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Abstract. Ultracold molecules offer brand new opportunities to probe the variation of fundamental constants with unprecedented sensitivity. This paper summarizes theoretical background and current constraints on the variation of the fine structure constant and electron-to-proton mass ratio, as well as proposals and experimental efforts to measure the variations based on ultracold molecules. In particular, we describe two novel spectroscopic schemes on ultracold molecules that have greatly enhanced sensitivity to fundamental constants: resonant scattering near Feshbach resonances and spectroscopy on close-lying energy levels of ultracold molecules.

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Contents

1. Introduction

Creation of ultracold molecules at temperatures below 1 μK by magnetoassociation [1, 2] or photoassociation [3]–[5] opens exciting prospects to test the variation of fundamental constants on a brand new level. Ultracold molecules offer two major advantages: firstly, the very low temperature allows the molecular samples to be fully polarized in one single quantum state and recent experiments have developed schemes to access any rovibrational and magnetic levels with very high fidelity. Secondly, the success in spatially confining a large number ($>10^4$) of ultracold molecules for a long storage time (>1 s) promises that an extremely high frequency resolution of $<1\,\mathrm{mHz}/\sqrt{\mathrm{Hz}}$ can be reached on molecular transitions. These features make ultracold molecules excellent candidates for performing new generation, very high resolution molecular spectroscopy.

Ultracold molecules can also be prepared in new, exotic regimes, which offer new strategies to measure the variation of fundamental constants. For example, Feshbach spectroscopy, which identifies coupling to weakly bound quantum states in atomic and molecular collisions, can precisely determine the value of the s-wave scattering length [6]. Here, the scattering length near Feshbach resonances can be an extremely sensitive probe on the variation of the electron–proton mass ratio [7]. As a second example, the variation of fundamental constants can also be strongly enhanced when the molecules are radiatively excited to close-lying, narrow energy levels. Several promising cases have been identified in cold molecule systems, including Cs_2 [8] and Sr_2 [9].

In this review paper, we will provide an overview on the experimental proposals for measuring the variation of fundamental constants based on ultracold molecules. As we will show below, molecular energy structure is mostly sensitive to two fundamental dimensionless constants: the fine-structure constant $\alpha = e^2/\hbar c$, which determines the strength of the electroweak interaction. Here $-e$ is the electron charge, $2\pi\hbar$ Planck's constant, and c the speed of light; the second fundamental constant is the electron-to-proton mass ratio $\beta = m_e/m_p$, which characterizes the strength of strong interactions in terms of the electroweak.

At present, NIST lists the following values of these constants [10]: $\alpha^{-1} = 137.035\,999\,679(94)$ and $\beta^{-1} = 1836.152\,672\,47(80)$.

Remarkably, in quantum chromodynamics (QCD) there is a similar coupling constant α_s for strong interaction to α for electroweak interaction. However, because of the highly nonlinear character of the strong interaction, this constant is not well defined. Instead of α_s, the strength of the strong interaction is usually characterized by the parameter Λ_{QCD}, which has the dimension of mass and is defined as the position of the Landau pole in the logarithm for the strong coupling constant, $\alpha_s(r) = C/\ln(r\,\Lambda_{QCD}/\hbar c)$, where C is a constant and r is the distance between two interacting particles.

In the Standard Model (SM), there is another fundamental parameter with the dimension of mass—the Higgs vacuum expectation value (VEV), which determines the electroweak unification scale. The electron mass m_e and quark masses m_q are proportional to the Higgs VEV. Consequently, the dimensionless parameters $X_e = m_e/\Lambda_{QCD}$ and $X_q = m_q/\Lambda_{QCD}$ link the electroweak unification scale with the strong scale. For the light quarks u and d, $X_q \ll 1$. Because of that, the proton mass m_p is proportional to Λ_{QCD} and $X_e \propto \beta$. Below we will use β instead of X_e because it is more directly linked to the observables in atomic and molecular experiments.

We begin by reviewing the theory and the state of the art of the search for the variation of α and β. Next, we discuss, in some detail, the dependence of molecular energy structure on α and β. Finally, we describe possible laboratory experiments with ultracold molecules on time-variation. Such experiments are a novelty, and the laboratory results obtained so far are not yet competitive. However, there are proposals for significant improvements, and several groups have already started implementing them.

