Enhanced effects of temporal variation of the fundamental constants in $^2\Pi_{1/2}$ term diatomic molecules: $^{207}$Pb$^{19}$F

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The $^{207}$Pb$^{19}$F molecule possesses a pair of closely spaced levels of opposite parity due to near cancelation of the omega-type doubling and magnetic hyperfine interaction energy shifts [Alphei et al. Phys. Rev. A, 83, 040501 (2011)]. We calculate the dependence of the transition frequency between these levels on the fine-structure constant $\alpha$ and the ratio of the light quark masses to the quantum chromodynamics scale ($m_q/\Lambda_{QCD}$), and find large enhancement of the relative effects of the variation of these parameters. Note that the effect of $\alpha$ variation appears mainly due to the significant difference in the relativistic correction factors for the fine and hyperfine structure. We hence suggest the $^{207}$Pb$^{19}$F molecule as a candidate system for investigating the possible temporal variation of the fundamental constants.

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I. INTRODUCTION

The $^{207}$Pb$^{19}$F molecule has been recently studied as a system with high sensitivity to P-odd and P,T-odd interactions [1, 2]. Here we want to point out that this molecule is also very sensitive to the variation of the fundamental constants of nature. The idea that such constants might vary with time can be traced as far back as the Large Numbers Hypothesis of Dirac, who hypothesized that the gravitational constant $G$ might be proportional to the reciprocal of the age of the universe [3–5]. In more recent times, the possibility of observing the space-time variation of the fundamental constants of nature has received renewed interest, with the possible variation of the fine-structure constant $\alpha = e^2/\hbar c$ and the electron-to-proton mass ratio $m_e/m_p$ receiving the most attention (see e.g. [6, 9]). Another dimensionless fundamental parameter for strong interactions is $m_q/\Lambda_{QCD}$, where $m_q$ is the light quark mass and $\Lambda_{QCD}$ is the QCD scale [10]. This parameter enters atomic physics through nuclear magnetic $g$-factors [12, 14].

At present, there are very strong upper bounds on the time variation of these constants from laboratory experiments (see e.g. [15–22]). More details about the current status of these experiments and on observational astrophysical and geophysical data can be found in a number of reviews [23–27]. All experiments cited above were performed with atoms, the only exception being experiment [19], which was done on the ro-vibrational transition of the SF$_6$ molecule. However, recently there has been a growing number of proposals to use different types of molecular transitions, where sensitivity to the variation of the fundamental constants is strongly enhanced compared to typical atomic transitions [28–31]. Molecules are also playing a very important role in astronomical studies of the possible variation of the fundamental constants on the cosmological time-scale (see, for example, review [32]).

In the present work, we propose another system for testing the possible temporal variation of the fundamental constants. Closely spaced levels of opposite parity are known to exist in the $^{207}$Pb$^{19}$F molecular radical species, with the separation between the levels experimentally known to be $\omega = 266.285$ MHz [1]. The close spacing between these levels is a result of the near cancelation between the shifts in the energies of these levels due to omega-type doubling and the magnetic hyperfine interaction. We show that the dependences on $\alpha$ and $m_q/\Lambda_{QCD}$ of these two nearly cancelling contributions are significantly different for omega-type doubling and magnetic hyperfine shifts, resulting in a sizeable enhancement in the $\alpha$- and $m_q/\Lambda_{QCD}$-dependence of the transition frequency $\omega$. Note that the effect of $\alpha$ variation appears mainly due to the large difference in the relativistic correction factors for the fine and hyperfine structure. The molecular energy levels of interest are also quite stable, making experiments using the $^{207}$Pb$^{19}$F molecule attractive for tests of the possible temporal variation of the fundamental constants.

The structure of this paper is as follows. In Section II we derive the non-linear dependence of the transition frequency $\omega$ on the omega-doubling, rotational and hyperfine interaction parameters. In Sec. III we derive the dependence of the transition frequency $\omega$ on $\alpha$. To solve this problem, we estimate higher order corrections in $Z\alpha$ to the fine structure and omega doubling intervals. In Sec. IV we derive the dependence of the transition frequency $\omega$ on $m_q/\Lambda_{QCD}$. Finally, in Sec. V we present the formula for the dependence of $\omega$ on both $\alpha$ and $m_q/\Lambda_{QCD}$, together with estimates for the sensitivity coefficients, and summarise our findings.
II. DEPENDENCE OF TRANSITION FREQUENCY ON OMEGA-DOUBLING AND HYPERFINE INTERACTION PARAMETERS

