

Nuclear matter radii from molecular rotations using ultra-high-resolution spectroscopy

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The rotational constant parametrizes the relative spacing between a molecule's rotational energy levels. It depends on the molecule's classical moments of inertia, which, in all studies, are expressed by treating the constituent nuclei as point masses separated by the bond length. We point out that treating the finite nuclear size leads to a correction to the rotational constant at the hertz level, which is resolvable with recently developed ultra-high-resolution molecular spectrometers. Nuclear-model-independent measurements of nuclear matter radii can thus be envisioned in the future using such apparatuses, advancing beyond the existing hadronic scattering experiments and further developing the intersection of nuclear and molecular physics. At the present time, it appears that the computational ability of *ab initio* quantum chemistry might be the limiting factor to the technical readiness of the approach. To test the premises of the proposed method, we call for benchmark experiments using HD^+ that are feasible with state-of-the-art experiment and theory.

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I. INTRODUCTION

Molecules are composed of two or more atoms joined by chemical bonds that couple the motion of the constituent nuclei. Even diatomic molecules, which have the simplest geometry, possess vibrational and rotational degrees of freedom. As a result, their spectra exhibit a vibrational structure for each electronic level and a rotational structure within each vibrational sublevel of each electronic level.

The rotational spectra of diatomic molecules have been extensively studied for more than a century [1], and it is well understood that the spacing between successive lines in a rotational spectrum is intimately linked to the moments of inertia of the molecule. Invariably, the point-nucleus approximation is used to express the molecular moments of inertia and thus to extract the rotational constants [1–4]. This approximation is certainly justified due to the large difference in scale between nuclear radii ($\sim 10^{-15}$ m) and the internuclear distance in a typical diatomic molecule ($\sim 10^{-10}$ m). Corrections due to treating the finite nuclear size can thus be expected to be extremely small and so far are considered negligible.

In the last few years, however, advances in microwave and infrared spectrometers with unprecedented resolution [5] and absolute accuracy [6] have been constructed and are capable of determining transition energies and thus rotational

constants with subhertz precision and kilohertz accuracy. Moreover, trap-based laser spectroscopy of light molecular ions has also demonstrated the control of statistical and systematic errors at the subkilohertz level [7,8]. Therefore, it is necessary to revisit the point-nucleus approximation in the molecular moment of inertia and consider the correction due to the full treatment of the finite nuclear size.

In light of these recent technical developments, here we point out that the emergent technology in molecular spectroscopy is sensitive to the matter radii of the constituent nuclei. We first provide the expression for the rotational constant in diatomic molecules where the constituent nuclei are treated as spheres of finite size. Given the resulting expression, we discuss how measurements of nuclear matter radii can be performed via ultra-high-resolution rotational spectroscopy of diatomic molecules with state-of-the-art and next-generation spectroscopic techniques. Compared to the existing and established experimental methods for measurements of the nuclear matter radius, the proposed approach offers a nuclear-model-independent determination of nuclear matter radii, with potentially higher precision and significantly smaller isotope-dependent systematic uncertainties.

II. MOLECULAR ROTATIONS

Depending on the size of the diatomic molecule, pure rotational spectra, which are composed of transitions between rotational levels within the same electronic-vibrational state, are observed between the microwave and millimeter-wave regions of the electromagnetic spectrum. The rotational lines of a diatomic molecule, characterized by the rotational quantum number J , follow a characteristic, diverging pattern at first order, which is given by the expression [1–3]

$$E(J) = B_v J(J + 1), \quad (1)$$

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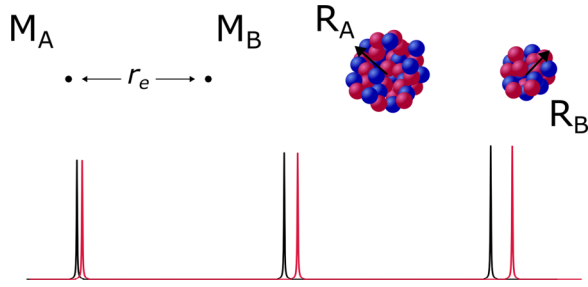


FIG. 1. Top: Conceptual comparison between a point-nucleus representation (left) and a finite-nucleus representation (right) of a diatomic molecule. Bottom: Schematic effect of a change in the rotational constant on the relative spacing of three successive rotational lines.

where B_v is called the rotational constant and generally shows a dependence on the vibrational quantum number v . A schematic example of the effect of changes in the rotational constant on the spacing of rotational lines is shown in Fig. 1. The values of the rotational constant for different values of v are related to an *equilibrium* rotational constant B_e through the expression [2]

$$B_v = B_e - \alpha_e(v + \frac{1}{2}), \quad (2)$$

where α_e is a constant that depends on the parameters of the Morse potential in the vibrational term of the molecular Hamiltonian [2] and B_e has the form

$$B_e = \frac{h}{8\pi^2 c I_e}. \quad (3)$$

In Eq. (3), I_e is the equilibrium moment of inertia. That is, the moment of inertia of the molecule assuming that the constituent nuclei are placed at a fixed distance from each other that is equal to the equilibrium bond length r_e .

In the point-nucleus approximation, the two nuclear masses M_A and M_B have an infinitely small radius and are separated by a distance r_e . Therefore, the point-nucleus moment of inertia is expressed as $I_e^p = \mu r_e^2$, where μ is the reduced molecular mass $\mu = \frac{M_A M_B}{M_A + M_B}$ and thus

$$B_e^p = \frac{h}{8\pi^2 c \mu r_e^2} \quad (4)$$

is the rotational constant for the point-nucleus case.

To arrive at the molecular moment of inertia when treating the nuclei as spheres of radius R_A and R_B , the parallel axis theorem can be used. Consider nucleus A as placed at a distance d_A from the center of mass of the molecule and nucleus B as placed at a distance d_B . Due to the symmetry of a diatomic molecule, the molecular center of mass will lie along the internuclear axis, and by the definition of the bond length, $r_e = d_A + d_B$.