2. Theoretical motivation

How might the variation of the physical constants and the violation of the local position invariance come about? Light scalar fields very naturally appear in modern cosmological models, affecting parameters of the SM including α and β (for the whole list of SM parameters see [11]). Cosmological variations of these scalar fields are, in turn, expected to take place because of the drastic changes in the composition of the Universe during its evolution.

Theories unifying gravity and other interactions suggest the possibility of spatial and temporal variation of physical 'constants' in the Universe [12]. Moreover, there exists a mechanism for making all coupling constants and masses of elementary particles both space- and time-dependent, and influenced by the local environment (see review [13]). Variation of the coupling constants could be nonmonotonic, such as, e.g. damped oscillations.

These variations are usually associated with the effect of massless (or very light) scalar fields. One such field is the dilaton: a scalar that appears in string theories together with the graviton, in a massless multiplet of closed-string excitations. Other scalars naturally appear in those cosmological models in which our Universe is a 'brane' floating in a space of a larger dimension. The scalars are simply brane coordinates in extra dimensions. However, the only relevant scalar field recently discovered, the cosmological dark energy, so far does not show visible variations. Observational limits on the variation of the physical constants given in section 3 are quite stringent, allowing only for scalar couplings, which are smaller than or, in a new class of 'chameleon-type models', comparable to gravity [14]. Preliminary observations suggest that there may be space variation of β at the level of $\delta\beta/\beta \sim 10^{-8}$ [15].

A possible explanation of the small observed variation was suggested by Damour *et al* [16, 17], who pointed out that cosmological evolution of scalars naturally leads to their self-decoupling. Damour and Polyakov [17] have further suggested that the variations should take place when the scalars become excited by some physical change in the Universe, such as phase transitions, or by other drastic changes in the equation of state of the Universe. They considered several phase transitions, but since the publication of their paper a new transition has been discovered, one from a matter dominated (decelerating) era to a dark-energy dominated (accelerating) era. This transition is a relatively recent event, corresponding to a cosmological redshift $z \approx 0.5$, or a look-back time of approximately five billion years.

The time dependence of the perturbation related to the transition from the decelerating to the accelerating era could be calculated [18, 19]. The calculation shows that the self-decoupling process is effective enough to explain why *after* this transition the variation of the constants is as small as observed in the present-time laboratory experiments: for α, see [29] and, for β, see [30]. However, the calculated time dependence is also consistent with the observations of the variation of the proton-to-electron mass ratio and the electromagnetic fine-structure constant at $z \geqslant 1$ [20]–[22].

3. Current constraints on the variation of α and β

The analysis of the data from the Big Bang nucleosynthesis [23], quasar absorption spectra and the Oklo natural nuclear reactor yields the space–time variation of the constants on the timescale of the lifetime of the Universe, i.e. from a few billion to more than ten billion years. In comparison, the frequencies of different atomic and molecular transitions in the laboratory experiments yield a time variation on the timescale from a few months to a few years. There is no model-independent connection between the variations on such different timescales. However, in order to compare the astrophysical and laboratory results, we often assume a linear time dependence of the constants. In this way, we can interpret all the results in terms of the time derivatives of the fundamental constants. Within this assumption, we can use the quasar absorption spectra to obtain the best current limit on the variation of the mass ratio β and of X_e, [24, 25]

$$\dot{\beta}/\beta = \dot{X}_e/X_e = (-1.2 \pm 1.4) \times 10^{-16}\,\mathrm{yr}^{-1}. \tag{1}$$

Combining this result with the atomic clock results [44], one can obtain upper bounds on the variation of α [26]–[28]. The best upper bound on the variation of α is provided by the single-ion optical clock experiments as [29]

$$\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17}\,\mathrm{yr}^{-1}. \tag{2}$$

The measurements at the Oklo natural reactor provide the best bound on the variation of $X_s = m_s/\Lambda_{QCD}$, where m_s is the strange quark mass [31]–[33],

$$|\dot{X}_s/X_s| < 10^{-18}\,\mathrm{yr}^{-1}. \tag{3}$$

Note that the Oklo data cannot yield any bound on the variation of α since the effect of α there is much smaller than the effect of X_s and should be neglected within the accuracy of the present theory [33].