The full Hamiltonian for the $^{207}$Pb$^{19}$F molecule is given in [1] and can be solved to give the value of $\omega$, provided that one knows all the necessary values of the rotational and hyperfine structure constants, see, for instance, Refs. [33-35]. The energy levels of interest are the closely spaced $F^p = 1/2^+$ and $F^p = 1/2^-$ states. Noting that the two most dominant contributions to $\omega$ are from omega-type doubling and the magnetic hyperfine interaction for lead, we ignore the magnetic hyperfine contribution from fluorine (which can be treated as a perturbation) and so instead consider the $F^p = 1^+$ and $F^p = 1^-$ states, the total angular momenta quantum numbers of which arise from the coupling of the angular momentum $J = 1/2$ with the nuclear spin angular momentum of lead $I = 1/2$ alone. The energies of the $F^p = 1^+$ and $F^p = 1^-$ states can be presented as follows [36]

$$E(J, F, p) = BJ(J + 1) + p(-1)^{F+1/2} \frac{\Delta}{2} \left(J + \frac{1}{2}\right) + U_{hf},$$  \hspace{1cm} (1)

where

$$U_{hf} = \frac{\chi A_{\perp}}{4}$$

$$+ 2(J - F) \left[ -\tau + s \sqrt{\tau^2 - \beta \left(\frac{\tau}{F + 1/2} - \beta\right)} \right],$$  \hspace{1cm} (2)

$$\chi = (-1)^{F+1} p,$$  \hspace{1cm} (3)

$$\tau = \left(B + \frac{\chi \Delta}{2}\right)(F + 1/2),$$  \hspace{1cm} (4)

$$\beta = \frac{A_{\parallel} - \chi A_{\perp}}{4},$$  \hspace{1cm} (5)

$$s = \text{sign}\left[\tau - \frac{\beta}{2F + 1}\right].$$  \hspace{1cm} (6)

Here $p$ denotes the parity of the state. The values of the rotational constant $B = 6917.9108$ MHz, the magnetic hyperfine splitting $\Delta = -4145.2304$ MHz and the hyperfine parameters for lead $A_{\parallel} = -7264.0388$ MHz, $A_{\perp} = 10146.6733$ MHz are known experimentally [1]. In Eq. (1), the first term represents the pure rotational energy contribution, the second term represents the magnetic hyperfine contribution that is present even in the absence of the hyperfine interaction, while the third term represents the contribution from the hyperfine interaction, which also includes non-linear rotational and magnetic hyperfine doubling contributions. Note that in Ref. [36], there is an error in the phase assignment in the molecular wavefunction used to calculate the energy levels. The relative phase between the basis functions of opposite projections of total electronic angular momentum on the molecular axis, linear combinations of which result in molecular wavefunctions of definite parity $p$, should be $(-1)^{J - S_p}$. For the $F = 0$ states, this results in the substitution $\chi \rightarrow -\chi$ in Eqs. (1) - (4) in Ref. [36]. For further details, we refer the reader to Refs. [34, 37].

We write the energy separation between the two $F = 1$ levels of interest in the following form

$$\omega = E(1/2, 1, +) - E(1/2, 1, -).$$  \hspace{1cm} (7)

Variation of (7) with respect to the omega-doubling, hyperfine interaction and rotational parameters leads to

$$\delta \omega = \frac{\partial \omega}{\partial \Delta} \delta \Delta + \frac{\partial \omega}{\partial A_{\perp}} \delta A_{\perp} + \frac{\partial \omega}{\partial A_{\parallel}} \delta A_{\parallel} + \frac{\partial \omega}{\partial B} \delta B.$$  \hspace{1cm} (8)

From Eqs. (11) - (17), we find

$$\frac{\partial \omega}{\partial \Delta} = -0.862,$$  \hspace{1cm} (9)

$$\frac{\partial \omega}{\partial A_{\perp}} = 0.497,$$  \hspace{1cm} (10)

$$\frac{\partial \omega}{\partial A_{\parallel}} = -0.139,$$  \hspace{1cm} (11)

$$\frac{\partial \omega}{\partial B} = 0.272.$$  \hspace{1cm} (12)

For comparison, we find from solving the full Hamiltonian (including the hyperfine interaction for fluorine) numerically, the corresponding values of the derivatives in Eqs. (9) - (12) to be $-0.863, 0.493, -0.140$ and $0.271$ respectively. In the present work, we use the analytical values given by (9) - (12) for the derivative values, but for the energy separation we use the experimentally determined value $\omega = 266.285$ MHz [1].

