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Calculation of a linear Stark effect on the 254-nm line of Hg

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An externally applied static electric field, by mixing opposite-parity states, can add electric-quadrupole and magnetic-dipole transition amplitudes to an allowed electric-dipole transition. The resulting interference among the amplitudes causes the absorption of resonance radiation to depend linearly on the static field and on the atomic polarization state. We present a calculation of this effect for the 254-nm line of Hg where the atomic polarization is specified by the ground-state nuclear spin, and the excited-state hyperfine structure is resolved. Possible experiments to measure this effect are pointed out.

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I. INTRODUCTION

It is well known that a type of Stark interference occurs when an $M1$ (magnetic-dipole) optical transition between levels of the same parity acquires an $E1$ (electric-dipole) component in the presence of a static electric field [1–4]. An analogous effect should occur when a static electric field induces $M1$ and $E2$ (electric-quadrupole) transitions in an allowed $E1$ transition [5]. This latter case has already been considered in detail for the Rb D lines in Ref. [5], where the vector structure of the interference effect is fully discussed, and it is shown that the fractional change in the absorptivity of the $J=\frac{1}{2}\rightarrow J=\frac{1}{2}$ allowed $E1$ transition is of the form

$$\frac{\delta\alpha}{\alpha}=(a_{E2}+a_{M1})(\hat{\epsilon}\cdot\mathbf{E}_S)(\hat{\mathbf{k}}\times\hat{\epsilon})\cdot\hat{\sigma}\ , \tag{1}$$

where a_{E2}, a_{M1} are of the order 2×10^{-8} (kV/cm)$^{-1}$ for Rb, $\hat{\epsilon}$ is the electric-field direction of the incident radiation, $\hat{\mathbf{k}}$ is the propagation direction of the incident radiation, $\mathbf{E}_S$ is the static electric field, and $\hat{\sigma}$ represents the atomic (electron-spin) polarization of the ground state.

We have now performed a similar calculation for the 254-nm absorption line of Hg, which is of interest because an interference term depending linearly on an applied electric field could be significant in the experimental search for a permanent electric dipole moment (PEDM) of the ^{199}Hg atom [6]. There are some important differences between Rb and Hg. For Rb, the ground-state polarization is specified by the electron-spin direction. For Hg, which has a $^1S_0$ ground-state electron configuration, the ground-state polarization is specified by the nuclear spin. The interference effect can then exist only if the excited-state hyperfine structure is resolved. Furthermore, the 254-nm line is an "intercombination line," requiring one to use intermediate coupling to describe the Hg wave functions. Finally, the Hg ground-state polarization (for nuclear spin $>\frac{1}{2}$) has a tensorial character which can lead to more complicated angular dependencies of the interference effect than are implied by Eq. (1).

We are specifically interested in the case of ^{199}Hg, which has nuclear spin $I=\frac{1}{2}$, and in the $F=\frac{1}{2}$ to $F=\frac{1}{2}$ transition, which is the optical transition used in the PEDM experiment mentioned above. The vector structure of this transition is the same as in Eq. (1) provided σ represents the ground-state nuclear spin rather than the electron spin. With minor modifications to the PEDM apparatus, an experimental measurement of this interference effect might be possible which would provide a calibration of the PEDM experiment as well as an interesting and useful test of atomic theory.

II. ELECTROMAGNETIC INTERACTION OPERATORS

We choose a simple geometry for the calculation which maximizes the effect in Eq. (1). The incident radiation propagates along $\hat{\mathbf{x}}$ with its electric-field vector along $\hat{\mathbf{y}}$:

$$\mathbf{E}(x,t)=E_0\cos(kx-\omega t)\hat{\mathbf{y}}\ . \tag{2}$$

The static electric field lies along $\hat{\mathbf{y}}$ also. We choose $\hat{\mathbf{z}}$ as the quantization axis (the radiation magnetic field lies along this axis).

