Penning trap mass measurements of the deuteron and the HD\(^+\) molecular ion

The masses of the lightest atomic nuclei and the electron mass\(^1\) are interlinked, and their values affect observables in atomic\(^2\), molecular\(^3\)–\(^5\) and neutrino physics\(^6\), as well as metrology. The most precise values for these fundamental parameters come from Penning trap mass spectrometry, which achieves relative mass uncertainties of the order of 10\(^{-11}\). However, redundancy checks using data from different experiments reveal considerable inconsistencies in the masses of the proton, the deuteron and the helion (the nucleus of helium-3), suggesting that the uncertainty of these values may have been underestimated. Here we present results from absolute mass measurements of the deuteron and the HD\(^+\) molecular ion using \(^{12}\)C as a mass reference. Our value for the deuteron mass, 2.013553212535(17) atomic mass units, has better precision than the CODATA value\(^7\) by a factor of 2.4 and differs from it by 4.8 standard deviations. With a relative uncertainty of eight parts per trillion, this is the most precise mass value measured directly in atomic mass units. Furthermore, our measurement of the mass of the HD\(^+\) molecular ion, 3.021378241561(61) atomic mass units, not only allows a rigorous consistency check of our results for the masses of the deuteron (this work) and the proton\(^8\), but also establishes an additional link for the masses of tritium\(^9\) and helium-3 (ref. \(^{10}\)) to the atomic mass unit. Combined with a recent measurement of the deuteron-to-proton mass ratio\(^11\), the uncertainty of the reference value of the proton mass\(^7\) can be reduced by a factor of three.

Penning traps allow the extremely precise determination of ratios of atomic masses. Over the years an extensive network has been created that connects individual masses via one or several links (see Fig. 1). The recently implemented redefinition of the international system of units\(^12\) generally allows expressing atomic masses in kilograms with relative uncertainties of the order of 10\(^{-11}\). However, especially for fundamental physics applications, a direct and trustworthy link from the lightest ions to the atomic mass unit (one-twelfth of the mass of a \(^{12}\)C atom) with higher precision is desirable to enable, for example, a connection to the electron mass, which is measured in atomic mass units. However, different links between the masses of the proton (\(m_p\)), the deuteron (\(m_d\)) and the helion (\(m_{he}\)) show a discrepancy of about 5 standard deviations, putting into question the reliability of the tabulated values for these important masses. To show this, we examine \(\Delta = m_p + m_d - m_{he}\).

This value, which is related to the proton separation energy of helium-3, can be derived in two ways: either by using measurements relating the involved masses directly to \(^{12}\)C (\(\Delta_{12}\))\(^{13}\), or by a mass ratio measurement of the HD\(^+\) molecular ion and the ‘He’ ion\(^10\) (\(\Delta_{HD}\)). Comparison of the two values using the measurements available at present yields a difference of \(\Delta_{12} - \Delta_{HD} = 484(97) \times 10^{-12}\) AMU (all uncertainties denote one standard deviation). In the 2016 atomic mass evaluation\(^{14}\), this problem was treated by omitting the direct helium-3 measurement from the adjustment process while still using the deuteron mass reported by the same group in the same measurement campaign, potentially leading to underestimated errors in the adjustment. In Fig. 1 we give an overview of the light-ion-mass measurements, including those conducted in this work and a recent measurement of the deuteron-to-proton mass ratio\(^11\). We note that conversion between the mass of ions and that of the corresponding atoms is possible without loss in precision in the low-mass regime.