III. VARIATION OF TRANSITION FREQUENCY WITH $\alpha$

It is known that the $\alpha$-dependence of the magnetic hyperfine interaction energy shift scales as $\alpha^2 F_{rel}^hf(Z\alpha)$, where $F_{rel}^hf(Z\alpha)$ is the Casimir relativistic correction factor, which for $s$- and $p$-waves with $j = 1/2$ is given approximately by

$$F_{rel}^hf = \frac{3}{\gamma_{1/2} (4\gamma_{1/2}^2 - 1)},$$  \hspace{1cm} (13)

see e.g. Refs. [38, 39]. We employ the standard notation $\gamma_j = \sqrt{(j + 1/2)^2 - (Z\alpha)^2}$ in Eq. (13) and throughout
this work. According to our numerical estimate based on the PbF wave function presented in [33], the magnetic hyperfine structure energy shift on accurate numerical many-body calculations of the dependence of the hyperfine structure energy shift on \( A \), where \( A \) is either \( A_0 \) or \( A_\perp \), with respect to \( \alpha \) thus leads to the following expression

\[
\frac{\delta A}{A} = (2 + K^{\text{hf}}_{\text{rel}}) \frac{\delta \alpha}{\alpha},
\]

where \( K^{\text{hf}}_{\text{rel}} \) is given by

\[
K^{\text{hf}}_{\text{rel}} = \frac{(Z\alpha)^2}{\gamma^2_{1/2}} \left( 12^{-\gamma^2_{1/2} - 1} \right)
\]

for both \( s_{1/2} \) and \( p_{1/2} \)-waves. For lead \((Z = 82)\), Eq. (15) gives \( K^{\text{hf}}_{\text{rel}} = 2.39 \). We note that more accurate numerical many-body calculations of the dependence of the hyperfine structure energy shift on \( \alpha \) give slightly larger values of the coefficient \( K^{\text{hf}}_{\text{rel}} \) than the analytical Casimir correction factor does for moderately heavy atomic and ionic species [41]. For instance, for Cs \((Z = 55)\), \( K^{\text{hf}}_{\text{rel}} = 0.83 \) numerically (instead of 0.74 analytically), while for Hg \((Z = 80)\), \( K^{\text{hf}}_{\text{rel}} = 2.28 \) numerically (instead of 2.18 analytically). However, for the purposes of the present work, it will suffice to use the analytical expression (15).

The omega-type doubling in interest in the \(^{207}\text{PbF}\) molecule occurs between the positive and negative-parity \(^2\text{Π}_{1/2}\) states. The Coriolis interaction can connect the \( \Omega = +1/2 \) and \( \Omega = -1/2 \) states to first order in perturbation theory, but cannot connect the \( \Lambda = +1 \) and \( \Lambda = -1 \) states directly without there being mixing of the \( \Lambda = +1 \) state with the \( \Lambda = 0 \) state via the spin-orbit interaction, and similarly mixing of the \( \Lambda = -1 \) state with the \( \Lambda = 0 \) state (see e.g. [13]). If we consider, for instance, the subspace spanned by the unperturbed states \( |\Lambda = +1\rangle \) and \( |\Lambda = 0\rangle \) in the two-level approximation, then in the presence of the spin-orbit interaction between these two states, the perturbed eigenfunction corresponding to the unperturbed state \( |\Lambda = +1\rangle \) in the lowest order approximation reads

\[
\left| \Lambda = +1 \right\rangle = \xi |\Lambda = +1\rangle + \eta |\Lambda = 0\rangle,
\]

where \( |\eta| \ll 1 \) is the spin-orbit mixing coefficient. These considerations imply that the \( \alpha \)-dependence of the omega-type doubling energy shift between the positive and negative-parity \(^2\text{Π}_{1/2}\) states in \(^{207}\text{PbF}\) scales in the same way as \( |\eta| \) does. We also know that

\[
|\eta| \approx |V_{so}| / \Delta \epsilon,
\]

\[
\Delta \epsilon \equiv E \left( ^3\Sigma_{1/2} \right) - E \left( ^3\Pi_{1/2} \right),
\]

which is to say that the \( \alpha \)-dependence of the omega-type doubling energy shift scales approximately in the same way as the spin-orbit interaction energy shift (in atomic units) does. Here \( V_{so} \) denotes the matrix element of the spin-orbit interaction operator between the states \(^2\Sigma_{1/2}\) and \(^2\Pi_{1/2}\), with projections of the orbital angular momentum on the molecular symmetry axis being \( \Lambda = 0 \) and \( \Lambda = +1 \) respectively.