The interaction of the radiation field with the atom is described by the following $E1$, $M1$, and $E2$ operators:

$$H_{E1}=e\mathbf{r}\cdot\mathbf{E}=eyE_0\cos\omega t\ , \tag{3}$$

$$H_{M1}=\frac{e}{2mc}(\mathbf{L}+2\mathbf{S})\cdot\mathbf{B}=\frac{e\hbar}{2mc}(L_z+2S_z)E_0\cos\omega t\ , \tag{4}$$

$$H_{E2}=\frac{e}{6}(3x_ix_j-\delta_{ij}r^2)\frac{\partial E_i}{\partial x_j}=\frac{e\omega}{2c}xyE_0\sin\omega t\ , \tag{5}$$

where the charge of the electron is $-e$, and the field and gradients are evaluated at the center of the atom ($x=0$). For the static field $\mathbf{E}_S$, the interaction is given by

$$H_S=e\mathbf{r}\cdot\mathbf{E}_S=eE_Sy\ . \tag{6}$$

The transition amplitude is determined by the matrix element connecting the initial (i) and final (f) states:

$$\langle\phi_f(t)|(H_{E1}+H_{E2}+H_{M1})|\phi_i(t)\rangle=(\mathcal{E}_1+\mathcal{M}_1+\mathcal{E}_2)e^{i\Delta\omega_{fi}t}\ , \tag{7}$$

where ϕ denotes the spin and space variables and includes the mixing due to H_S, and we have used the rotating-wave approximation $\Delta\omega_{fi} \ll \omega$, where

$$\Delta\omega_{fi}=\frac{W_f-W_i}{\hbar}-\omega ,$$

with $W_{f,i}$ the energies of the states ($W_f > W_i$). Denoting the (time-independent) atomic states in the absence of the external field by ϕ^0, we may write the following expressions for the multipole amplitudes in Eq. (7):

$$\mathcal{E}_1=\langle\phi_f^0|eE_0y|\phi_i^0\rangle , \tag{8}$$

$$\mathcal{M}_1=\frac{e^2E_SE_0\hbar}{4mc}\sum_n\left[\frac{\langle\phi_f^0|y|\phi_n^0\rangle\langle\phi_n^0|(L_z+2S_z)|\phi_i^0\rangle}{W_f-W_n}+\frac{\langle\phi_f^0|(L_z+2S_z)|\phi_n^0\rangle\langle\phi_n^0|y|\phi_i^0\rangle}{W_i-W_n}\right] , \tag{9}$$

$$\mathcal{E}_2=\frac{ie^2\omega E_SE_0}{4c}\sum_n\left[\frac{\langle\phi_f^0|y|\phi_n^0\rangle\langle\phi_n^0|xy|\phi_i^0\rangle}{W_f-W_n}-\frac{\langle\phi_f^0|xy|\phi_n^0\rangle\langle\phi_n^0|y|\phi_i^0\rangle}{W_i-W_n}\right] . \tag{10}$$

Note that $W^0=W$ to this order in E_S and E_0. In the bracketed expressions above, the first and second terms give the perturbations by the static field of the final and initial states, respectively.

It will be convenient later to introduce the irreducible multipole operator

$$T_q^{(k)}=\left[\frac{4\pi}{2k+1}\right]^{1/2}r^kY_{kq}(\theta,\phi) , \tag{11}$$

in terms of which the operators in Eqs. (8), (9), and (10) can be written

$$y=-i\frac{1}{\sqrt{2}}(T_1^1+T_{-1}^1) , \tag{12}$$

$$xy=-i(\tfrac{2}{3})^{1/2}(T_2^2-T_{-2}^2) . \tag{13}$$

It is straightforward to work out the interference effect. The transition probability is proportional to the square of the total amplitude in Eq. (7), which to first order in $\mathcal{M}_1$ and $\mathcal{E}_2$ can be written

$$P_{fi}\propto|\mathcal{E}_1+\mathcal{M}_1+\mathcal{E}_2|^2=|\mathcal{E}_1|^2+2\,\mathrm{Re}[(\mathcal{M}_1+\mathcal{E}_2)\mathcal{E}_1^*]+\cdots .$$

Thus, the fractional change in absorbtivity due to the presence of the (small) $\mathcal{M}_1$ and $\mathcal{E}_2$ amplitudes is

$$\frac{\delta\alpha}{\alpha}=\frac{2\,\mathrm{Re}[(\mathcal{M}_1+\mathcal{E}_2)\mathcal{E}_1^*]}{|\mathcal{E}_1|^2}=2\,\mathrm{Re}\left[\frac{\mathcal{M}_1+\mathcal{E}_2}{\mathcal{E}_1}\right] . \tag{14}$$

We will evaluate these amplitudes using a central-field model of the Hg atom.