The moment of inertia of a solid sphere about any axis going through its center is

$$I_{\text{sphere}} = \frac{2}{5}MR^2, \quad (5)$$

where M is the sphere's mass and R is its radius. From the parallel axis theorem, the moment of inertia of a solid sphere

about an axis at a distance d from its center is

$$I = I_{\text{sphere}} + Md^2. \quad (6)$$

For two nuclei rotating about the same axis in the same direction, the total moment of inertia of the molecule is equal to the sum of the moments of inertia of the nuclei. Therefore, using Eqs. (5) and (6), the moment of inertia of the diatomic molecule is

$$\begin{aligned} I_e^s &= \frac{2}{5}M_A R_A^2 + M_A d_A^2 + \frac{2}{5}M_B R_B^2 + M_B d_B^2 \\ \Leftrightarrow I_e^s &= \frac{2}{5}(M_A R_A^2 + M_B R_B^2) + M_A d_A^2 + M_B d_B^2. \end{aligned} \quad (7)$$

The last two terms are equivalent to the point-nucleus moment of inertia I_e^p . This can be seen by considering the molecule's center of mass as defining the zero coordinate of the internuclear axis. The locations of nuclei A and B are thus

$$d_A = -\frac{M_B r_e}{M_A + M_B}, \quad (8)$$

$$d_B = \frac{M_A r_e}{M_A + M_B}. \quad (9)$$

Therefore,

$$\begin{aligned} M_A d_A^2 + M_B d_B^2 &= \frac{M_A M_B^2 r_e^2}{(M_A + M_B)^2} + \frac{M_B M_A^2 r_e^2}{(M_A + M_B)^2} \\ &= \frac{M_A M_B M_B + M_B M_A M_A}{(M_A + M_B)^2} r_e^2 \\ &= \frac{M_A M_B (M_A + M_B)}{(M_A + M_B)^2} r_e^2 = \frac{M_A M_B}{M_A + M_B} r_e^2, \end{aligned}$$

and thus,

$$M_A d_A^2 + M_B d_B^2 = \mu r_e^2. \quad (10)$$

Equation (7) is therefore equal to

$$I_e^s = \frac{2}{5}(M_A R_A^2 + M_B R_B^2) + I_e^p \quad (11)$$

At the point-nucleus limit, where $R_A = R_B = 0$, $I_e^s = I_e^p$, as expected. The equilibrium rotational constant for a diatomic molecule can thus be expressed as

$$B_e = \frac{h}{8\pi^2 c} \frac{1}{\frac{2}{5}(M_A R_A^2 + M_B R_B^2) + \mu r_e^2}. \quad (12)$$

III. NUCLEAR MATTER RADII

As per Eq. (11), the moment of inertia of a diatomic molecule when treating the finite nuclear size has a correction that depends on the constituent nuclear masses and radii. Figure 2 shows how the correction scales as a function of the equilibrium bond length r_e for three diatomic molecules with different masses. Evidently, the correction to the rotational constant, quantified as the difference between the point-nucleus and finite-nucleus rotational constants B_e^p and B_e^s , is on the order of a few tens of hertz for both the lightest possible molecule (H_2) and the actinide molecule ThF^+ .

With subkilohertz resolution, the state of the art in molecular spectroscopy is already capable of determining the rotational constants of diatomic molecules with hertz- or subhertz-level uncertainty, and further improvements can be expected in the future. Therefore, it is worthwhile considering

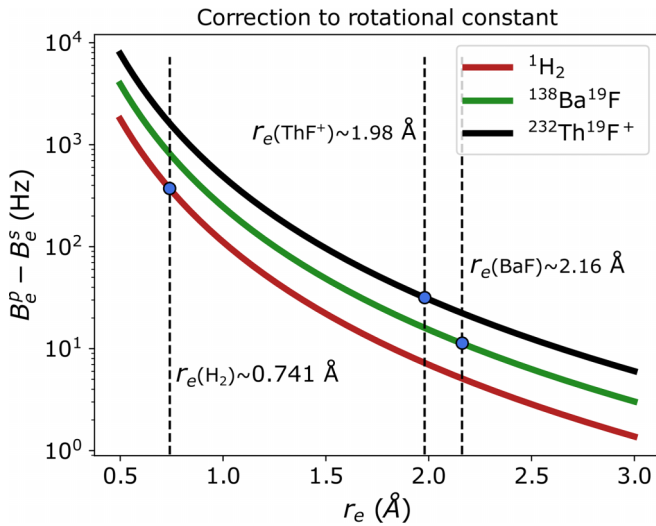


FIG. 2. Calculation of the correction (in Hz) to the rotational constant due to treating the finite size of the nuclei as opposed to the point-nucleus approximation. The nuclear matter radii used to calculate the corrections were approximated as being equal to the charge radii and taken from Ref. [9]. Nuclear masses were taken from the 2020 Atomic Mass Evaluation [10], and equilibrium bond lengths were taken from the NIST Chemistry WebBook.

how such precision can be utilized to measure nuclear matter radii.

The size of a nucleus is most often discussed in terms of two observables; the mean-square nuclear charge radius $\langle r^2 \rangle_{\text{ch}}$, which is determined solely by the proton distribution, and the mean-square nuclear matter radius $\langle r^2 \rangle_{\text{m}}$, which is determined by both the proton and neutron distributions.

The charge radius can be measured through a variety of complementary experimental techniques. Muonic-atom x-ray spectroscopy [11] and electron scattering experiments [12,13] have provided measurements of the absolute nuclear charge radii of stable isotopes for decades [9]. Laser spectroscopy, on the other hand, provides high-precision measurements of the relative change in the root-mean-square (rms) nuclear charge radius between isotope pairs in a nuclear-model-independent manner, through the isotope shift [14]. By combining absolute measurements in stable isotopes and relative measurements in radioactive isotopes, the charge radii of a great number of nuclei far from nuclear stability have been measured [15]. The study of nuclear charge radii has thus become a cornerstone of modern nuclear structure research, pursued to investigate the emergence of new magic numbers [16,17], the disappearance and inversion of odd-even staggering [18,19], signatures of rare nuclear effects [20], and more. Recently, muonic-atom and electron scattering experiments on radioactive isotopes were demonstrated for the first time [21,22], opening a new pathway towards absolute charge radius determination in unstable nuclei.