It is well known that the spin-orbit matrix elements in atomic units scale as \( Z^2 \alpha^2 \). For the hyperfine interaction, higher order \( Z^2 \alpha^2 \) corrections are very important; they even produce a singularity for \( Z^2 \alpha^2 = 3/4 \) for the point-like nucleus case - see Eq. (13). Therefore, we should estimate higher order \( Z^2 \alpha^2 \) corrections for the spin-orbit splitting and omega doubling. Relativistic effects, such as the spin-orbit interaction, arise predominantly at small distances \( r \ll a_B / Z \), where screening of the nuclear Coulomb field is negligible [43]. Also, the binding energy of the unpaired electron in \(^{207}\text{PbF}\) is small compared with the Coulomb potential energy. Thus for \( r \ll a_B / Z \), the wavefunction is proportional to the hydrogen-like ion wavefunction with a large principal quantum number \( n \). These points imply that the \( \alpha \)-dependence of the spin-orbit matrix elements may be found from the spin-orbit splitting \( np_{3/2} - np_{1/2} \) in hydrogen-like ions. The relativistic Dirac formula for the energy levels of a hydrogen-like species reads (see e.g. [44])

\[
E_{n,j} = \frac{mc^2}{\left[ 1 + \frac{(Z\alpha)^2}{(\gamma_{n} + \eta_{n})^2} \right]^{1/2}},
\]

where \( n = j + 1/2 + n' \). To work with dimensionless quantities, we take the ratio of (19) to the non-relativistic energy scale, \( mc^2 (Z\alpha)^2 / 2n^2 \), giving

\[
\varepsilon_{n,j} = \frac{2n^2}{(Z\alpha)^2} \left[ 1 + \frac{(Z\alpha)^2}{(\gamma_{n} + \eta_{n})^2} \right]^{1/2}.
\]

We take the limit \( n' \to \infty \) (note again that \( n = j + 1/2 + n' \)) and find that the \( \alpha \)-dependence of the energy difference \( \varepsilon_{n,3/2} - \varepsilon_{n,1/2} \) scales as

\[
C_{\text{rel}}^{so} = \frac{Z^2 \alpha^2}{4} F_{\text{rel}}^{so} = \gamma_{3/2} - \gamma_{1/2} - 1.
\]

The first term in the expansion of the right-hand-side gives the usual \( Z^2 \alpha^2 \) dependence, while higher orders give the relativistic correction factor \( F_{\text{rel}}^{so} \) for the spin-orbit interaction. The difference between the relativistic correction factor in Eq. (21) compared with the relativistic correction factor for the hyperfine interaction in Eq. (13) is very significant: the relativistic factor for the spin-orbit interaction remains finite (< 3) for any \( Z\alpha < 1 \), i.e. the relativistic corrections are significantly smaller than that for the hyperfine interaction (which become infinite for \( Z^2 \alpha^2 = 3/4 \)). Variation of (21) with respect to \( \alpha \) gives

\[
2 + K^{so}_{\text{rel}} = \frac{\partial C_{\text{rel}}^{so}}{\partial \alpha} \frac{1}{C_{\text{rel}}^{so}} = \frac{(Z\alpha)^2}{\gamma_{3/2} - \gamma_{1/2} - 1}.
\]
For $Z = 82$, Eq. (22) gives $2 + K_{\text{rel}}^{\alpha} = 2.42$, i.e. higher order relativistic corrections increase the result by 20%. This gives the following variation of $\Delta$ with respect to $\alpha$

$$\frac{\delta \Delta}{\Delta} = (2 + K_{\text{rel}}^{\alpha}) \frac{\delta \alpha}{\alpha}. \quad (23)$$

