from the $4s_{1/2}, 4p_{1/2}, \text{ and } 4p_{3/2} \text{ semicore subshells by the valence electrons must be taken into account. Further improvements are achieved when one adds to this set, triple excitations from the valence electrons into the } n=6 \text{ shell. Experimental results are also shown for purpose of comparison. One notes that the results obtained are in satisfactory agreement with experiment since the MCDH $\Delta E$ values differ from the experimental values by only } \pm 2379 \text{ cm}^{-1} (\sim 8.1 \%) \text{ and } \pm 2364 \text{ cm}^{-1} (7.8 \%), \text{ respectively, for the } ^2P_{1/2} \text{ and } ^2P_{3/2} \text{ levels, and by } \pm 2022 \text{ cm}^{-1} (6.7 \%) \text{ and } \pm 2133 \text{ cm}^{-1} (6.1 \%) \text{ for the } ^2D_{5/2} \text{ and } ^2D_{3/2} \text{ respectively. For the CI calculations that includes Breit interaction and vacuum polarization, the results tend to be worse than the MCDH ones if one only deals with valence correlation. The semicore-valence correlation (using the } \{6SD\} \cup \{7SD\} \text{ basis set} \text{ must be considered in order to obtain results which are in very good agreement with experiment. In this case, the calculated } \Delta E \text{ values differ from the experimental values by only } \pm 2030 \text{ cm}^{-1} (6.9 \%) \text{ and } \pm 2062 \text{ cm}^{-1} (6.8 \%) \text{ respectively for the } ^2P_{1/2} \text{ and } ^2P_{3/2} \text{ levels.}
TABLE I. Calculated values of the energy $E$ (Hartree) of the ground state and the lowest-lying excited states as functions of the number $n_e$ of CSFs involved in the CI calculations. Calculated values of the energy $\Delta E$ (cm$^{-1}$) of the states with respect to the energy of the ground state as functions of the number $n_e$ of CSFs involved in the MCDF and CI calculations. Experimental values from Ref. [17] are also reported.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>$n_e$</th>
<th>$E$</th>
<th>$n_e$</th>
<th>$\Delta E$</th>
<th>$n_e$</th>
<th>$\Delta E$</th>
<th>$n_e$</th>
<th>$\Delta E$</th>
<th>$n_e$</th>
<th>$\Delta E$</th>
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<tr>
<td>$^2S_{1/2}^o$</td>
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<td>0</td>
<td>2532</td>
<td>27173</td>
<td>4387</td>
<td>28109</td>
<td>4399</td>
<td>32265</td>
<td>3732</td>
<td>36847</td>
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<tr>
<td>$^2P_{3/2}^o$</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^2D_{5/2}^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$MCDF calculation

$^b$CI calculation, vaIence correlation

$^c$CI calculations, including vaIence and secIemov-valence correlation

$^d$Experiment

levels, and by only $-399$ cm$^{-1}$ ($-1.3\%$) and $-421$ cm$^{-1}$ ($-1.2\%$) for the $^2D_{5/2}^e$ and $^2D_{5/2}^o$, respectively.

Table II gives the calculated values of the reduced matrix elements between the ground state and the $4d^{10} \, np^2 \, F_{1/2,3/2}$ states and between the upper state and the $4d^{10} \, np^2 \, F_{1/2,3/2}$ states. Table III summarizes the values of the Einstein coefficient, lifetime, and width of the clock transition obtained by the different methods.

IV. LIGHT SHIFT, BLACKBODY RADIATION, AND OTHER SYSTEMATIC ERRORS AFFECTING THE CLOCK TRANSITION

A. Light shift of atomic hyperfine levels

Within a laser field $\vec{E}(\omega_L, \vec{e})$, the transition frequency between the states $|\gamma J F M_F \rangle$ and $|\gamma' J' F' M_{F'} \rangle$ is subjected to an ac Stark shift by

$$\omega_{\gamma 0} = \omega_0 - \Delta \alpha(\omega_L, \vec{e}) \vec{E}(\omega_L, \vec{e})^2/4\hbar + O(\vec{E}^2),$$

where $\omega_0$ the unperturbed atomic resonance frequency and $\Delta \alpha(\omega_L, \vec{e})$ denotes the differential ac dipole polarizability. In the case where the laser field is linearly polarized along the $z$ axis, the Stark Hamiltonian $H_{EE}$ is, in the second-order perturbation theory, given by [18,19]

$$H_{EE} = -\frac{1}{4} \alpha^{(0)}(\gamma J | \vec{E}^2 | \gamma J) - \frac{1}{4} \alpha^{(2)}(\gamma J$$

$$\times \sum_{F M_F F' M_{F'}} (F M_F)(F' M_{F'}) \times |\vec{E}|^2 \left[ \begin{array}{c} 1 \\ 2 \\ 1 \\ 0 \\ 0 \\ 0 \end{array} \right]$$

$$\times \left[ \frac{15(J+1)(2J+1)(2J+3)}{2J(2J-1)} \right]^{1/2}.$$
TABLE II. Reduced matrix elements between the low-lying states of neutral silver atoms (in a.u.).