Measurements of the nuclear matter radius [23,24], on the other hand, are significantly more challenging. Since the pioneering experiments by Rutherford and his group [25], charged-particle scattering experiments have undergone continuous development and to this day are the most widespread approach to measuring the distribution of nuclear matter [26],

together with matter-antimatter annihilation approaches [27]. Extracting the nuclear matter radius from hadronic scattering requires modeling the underlying hadron dynamics, knowledge of which remains incomplete. Therefore, nuclear matter radii from hadronic scattering have large systematic uncertainties that are isotope dependent and mostly uncontrolled [28]. So far, only the Lead Radius EXperiment (PREX-2) [29] experiment has come close to extracting the nuclear matter radius at the 1% level in statistical and systematic uncertainties based on the determination of the neutral weak form factor from elastic electron scattering, thus avoiding the uncontrolled systematics of hadronic models.

As a result, while knowledge of the nuclear matter radius and the neutron distribution is highly important in nuclear physics, for instance, to explore the formation of neutron skins [29], the equation of state in neutron stars [30,31], the structure of nuclear halos [32,33], and the limits of the nuclear landscape [34,35], their experimental study requires large-scale and costly reaction spectrometers at specialized facilities. Accessing the nuclear matter radius via ultra-high-resolution rotational spectroscopy of diatomic molecules thus offers an alternative experimental tool of great value, with a reduced cost, potential for lower statistical uncertainties, and controlled, isotope-independent systematic uncertainties.

The moment of inertia in Eq. (11) defines an equilibrium rotational constant B_e [Eq. (12)] for a diatomic molecule composed of realistic, finite-size nuclei. The equilibrium rotational constant, however, is not directly measurable in the laboratory. Instead, the vibrational-state-dependent constants B_v are measured, which are related to B_e via Eq. (2).

The constant α_e in Eq. (2) is related to the parameters of the internuclear potential used in the molecular Hamiltonian. For the most commonly used Morse potential, α_e depends on the three Morse potential parameters α , D , and r_e as [2]

$$\alpha_e = \frac{3h^2\omega_e}{16\pi^2\mu r_e^2 D} \left(\frac{1}{\alpha r_e} - \frac{1}{\alpha^2 r_e^2} \right), \quad (13)$$

where $\omega_e = \frac{\alpha}{2\pi c} \sqrt{\frac{2D}{\mu}}$ is the harmonic frequency of the electronic state.

Consider a diatomic molecule with atoms A and B for which the atomic masses of both nuclei are known with high precision and accuracy (a precision of 10^{-9} atomic mass units or better [10]) and the nuclear matter radius for atom B was measured in a scattering experiment. Combining Eqs. (2), (12), and (13), it is seen that for each value of v , an equation with R_A , α , D , and r_e as unknowns is constructed.

Therefore, a value for R_A can be extracted if B_v is measured for enough different values of v . For the Morse potential and alternative functions [36], which are described by three parameters, B_v would have to be measured for at least $v = 0-3$. With four values of B_v , a set of four equations and four unknowns is formed. Adding further measurements of B_v for higher values of v will help reduce the uncertainty in the extracted parameters by constraining the linear form of Eq. (2). While spectroscopy of excited vibrational states is not typical for cryogenic buffer-gas-cooled spectrometers, vibrational relaxation through buffer-gas collisions is significantly more inefficient than rotational and translational cooling [37], which makes such spectrometers compatible with the

proposed approach. For ion trap experiments, excited vibrational states can be studied via optical or infrared excitations of overtone vibrational transitions.

A significant aspect of the approach proposed here is its versatility, as practically no electronic-state requirements are imposed on the system or technique chosen for the measurement of the rotational constant. As a result, the measurements can be performed in either neutral or ionic systems in the ground or metastable states.

IV. HIGHER-ORDER CORRECTIONS

Beyond the correction due to the finite nuclear size considered here, other corrections to the molecular rotational constant are to be expected at the level of precision that is necessary to extract the nuclear matter radius, such as quantum electrodynamics (QED) corrections. Hyperfine effects and the influence of the nuclear charge radius on the bond length may also need to be considered at this level of precision.

The presently described method proposes extracting the nuclear matter radius by determining B_e with very high precision and then using the relation between the moment of inertia and B_e to extract the matter radius. The extraction of B_e can be done by measuring B_v for several vibrational states of the electronic ground state and then performing a fit as per Eq. (2). In a fit of B_v versus $(v + \frac{1}{2})$, the y intercept gives B_e , and the slope is related to the parameters of the vibrational potential used in the molecular Hamiltonian. One of these parameters is the equilibrium bond length r_e , knowledge of which is also necessary to use Eq. (12) and extract the nuclear matter radii. Depending on the vibrational potential used in the Hamiltonian, r_e could be extracted from the fit's slope.

So far we have considered that if B_v is measured for a sufficient number of vibrational states with high precision, then B_e and r_e can be extracted and provide the nuclear matter radius of interest without the need to calculate any properties of the molecule with *ab initio* quantum chemistry. However, at the level of precision discussed here, there are several points that require consideration.

Most importantly, it is not clear to what degree the relation between B_e and B_v in Eq. (2) is exact at this level—in fact, it is certainly not fully linear. The description of this relation might depend to some extent on the potential energy function used, and it is known that the most commonly used Morse potential energy function for diatomic molecules has limited accuracy, leading to the development of more elaborate potential energy functions (see Refs. [36,38,39] and references therein). However, none of these potentials have been held to the test of ultra-high-precision spectroscopy so far.