In Penning trap mass ratio measurements, the cyclotron frequency \(\nu_C = \frac{1}{2\pi} \frac{eB}{m} \) of a single ion with charge \(q\) and mass \(m\) in a homogeneous magnetic field \(B\) is compared to the cyclotron frequency of a reference ion in the same magnetic field. Using \(^{12}\)C\(^+\) as reference, the mass of the deuteron is given by

\[
m_d = \frac{1}{6} \frac{\nu_C(^{12}\text{C}^+)}{\nu_C(^{1}\text{H}^+)} m(^{12}\text{C}^+) - \frac{1}{6} \nu_C(^{1}\text{C}^+) m(^{1}\text{C}^+).
\]

The atomic mass of the highly charged carbon ion is known very well because the electron’s mass and the ionization energies of carbon\(^14\) are known with sufficient precision: \(m(^{12}\text{C}^+) = 11.99760962641246(35)\) AMU with a relative uncertainty of 0.03 parts per trillion (ppt). The experiment therefore comes down to measuring the cyclotron frequency ratio \(R^2\) as precisely as possible.

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1Max-Planck-Institut für Kernphysik, Heidelberg, Germany. 2GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany. 3Johannes Gutenberg-Universität, Mainz, Germany. 4Helmholtz-Institut Mainz, Germany. 5PRISMA+ Cluster of Excellence, Johannes Gutenberg-Universität, Mainz, Germany. 6e-mail: sascha.rau@mpi-hd.mpg.de

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transfers the phase of the modified cyclotron motion to the axial motion. This method is lineshape-independent, but one must correct for relativistic frequency shifts due to the excited radius during the phase evolution. The magnetron frequency was measured at various times throughout the data taking using the ‘double-dip’ technique as in our previous campaign. For this purpose, the drive strength was varied and extrapolated to zero.

In our trap chamber, we reach a virtually perfect vacuum (better than 10⁻¹⁰ mbar), which is measurable only via the absence of charge exchange of trapped highly charged ions. This is enabled by a pinch-off technique, which hermetically seals the trap chamber, and cryopumping at 4.2 K. The sealed trap chamber necessitates the production of ions inside it, which is done using a miniature electron-beam ion source (mEBIS). There, electrons are emitted from a field-emission point, pass through a hole in our target and are reflected back and forth inside the mEBIS. Owing to space charge, the electron beam widens and finally hits the target, where atoms and molecules are ablated. The target is made of a plastic compound with carbon nanotubes (TECAPEEK) to ensure electrical conductivity. On top of the target surface, we put a printed layer of deuterated molecules to allow efficient production of deuteron atomic and molecular ions. To this end, deuterated thymidine was dissolved in heavy water. From this solution (concentration of 5 mg ml⁻¹) we put 458 5-nl drops in two layers in an octagonal pattern on top of our target using a drop-on-demand printing system; see also Fig. 2.

The main systematic limitation in our past experiments has been the residual quadratic component of the magnetic inhomogeneity: the field generated by the superconducting magnet at the position of our trap, although very homogeneous, has a slight (in our case, positive) quadratic dependence on the axial position. Hence, when an ion moves with its thermal amplitude, it experiences a higher magnetic field compared to a situation without inhomogeneity. This field then depends mainly on the temperature of the axial motion. We reduce this effect by implementing a closed-loop superconducting coil placed directly around the trap chamber inside our magnet. This coil can be charged from outside the magnet to shunt the magnetic field in situ while simultaneously monitoring the effect on the ion. With this technique, we were able to reduce the quadratic magnetic-field inhomogeneity by a factor of 100, from B₁/2B₀ = 7.2(4) × 10⁻⁸ mm⁻² during the proton mass measurement campaign²⁵ to B₁/2B₀ = 6.5(6.5) × 10⁻¹⁰ mm⁻², making the systematic effect on the frequency ratio negligible (see also Table 1). Here, Bₙ and B₀ are defined through a series expansion of the magnetic field B along the axial direction, B = Bₙ + B₂z + B₄z², where the Bₙ term does not lead to a relevant systematic uncertainty. Construction details for these coils can be found in ref. ³. To reach a better stability for the frequency ratio R², we implemented a pressure-stabilization system for the liquid-nitrogen and liquid-helium reservoirs. Because the boiling point of cryoliquids is strongly pressure-dependent, this potentially reduces magnetic-field drifts. With this system we can keep the pressure to within ~4 μbar of its nominal value, slightly above ambient pressure. Furthermore, we have added three set screws that can be actuated from the room-temperature stage to allow an exact in situ alignment of the trap with respect to the magnetic field. These improvements enabled a stability of R² of 1.6 × 10⁻⁵ per measured frequency ratio.