III. Hg WAVE FUNCTIONS

The Hg 254-nm line connects the energy levels labeled $6\,^3P_1$ and $6\,^1S_0$. In the case of pure LS states, such a transition would be a highly forbidden intercombination electric-dipole line. However, for heavy atoms, LS coupling begins to fail and the angular-momentum states are no longer pure LS states. For the Hg excited state which is a $6s6p$ electron configuration, we have the following spectroscopic states with the experimentally observed energies

$$^3\bar{P}_2(5.43\ \mathrm{eV}) ,\ ^3\bar{P}_1(4.86\ \mathrm{eV}) ,$$
$$^1\bar{P}_1(6.67\ \mathrm{eV}) ,\ ^3\bar{P}_0(4.64\ \mathrm{eV}) .$$

The intermediate coupling states are of definite $J=L+S$; therefore, what we call $^1\bar{P}_1$ and $^3\bar{P}_1$ are really an admixture of the LS states. This admixture can be readily determined by diagonalizing the LS plus electrostatic matrix [7]:

$$\begin{array}{c|cccc|}
 & ^3P_2 & ^3P_1 & ^1P_1 & ^3P_0 \\
\hline
^3P_2 & \frac{1}{2}\zeta+F_0-G_1 & & & \\
^3P_1 & & -\frac{1}{2}\zeta+F_0-G_1 & \frac{\sqrt{2}}{2}\zeta & \\
^1P_1 & & \frac{\sqrt{2}}{2}\zeta & F_0+G_1 & \\
^3P_0 & & & & -\zeta+F_0-G_1
\end{array} ,$$

where ζ is the LS coupling strength and F_0, G_1 determine the electrostatic interaction. These constants can be determined from the observed energies (eigenvalues) for the four spectroscopic terms. It is evident that only the $^1P_1$ and $^3P_1$ states are mixed. After determining the various constants in the above matrix, the eigenvectors are readily determined. We find

$$^1\bar{P}_1=\alpha\,^1P_1-\beta\,^3P_1 , \tag{15}$$

$$^3\bar{P}_1=\alpha\,^3P_1+\beta\,^1P_1 , \tag{16}$$

where, as above, the bar indicates the spectroscopic LS states, $\alpha=0.98$, and $\beta=0.20$. As for the d states and those states with principal quantum number greater than

6, they are pure LS states to a very good approximation.

The radial wave functions were determined by use of a relativistic Hartree-Fock-Dirac (RHFD) numerical algorithm which uses the central-field approximation [8] or by numerical solution of the ordinary Schrödinger equation (SE) with a shielded Coulomb potential from the RHFD solution to the Hg^+ ion ground state. We are interested primarily in the $6s$, $6p$, and nd radial functions.

The RHFD wave functions for the $6p$ electron are different for the two j states, that is, for the $6p_{1/2}$ and $6p_{3/2}$ states. As expected, the large part of the RHFD $p_{3/2}$ and SE solutions are nearly equal. As a comparison, the expectation values of r^2 for the $6p_{1/2}$ state and for the $6p_{3/2}$ state are (in atomic units)

$$\langle 6p_{1/2}|r^2|6p_{1/2}\rangle = 29.41 \ ,$$

$$\langle 6p_{3/2}|r^2|6p_{3/2}\rangle = 35.99 \ .$$

Thus, to achieve the desired level of accuracy (about 30%), it will make little difference which radial wave functions we use. It should be noted that in general, the LS states of the sp configuration are linear combinations of the $p_{1/2}$ and $p_{3/2}$ states. It is straightforward to show through projection onto the various angular momentum states (see Table 1 [9] in Ref. [7]) that, for example,

$$^1P_1 \rightarrow \frac{\sqrt{2}}{\sqrt{3}}p_{3/2} - \frac{1}{\sqrt{3}}p_{1/2} \ .$$

The $6s$ wave function and eigenvalue from the RHFD algorithm are quite different from the SE solution; we therefore use the RHFD $6s$ state in our calculation. The eigenvalue for the $6p$ state differs by 30% between the two methods. In general, as the principal quantum number and angular momentum increase, the results of the two methods become similar. To achieve the required level of accuracy, for all radial functions other than the $6s$ and $6p$ states, we can use the L states of the ordinary Schrödinger equation.

The calculations are greatly facilitated by use of the Wigner-Eckart theorem [10]:

$$\langle n'L'M'|T_q^{(k)}|nLM\rangle = (-1)^{L+k+M'} \begin{pmatrix} L & k & L' \\ M & q & -M' \end{pmatrix} \times \langle n'L'\|T^k\|nL\rangle \ , \tag{17}$$

where the matrix is a 3-j symbol and $T_q^{(k)}$ is the multipole operator of Eq. (11). The reduced matrix element, in terms of the radial wave function, is [11]

$$\langle n'L'\|T^k\|nL\rangle = (-1)^{L-k}\sqrt{L+1}\sqrt{L'+1} \begin{pmatrix} L & k & L' \\ 0 & 0 & 0 \end{pmatrix} \times \int_0^\infty dr\, r^{k+2} R^*_{n'L'}(r) R_{nL}(r) \ , \tag{18}$$

where R is the radial part of the wave function. Later, the integral will be written as $\langle n'L'|r^k|nL\rangle$.