4. Dependence of atomic and molecular spectra on α and β

Atomic and molecular spectra are most naturally described in atomic units ($\hbar = m_e = e = 1$), with the energy measured in Hartrees ($1\,\text{Hartree} = e^4 m_e/\hbar^2 = 2\,\text{Rydberg} = 219\,474.631\,3705(15)\,\text{cm}^{-1}$). In these units, the nonrelativistic Schrödinger equation for an atom with an infinitely heavy pointlike nucleus does not include any dimensional parameters. The dependence of the spectrum on α appears only through relativistic corrections, which describe the fine structure, the Lamb shift, etc. The dependence of atomic energies on β is known as the isotope effect and is caused by a finite nuclear mass and volume. There are even smaller corrections to atomic energies, which depend on both α and β and are known as the hyperfine structure.

One could argue that the atomic energy unit itself depends on α as it can be expressed as $\alpha^2 m_e c^2$, with $m_e c^2$ the rest energy of a free electron. However, an experimental search for a possible variation of the fundamental constants relies on the observation of the time-variations of the ratios of different transition frequencies to one another. In such ratios, the dependence of the units on the fundamental constants cancels out. Below we will use atomic units unless stated otherwise.

The relativistic corrections to the binding energies of the atomic valence electrons are of the order of $\alpha^2 Z^2$, where Z is the atomic number, and become quite large for heavy elements. For our purposes, it is convenient to consider the dependence of the atomic transition frequencies on α^2 in the form

$$\omega = \omega_0 \left(1 + \frac{K}{2} x\right), \tag{4}$$

where $x = (\alpha/\alpha_0)^2 - 1 \approx 2\delta\alpha/\alpha$ and ω_0 is a transition frequency for $\alpha = \alpha_0$. Rough estimates of the enhancement factor $K = \delta(\log\omega)/\delta(\log\alpha)$ can be obtained from simple one-particle models, but in order to obtain accurate values one has to account for electronic correlations via large-scale numerical calculations. Recently, such calculations have been carried out for many atoms and ions [34]–[41].

Isotope effects in atoms are of the order of $\beta \sim 10^{-3}$ and the magnetic hyperfine structure roughly scales as $\alpha^2 \beta Z g_{\text{nuc}} \sim 10^{-7} Z g_{\text{nuc}}$, where g_{nuc} is nuclear g-factor. One has to keep in mind that g_{nuc} depends on the quark parameters X_q. This dependence has to be considered when comparing, e.g. the frequency of the hyperfine transition in ^{133}Cs (Cs frequency standard) [26] or the hydrogen 21 cm hyperfine line [42, 43] with various optical transitions [26]. At present, there are many very accurate experiments comparing different optical and microwave atomic clocks [29, 30], [44]–[53]. A detailed discussion of the atomic experiments can be found in recent reviews [54, 55].

Molecular spectroscopy opens additional possibilities to study the variation of fundamental constants. It is known that β defines the scales of electronic, vibrational, and rotational intervals in molecular spectra, $E_{\text{el}} : E_{\text{vib}} : E_{\text{rot}} \sim 1 : \beta^{1/2} : \beta$. In addition, molecules have fine and hyperfine structures, Λ-doubling, hindered rotation, etc. All these effects have different dependences on the fundamental constants.

The sensitivity to temporal variation of the fundamental constants may be strongly enhanced in coupling between molecular levels and continuum, as well as transitions between narrow close-lying levels of different types.

In the following, we describe selected cases to illustrate the potential of ultracold molecules in probing the constants: scattering lengths of ultracold atomic and molecular collisions, narrow

close-lying levels of diatomic molecules and the proposed experiment with ultracold Cs_2 and Sr_2 molecules. Enhancement of the relative variation $\delta\omega/\omega$ can also occur in transitions between nearly degenerate levels of atoms [34, 35, 37, 56, 57], thermal molecules [8, 24], [58]–[60] and nuclei [61, 62].