Therefore, the validity of Eq. (2) at the precision required by this method remains to be confirmed. It is expected that additional terms will need to be considered in Eq. (2) at higher orders of $(v + \frac{1}{2})$. These corrections would make Eq. (2) nonlinear but would not affect the extraction of B_e through the y intercept of a fit between B_v and $(v + \frac{1}{2})$; the higher-order terms do not need to be understood at an analytical, first-principles level to extract B_e from the y intercept. Nevertheless, these terms will impact the ability to extract r_e , and theoretical and experimental investigations into the applicability of Eq. (2) at very high precision are still necessary.

Most likely, extracting the nuclear matter radius from B_e will at least partly require input from *ab initio* calculations, for instance, via a highly precise calculation of r_e . In this case, further corrections need to be considered, such as the influence of the nuclear charge radii on r_e , as well as radiative and relativistic corrections.

Especially for the correction due to the finite nuclear charge radius, there are indications that the correction can be at the kilohertz level or higher. Within the Dunham parametrization of the rovibrational energy levels of diatomic molecules [40], the rotational constant B is expressed as the $k, l = 0, 1$ Dunham parameter Y_{01} . While early studies considered that the Dunham parameters needed to be scaled only by the reduced molecular mass upon isotopic substitution of the constituent nuclei [1,40], it has long been noticed that this relation is incomplete, and instead, the nuclear mass and nuclear charge radius need to be taken into account in an explicit manner [41,42]. Recently, we showed that the nuclear radius and mass corrections to the Dunham expansion can be viewed as the molecular equivalent of the more familiar atomic field and mass shifts and can be utilized directly in a King plot with atomic data [43].

Despite the extensive evidence of the validity of the nuclear mass and field corrections to the Dunham parameters, however, they are not routinely considered in the expression of the molecular rotational constant in spectroscopic studies. Instead, their influence is typically “absorbed” into an effective equilibrium bond distance that is extracted from the measured spectra using the definition in Eq. (4). With current and planned advances in the accuracy and precision of state-of-the-art spectroscopic equipment, these corrections need to be taken into consideration in a systematic and consistent manner. Especially for the accurate extraction of nuclear matter radii, as proposed here, an accurate value for the equilibrium bond length r_e needs to be determined, and these corrections must therefore be fully treated. Further corrections beyond the nuclear mass and field shifts also need to be explored.

To assess the magnitude of these corrections to r_e , *ab initio* molecular theory has to be employed. However, the correction to the rotational constant due to the matter radius decreases for heavier molecules (Fig. 2), and typically, so does the computational precision of quantum chemistry. Meanwhile, higher-order corrections to the bond length might increase in significance for heavier molecules, such as the correction due to the nuclear charge radius and QED effects.

While QED corrections to electronic transition energies have been calculated for heavy molecules, even up to the theoretical superheavy molecule E(120)F [44], the computational accuracy and precision remain limited considering the requirements of our proposed method. Progress in *ab initio* relativistic calculations relevant to multielectron systems is ongoing, but the computational precision and accuracy are still many orders of magnitude from the level required by the method presented here.

As a result, only light molecules appear accessible by the currently proposed method at the present time. This does not eliminate the near-term nuclear-physics impact of the proposed method since accurate and precise determination of the nuclear matter radius in light nuclei can be used as a benchmark for a large number of emerging *ab initio* nuclear

theory techniques [45,46], whose applicability is often limited to light nuclei. This research potential also includes direct benchmarks for large-scale lattice quantum chromodynamics calculations using the structure of light nuclei [47–49].

V. PROPOSED CASES

A. HD^+

Extracting the nuclear matter radius via the method proposed here introduces a systematic uncertainty depending on the values used for the matter radii of the other nuclei in the molecule. As a result, diatomic molecules are highly preferable. Specifically, monohydrides are ideal since the nuclear matter and charge radii of ^1H are identical, and progress is ongoing towards resolving the proton radius puzzle [50].

Hydrogen compounds remain the subject of several high-precision experimental and theoretical studies [7,8,51–62]. HD^+ , in particular, possessing only one electron, is an ideal probe to test the quantum-mechanical description of a three-body system at the parts-per-trillion level [7,8,60] without electron correlation effects. As a result, it also provides an excellent system to investigate the magnitude of the higher-order corrections required for reliable extraction of nuclear matter radii. As per Fig. 2, the finite-radius correction in H_2 is expected to be on the order of 10^2 Hz, owing to the short bond length of the system, so the nuclear matter radius should be accessible with the precision already demonstrated with optical spectroscopy.

Major breakthroughs have been achieved in the last decade on the vibrational-rotational structure of HD^+ [8,51,53,60–62], including high-precision investigations of the potential energy surface in hydrogen compounds. The dissociation energy of molecular hydrogen was the first observable for which QED effects were explicitly calculated in a molecule [63]. More recently, the theoretical value of the dissociation energy of H_2 [64] was successfully benchmarked by a highly precise measurement that achieved an uncertainty of less than 5 kHz [65].

For several of the higher-order corrections mentioned in the previous section, results have already been reported for HD^+ . In their recent work on the precision spectroscopy of HD^+ [7], Alighanbari *et al.* provided an uncertainty breakdown for the *ab initio* calculation of a rotational transition frequency in HD^+ that included QED and finite-size corrections and reached a theoretical uncertainty of 18 Hz. These *ab initio* calculations were successfully benchmarked for several hyperfine components of the rotational transition, confirming the validity of the presented theoretical results at the $\sim 10^1$ -Hz level.

Importantly, the relativistic and finite-charge-radius corrections to the rotational transition frequency in HD^+ were calculated to be the most dominant, making a relative contribution of 10^{-5} to the total transition frequency [7]. For a larger system containing a heavier nucleus with a larger charge and charge radius, both corrections would be expected to increase in absolute and relative magnitude even further, and thus, their accurate calculation is critical.