**Data analysis**

For the deuteron mass, the data consist of four different sets of (d, C⁶⁺) pairs with varied spatial ordering to exclude systematic effects, obtained over 41 runs. The ion pairs were trapped for 1–4 months and were lost owing to communication problems between the computer control system and the devices used in the setup. In each run, the settings for the excitation strengths A for the PNA remained constant; one run typically contained 27 frequency ratios. For each frequency ratio, the ion to be measured first was chosen randomly and shuttled into the precision trap while the other ion was stored in an adjacent storage.
After measuring the frequencies of the first ion, the second ion was transported into the precision trap, and the first ion was placed in a storage trap. The measurement cycle is described in more detail in ref. 8. The ions are measured using identical trapping potentials, which is possible by tuning the resonator frequency using a varactor diode as described in ref. 8.

To extrapolate energy-dependent shifts occurring during the PNA, we took measurements with various independently varied excitation strengths for both the deuteron and the carbon ion. The radius of the modified cyclotron motion $r_{\text{exc}}$ is proportional to the excitation strength, $r_{\text{exc}} \propto \kappa A_\text{e} x$, where $\kappa$ is a proportionality constant that depends on the particle. The energy associated with this motion leads to a relativistic mass increase and therefore to a frequency shift proportional to $r_{\text{exc}}^2$. As an example, this shift amounts to $\Delta \nu / \nu = -19 \times 10^{-12}$ for carbon and $-18 \times 10^{-12}$ for the deuteron at the lowest excitation amplitude of about 10 μm used in the PNA.

In the analysis, this is treated by fitting a plane to the tuples $(A_\text{e} x (d)^2, A_\text{e} x (^{12}\text{C}^+) ^2, R_{\text{CF}})$ in a manner similar to that described in ref. 16. The results of this fit are a ratio, denoted as $R_{\text{CF}}^\text{stat}$, extrapolated to zero excitation energy for both ions, and a calibration for the excitation strength, $A_\text{e} x$, obtained using the known formula for the relativistic shift. To further exclude systematic effects, data were measured with the fourth and fifth ion pairs using a different arbitrary waveform generator (AWG) for the excitations. The datasets with the two AWGs were analysed separately and subsequently averaged. In Fig. 3 the measured ratios for ion pairs 1 and 2 are shown for different PNA settings, after correction to zero-excitation amplitude using the fit. For the other two ion pairs, the data are shown in Supplementary Table 1 | Systematic effects in the deuteron measurement

| Effect                      | Shift of $\nu_c$ for $d$ | Correction to $R_{\text{CF}}^\text{stat}$ | Uncertainty |
|-----------------------------|--------------------------|------------------------------------------|-------------|
| Image charge                | $-16.6$                  | $-98.7$                                  | 82.1        |
| Special relativity (thermal)| $-3.4$                   | $-0.6$                                   | 2.9         |
| Magnetic inhomogeneity      | 0.4                      | 0.1                                      | 0.3         |
| Electrostatic anharmonicity | 0                        | 0                                         | 0.1         |
| Dip lineshape               | 0                        | 0                                         | 4.7         |
| Magnetron frequency         | 0                        | 0                                         | 0.4         |
| Total                       | $-19.6$                  | $-99.2$                                  | 79.6        |