We are interested in matrix elements between states of $F = I + J$ when there is no coupling of the radiation field to the nuclear spin. In this case, the reduced matrix element is modified by dilution with the nuclear spin. For example [12],

$$\langle n'F'L'I\|T^k\|nFLI\rangle = (-1)^{I+k+F+L'}\sqrt{(2L'+1)(2L+1)} \times \begin{Bmatrix} L & F & I \\ F' & L' & k \end{Bmatrix} \langle n'L'\|T^k\|nL\rangle \ , \tag{19}$$

where the matrix is a 6-j symbol and it is understood that T^k operates only on the orbital angular momentum.

As an additional check, we can compare the radial matrix element and α and β as determined from the measured lifetimes of the $^3P_1$ (115 ns) and $^1P_1$ (1.31 ns) excited states with the results of our calculations. We find $|\alpha| = 0.18$ and $|\beta| = 0.98$ from the excited-state lifetimes, which compares well with the values determined by diagonalizing the LS plus electrostatic interaction matrix. The radial matrix elements for the electric dipole transition are

$$|\langle 6p|r|6s\rangle| = \begin{cases} 3.1 & \text{calculated} \\ 2.6 & \text{from lifetimes} \ , \end{cases}$$

which are also in reasonable agreement.

Finally, we note that while it is important to take into account the LS mixing in calculating transition amplitudes, the effect on energies is smaller and may be ignored for our accuracy. Hence we will assume that the energies of a spectroscopic P state and its corresponding pure LS state are the same.

IV. MAGNETIC-DIPOLE INTERFERENCE

The $M1$ amplitude is the easiest to calculate. The operators L_z and S_z cannot change the principal quantum number n, nor can they change L, S, M_L, M_S, or $M_F = m$, but they can change F. Equation (9) reduces to

$$\mathcal{M}_1 = \frac{e^2 E_S E_0 \hbar}{4mc} \sum_{F',m'} \langle 6\,^3\bar{P}_1 Fm|(L_z + 2S_z) \times \left[\frac{|6\,^3\bar{P}_1 F'm'\rangle\langle 6\,^3\bar{P}_1 F'm'|}{-W_{6\,^3P_1}} + \frac{|6\,^1\bar{P}_1 F'm'\rangle\langle 6\,^1\bar{P}_1 F'm'|}{-W_{6\,^1P_1}} \right] \times y|6\,^1S_0 I\mu\rangle \ , \tag{20}$$

where we reference the excited-state energies to the ground state and denote the angular momentum of the final state by F and m and of the initial state by the nuclear spin I and its projection μ.

Introducing the multipole operator from Eq. (12) and the LS states from Eqs. (15) and (16), we obtain

$$\mathcal{M}_1=-i\frac{e^2\hbar E_S E_0}{4\sqrt{2}mc}\sum_{F',m'}\Bigg[\left[\frac{\alpha^2\beta}{-W_{6\,^1P_1}}+\frac{\beta^3}{-W_{6\,^3P_1}}\right]\langle 6\,^1P_1Fm|L_z|6\,^1P_1F'm'\rangle$$

$$+\left[\frac{\alpha^2\beta}{-W_{6\,^3P_1}}-\frac{\alpha^2\beta}{-W_{6\,^1P_1}}\right]\langle 6\,^3P_1Fm|(L_z+2S_z)|6\,^3P_1F'm'\rangle\Bigg]$$

$$\times\langle 6\,^1P_1F'm'|(T^1_1+T^1_{-1})|6\,^1S_0I\mu\rangle\ . \tag{21}$$

For the singlet state, $L_z=J_z$, while for the triplet state, $L_z=\frac{3}{2}J_z$. The matrix elements for J_z can be readily determined:

$$\langle Fm|J_z|F'm'\rangle=\delta_{mm'}(2F+1)^{1/2}(2F'+1)^{1/2}\sum_{m_i,m_J}m_J\begin{bmatrix}I & 1 & F\\ m_i & m_J & -m\end{bmatrix}\begin{bmatrix}I & 1 & F'\\ m_i & m_J & -m'\end{bmatrix}\ .$$