5. Enhanced sensitivity of scattering length on β in ultracold atomic and molecular collisions near Feshbach resonances

An interesting case of the enhancement of the effect of the variation of fundamental constants arises in collisions of ultracold atoms and molecules near Feshbach resonances [7]. In cold collisions, scattering phase shift ϕ is very sensitive to the change of the electron–proton mass ratio β. This dependence can be understood as ϕ depends on the ratio of the molecular potential V and the atomic mass $m_{\rm at}$, namely, $\phi \propto (V/m_{\rm at})^{1/2}$. Since the molecular potential V is predominately electronic and the atomic mass is essentially baryonic, we have $\phi \sim (V/m_{\rm at})^{1/2} \sim (m_{\rm e}/m_{\rm p})^{1/2} \sim \beta^{1/2}$. A model potential calculation shows that, among other cold collisions properties, scattering length A can be extremely sensitive to β. A fractional variation of β can be amplified to a change of A according to:

$$\frac{\delta A}{A} = K\frac{\delta\beta}{\beta}, \tag{5}$$

where the enhancement factor $K = \delta(\log A)/\delta(\log\beta)$ can be as large as $10^9 \sim 10^{12}$ near narrow or optical Feshbach resonances. The enhancement results from the resonance character of the scattering length near the pole and the increased sensitivity to probe Feshbach molecular states with different spin symmetry and thus different dependence on β [7]. Currently, the best measurement on the scattering length has an uncertainty of 10^{-4}, which can potentially probe the variation of β on the level of $10^{-13} \sim 10^{-16}$.

Recently, the Gibble group at Penn State University demonstrated that an atomic-clock-type experiment can determine the scattering phase shift with very high precision [63]. They concluded that 1 ppm (10^{-6}) measurement on the scattering length can be reached [63]. If such a measurement is performed near narrow Feshbach resonances in two consecutive years, variation of β can be probed on the level of 10^{-15}–$10^{-18}\,{\rm yr}^{-1}$.

Note that the calculation of the factor K in [7] is based on the analytic formula for the scattering length derived in [64]. This formula is valid for an arbitrary interatomic potential with an inverse-power long-range tail ($-C_6/r^6$ for neutral atoms, where C_6 is the van der Waals potential constant and r is the atomic separation), i.e. it includes all anharmonic corrections.

To the best of our knowledge, this is the only suggested experiment on time-variation where the observable is not a frequency. However, another parameter, L, with the dimension of length is needed to compare A with and thus render it dimensionless. In [7], the scattering length was defined in atomic units (a_B). It is important, however, that because of the large enhancement in equation (5), the possible dependence of L on β becomes irrelevant. For example, if we measure A in conventional units, meters, which are linked to the Cs standard, then $\delta L/L = -\delta\beta/\beta$, and

$$\frac{\delta(A/L)}{(A/L)} = (K+1)\frac{\delta\beta}{\beta}. \tag{6}$$

As long as $K \gg 1$, the dependence of the units used on the fundamental constants can be neglected. Below, we discuss several other experiments with huge enhancement factors, where this argument can also be applied.

6. Narrow close-lying levels of diatomic molecules

In this section, we focus on narrow close-lying levels of varying nature in diatomic molecules. Such levels may occur due to the cancelation between either hyperfine and rotational structures [58], or between the fine and vibrational structures within the electronic ground state [60]. The intervals between the levels correspond to microwave frequencies, which are experimentally accessible, and have narrow linewidths, typically $\sim 10^{-2}$ Hz. The enhancement of the relative variation K can exceed 10^5 in such cases. Practically, molecular transitions with weak dependence on external fields are particularly favorable candidates.

6.1. Molecules with cancelation between hyperfine structure and rotational intervals

Consider diatomic molecule with the $^2\Sigma$ ground state (one unpaired electron). Examples of such molecules include LaS, LaO, LuS, LuO and YbF [65]. The hyperfine interval $\Delta_{\rm hfs}$ is proportional to $\alpha^2 Z F_{\rm rel}(\alpha Z)\beta g_{\rm nuc}$, where $F_{\rm rel}$ is an additional relativistic (Casimir) factor [66]. The rotational interval $\Delta_{\rm rot} \propto \beta$ is approximately independent of α. If we find a molecule with $\Delta_{\rm hfs} \approx \Delta_{\rm rot}$, the splitting ω between hyperfine and rotational levels will depend on the following combination:

$$\omega \propto \beta \left[\alpha^2 F_{\rm rel}(\alpha Z)\, g_{\rm nuc} - \text{const}\right]. \tag{7}$$

