Effect of $\alpha$ variation on the vibrational spectrum of $\text{Sr}_2$

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We consider the effect of $\alpha$ variation on the vibrational spectrum of $\text{Sr}_2$ in the context of a planned experiment to test the stability of $\mu \equiv m_e/m_p$ using optically trapped $\text{Sr}_2$ molecules [Zelevinsky et al., Phys. Rev. Lett. 100, 043201; Kotochigova et al., Phys. Rev. A 79, 012504]. We find the prospective experiment to be 3 to 4 times less sensitive to fractional variation in $\alpha$ as it is to fractional variation in $\mu$. Depending on the precision ultimately achieved by the experiment, this result may give justification for the neglect of $\alpha$ variation or, alternatively, may call for its explicit consideration in the interpretation of experimental results.

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I. INTRODUCTION

In the endeavor to understand nature on its most fundamental level, physicists are striving for a description of all fundamental forces within a single unified theory. Some promising theories suggest that observable quantities such as the electron-to-proton mass ratio $\mu \equiv m_e/m_p$ or the fine structure constant $\alpha \equiv e^2/\hbar c$ may not have fixed values [1]. A detected drift in $\mu$ or $\alpha$ could thus provide valuable insight into the fundamental workings of nature beyond our current understanding. To date, laboratory measurements have verified the stability of $\mu$ and $\alpha$ on the fractional level of $10^{-11}$ [2] and $10^{-17}$ [3] per annum, respectively. More stringent laboratory tests are further motivated by recent evidence of a spatial gradient in the value of $\alpha$ based on an analysis of quasar absorption spectra [4]. It has been suggested that the Earth’s motion relative this gradient may lead to measurable effects in the laboratory [5].

The Ye group at JILA (Boulder) aims to test the stability of $\mu$ to high precision using $\text{Sr}_2$ molecules confined in an optical lattice [6]. The experimental protocol, as outlined by Zelevinsky et al. [7, 8], calls for optical Raman spectroscopy between select vibrational levels of the $X^1\Sigma_g^+$ ground electronic potential. A variation in $\mu$ alters the vibrational spectrum, and experimental sensitivity to this change may be optimized with a prudent choice of levels to incorporate into the spectroscopic scheme. It was shown in Refs. [7, 8] that, with respect to variation in $\mu$, the lowest and highest vibrational levels experience minimal displacement relative to the potential, whereas levels in the intermediate part of the spectrum experience a much larger shift. Zelevinsky et al. have focused on transitions between the $n = 27$ intermediate level ($n$ being the vibrational quantum number) and “anchor” levels at the bottom and top of the spectrum. Fig. 1 illustrates the basic objective of the experiment. A detected drift in the frequency ratio $R$ (see Figure) is to be interpreted as a drift in the electron-to-proton mass ratio.

Here we investigate the effect of $\alpha$ variation on this promising experiment. The electronic potential depends on $\alpha$ through relativistic effects of electron motion. A variation of $\alpha$ alters the potential and, consequently, the vibrational spectrum supported by it. Thus, a measured drift in $R$ may be due (or partially due) to $\alpha$ variation, threatening misinterpretation of the experimental results.

The experiment described by Zelevinsky et al. is similar in spirit to an experiment posed simultaneously by DeMille et al. [9] to test the stability of $\mu$ using diatomic molecules. A key difference is that, whereas Zelevinsky et al. focus on a single electronic potential, DeMille et al. suggest probing the splitting between vibrational lev-
els supported by different electronic potentials. Recently, we analyzed the influence of \( \alpha \) variation on the experiment of DeMille et al. using a semi-classical (WKB) approach, specifically focusing on the system Cs\(_2\) [10]. We found the experiment to be order-of-magnitude as sensitive to fractional variation in \( \alpha \) as it is to fractional variation in \( \mu \). Considering the anticipated precision of this experiment [9], together with the current laboratory limit on \( \alpha \) variation [3], we concluded that \( \alpha \) variation may not be negligible for the proposed experiment. This finding largely motivated our present work.

II. PRELIMINARY SET-UP

Strictly speaking, only variations in dimensionless quantities have physical meaning. For a given vibrational level \( n \), we will concern ourselves with the normalized energy \( \mathcal{E}_n = \frac{E_n}{D} \), where \( E_n \) is the vibrational energy relative to the bottom of the potential and \( D \) is the potential depth. Clearly, \( \mathcal{E}_n \) is limited to the range \( 0 < \mathcal{E}_n < 1 \). Variations in \( \mu \) and \( \alpha \) induce a shift in \( \mathcal{E}_n \),

\[
\delta \mathcal{E}_n = (\partial_\mu \mathcal{E}_n) \frac{\delta \mu}{\mu} + (\partial_\alpha \mathcal{E}_n) \frac{\delta \alpha}{\alpha},
\]

where we employ the shorthand notation

\[
\partial_\mu \equiv \frac{\partial}{\partial \ln \mu}, \quad \partial_\alpha \equiv \frac{\partial}{\partial \ln \alpha}.
\]

The quantities \( \partial_\mu \mathcal{E}_n \) and \( \partial_\alpha \mathcal{E}_n \) quantify the sensitivity of the vibrational level \( n \) to fractional variations in the electron-to-proton mass ratio and the fine structure constant, respectively.