<table>
<thead>
<tr>
<th>$n$</th>
<th>RHF</th>
<th>MCDF</th>
<th>MCHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4d$^{10}$5s$^2$S$^1/2$</td>
<td>2.71626</td>
<td>3.15676</td>
</tr>
<tr>
<td>6</td>
<td>4d$^{10}$np$^2$P$^3/2$</td>
<td>0.25713</td>
<td>0.28695</td>
</tr>
<tr>
<td>7</td>
<td>0.07804</td>
<td>0.46984</td>
<td>0.27075</td>
</tr>
<tr>
<td>8</td>
<td>0.02411</td>
<td>0.00753</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.00753</td>
<td>0.00753</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.00824</td>
<td>0.00824</td>
<td></td>
</tr>
</tbody>
</table>

ac polarizabilities of the $5^2S_{1/2}$ and $5^2D_{5/2}$ incorporate, respectively, the coupling with the states states $np^2P_{3/2,1/2}$ and $np^2P_{3/2}$. We perform a RHF calculation of the reduced matrix elements for the states $np^2P_{3/2,1/2}$ for $n=\{5–10\}$. Results show that the $\langle 5^2S_{1/2} || D || 5^2P_{3/2,1/2} \rangle$ contribute for 95% of the ground state polarizability and the $\langle 5^2D_{5/2} || D || 5^2P_{3/2} \rangle$ element contribute for 61% of the upper state polarizability. Figure 1 represents the scalar polarizabilities of both levels as functions of laser wavelength.

More accurate calculations have been performed for $n\leq 7$ using the MLTPOL program [20] with the wave functions issue from MCHF+BP+CI calculation and by means of RELCI program [21] with the wave functions issue from MCDF+CI calculation. Using the MCDF+CI value for $\lambda_L = 661.2$ nm, we obtain for the scalar polarizabilities $\alpha^{(0)}[5S_{1/2}]=42.47485 \times 10^{-4}$ (Hz m$^2$)/W, $\alpha^{(0)}[5D_{5/2}]=23.58621 \times 10^{-6}$ (Hz m$^2$)/W, and for the tensor polarizability $\alpha^{(2)}[5D_{5/2}]=-\alpha^{(0)}[5D_{5/2}]$. When compared to the $E1$ scalar polarizability $\alpha^{E1}$, the higher orders multipole corrections from the magnetic dipole $M1$ and the electric-dipole $E2$ were found negligible. Numerical estimates give $\alpha^{E2}=\alpha^{M1}=10^{-10}\alpha^{E1}$ for both levels. The resulting frequency shift is then given by

$$\delta\omega/2\pi \text{ (Hz)} = -1.421 \times 10^{-3} (P/S) \text{ (W/m}^2\text{)}.$$  

(16)

The values obtained by the MCHF+BP+CI and RHF method are, respectively, $-1.416 \times 10^{-3}$ (Hz m$^2$)/W and $-1.063 \times 10^{-3}$ (Hz m$^2$)/W. One can notice a good agreement between the value obtained by the MCDF and MCHF methods. The value obtained by the RHF method is lower but still in good agreement with the other results. This could easily be explained if we take into account that the core-core and core-valence effects are not considered in this method. This frequency shift can be reduced below to $10^{-18}$ in relative value if the laser intensity fluctuations are below to 1 W/cm$^2$. Figure 2 gives the light shift of the transition from the $5^2S_{1/2}(F=0,M=0)$ sublevel to the $5^2D_{5/2}(F'=2,M_{F'}=0)$ sublevel as a function of the laser field intensity. The value of the wavelength of the laser field is chosen to be $\lambda = 661.2$ nm.
B. Blackbody radiation