Corrections of even higher order than those considered by Alighanbari *et al.* [7], that is, going beyond three-loop

radiative corrections, can be expected to contribute less than 100 Hz to the rotational transition frequency, while the finite-matter-radius correction to the rotational constant is estimated to be a few hundred hertz (see Fig. 2). As the quantity of interest for our method is the rotational constant B_e , rather than individual rotational transition frequencies, the theoretical uncertainty of interest can be expected to be even better than the 18 Hz reported in Ref. [7]. The reason is that corrections that shift individual rotational transitions the same way will be significantly suppressed when determining the rotational constant, as the latter is determined from the relative difference between rotational transitions (see, for example, Refs. [66,67], where order-of-magnitude higher precision is achieved for the rotational constant compared to the individual transition frequencies for light molecules).

References [7,8,62] also demonstrated the control of systematic shifts in the spectroscopy of rotational and rovibrational lines to the subkilohertz level. These shifts are likely to also be suppressed when translated into a rotational-constant uncertainty, allowing the matter radius to be extracted without the further need for an order of magnitude improvement in the control of systematics. However, this has to be investigated directly. It is also important to note that systematic shifts were controlled to this level in ion trap experiments, and a similar level of control remains to be demonstrated in the more universally applicable cryogenic buffer-gas cell approaches of Refs. [5,6].

Overall, with statistical and systematic uncertainties already under control at the required level in both experiment and theory, a campaign could be pursued with HD^+ to measure multiple overtone rovibrational transitions to different upper vibrational states and determine B_v for a range of v (for instance, such measurements were performed in Ref. [68] for neutral HD, but at a much lower precision than required for this method). These measurements could then be used to test the linearity of B_v as a function of $(v + \frac{1}{2})$ at the hertz level and test the validity of Eq. (2). As a next step, the consistency of Eq. (12) could be tested with this molecule to extract the matter radius of the deuteron and compare it to the literature value from reaction experiments and nucleon-nucleon potential calculations [69].

B. Calcium radii

Once the premises of the proposed method are tested with the spectroscopy of HD^+ , a measurement of the nuclear matter radii of $^{40,48}\text{Ca}$ could also be pursued. The calcium isotopic chain ($Z = 20$) is of central interest in nuclear structure research, as it has a magic proton number and two stable isotopes with a magic neutron number (at $N = 20, 28$), thus being doubly magic. The nuclear ground states of the doubly magic $^{40,48}\text{Ca}$ are more energetically stable compared to nuclei in their vicinity, as seen through their binding energies, two-neutron separation energies, and transition energies, and cross sections to their first excited states [70]. These observations have been acknowledged since the early development of the nuclear shell model, and they form a staple of nuclear physics knowledge to this day.

Despite an excess of eight neutrons, the nuclear charge radius of ^{48}Ca is astonishingly similar to that of ^{40}Ca [16].

This is surprising and indicates either a deviation from the constancy of nucleon density within the nucleus as observed throughout the nuclear chart [70] or, much more likely, the formation of a thick neutron skin in ^{48}Ca .

To explore these conclusions, knowledge of the nuclear matter radii, which have been measured with proton elastic scattering [71–73] and collisions with a carbon target [74], is necessary. While different studies point to the formation of a considerably thicker neutron skin in ^{48}Ca compared to ^{40}Ca , there is noticeable statistical scatter between the different values reported for the rms nuclear matter radii of $^{40,48}\text{Ca}$ that originates from the different nuclear-model assumptions employed in each analysis. On the other hand, the measured electric dipole polarizability of ^{48}Ca implies a small neutron skin [75]. Last, Tanaka *et al.* [74] reported an abrupt and prominent increase in the rms nuclear matter radius beyond $N = 28$, which requires independent validation.

To extract the matter radius of calcium nuclei using the current method, calcium monohydride (CaH) would be the most reasonable choice due to the precise knowledge of the proton radius. CaH, which is the lightest possible calcium molecule, is significantly heavier than the hydrogen compounds discussed above. As a result, it cannot reasonably be expected that the theoretical precision achieved for HD^+ can also be achieved for CaH at the present time. We thus also call for the development of precision calculations of this and other light calcium molecules to assess the readiness level of applying the currently proposed method to CaH and other calcium molecules for the extraction of nuclear matter radii.

VI. CONCLUSION

By including the finite nuclear size in the expression of the equilibrium rotational constant, we pointed out that

ultra-high-resolution molecular spectroscopy techniques are already sensitive to the influence of nuclear matter radii on the rotational structure of diatomic molecules. With further improvements in calculations of the molecular bond length, ultra-high-resolution molecular spectroscopy could offer an alternative route to measuring nuclear matter radii at a much reduced cost and with lower systematic uncertainties compared to hadronic scattering experiments.

The main limitation of the proposed method appears to be the precision and accuracy of *ab initio* molecular calculations that might be required to determine the equilibrium bond length r_e , which is involved in the expression that relates the nuclear matter radii and the equilibrium rotational constant B_e . The necessary precision and accuracy of such calculations has been demonstrated in the case of HD^+ , and achieving similar performance in calculations of heavier systems is necessary.

To test the validity of our proposal at the required level of precision, we propose that high-precision spectroscopy of HD^+ be pursued. Measurements and *ab initio* calculations at the part-per-trillion level have already been achieved for this molecule, and existing experimental setups could be used to test the premises of our proposed method. We also propose carrying out spectroscopy of CaH to determine the nuclear matter radii of $^{40,48}\text{Ca}$ as a case of high nuclear physics importance [74,75].