In this work, we deal with a heavy Pb atom. The spin-orbit interaction rapidly increases with $Z^2 \alpha^2$. In the hypothetical case of a very large spin-orbit interaction, which exceeds an interval between the $\Lambda = 1$ and $\Lambda = 0$ terms, omega doubling does not depend on the spin-orbit interaction, since the state with definite electronic angular momentum $j = 1/2$ already contains both $\Lambda = 1$ and $\Lambda = 0$ components. This means that, in this limit, the $\alpha$ dependence of the omega doubling vanishes. In the realistic case of the PbF molecule, this does not happen. However, there exists a further non-linear correction to Eq. (23), which followed from perturbation theory for closely spaced states. We again restrict our attention to the subspace spanned by the unperturbed states $|\Lambda = \pm 1\rangle$ and $|\Lambda = 0\rangle$ in the two-level approximation. The spin-orbit mixing coefficient in Eq. (16) can be expressed as follows [15]

$$|\eta| = \frac{1}{\sqrt{2}} \sqrt{1 - \frac{\Delta \varepsilon}{\varepsilon}}, \quad (24)$$

where $\Delta \varepsilon$ is defined by Eq. (18) and

$$\varepsilon = \sqrt{\Delta \varepsilon^2 + 4|V_{so}|^2}. \quad (25)$$

Noting that $|V_{so}|/\Delta \varepsilon \ll 1$, we find

$$|\eta| \approx \frac{|V_{so}|}{\Delta \varepsilon} \left[1 - \frac{3}{2} \frac{|V_{so}|^2}{|\Delta \varepsilon|^2}\right], \quad (26)$$

from which the following equation follows directly

$$\frac{\partial |\eta|}{\partial \alpha} |\eta| = \frac{\partial |V_{so}|}{\partial \alpha} \frac{\alpha}{|V_{so}|} \left[1 - \frac{9}{4} \frac{|V_{so}|^2}{|\Delta \varepsilon|^2} \right]$$

$$\approx (2 + K_{\text{rel}}^{\alpha}) \left[1 - 3 \frac{|V_{so}|^2}{|\Delta \varepsilon|^2}\right]. \quad (27)$$

The second term in square brackets in the last line of Eq. (27) is the non-linear correction factor $\chi$ to Eq. (23)

$$\frac{\delta \Delta}{\Delta} = (2 + K_{\text{rel}}^{\alpha}) \chi \frac{\delta \alpha}{\alpha}. \quad (28)$$

From numerical calculations [33], we know that $|V_{so}/\Delta \varepsilon| = 0.19$ and so we find that $\chi = 0.89$.

Finally, we estimate the $\alpha$ dependence of the contribution of the molecular rotational constant $B$ to the variation of the energy separation $\omega$ as follows. The effect of this contribution to the sensitivity coefficient for $\alpha$ in our final expression [34] is very small, so a refined calculation is not necessary here. The rotational constant of interest here ($B = B_{1/2}$) is that for the $2^2\Pi_{1/2}$ state, which near the Pb nucleus is dominated by the $p_{1/2}$ atomic orbital (over 80% — see [33]). The $\alpha$ dependence of $B_{1/2}$ arises due to the relativistic correction to the potential $V_{\text{rel}}(r)$, which is located near the Pb nucleus where the Coulomb potential is not screened and the energy of the valence electron may be neglected. In this region, the valence electron wave function is proportional to the Coulomb wave function with a large principal quantum number $n$. From the relativistic energy shifts of the high Coulomb levels in Eq. (19), we know that $\langle n_{p1/2}|V_{\text{rel}}|n_{p1/2}\rangle \approx 2 \langle n_{p3/2}|V_{\text{rel}}|n_{p3/2}\rangle$. This gives the following relations between the relativistic shifts of the rotational constants

$$B_{1/2}^{\text{rel}} = 2B_{3/2}^{\text{rel}} = 2(B_{1/2} - B_{3/2}) = \text{const} (Z\alpha)^2, \quad (29)$$

where $B_{3/2}$ is the rotational constant for the $2^2\Pi_{3/2}$ state, and from which we find that

$$\frac{\delta B_{1/2}}{B_{1/2}} = \frac{2B_{1/2}^{\text{rel}} \delta \alpha}{\alpha} = 2 \delta \frac{\alpha}{\alpha}. \quad (30)$$

We use the experimentally determined rotational constant values $B_{1/2} = 0.23403 \text{ cm}^{-1}$ and $B_{3/2} = 0.22875 \text{ cm}^{-1}$ for $^{208}\text{Pb}^{19}\text{F}$ [46], giving $\nu = -0.046$.