The interaction between atoms and the electric fields of blackbody radiation (BBR) both induces transitions and produces nonresonant Stark and Zeeman shifts of the atomic transitions [22]. The nonresonant ac Stark shift $\Delta W^{(j)}$ of the energy of state $|\gamma J\rangle$ induced by the level $|\gamma J\rangle$ is given by [23]

$$\Delta W^{(j)}|\gamma J\rangle = -\frac{1}{\hbar} \sum_{\gamma'} S_{\gamma\gamma'} \int_0^{+\infty} \frac{\omega_{\gamma\gamma'}^2}{\omega_{\gamma\gamma'}^2 - \omega^2} \xi^2(\omega) d\omega,$$  

where $e$ is the electron charge and $\xi^2(\omega)$ is the quadratic electric field strength of BBR. At room temperature ($T=300$ K), BBR has its peak spectral density around a frequency $\omega_{\text{max}}/2\pi=17$ THz which is far below the minimum value of $\omega_{\gamma\gamma'}$ corresponding to the D1 and D2 transitions in silver. Hence, it is possible to omit the $\omega^2$ term in the denominator of Eq. (17) avoiding the singularity of the integrand [24]. It is assumed that the perturbing BBR is isotropic and unpolarized. Only the scalar polarizability contributes to the BBR shift. Furthermore, due to the very low intensity of the BBR field, the hyperpolarizability effect is negligible. The relation (17) becomes

$$\Delta W^{(j)}|\gamma J\rangle = -\frac{1}{\hbar} \sum_{\gamma'} S_{\gamma\gamma'} |\gamma J\rangle \langle \xi^2_{\text{BBR}}(t)|,$$  

where

$$a_{0}|\gamma J\rangle = \frac{2}{\hbar} \sum_{\gamma'} \frac{S_{\gamma\gamma'}}{\omega_{\gamma\gamma'}}$$  

is the dc Stark coefficient. The time averaged quadratic electric field strength is given by the Stephan-Boltzmann law.

C. Quadratic Zeeman shift

While the $(F=0,M_F=0)$ to $(F'=2,M_{F'}=0)$ hyperfine component has no linear Zeeman shift, it does have a quadratic Zeeman shift that must be accounted for. Let $H_S$ and $H_D$ be the effective Hamiltonian operators that operate within the subspaces of hyperfine sublevels associated with the levels $5^2S_{1/2}$ and $5^2D_{3/2}$, respectively.
where $A_S$ and $A_D$ are the dipole hyperfine constants and $\mu_B$ is the Bohr magneton. All of the parameters entering in $H_S$ and $H_D$ are known from experiments. The ground-state hyperfine constant $A_S$ and the excited-state hyperfine constant $A_D$ have been measured in Ref. [25,26] to be, respectively, 1976.93(4) and $-145.1584(5)$ MHz. For low magnetic fields ($B$ less than 1 mT), it is sufficient to calculate the energy levels to second order in $B$. To this order in $B$, the energies of the hyperfine-Zeeman sublevels for the states denoted $|gJF\rangle$ are

$$
\langle 5s\ 1/2\ 0 | H_S | 5s\ 1/2\ 0 \rangle = E_S - \frac{3hA_S}{4} - \frac{(g_J - g_I)^2\mu_B^2B^2}{4hA_S},
$$

$$
\langle 5s\ 5/2\ 2\ 0 | H_D | 5s\ 5/2\ 2\ 0 \rangle = E_D - \frac{7hA_D}{4} - \frac{(g_J - g_I)^2\mu_B^2B^2}{12hA_D},
$$

where $E_S$ and $E_D$ are the unperturbed energy levels of the corresponding states. We obtained $-993.32(2)$ Hz/G$^2$ for the ground state and 1621.02(1) Hz/G$^2$ for the upper state. This leads to a total shift of 627.70(2) Hz/G$^2$. To reach a relative accuracy of $10^{-18}$, one has to control the surrounding magnetic field within 1 mG which is currently the case in Cs atomic clocks.

V. SUMMARY AND CONCLUSION

We report ab initio calculations of the frequency shifts of the quadrupolar optical clocks transition in neutral silver atoms due to external fields. We found that the fractional frequency shift due to the laser field can be reduced to $10^{-18}$ if the laser intensity fluctuations are within 0.1 mW/cm$^2$. The BBR frequency shift is equal to $-160$ MHz at $T=293$ K. Fractional BBR shift can be reduced to $10^{-18}$ by controlling the fluctuations of the surrounding medium temperature to $\Delta T \lesssim 0.5$ K. The effect of the quadrupolar Zeeman shift can also be negligible ($\lesssim 10^{-18}$) if the magnetic field variations of the surrounding medium are within $\Delta B \lesssim 1$ mG. The lifetime of the upper metastable level has been evaluated to $\tau = 115$ ms. Hence, the neutral silver atom appears as a promising candidate for the next generation of atomic optical clocks. Recently, this transition has been observed for the first time by the group at CNAM using a thermal atomic beam [27].

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[19] The vector light shift vanishes if the laser beams are not circularly polarized. Using a polarizer with an extinction ratio of $10^{-5}$ could guarantee a residual vector light shift less than 1 mHz on the clock transition (see Ref. [5]).
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