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- [1] G. Herzberg, *Molecular Spectra and Molecular Structure* (van Nostrand, Toronto, Canada, 1945).
 - [2] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics with Applications to Chemistry* (Courier Corporation, New York, 2012).
 - [3] J. M. Brown and A. Carrington, *Cambridge Molecular Science* (Cambridge University Press, Cambridge, 2003).
 - [4] P. Atkins and J. de Paula, *Atkins' Physical Chemistry* (Oxford University Press, Oxford, 2014).
 - [5] L. Satterthwaite, G. Koumariou, D. Sorensen, and D. Patterson, Sub-Hz differential rotational spectroscopy of enantiomers, *Symmetry* **14**, 28 (2022).
 - [6] R. Aiello, V. Di Sarno, M. G. Delli Santi, M. De Rosa, I. Ricciardi, P. De Natale, L. Santamaria, G. Giusfredi, and P. Maddaloni, Absolute frequency metrology of buffer-gas-cooled molecular spectra at 1 kHz accuracy level, *Nat. Commun.* **13**, 7016 (2022).
 - [7] S. Alighanbari, G. S. Giri, F. L. Constantin, V. I. Korobov, and S. Schiller, Precise test of quantum electrodynamics and determination of fundamental constants with HD^+ ions, *Nature (London)* **581**, 152 (2020).
 - [8] S. Patra, M. Germann, J. P. Karr, M. Haidar, L. Hilico, V. I. Korobov, F. M. Cozijn, K. S. Eikema, W. Ubachs, and J. C. Koelemeij, Proton-electron mass ratio from laser spectroscopy of HD^+ at the part-per-trillion level, *Science* **369**, 1238 (2020).
 - [9] I. Angeli and K. P. Marinova, Table of experimental nuclear ground state charge radii: An update, *At. Data Nucl. Data Tables* **99**, 69 (2013).
 - [10] M. Wang, W. J. Huang, F. G. Kondev, G. Audi, and S. Naimi, The AME 2020 atomic mass evaluation (II). Tables, graphs and references, *Chin. Phys. C* **45**, 030003 (2021).
 - [11] R. Engfer, H. Schneuwly, J. L. Vuilleumier, H. K. Walter, and A. Zehnder, Charge-distribution parameters, isotope shifts, isomer shifts, and magnetic hyperfine constants from muonic atoms, *At. Data Nucl. Data Tables* **14**, 509 (1974).
 - [12] R. Hofstadter, Electron scattering and nuclear structure, *Rev. Mod. Phys.* **28**, 214 (1956).
 - [13] H. De Vries, C. W. De Jager, and C. De Vries, Nuclear charge-density-distribution parameters from elastic electron scattering, *At. Data Nucl. Data Tables* **36**, 495 (1987).
 - [14] W. H. King, *Isotope Shifts in Atomic Spectra* (Springer, New York, 2013).
 - [15] X. F. Yang, S. J. Wang, S. G. Wilkins, and R. F. Garcia Ruiz, Laser spectroscopy for the study of exotic nuclei, *Prog. Part. Nucl. Phys.* **129**, 104005 (2023).