**IV. VARIATION OF TRANSITION FREQUENCY WITH $m_{\bar{g}}/\Lambda_{\text{QCD}}$**

The omega-type doubling and rotational energy shifts are obviously independent of the nuclear magnetic moment $\mu$. The $\mu$-dependence of the hyperfine interaction energy shift, however, scales linearly with $\mu$. The variation of $A$ with respect to $\mu_{\text{N}}$ is thus

$$\frac{\delta A}{A} = \frac{\delta \mu_{\text{N}}}{\mu_{\text{N}}}, \quad (31)$$

which can also be expressed as follows [14]

$$\frac{\delta A}{A} = \kappa_{\text{N}} \left(\frac{m_{\bar{g}}/\Lambda_{\text{QCD}}}{m_{\bar{g}}/\Lambda_{\text{QCD}}}\right). \quad (32)$$

Noting that there is little sensitivity of $\delta \mu/\mu$ to core polarization effects in odd-neutron, even-proton nuclei [14], we can estimate $\kappa_{\text{N}}$ from known data. The $^{207}\text{Pb}$ nucleus in the ground state has $I' = 1/2^-$ and nuclear magnetic moment $\mu = +0.592583 \mu_N$, while the $^{199}\text{Hg}$ nucleus in the ground state has $I' = 1/2^-$ and nuclear magnetic moment $\mu = +0.5058855 \mu_N$ [47]. Without account of nuclear radius variation, $\kappa_{\text{Hg}} = -0.09$ [44] [48]. However, with account of the effect of nuclear radius variation on the hyperfine structure, $\kappa_{\text{Hg}} = -0.111$ [49]. Since the values and origin of the $^{207}\text{Pb}$ and $^{199}\text{Hg}$ nuclear magnetic moments, as well as their radii are similar, we take $\kappa_{\text{N}} \approx \kappa_{\text{Hg}} = -0.111$ for our estimate of $\kappa_{\text{N}}$. 
V. SUMMARY AND CONCLUSIONS

The variation of $\omega$ (in atomic units) with respect to $\alpha$ and $m_q/\Lambda_{\text{QCD}}$ reads

$$\frac{\delta \omega}{\omega} = \left[ \chi(2 + K_{\text{rel}}) \frac{\partial \omega}{\partial \Delta} + 2 \nu B \frac{\partial \omega}{\partial B} + \frac{(2 + K_{\text{rel}}^h)}{\omega} \left( A_1 \frac{\partial \omega}{\partial A_1} + A_2 \frac{\partial \omega}{\partial A_2} \right) \frac{\delta \alpha}{\alpha} + \frac{\kappa \rho}{\omega} \left( A_1 \frac{\partial \omega}{\partial A_1} + A_2 \frac{\partial \omega}{\partial A_2} \right) \frac{\delta (m_q/\Lambda_{\text{QCD}})}{(m_q/\Lambda_{\text{QCD}})} + \frac{\delta (m_e/m_p)}{(m_e/m_p)} \right].$$

(33)

Substituting all the known quantities into Eq. (33) and taking into account that $\Delta, A_1, A_2$ and $B$ all have linear dependence on the electron-to-proton mass ratio, $m_e/m_p$, gives

$$\frac{\delta \omega}{\omega} \approx -55 \frac{\delta \alpha}{\alpha} + 2.1 \frac{\delta (m_q/\Lambda_{\text{QCD}})}{(m_q/\Lambda_{\text{QCD}})} + \frac{\delta (m_e/m_p)}{(m_e/m_p)}.$$  

(34)

With the approximations made in deriving relation (34), the uncertainties in the sensitivity coefficients in Refs. [14, 15, 20] are $\sim 20\%$. Note that the effect of the variation of $m_e/m_p$ is not enhanced.

We see that the $^{207}$Pb$^{19}$F molecular radical species can offer a one to two order of magnitude enhancement of the relative effect of $\alpha$-variation. This is comparable to the enhancements in some other molecular species [28–31]. Even more interestingly, the sensitivity coefficient for $m_q/\Lambda_{\text{QCD}}$ is enhanced by two orders of magnitude compared with the ratio of frequencies of $^{133}$Cs and $^{87}$Rb atomic clocks, which use electronic hyperfine transitions as their frequency standards [14, 15, 19] and currently provide the best limit on the variation of $m_q/\Lambda_{\text{QCD}}$ [20]. Furthermore, the natural widths of the closely spaced energy levels of interest are quite small, since both states lie merely $\sim 8000$ MHz above the ground state. An additional advantage is that this molecule is already considered for high precision experiments to study the P-odd anapole moment of the nucleus $^{207}$Pb and to search for the electron EDM [1]. We hence suggest the $^{207}$Pb$^{19}$F molecule as a candidate system for investigating the possible temporal variation of the fundamental constants.