Using Eq. (19), we find

$$\mathcal{M}_1^{m\mu}=-i\frac{e^2\hbar E_S E_0}{4\sqrt{2}mc}\left[\frac{\alpha^2\beta}{2W_{6\,^1P_1}}-\frac{3\alpha^2\beta+2\beta^3}{2W_{6\,^3P_1}}\right](2F+1)^{1/2}(2F'+1)^{1/2}$$

$$\times\sum_{m_i,m_J}m_J\begin{bmatrix}I & 1 & F\\ m_i & m_J & -m\end{bmatrix}\begin{bmatrix}I & 1 & F'\\ m_i & m_J & -m'\end{bmatrix}\sum_{\epsilon=\pm1}(-1)^{I+1+m}\begin{bmatrix}I & 1 & F\\ \mu & \epsilon & -m\end{bmatrix}\frac{\langle F\|T^1\|I\rangle}{\sqrt{2}}\ . \tag{22}$$

Similarly, we find the electric dipole amplitude from Eq. (8):

$$\mathcal{E}_i^{m\mu}=-i\beta\frac{E_0}{2}(-1)^{I+1+m}\sum_{\epsilon=\pm1}\begin{bmatrix}I & 1 & F\\ \mu & \epsilon & -m\end{bmatrix}\frac{\langle F\|T^1\|I\rangle}{\sqrt{2}}\ . \tag{23}$$

The fractional change in absorptivity due to the $M1$ amplitude is obtained by substituting Eqs. (22) and (23) into Eq. (14). Neglecting the term in β^3,

$$\left[\frac{\delta\alpha}{\alpha}\right]^{\mu}_{M1}=-E_S\frac{e\hbar}{2mc}\alpha^2\left[\frac{1}{W_{6\,^1P_1}}-\frac{3}{W_{6\,^3P_1}}\right](2F+1)^{1/2}(2F'+1)^{1/2}$$

$$\times\frac{\displaystyle\sum_{m,m_i,m_J,\epsilon}m_J\begin{bmatrix}I & 1 & F\\ m_i & m_J & -m\end{bmatrix}\begin{bmatrix}I & 1 & F'\\ m_i & m_J & -m'\end{bmatrix}\begin{bmatrix}I & 1 & F\\ \mu & \epsilon & -m\end{bmatrix}^2}{\displaystyle\sum_{m,\epsilon}\begin{bmatrix}I & 1 & F\\ \mu & \epsilon & -m\end{bmatrix}^2}\ . \tag{24}$$

The factor multiplying the angular momentum terms is

$$B_{M1}E_S=-E_S\left[\frac{e\hbar}{2mc}\right]\alpha^2\left[\frac{1}{W_{6\,^1P_1}}-\frac{3}{W_{6\,^3P_1}}\right]$$

$$=-[8.65\times10^{-9}\ (\mathrm{kV/cm})^{-1}]E_S\ . \tag{25}$$

Thus, from the $M1$ part of the interference, we can expect a fractional change in absorptivity of order 10^{-7} for a static field of 10 kV/cm.

For the $F=\frac{1}{2}$ to $F=\frac{1}{2}$ transition (for ^{199}Hg), the angular momentum sum gives

$$\left[\frac{\delta\alpha}{\alpha}\right]^{\pm1/2}_{M1}=\mp0.9017\ldots B_{M1}E_S\ . \tag{26}$$

In the case of the $F=\frac{3}{2}$ to $F=\frac{5}{2}$ transition (for ^{201}Hg),

$$\left[\frac{\delta\alpha}{\alpha}\right]^{\mu}_{M1}=B_{M1}E_S\begin{cases}\pm0.793\,66\ldots, & \mu=\pm\frac{3}{2}\\ \pm\frac{1}{3}\ , & \mu=\pm\frac{1}{2}\ .\end{cases}$$

It is evident that the interference depends both on the dipole and (weakly) on the octupole components of the ground-state polarization. In fact, the presence of the factor m_J in the sum in Eq. (24) can in general make the interference proportional to all odd-order polarization multipole moments. We include the $F=\frac{3}{2}$ to $F=\frac{5}{2}$ result only to demonstrate the possible sensitivity to higher moments of the polarization; we will only consider the $F=\frac{1}{2}$ to $F=\frac{1}{2}$ transition throughout the rest of this paper. For this transition, the $M1$ coefficient in Eq. (1) is found from Eqs. (25) and (26) to be

$$a_{M1}=7.80\times10^{-9}\ (\mathrm{kV/cm})^{-1}\ . \tag{27}$$

V. "P-CHANNEL" ELECTRIC-QUADRUPOLE INTERFERENCE

To evaluate the $E2$ amplitude in Eq. (10), we first consider the second term in brackets, in which the static field mixes the P_1 states with the ground state (the P channel). In Sec. VI we will consider the first term in the brackets, in which the ${}^1D_2$ states are mixed with the ${}^3P_1$ state (the D channel).