The relative variation is then given by

$$\frac{\delta\omega}{\omega} \approx \frac{\Delta_{\rm hfs}}{\omega}\left[(2+K)\,\frac{\delta\alpha}{\alpha} + \frac{\delta g_{\rm nuc}}{g_{\rm nuc}}\right] + \frac{\delta\beta}{\beta}, \tag{8}$$

where the factor K comes from the variation of $F_{\rm rel}(\alpha Z)$ and for $Z \sim 50$, $K \approx 1$. As long as $\Delta_{\rm hfs}/\omega \gg 1$, we can neglect the last term in equation (8).

Data on the hyperfine structure of diatomics are hard to come by and usually not very accurate. Using the data from [65], one can find that $\omega = (0.002 \pm 0.01)\,\text{cm}^{-1}$ for $^{139}\text{La}^{32}\text{S}$ [58]. Note that for $\omega = 0.002\,\text{cm}^{-1}$, the relative frequency shift is

$$\frac{\delta\omega}{\omega} \approx 600\,\frac{\delta\alpha}{\alpha}. \tag{9}$$

As new data on molecular hyperfine constants become available, it is likely that other molecular candidates with the cancelation effect will be found.

6.2. Molecules with cancelation between fine-structure and vibrational intervals

The fine-structure interval, $\omega_{\rm f}$, increases rapidly with the nuclear charge Z:

$$\omega_{\rm f} \sim Z^2\alpha^2, \tag{10}$$

In contrast, the vibrational energy quantum decreases with the atomic mass

$$\omega_{\rm vib} \sim M_{\rm r}^{-1/2}\beta^{1/2}, \tag{11}$$

where the reduced mass for the molecular vibration is $M_{\rm r}m_{\rm p}$. Therefore, we obtain an equation $Z = Z(M_{\rm r}, v)$ for the spectral lines at fixed $Z, M_{\rm r}$ where we can expect an approximate cancelation between the fine-structure and vibrational intervals:

$$\omega = \omega_{\rm f} - v\,\omega_{\rm vib} \approx 0, \quad v = 1, 2, \ldots\ . \tag{12}$$

Using equations (10)–(12), it is easy to find the dependence of the transition frequency on the fundamental constants

$$\frac{\delta\omega}{\omega} = \frac{1}{\omega}\left(2\omega_{\rm f}\frac{\delta\alpha}{\alpha} + \frac{v}{2}\omega_{\rm vib}\frac{\delta\beta}{\beta}\right) \approx K\left(2\frac{\delta\alpha}{\alpha} + \frac{1}{2}\frac{\delta\beta}{\beta}\right), \tag{13}$$

where the enhancement factor, $K = \omega_{\rm f}/\omega$, is due to the relative frequency shift for a given change of the fundamental constants. Large values of the factor K are experimentally favorable, as the correspondingly large relative shifts can be more easily detected. However, large value of K do not always guarantee a more sensitive measurement. In some cases of quasi-degenerate levels, this factor may become irrelevant [56]. Thus, it is also important to consider the absolute values of the shifts and compare them with the linewidths of the transitions in question.

Assuming $\delta\alpha/\alpha \sim 10^{-17}$ and $\omega_{\rm f} \sim 500\,{\rm cm}^{-1}$, we obtain $\delta\omega \sim 10^{-14}\,{\rm cm}^{-1} \sim 3\times 10^{-4}\,{\rm Hz}$. In order to obtain a similar sensitivity from a comparison of the hyperfine transition frequencies of Cs or Rb, one would have to measure the shifts with an accuracy of $\sim 10^{-7}\,{\rm Hz}$. Note that the narrow close levels discussed here exist, for example, in the molecular ion Cl_2^+ and in the molecule SiBr [59].

7. Proposed experiments with Cs_2 and Sr_2

In this section, we discuss two recently proposed experiments with cold diatomic molecules, one with Cs_2 at Yale [8, 67] and one with Sr_2 at JILA [9].