- [16] R. F. Garcia Ruiz *et al.*, Unexpectedly large charge radii of neutron-rich calcium isotopes, *Nat. Phys.* **12**, 594 (2016).
- [17] A. Koszorús *et al.*, Charge radii of exotic potassium isotopes challenge nuclear theory and the magic character of $N = 32$, *Nat. Phys.* **17**, 439 (2021).
- [18] R. P. de Groote *et al.*, Measurement and microscopic description of odd-even staggering of charge radii of exotic copper isotopes, *Nat. Phys.* **16**, 620 (2020).
- [19] E. Verstraelen, A. Teigelhöfer, W. Ryssens, F. Ames, A. Barzakh, M. Bender, R. Ferrer, S. Goriely, P. H. Heenen, M. Huyse, P. Kunz, J. Lassen, V. Manea, S. Raeder, and P. Van Duppen, Search for octupole-deformed actinium isotopes using resonance ionization spectroscopy, *Phys. Rev. C* **100**, 044321 (2019).
- [20] A. J. Miller, K. Minamisono, A. Klose, D. Garand, C. Kujawa, J. D. Lantis, Y. Liu, B. Maaß, P. F. Mantica, W. Nazarewicz, W. Nörtershäuser, S. V. Pineda, P.-G. Reinhard, D. M. Rossi, F. Sommer, C. Sumithrarachchi, A. Teigelhöfer, and J. Watkins, Proton superfluidity and charge radii in proton-rich calcium isotopes, *Nat. Phys.* **15**, 432 (2019).
- [21] A. Adamczak *et al.*, Nuclear structure with radioactive muonic atoms, *EPJ Web Conf.* **193**, 04014 (2018).
- [22] K. Tsukada, Y. Abe, A. Enokizono, T. Goke, M. Hara, Y. Honda, T. Hori, S. Ichikawa, Y. Ito, K. Kurita, C. Legris, Y. Maehara, T. Ohnishi, R. Ogawara, T. Suda, T. Tamae, M. Wakasugi, M. Watanabe, and H. Wauke, First observation of electron scattering from online-produced radioactive target, *Phys. Rev. Lett.* **131**, 092502 (2023).
- [23] I. Brissaud, Y. Le Bornec, B. Tatischeff, L. Bimbot, M. K. Brussel, and G. Duhamel, Détermination du rayon de la distribution de neutrons de certains noyaux par l'étude de la diffusion élastique de particules alpha de 166 mev, *Nucl. Phys. A* **191**, 145 (1972).
- [24] G. D. Alkhazov, S. L. Belostotsky, and A. A. Vorobyov, Scattering of 1 GeV protons on nuclei, *Phys. Rep.* **42**, 89 (1978).
- [25] E. Rutherford, LXXIX. The scattering of α and β particles by matter and the structure of the atom, *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **21**, 669 (1911).
- [26] C. J. Batty, E. Friedman, H. J. Gils, and H. Rebel, in *Experimental Methods for Studying Nuclear Density Distributions*, edited by J. W. Negele and E. Vogt, *Advances in Nuclear Physics* Vol. 19 (Springer, Boston, MA, 1989), pp. 1–188.
- [27] T. Aumann *et al.*, PUMA, antiProton unstable matter annihilation, *Eur. Phys. J. A* **58**, 88 (2022).
- [28] M. Thiel, C. Sfienti, J. Piekarewicz, C. J. Horowitz, and M. Vanderhaeghen, Neutron skins of atomic nuclei: Per aspera ad astra, *J. Phys. G* **46**, 093003 (2019).
- [29] D. Adhikari *et al.*, Accurate determination of the neutron skin thickness of ^{208}Pb through parity-violation in electron scattering, *Phys. Rev. Lett.* **126**, 172502 (2021).
- [30] J. M. Lattimer and M. Prakash, Nuclear matter and its role in supernovae, neutron stars and compact object binary mergers, *Phys. Rep.* **333–334**, 121 (2000).
- [31] B. T. Reed, F. J. Fattoyev, C. J. Horowitz, and J. Piekarewicz, Implications of PREX-2 on the equation of state of neutron-rich matter, *Phys. Rev. Lett.* **126**, 172503 (2021).
- [32] P. Egelhof *et al.*, Nuclear-matter distributions of halo nuclei from elastic proton scattering in inverse kinematics, *Eur. Phys. J. A* **15**, 27 (2002).
- [33] A. V. Dobrovolsky *et al.*, Study of the nuclear matter distribution in neutron-rich Li isotopes, *Nucl. Phys. A* **766**, 1 (2006).
- [34] J. Erler, N. Birge, M. Kortelainen, W. Nazarewicz, E. Olsen, A. M. Perhac, and M. Stoitsov, The limits of the nuclear landscape, *Nature (London)* **486**, 509 (2012).
- [35] N. Tsunoda, T. Otsuka, K. Takayanagi, N. Shimizu, T. Suzuki, Y. Utsuno, S. Yoshida, and H. Ueno, The impact of nuclear shape on the emergence of the neutron dripline, *Nature (London)* **587**, 66 (2020).
- [36] P. Q. Wang, J. Y. Liu, L. H. Zhang, S. Y. Cao, and C. S. Jia, Improved expressions for the Schiöberg potential energy models for diatomic molecules, *J. Mol. Spectrosc.* **278**, 23 (2012).
- [37] N. R. Hutzler, M. F. Parsons, Y. V. Gurevich, P. W. Hess, E. Petrik, B. Spaun, A. C. Vutha, D. DeMille, G. Gabrielse, and J. M. Doyle, A cryogenic beam of refractory, chemically reactive molecules with expansion cooling, *Phys. Chem. Chem. Phys.* **13**, 18976 (2011).
- [38] A. Del Sol Mesa, C. Quesne, and Yu F. Smirnov, Generalized Morse potential: Symmetry and satellite potentials, *J. Phys. A* **31**, 321 (1998).
- [39] M. Abu-Shady and E. M. Khokha, A precise estimation for vibrational energies of diatomic molecules using the improved Rosen-Morse potential, *Sci. Rep.* **13**, 11578 (2023).
- [40] J. L. Dunham, The energy levels of a rotating vibrator, *Phys. Rev.* **41**, 721 (1932).
- [41] J. Schlembach and E. Tiemann, Isotopic field shift of the rotational energy of the Pb-chalcogenides and Tl-halides, *Chem. Phys.* **68**, 21 (1982).
- [42] S. Knecht and T. Saue, Nuclear size effects in rotational spectra: A tale with a twist, *Chem. Phys.* **401**, 103 (2012).
- [43] M. Athanasakis-Kaklamanakis, S. G. Wilkins, A. A. Breier, and G. Neyens, King-plot analysis of isotope shifts in simple diatomic molecules, *Phys. Rev. X* **13**, 011015 (2023).
- [44] L. V. Skripnikov, D. V. Chubukov, and V. M. Shakhova, The role of QED effects in transition energies of heavy-atom alkaline earth monofluoride molecules: A theoretical study of Ba^+ , BaF , RaF , and E120F , *J. Chem. Phys.* **155**, 144103 (2021).
- [45] P. Navrátil, S. Quaglioni, G. Hupin, C. Romero-Redondo, and A. Calci, Unified *ab initio* approaches to nuclear structure and reactions, *Phys. Scr.* **91**, 053002 (2016).
- [46] H. Hergert, A Guided Tour of *ab initio* nuclear many-body theory, *Front. Phys.* **8**, 379 (2020).
- [47] S. R. Beane, E. Chang, S. Cohen, W. Detmold, H. W. Lin, K. Orginos, A. Parreño, M. J. Savage, and B. C. Tiburzi (NPLQCD Collaboration), Magnetic moments of light nuclei from lattice quantum chromodynamics, *Phys. Rev. Lett.* **113**, 252001 (2014).
- [48] E. Chang, W. Detmold, K. Orginos, A. Parreño, M. J. Savage, B. C. Tiburzi, and S. R. Beane (NPLQCD Collaboration), Magnetic structure of light nuclei from lattice QCD, *Phys. Rev. D* **92**, 114502 (2015).
- [49] A. Parreño, P. E. Shanahan, M. L. Wagman, F. Winter, E. Chang, W. Detmold, and M. Illa (NPLQCD Collaboration), Axial charge of the triton from lattice QCD, *Phys. Rev. D* **103**, 074511 (2021).
- [50] H. Gao and M. Vanderhaeghen, The proton charge radius, *Rev. Mod. Phys.* **94**, 015002 (2022).
- [51] J. C. J. Koelemeij, B. Roth, A. Wicht, I. Ernsting, and S. Schiller, Vibrational spectroscopy of HD^+ with 2-ppb accuracy, *Phys. Rev. Lett.* **98**, 173002 (2007).