A major difference between the $M1$ and $E2$ interference calculations is that the $E2$ operator can mix states of different principal quantum number; we thus have to consider an infinite sum over intermediate states. However, the angular momentum construction of each of these states is identical; the sum over principal quantum number can be easily carried out, as will be demonstrated shortly, leaving a radial integral to be evaluated.

Including just the P channel, Eq. (10) may be written

$$\mathcal{E}_{2,P}=\frac{ie^2kE_SE_0}{4\sqrt{3}}\sum_{n,F',m'}\langle 6\,{}^3\bar{P}_1Fm|(T_2^2-T_{-2}^2)\left[\frac{|n\,{}^3\bar{P}_1F'm'\rangle\langle n\,{}^3\bar{P}_1F'm'|}{W_{6\,{}^1S_0}-W_{n\,{}^3P_1}}+\frac{|n\,{}^1\bar{P}_1F'm'\rangle\langle n\,{}^1\bar{P}_1F'm'|}{W_{6\,{}^1S_0}-W_{n\,{}^1P_1}}\right]$$

$$\times(T_1^1+T_{-1}^1)|6\,{}^1S_0I\mu\rangle\ , \tag{28}$$

where k is the wave number of the incident radiation and where we have inserted the multipole operators from Eqs. (12) and (13). Using Eqs. (15) and (16) to transform to the LS basis and ignoring terms of order β^2, we obtain

$$\mathcal{E}_{2,P}=\frac{ie^2kE_SE_0}{4\sqrt{3}}\sum_{n,F',m'}\sum_{\epsilon,\epsilon'=\pm1}[\beta(6)\alpha^2(n)\langle 6\,{}^1P_1Fm|\epsilon T_{2\epsilon}^2|n\,{}^1P_1F'm'\rangle+\alpha(6)\alpha(n)\beta(n)\Delta_3^1(n)\langle 6\,{}^3P_1Fm|T_{2\epsilon}^2|n\,{}^3P_1F'm'\rangle]$$

$$\times\frac{\langle n\,{}^1P_1F'm'|T_{1\epsilon'}^1|6\,{}^1S_0I\mu\rangle}{W_{6\,{}^1S_0}-W_{n\,{}^1P_1}}\ , \tag{29}$$

where

$$\Delta_3^1(n)\equiv\frac{W_{n\,{}^3P_1}-W_{n\,{}^1P_1}}{W_{6\,{}^1S_0}-W_{n\,{}^3P_1}}\ .$$

In Eq. (29) we have written α and β as functions of the principal quantum number with the definition $\beta=\beta(6)$. To a very good approximation, $\beta(n\neq6)=0$ and $\alpha(n)=1$. We thus have an infinite sum over the $\alpha(n)$ terms and a single term for $\beta(n)=\beta(6)$.

By direct computation, it is straightforward to show that

$$\langle 6\,{}^3P_1Fm|T_{\pm2}^2|n\,{}^3P_1F'm'\rangle=-\tfrac{1}{2}\langle 6\,{}^1P_1Fm|T_{\pm2}^2|n\,{}^1P_1F'm'\rangle\ ,$$

which may be used together with Eqs. (17) and (19) to reduce Eq. (29) to the form

$$\mathcal{E}_{2,P}=\frac{ie^2kE_SE_0}{4\sqrt{3}}\beta\sum_{F',m'}3\sqrt{3}(-1)^{2F'+m+m'}\frac{\sqrt{6}}{\sqrt{5}}K\sum_{\epsilon,\epsilon'}\begin{bmatrix}F' & 2 & F\\ m' & 2\epsilon & -m\end{bmatrix}\epsilon\begin{bmatrix}I & 1 & F'\\ \mu & \epsilon' & -m'\end{bmatrix}\begin{Bmatrix}1 & F' & I\\ F & 1 & 2\end{Bmatrix}\begin{Bmatrix}0 & I & I\\ F' & 1 & 1\end{Bmatrix}\ , \tag{30}$$

where

$$K=\frac{\sqrt{5}}{\sqrt{6}}\left[1-\frac{\delta(n,6)}{2}\Delta_3^1(n)\right]\sum_n\frac{\langle 6P\|T^2\|nP\rangle\langle nP\|T^1\|6S\rangle}{W_{6S}-W_{n\,{}^1P_1}}\ . \tag{31}$$