We could, if desired, regard \( \delta E_n = \delta \mathcal{E}_n \times D \) as an “absolute” energy shift, an association which amounts to arbitrarily assuming the potential depth to be fixed with respect to any variation. Fixing any other energy reference—such as the atomic unit of energy, given by \( \epsilon^4m_e/\hbar^2 = \alpha^3m_e\epsilon^2 \), or the SI unit of energy, which itself references the hyperfine frequency of Cs as well as a platinum-iridium prototype mass held in Paris [11]—would be equally justified and would generally yield a different “absolute” energy shift. Here we actively avoid the possibly slippery notion of absolute energy shift and quote results for \( \partial_\mu \mathcal{E}_n \) and \( \partial_\alpha \mathcal{E}_n \), as these are unambiguously defined.

III. THE MORSE POTENTIAL

The Morse potential represents an idealized electronic potential for a diatomic molecule. It is given by

\[
V(r) = D \left[ 1 - e^{-a(r-r_0)} \right]^2,
\]

where \( r \) is the internuclear separation, with \( r_0 \) being the equilibrium distance, and \( a^{-1} \) is directly related to the width of the potential. The normalized vibrational energies for the Morse potential are given precisely by the formula

\[
\mathcal{E}_n = \epsilon \left( n + \frac{1}{2} \right) - \frac{1}{4} \epsilon^2 \left( n + \frac{1}{2} \right)^2, \tag{1}
\]

where \( \epsilon \equiv \hbar\sqrt{2/DM} \) and \( M \) is the reduced nuclear mass.

From Eq. \( \text{(1)} \) we see that a variation in \( \mathcal{E}_n \) may be attributed solely to a variation in the parameter \( \epsilon \). Specifically, we may write

\[
\delta \mathcal{E}_n = f(\mathcal{E}_n) \frac{\delta \epsilon}{\epsilon} = f(\mathcal{E}_n) \left[ (\partial_\mu \ln \epsilon) \frac{\delta \mu}{\mu} + (\partial_\alpha \ln \epsilon) \frac{\delta \alpha}{\alpha} \right], \tag{2}
\]

where \( f(x) = 2 \left[ x - 1 + \sqrt{1-x} \right] \). The function \( f(x) \) is displayed in Fig. 2. This function modulates the sensitivity of the various levels of the vibrational spectrum to variations in \( \mu \) and \( \alpha \). Notably it approaches zero in the limits \( x \rightarrow 0 \) and \( x \rightarrow 1 \) and has a maximum at \( x = 3/4 \). This translates to minimal sensitivities for the lowest and highest vibrational levels, with the largest sensitivities occurring for levels in the intermediate part of the spectrum.

We may go a step further and, based on physical reasoning, deduce a numerical value for the factor \( (\partial_\mu \ln \epsilon) \) appearing in Eq. \( \text{(2)} \). This is accomplished most transparently by assuming atomic units, though we reiterate that \( \epsilon \) itself is dimensionless. When expressed in atomic units, the molecular potential (and its depth, width, etc.) is independent of the electron-to-proton mass ratio, whereas the reduced mass has a value which is inversely proportional to \( \mu \). From the definition of \( \epsilon \), it follows that \( (\partial_\mu \ln \epsilon) = 1/2 \).

FIG. 2. The function \( f(x) = 2 \left[ x - 1 + \sqrt{1-x} \right] \). For the Morse potential, this function modulates the level sensitivities to both \( \mu \) and \( \alpha \) variation across the vibrational spectrum, with the argument \( x \) taken as \( \mathcal{E}_n \equiv E_n/D \). The most deeply \( (\mathcal{E}_n \rightarrow 0) \) and loosely \( (\mathcal{E}_n \rightarrow 1) \) bound levels are insensitive to variations, while intermediate levels have much larger sensitivities.
In contrast to \((\partial_n \ln \epsilon)\), there is not a simple analytical result for the factor \((\partial_n \ln \epsilon)\). Nevertheless, we may provide a physically reasonable estimate of \((\partial_n \ln \epsilon)\) by realizing that, in atomic units, the electronic potential is independent of \(a\) in the nonrelativistic limit, having relativistic corrections which scale as \((\alpha Z)^2\), with \(Z\) being the nuclear charge number. This suggests that \((\partial_n \ln \epsilon) \sim (\alpha Z)^2\). From this reasoning, we may suspect the vibrational spectrum of \(\text{Sr}_2\) to be nearly as sensitive to \(a\) variation as it is to \(\mu\) variation.