- [52] U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, and S. Schiller, Manipulation of individual hyperfine states in cold trapped molecular ions and application to HD^+ frequency metrology, *Phys. Rev. Lett.* **108**, 183003 (2012).
- [53] G. D. Dickenson, M. L. Niu, E. J. Salumbides, J. Komasa, K. S. E. Eikema, K. Pachucki, and W. Ubachs, Fundamental vibration of molecular hydrogen, *Phys. Rev. Lett.* **110**, 193601 (2013).
- [54] J. Biesheuvel, J.-P. Karr, L. Hilico, K. S. E. Eikema, W. Ubachs, and J. C. J. Koelemeij, Probing QED and fundamental constants through laser spectroscopy of vibrational transitions in HD^+ , *Nat. Commun.* **7**, 10385 (2016).
- [55] J. Biesheuvel, J.-P. Karr, L. Hilico, K. S. E. Eikema, W. Ubachs, and J. C. J. Koelemeij, High-precision spectroscopy of the HD^+ molecule at the 1-p.p.b. level, *Appl. Phys. B* **123**, 23 (2017).
- [56] V. I. Korobov, L. Hilico, and J.-P. Karr, Fundamental transitions and ionization energies of the hydrogen molecular ions with few ppt uncertainty, *Phys. Rev. Lett.* **118**, 233001 (2017).
- [57] D. T. Aznabayevev, A. K. Bekbaev, and V. I. Korobov, Leading-order relativistic corrections to the rovibrational spectrum of H_2^+ and HD^+ molecular ions, *Phys. Rev. A* **99**, 012501 (2019).
- [58] D. J. Fink and E. G. Myers, Deuteron-to-proton mass ratio from the cyclotron frequency ratio of H_2^+ to D^+ with H_2^+ in a resolved vibrational state, *Phys. Rev. Lett.* **124**, 013001 (2020).
- [59] S. Rau, F. Heiße, F. Köhler-Langes, S. Sasidharan, R. Haas, D. Renisch, C. E. Düllmann, W. Quint, S. Sturm, and K. Blaum, Penning trap mass measurements of the deuteron and the HD^+ molecular ion, *Nature (London)* **585**, 43 (2020).
- [60] M. Germann, S. Patra, J. P. Karr, L. Hilico, V. I. Korobov, E. J. Salumbides, K. S. Eikema, W. Ubachs, and J. C. Koelemeij, Three-body QED test and fifth-force constraint from vibrations and rotations of HD^+ , *Phys. Rev. Res.* **3**, L022028 (2021).
- [61] I. V. Kortunov, S. Alighanbari, M. G. Hansen, G. S. Giri, V. I. Korobov, and S. Schiller, Proton-electron mass ratio by high-resolution optical spectroscopy of ion ensembles in the resolved-carrier regime, *Nat. Phys.* **17**, 569 (2021).
- [62] S. Alighanbari, I. V. Kortunov, G. S. Giri, and S. Schiller, Test of charged baryon interaction with high-resolution vibrational spectroscopy of molecular hydrogen ions, *Nat. Phys.* **19**, 1263 (2023).
- [63] J. Komasa, K. Piszczatowski, G. Łach, M. Przybytek, B. Jeziorski, and K. Pachucki, Quantum Electrodynamics effects in rovibrational spectra of molecular hydrogen, *J. Chem. Theory Comput.* **7**, 3105 (2011).
- [64] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki, Nonadiabatic QED correction to the dissociation energy of the hydrogen molecule, *Phys. Rev. Lett.* **122**, 103003 (2019).
- [65] N. Hölsch, M. Beyer, E. J. Salumbides, K. S. E. Eikema, W. Ubachs, C. Jungen, and F. Merkt, Benchmarking theory with an improved measurement of the ionization and dissociation energies of H_2 , *Phys. Rev. Lett.* **122**, 103002 (2019).
- [66] M. Dulick, K.-Q. Zhang, B. Guo, and P. F. Bernath, Far- and mid-infrared emission spectroscopy of LiH and LiD , *J. Mol. Spectrosc.* **188**, 14 (1998).
- [67] C. R. Markus, J. N. Hodges, A. J. Perry, G. S. Kocheril, H. S. P. Müller, and B. J. McCall, High precision rovibrational spectroscopy of OH^+ , *Astrophys. J.* **817**, 138 (2016).
- [68] A. R. W. McKellar, W. Goetz, and D. A. Ramsay, The rotation-vibration spectrum of HD -Wavelength and intensity measurements of the 3-0, 4-0, 5-0, and 6-0 electric dipole bands, *Astrophys. J.* **207**, 663 (1976).
- [69] C. W. Wong, Deuteron radius and nuclear forces in free space, *Int. J. Mod. Phys. E* **03**, 821 (1994).
- [70] R. F. Casten, *Nuclear Structure from a Simple Perspective*, (Oxford University Press, Oxford, 2000).
- [71] G. Igo *et al.*, Elastic differential cross sections and analyzing powers for $p+^{40,42,44,48}\text{Ca}$ at 0.8 GeV, *Phys. Lett. B* **81**, 151 (1979).
- [72] R. H. McCamis, T. N. Nasr, J. Birchall, N. E. Davison, W. T. H. van Oers, P. J. T. Verheijen, R. F. Carlson, A. J. Cox, B. C. Clark, E. D. Cooper, S. Hama, and R. L. Mercer, Elastic scattering of protons from $^{40,42,44,48}\text{Ca}$ from 20 to 50 MeV and nuclear matter radii, *Phys. Rev. C* **33**, 1624 (1986).
- [73] J. Zenihiro, H. Sakaguchi, S. Terashima, T. Uesaka, G. Hagen, M. Itoh, T. Murakami, Y. Nakatsugawa, T. Ohnishi, H. Sagawa, H. Takeda, M. Uchida, H. P. Yoshida, S. Yoshida, and M. Yosoi, Direct determination of the neutron skin thicknesses in $^{40,48}\text{Ca}$ from proton elastic scattering at $E_p = 295$ MeV, [arXiv:1810.11796](https://arxiv.org/abs/1810.11796).
- [74] M. Tanaka *et al.*, Swelling of doubly magic ^{48}Ca core in Ca isotopes beyond $N = 28$, *Phys. Rev. Lett.* **124**, 102501 (2020).
- [75] J. Birkhan, M. Miorelli, S. Bacca, S. Bassauer, C. A. Bertulani, G. Hagen, H. Matsubara, P. von Neumann-Cosel, T. Papenbrock, N. Pietralla, V. Y. Ponomarev, A. Richter, A. Schwenk, and A. Tamii, Electric dipole polarizability of ^{48}Ca and implications for the neutron skin, *Phys. Rev. Lett.* **118**, 252501 (2017).