Using Eq. (18),

$$\langle 6P\|T^2\|nP\rangle\langle nP\|T^1\|6S\rangle=\frac{\sqrt{6}}{\sqrt{5}}\langle 6P|r^2|nP\rangle\langle nP|r|6S\rangle\ . \tag{32}$$

Therefore,

$$K=-\tfrac{1}{2}\Delta_3^1(6)\langle 6P|r^2|6P\rangle\langle 6P|r|6S\rangle+\sum_n\frac{\langle 6P|r^2|nP\rangle\langle nP|r|6S\rangle}{W_{6S}-W_{n\,{}^1P_1}}\ . \tag{33}$$

The first term can be calculated directly from the $6S$ and $6P$ wave functions and energies. By a standard technique [13], the second term can be transformed into a single matrix element $\langle 6P|r^2|\Psi_P\rangle$, where the new function $|\Psi_P\rangle$ is defined by the inhomogeneous differential equation

$$(H-W_{6S})|\Psi_p\rangle=-r|6S\rangle\ . \tag{34}$$

We define another function $|\Psi_p\rangle=P(r)/r$, and also $|6S\rangle=U_{6S}(r)/r$, to obtain the differential equation

$$\left[\frac{d^2}{dr^2}-\frac{L(L+1)}{r^2}+2(W_{6S}-V(r))\right]P(r)=2U_{6S}(r)\ , \tag{35}$$

where $L=1$ and we have taken the shielded Coulomb potential of the Hg^+ ion as $V(r)$. We have the boundary conditions that $P(r)=0$ at $r=0$ and infinity. The equation was solved by use of a second-order Runge-Kutta integration [14]. The value of $P'(0)$ to give the proper boundary conditions was determined by iteration. U_{6S} and W_{6S} were obtained using the RHFD method. Using the RHFD radial functions and eigenvalues, we find (in atomic units)

$$K=82+\langle 6P|r^2|\psi_p\rangle=390\ . \tag{36}$$

Thus,

$$\mathcal{E}_{2,P}^{m\mu}=i\frac{3\sqrt{3}}{2\sqrt{5}}e^2kE_SE_0\beta K\sum_{F',m',\epsilon,\epsilon'}(-1)^{2F'+m'+m}\begin{bmatrix}F' & 2 & F\\ m' & 2\epsilon & -m\end{bmatrix}\epsilon\begin{bmatrix}I & 1 & F'\\ \mu & \epsilon' & -m'\end{bmatrix}\begin{Bmatrix}1 & F' & I\\ F & 1 & 2\end{Bmatrix}\begin{Bmatrix}0 & I & I\\ F' & 1 & 1\end{Bmatrix}\ . \tag{37}$$

We next need the $E1$ amplitude. Using Eq. (23) with Eqs. (17), (18), and (19),

$$\mathcal{E}_1^{m\mu}=-i\beta\frac{E_0}{2}\frac{\sqrt{3}}{\sqrt{2}}(-1)^{3I+1+m}\sum_{\epsilon}\begin{bmatrix}I & 1 & F\\ \mu & \epsilon & -m\end{bmatrix}\begin{Bmatrix}0 & I & I\\ F & 1 & 1\end{Bmatrix}\langle 6P|r|6S\rangle\ . \tag{38}$$

From integration of the wave functions, $\langle 6P|r|6S\rangle=-3.1$. Using Eq. (13), for $I=\frac{1}{2}$ to $F=\frac{1}{2}$,

$$\left[\frac{\delta\alpha}{\alpha}\right]_{E2,P}^{\pm 1/2}=\frac{6}{\sqrt{5}}\left[\mp\frac{1}{4\sqrt{5}}\right]K\frac{ekE_S}{\langle 6P|r|6S\rangle}=\mp[0.96\times 10^{-7}\ (\mathrm{kV/cm})^{-1}]E_S\ , \tag{39}$$

which, using Eq. (1), yields

$$a_{E2,P}=-0.96\times 10^{-7}\ (\mathrm{kV/cm})^{-1}\ . \tag{40}$$

VI. "*D*-CHANNEL" ELECTRIC-QUADRUPOLE INTERFERENCE

The D-channel calculation proceeds similarly to the P channel with the exception that the $n\,^1D_2$ states are pure LS. Referring to Eqs. (10) and (16), we now have

$$\mathcal{E}_{2,D}=-\frac{ie^2kE_SE_0}{4\sqrt{3}}\beta\sum_{n,F',m'}\sum_{\epsilon,\epsilon'=\pm 1}\frac{\langle 6\,^1P_1Fm|T_\epsilon^1|n\,^2D_2F'm'\rangle\langle n\,^2D_2F'm'|\epsilon' T_{2\epsilon'}^2|6\,^1S_0I\mu\rangle}{W_{6\,^3P_1}-W_{n\,^1D_2}}\ . \tag{41}$$