The exercise of this section provides us with useful insight which is applicable to real physical systems. A true potential, of course, is not restricted to the form of a Morse potential. Nevertheless, the function \(f(x)\) displayed in Fig. 2 is expected to give a qualitatively accurate depiction of the sensitivities \(\partial_n \mathcal{E}_n\) and \(\partial_n \mathcal{E}_n\) versus the normalized energy \(\mathcal{E}_n\). In the vicinity of the equilibrium distance, the potential resembles that of a harmonic oscillator. The lower portion of the energy spectrum is then well-described by a single term, proportional to \((n + \frac{1}{2})^2\), in a Dunham-type expansion. Across this region, \(\partial_n \mathcal{E}_n\) vs \(\mathcal{E}_n\) and \(\partial_n \mathcal{E}_n\) versus \(\mathcal{E}_n\) are essentially linear. Approaching the dissociation limit, anharmonic effects become important and the remaining terms in the Dunham expansion, proportional to \((n + \frac{1}{2})^2\), \((n + \frac{1}{2})^3\), etc., then drive the sensitivities back to zero. The fact that the sensitivities approach zero in the limits \(\mathcal{E}_n \rightarrow 0\) and \(\mathcal{E}_n \rightarrow 1\) is a consequence of our choice for the zero of energy (bottom of the potential) and our choice to normalize energy to the dissociation energy.

**IV. AB INITIO CALCULATIONS FOR LEVEL SENSITIVITIES**

We have calculated the \(X^1\Sigma^+\) potential of \(\text{Sr}_2\) using the relativistic computation chemistry program \textsc{dirac10}\cite{12}. In order to reduce computational effort we employed the infinite order two-component relativistic Hamiltonian obtained after the Barysz-Sadlej-Snijders (BSS) transformation of the Dirac Hamiltonian in a finite basis set\cite{12}. This approximation includes both scalar and spin-orbit relativistic effects to infinite order and is one of the most computer time efficient and accurate approximations to the four-component Dirac-Coulomb Hamiltonian. Electron correlation was taken into account using closed-shell single-reference coupled-cluster theory including single, double, and perturbative triple excitations [CCSD(T)]. The Faegri dual family basis set\cite{14} was used, augmented by diffuse and high angular momentum exponents to obtain 21s18p12d6f2g Gaussian orbitals. Virtual orbitals with energies above 45 a.u. were omitted, and the 56 outer core electrons were correlated.

We subsequently fed our CCSD(T) potential curve into a Matlab routine to solve the Schrödinger equation for the nuclear part of the molecular wave function within the Born-Oppenheimer approach. A symmetric three-point finite difference method was applied to obtain the nuclear eigenfunctions together with their corresponding vibrational energies. For the discretization of the internuclear distance a step size of \(7 \times 10^{-3}\) Å was chosen.

We may gauge the accuracy of our \textit{ab initio} method through direct comparison with experimental results of Gerber et al.\cite{15}. These authors have tabulated energies for the \(n = 0\) through \(n = 35\) portion of the \(X^1\Sigma^+_g\) vibrational spectrum. Furthermore, they have determined the dissociation energy of this state to be \(D = 1060(30)\) cm\(^{-1}\). Our computed dissociation energy, \(D = 993\) cm\(^{-1}\), is about 2σ lower than the experimental value. Comparing individual levels, we find that our computed vibrational energies differ from experimental values by no more than 2 cm\(^{-1}\) for levels spanning the lower half of the potential depth (\(n = 0\) through \(n = 15\)). Above this, our computed energies steadily diverge from experiment values, with our values being increasingly smaller in comparison. For example, for \(n = 27\) our computed energy \(E_n = 789\) cm\(^{-1}\) is 3% lower than the experimental value \(E_n = 811\) cm\(^{-1}\), whereas for \(n = 35\) our computed energy \(E_n = 889\) cm\(^{-1}\) is 5% lower than the experimental value \(E_n = 940\) cm\(^{-1}\). This divergence in the upper part of the spectrum is undoubtedly correlated to the fact that our dissociation energy is lower than the experimental dissociation energy.