Since the effects of the variation of fundamental constants in the $^{207}$Pb$^{19}$F molecule are significantly enhanced, it does not matter what system will be used to provide the reference frequency. In fact, we presented the result of the variation of the ratio $\omega/(\text{atomic unit})$. In order to use a specific frequency standard, such as caesium or rubidium, one should subtract the effect of the variation of the corresponding standard frequency, which is presented (also in atomic units) in Refs. [14, 15, 19]. This will provide only small corrections to Eq. (34).

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(2011); arXiv:1111.0092.
[25] J.-P. Uzan, Living Reviews in Relativity 14, 2 (2011), URL http://www.livingreviews.org/lrr-2011-2
[26] J. C. Berengut and V. V. Flambaum, Journal of Physics Conference Series 264, 012010 (2011); arXiv:1009.3693.
[27] J. C. Berengut, V. V. Flambaum, and A. Ong, in European Physical Journal Web of Conferences (2013), vol. 57 of European Physical Journal Web of Conferences, p. 2001.
[28] V. V. Flambaum, Phys. Rev. A 73, 034101, (2006).
[29] V. V. Flambaum, and M. G. Kozlov, Phys. Rev. Lett. 99, 150801 (2007); arXiv:0705.0849.
[30] D. DeMille, S. Sainis, J. Sage, T. Bergeman, S. Kotochigova, and E. Tiesinga, Phys. Rev. Lett. 100, 043202 (2008); arXiv:0709.0963.
[31] T. Zelevinsky, S. Kotochigova, and J. Ye, Phys. Rev. Lett. 100, 043201 (2008); arXiv:0708.1806.
[32] M. G. Kozlov and S. A. Levshakov, Annalen der Physik 525, 452 (2013); arXiv:1304.4510.
[33] M. G. Kozlov, V. I. Fomichev, Yu. Yu. Dmitriev, L. N. Labzovsky, and A. V. Titov, J. Phys. B 20, 4939, (1987).
[34] K. I. Baklanov, A. N. Petrov, A. V. Titov, and M. G. Kozlov, Phys. Rev. A 82, 060501(R), (2010).
[35] A. N. Petrov, L. V. Skripnikov, A. V. Titov, and R. J. Mawhorter, Phys. Rev. A 88, 010501(R), (2013).
[36] C. P. McRaven, P. Sivakumar, and N. E. Shafer-Ray, Phys. Rev. A 78, 054502, (2008).
[37] J. M. Brown, and A. Carrington, Rotational Spectroscopy of Diatomic Molecules, (Cambridge University Press, Cambridge, 2003).
[38] J. D. Prestage, R. L. Tjoelker, and L. Maleki, Phys. Rev. Lett. 74, 3511, (1995).
[39] I. B. Khriplovich, Parity Nonconservation in Atomic Phenomena, (Gordon and Breach, Philadelphia, 1991).
[40] C. Schwartz, Phys. Rev. 97, 380, (1955).
[41] V. A. Dzuba, V. V. Flambaum, and J. K. Webb, Phys. Rev. A 59, 230, (1999).
[42] M. G. Kozlov, Phys. Rev. A 80, 022118, (2009).
[43] H. B. G. Casimir, On the Interaction Between Atomic Nuclei and Electrons, (Teyler’s Tweede Genootschap, Haarlem, 1936).
[44] J. J. Sakurai, and J. Napolitano, Modern Quantum Mechanics, 2nd Ed. (Addison-Wesley, San Fransisco, 2011).
[45] L. D. Landau, and E. M. Lifshitz, Quantum Mechanics (Non-relativistic Theory), 3rd Ed. (Butterworth-Heinemann, Oxford, 1977).
[46] National Institute of Standards and Technology, Chemistry WebBook, last updated 2011, URL http://webbook.nist.gov/.
[47] N. J. Stone, At. Data. Nucl. Data. Tables 90, 75, (2005).
[48] J. C. Berengut, V. V. Flambaum, and E. M. Kava, Phys. Rev. A 84, 042510, (2011).
[49] T. H. Dinh, A. Dunning, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A 79, 054102, (2009).