Using Eqs. (17), (18), and (19),

$$\langle Fm|T_\epsilon^1|nF'm'\rangle\langle nF'm'|\epsilon' T_{2\epsilon'}^2|I\mu\rangle$$
$$=6\epsilon'(-1)^{4I+2F'+m'+m}\begin{Bmatrix}2 & F' & I\\ F & 1 & 1\end{Bmatrix}\begin{Bmatrix}0 & I & I\\ F' & 2 & 2\end{Bmatrix}\begin{bmatrix}F' & 1 & F\\ m' & \epsilon & -m\end{bmatrix}\begin{bmatrix}I & 2 & F'\\ \mu & 2\epsilon' & -m'\end{bmatrix}\langle 6P|r|nD\rangle\langle nD|r^2|6S\rangle\ . \tag{42}$$

Again, we have to sum over states; referring to Eqs. (30)–(33),

$$K'=\sum_n\frac{\langle 6P|r|nD\rangle\langle nD|r^2|6S\rangle}{W_{6\,^3P_1}-W_{n\,^1D_2}}\ . \tag{43}$$

As before, the sum can be transformed into a differential equation,

$$\left[\frac{d^2}{dr^2}-\frac{L(L+1)}{r^2}+2(W_{6\,^3P_1}-V(r))\right]D(r)=2U_{6P}(r)\ , \tag{44}$$

with $L=2$. Solving as before, we find

$$K'=\langle\Psi_d|r^2|6S\rangle=49.2\ . \tag{45}$$

Using Eqs. (13), (38), (42), and (45), we obtain

$$\left[\frac{\delta\alpha}{\alpha}\right]_{E2,D}^{\pm 1/2}=\frac{2\sqrt{2}K'ekE_S}{\langle 6P|r|6S\rangle}\left[\pm\frac{\sqrt{3}}{\sqrt{400}}\right]$$
$$=\pm[2.2\times 10^{-8}\ (\mathrm{kV/cm})^{-1}]E_S\ , \tag{46}$$

or, from Eq. (1),

$$a_{E2,D}=2.2\times 10^{-8}\ (\mathrm{kV/cm})^{-1}\ , \tag{47}$$

which is much smaller than the P-channel result.

VII. COMBINED EFFECT AND PROPOSALS FOR EXPERIMENTAL VERIFICATION

Combining the results [Eqs. (27), (40), and (47)], we find

$$a=-6.6\times10^{-8}\ (\mathrm{kV/cm})^{-1}\ . \tag{48}$$

We estimate the error to be ±30%, which is due to uncertainty in the radial wave functions and the simple *LS* coupling scheme used. The magnitude of the interference in Hg is thus nearly five times as large as the effect in Rb.

With minor modifications, the Hg PEDM apparatus [6] would be quite suitable to measure this effect. Nuclear spin polarization is created by optical pumping in mercury vapor cells within which 10-kV/cm electric fields can be applied. A major source of error in the PEDM measurement itself, stray magnetic fields, would have little effect on the interference measurement. Not only would the noise be smaller, but larger electric fields and faster field-reversal rates could be used since the limiting voltage is determined by electrical breakdown in the cell, not by leakage-current-induced magnetic fields as in the PEDM experiment. Measuring a change in absorption of the size predicted in Eq. (48) should then be feasible.

VIII. CONCLUSION

We have calculated a linear Stark interference effect in Hg and have concentrated on the effect in ^{199}Hg where the nuclear spin $I=\frac{1}{2}$. The result is about five times greater in magnitude over a similar calculation for the Rb *D* lines for which this effect was originally suggested. The important differences between Hg and Rb are that for Hg the hyperfine structure is resolved, the atomic polarization is defined by the nuclear spin, and the 254-nm line of interest is an intercombination line. The effect is large enough to be measured (in a quite reasonable averaging time) with a modified version of the Hg permanent-electric-dipole-moment apparatus.

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