To see how the normalized energies change with respect to variations in \(\mu\) and \(\alpha\), we recomputed the potential energy curve, as well as the vibrational spectrum supported by it, for various values of \(\mu\) and \(\alpha\) in the neighborhood of \(\mu = 1/1836\) and \(\alpha = 1/137\). The computational chemistry programs assume atomic units; numerical variations in \(\mu\) and \(\alpha\) are effected by modifying parameter values for the reduced mass within our Matlab routine and the speed of light within \textsc{dirac10} \((M = 44\) μ\(^{-1}\) a.u. for 8\(^8\)Sr\(_2\) and \(c = 1/\alpha\) a.u., where a.u. denotes the respective atomic units of mass and velocity). We then obtain the sensitivities \(\partial_\mu \mathcal{E}_n\) and \(\partial_\alpha \mathcal{E}_n\) from numerical differentiation with respect to \(\mu\) and \(\alpha\). We emphasize that our method for obtaining these sensitivities treats variations in \(\mu\) and \(\alpha\) in a similar manner and on equal footing. Figure 3 displays our results for \(\partial_\mu \mathcal{E}_n\) and \(\partial_\alpha \mathcal{E}_n\) for the levels \(n = 0\) through \(n = 35\); these level sensitivities are plotted versus the normalized energy \(\mathcal{E}_n\). We note a behavior which resembles that “predicted” by the Morse potential. Namely, both sensitivity curves approach the appropriate limits for \(\mathcal{E}_n \rightarrow 0\) and \(\mathcal{E}_n \rightarrow 1\), while simultaneously peaking at \(\mathcal{E}_n \approx 3/4\). Moreover, the curves are found to be essentially proportional, with the ratio \(\partial_\alpha \mathcal{E}_n/\partial_\mu \mathcal{E}_n\) being \(0.28\pm0.02\) across the entire range of data (and \(0.28\) at the common maximum of the two curves).

**V. CONCLUSION**

Here we have considered the influence of \(\alpha\) variation on the experiment proposed by Zelevinsky et al.\cite{7,8} to probe variation in the electron-to-proton mass ratio using
the vibrational spectrum of Sr$_2$. The relevant observable in this experiment is the frequency ratio $R$, illustrated in Fig. 1. With one “anchor” level taken at the bottom of the spectrum and another at the top, the frequency ratio is given approximately by

$$R \approx 2\varepsilon_n - 1,$$

where $n$ labels the intermediate level (e.g., $n = 27$ in Fig. 1). Our ab initio computations predict that the frequency ratio $R$ is only 3 to 4 times less sensitive to variation in $\mu$ as it is to variation in $\alpha$. Specifically, we find that variations in $\mu$ and $\alpha$ induce a variation in $R$ according to the relation

$$\delta R = K \left( \frac{\delta \mu}{\mu} + 0.28 \frac{\delta \alpha}{\alpha} \right).$$

Equation (3) summarizes the principle result of this work. The factor $K$ here is given approximately by $K \approx 2 \times \partial_{\mu} \varepsilon_n$; non-zero shifts in the two anchor levels amount to small corrections which reduce $K$ from this value.

As suggested by Eq. (3), a measured drift in the frequency ratio $R$ cannot, by itself, be used to distinguish between $\mu$ variation or $\alpha$ variation. To extract information about variations in the respective constants themselves requires further experimental input. Optical ion clocks have been used to test the stability of $\alpha$, with the ratio of clock frequencies being insensitive to $\mu$ variation. The current best limit on $\alpha$ variation allows for a drift on the fractional level of $4 \times 10^{-17}$/year $^3$. For the proposed experiment of Zelevinsky et al., this result may be used with Eq. (3) to justify neglect of $\alpha$ variation, which has been implicitly assumed in previous works $^{[7,8]}$. On the other hand, for high experimental precision—namely, experimental precision capable of detecting a drift in $\mu$ at the fractional level of $1 \times 10^{-17}$/year—equation $^9$ indicates that $\alpha$ variation should not be neglected. Such high precision is conceivable; in the related proposal of DeMille et al. $^3$, referred to in the Introduction, the authors argued that their method could plausibly detect fractional variations in $\mu$ at $\lesssim 10^{-17}$.

For such high experimental precision, additional experimental input could perhaps be obtained by substituting Sr$_2$ with another species, such as Yb$_2$, in the experiment. Yb has a similar valence structure as Sr and also has isotopes which lack nuclear spin ($^{168,170,172,174,176}$Yb). Moreover, as with Sr, high precision spectroscopy on optically trapped Yb has become a refined art $^{[16,17]}$. From the $(\alpha Z)^2$ scaling of the relativistic corrections to the electronic potential, we may presume that an Yb$_2$ experiment would be about equally sensitive to $\alpha$ variation as to $\mu$ variation, with an estimated sensitivity ratio $0.28 \times (70/38)^2 = 0.95$. Using Sr$_2$ and Yb$_2$ results in conjunction, one could conceivably determine both $\mu$ and $\alpha$ variation to high precision with the proposed experiment of Zelevinsky et al.

VI. ACKNOWLEDGEMENTS

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