The Yale experiment is based on the idea described in [8] to match the electronic energy with a large number of vibrational quanta. The difference compared with equations (10)–(12) is that here the electronic transition is between a $^1\Sigma_{\rm g}^+$ ground state and a $^3\Sigma_{\rm u}^+$ excited state and thus, to the first approximation, its frequency is independent of α. The energy of this transition is about $3300\,{\rm cm}^{-1}$ and the number of the vibrational quanta needed to match it is of the order of 100. For the vibrational quantum number $v \sim 100$, the density of the levels is high due to the anharmonicity of the potential and hence it is possible to find two nearby levels belonging to two different potential energy curves. This leads to an enhanced sensitivity to variation of β, as in equation (12). Cold Cs_2 molecules in a particular quantum state can be produced by the photoassociation of cold Cs atoms in a trap.

Let us estimate the sensitivity of this proposed experiment to the variation of α and β. If we neglect the anharmonicity, we can write the transition frequency between the closely spaced vibrational levels of the two electronic terms as

$$\omega = \omega_{\rm el,0} + qx + \left(v_2 + \frac{1}{2}\right)\omega_{\rm vib,2} - \left(v_1 + \frac{1}{2}\right)\omega_{\rm vib,1}, \tag{14}$$

where $v_2 \ll v_1$. The dependence of this frequency on α and β is given by

$$\delta\omega \approx 2q\frac{\delta\alpha}{\alpha} - \frac{\omega_{\rm el,0}}{2}\frac{\delta\beta}{\beta}, \tag{15}$$

where we made use of the inequality $\omega \ll \omega_{\rm el,0}$. For the ground state of atomic Cs, the q-factor is about $1100\,{\rm cm}^{-1}$, which is close to $(1/4)\alpha^2 Z^2 E_{6s}$, where E_{6s} is the ground-state binding energy. If we assume that the same relation holds for the electronic transition in the molecule, we obtain $|q| \sim (1/4)\alpha^2 Z^2 \omega_{\rm el,0} \sim 120\,{\rm cm}^{-1}$. Using this rough estimate and equation (15) we have (in ${\rm cm}^{-1}$)

$$\delta\omega \approx -240\frac{\delta\alpha}{\alpha} - 1600\frac{\delta\beta}{\beta}, \tag{16}$$

where we assumed that the relativistic corrections reduce the dissociation energy of the molecule, as a result of which q is negative. This estimate shows that the experiment with Cs_2 is mostly sensitive to the variation of β.

As noted above, for high vibrational states, the potential is highly anharmonic. This significantly decreases the sensitivity as estimated by equation (16). This can be seen either from the Wentzel–Kramers–Brillouin (WKB) approximation [8, 67], or from an analytic solution for the Morse potential [9]. The quantization condition for the vibrational spectrum in the WKB approximation

$$\int_{R_1}^{R_2} \sqrt{2M(U(r)-E_n)}\,\mathrm{d}r = \left(v+\frac{1}{2}\right)\pi \tag{17}$$

yields, by differentiation with respect to β, the following result:

$$\delta E_v = \frac{v+\frac{1}{2}}{2\rho(E_v)}\frac{\delta\beta}{\beta}\,, \tag{18}$$

where $\rho(E_v) \equiv (\partial E_v/\partial v)^{-1} \approx (E_v - E_{v-1})^{-1}$ is the level density. For the harmonic part of the potential, $\rho = \text{const}$ and the shift δE_v increases linearly with v, but for vibrational states near the dissociation limit, the level density $\rho(E) \longrightarrow \infty$ and $\delta E_v \longrightarrow 0$. Consequently, the maximum sensitivity $\sim 1000\,\mathrm{cm}^{-1}$ is reached at $v \approx 60$, and rapidly drops for higher v. The Yale group has found a conveniently close vibrational level of the upper $^3\Sigma_u$ state with $v = 138$. The sensitivity for this level is, however, only $\sim 200\,\mathrm{cm}^{-1}$ [67]. There are still good prospects for finding other close-lying levels with smaller v, for which the sensitivity may be several times higher.

The sensitivity as given by equation (16) towards the variation of α is also reduced by the anharmonicity of the potential. For the highest vibrational levels of the electronic ground state as well as for all levels of the upper (weakly bound) electronic state, the separation between the nuclei is large, $R \approx 12$ au. Thus, both electronic wave functions are close to either symmetric (for $^1\Sigma_g^+$) or antisymmetric combination (for $^3\Sigma_u^+$) of the atomic $6s$ functions,

$$\Psi_{g,u}(r_1, r_2) \approx \frac{1}{\sqrt{2}}\left(6s^a(r_1)6s^b(r_2) \pm 6s^b(r_1)6s^a(r_2)\right). \tag{19}$$

As a result, all the relativistic corrections are (almost) the same for both electronic states.

The deleterious effect of the anharmonicity on the sensitivity to the variation of β and α can also be obtained from the analysis of the Morse potential. Its eigenvalues are given by

$$E_v = \omega_0\left(v+\frac{1}{2}\right) - \frac{\omega_0^2(v+\frac{1}{2})^2}{4d} - d, \tag{20}$$

with $\omega_0 = 2\pi a\sqrt{2d/M}$ and d the dissociation energy. The last eigenvalue E_N is found from the conditions $E_{N+1} \leqslant E_N$ and $E_{N-1} \leqslant E_N$. Clearly, E_N is very close to zero and is independent of β and α and thus of their variation.

We note that the highest absolute sensitivity can be expected for vibrational levels in the middle of the potential energy curve. However, in this part of the spectrum, there are no close-lying levels of a different state that would allow to maximize the relative sensitivity $\delta\omega/\omega$. Zelevinsky *et al* [9] proposed to measure molecular transition with the highest sensitivity to β using a frequency comb. In the proposed experiment, an optical lattice is used to trap Sr_2 molecules formed in one of the uppermost vibrational levels of the ground electronic states by photoassociation. In the next step, a Raman transition is proposed to create molecules in one

of the most sensitive levels in the middle of the potential well. To minimize light shifts on the relevant transition, the optical lattice is formed by a laser operated at the 'magic' wavelength [9]. Sensitivity to the external magnetic field can also be greatly reduced by choosing molecular levels with identical magnetic moment.

The frequency comb scheme offers the highest possible absolute sensitivity for a given molecule. Unfortunately, the dissociation energy of Sr_2 is only about $1000\,cm^{-1}$, which is three times smaller than that of Cs_2. Consequently, the highest sensitivity for the Sr_2 molecule occurs at about $270\,cm^{-1}$, i.e. only slightly higher than for the $v = 138$ level in Cs_2. Therefore, it may be useful to try to apply this scheme to another molecule with a larger dissociation energy. Finally, we note that the sensitivity to α-variation in the Sr_2 experiment is additionally reduced by a factor $(55/38)^2 \approx 2$ because of the smaller Z.

8. Conclusions

Astrophysical observations of the spectra of diatomic and polyatomic molecules can reveal a possible variation of the electron-to-proton mass ratio β on a timescale from 6 to 12 billion years. However, the astrophysical results obtained so far are inconclusive. Much the same can be said about the astrophysical search for an α-variation.

The use of cold molecules holds promise to dramatically enhance the sensitivity of molecular experiments. An example is the scattering length in cold collisions of atoms and molecules near narrow Feshbach resonances, which can have a surprisingly high sensitivity to the variation of β [7]. Measurement of scattering phase shift in atomic-clock-type experiments [63] can potentially test the fractional variation of β on the level of 10^{-15}–$10^{-18}\,yr^{-1}$.

Preliminary spectroscopic experiments with ultracold Cs_2 molecules have been recently performed at Yale [67]. The electronic transition between the $^3\Sigma_u^+$ and $^1\Sigma_g^-$ states of Cs_2 is independent, to the first approximation, of α. On the other hand, the sensitivity to β-variation may be enhanced because of the large number of vibrational quanta needed to match the electronic transition. However, the anharmonicity of the potential suppresses this enhancement for very high vibrational levels near the dissociation limit. As a result, the sensitivity to the variation of β for the $v = 138$ level is about the same as that given in equation (13). It is possible that there are other close-lying levels with smaller vibrational quantum number which, consequently, would allow for a higher sensitivity. Even if such levels are not found, the experiment with the $v = 138$ level may improve the current limit on the time-variation of β by several orders of magnitude.

An experiment with the Sr_2 molecule has been recently proposed at JILA [9]. This experiment has a similar sensitivity to the time-variation of β as the experiment with Cs_2; these experiments are complementary to the experiments with molecular radicals, which are mostly sensitive to the time-variation of α [60].

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