Systematic shifts and their uncertainties after extrapolation to zero-excitation amplitude. All values are relative and expressed in parts per trillion. For details see text.
The deuteron mass reported here deviates significantly from the current CODATA (Committee on Data for Science and Technology) value; see Fig. 4. To further validate our measurement, we can compare the directly measured mass of HD$^+$ with that derived from its constituents. Using our previously reported proton mass$^8$, the deuteron mass measured by our group$^9$, the deuteron-to-proton mass ratio reported by UW$^{13}$, the deuteron-to-proton mass ratio measured by FSU$^{12}$ combined with the current CODATA value for the proton mass$^7$, and the mass value reported in this work. The CODATA value$^8$, which coincides with the value reported by UW, is shown as a grey band with dashed borders. All error bars correspond to the 1σ confidence interval (68%).

Discussion

The deuteron mass reported here deviates significantly from the current CODATA (Committee on Data for Science and Technology) value; see Fig. 4. To further validate our measurement, we can compare the directly measured mass of HD$^+$ with that derived from its constituents. Using our previously reported proton mass$^8$, the deuteron mass reported here, the electron mass$^9$ and the binding energy of a three-body system$^8$, one arrives at the following value for the mass of the HD$^+$ molecular ion: $m(\text{HD}^+)_{\text{p+d}} = 3.021378241576(37)$ AMU. This value agrees with the directly measured one on a 1σ level,
Table 2 | Mass values of light nuclei

| Quantity | Value (amu) | Relative uncertainty (×10⁻¹¹) |
|----------|-------------|---------------------------------|
| Proton mass, m⁰ | 1.00727464665801(17) | 1.7 |
| Deuteron mass, m_d | 2.013553212538(16) | 0.8 |
| Neutron mass, m_n | 1.00866491604(42) | 42 |
| Δ_c | 0.005897432449(50) |
| Δ_{FSU} | 0.005897432197(70) |

Shown are the mass values and uncertainties of the proton, the deuteron and the neutron in atomic mass units, derived from the least-squares adjustment described in the text. The resulting value for Δ_c and Δ_{FSU} are added for convenience. The values are correlated, with correlation coefficients r(m_proton, m_deuteron) = 0.26, r(m_deuteron, m_neutron) = -0.03 and r(m_proton, m_neutron) = 0.03.

The measurement of m(HD⁺)_{direct} = 15(71) × 10⁻¹² amu if one uses the deuteron mass reported by the University of Washington.11 This difference amounts to 225(80) × 10⁻¹⁲ amu, or 517(158) × 10⁻¹² amu if one also uses their previously reported proton mass.28 We regard the striking agreement between our measurements and results obtained with different masses and systems as a profound consistency check, substantiating our measurement methods. Using our measurements, we can also extract a deuteron-to-proton mass ratio of m_d/m_proton (LIONTRAP) = 1.99900750122(859). This value agrees with a direct measurement using H₂O molecular ions recently reported by Florida State University on a lo level. The agreement between the measurements of m_n (ref. 3), m_d and m(HD⁺) (this work) with the deuteron-to-proton mass ratio10 opens up the possibility for a least-squares adjustment of m_n and m_d with only the listed measurements as input and using the techniques described in ref. 10. The resulting masses are listed in Table 2. The main advantage of this adjustment is a reduction in the uncertainty of the proton mass (in amu) by a factor of 2 compared to the direct measurement. With these adjusted masses and the measured nuclear binding energy of the deuteron, S_d = 0.00238817008(42) amu (ref. 30), which was adjusted with an updated value for the lattice constant of the crystal used in the measurement (see also Supplementary Information) 31, the neutron mass becomes m_n = 1.00866491604(42) amu, which is shifted by 9 × 10⁻¹² amu compared to the CODATA 2018 value.2 The uncertainty, however, remains the same owing to the limitation by the measurement uncertainty of S_d. When using the adjusted values here, the light-ion mass discrepancy is reduced to Δ_{FSU} = Δ_c = 258(86) × 10⁻¹² amu, strengthening the credibility of the mass difference between the tritium and helium-3 nuclei needed for the KATRIN experiment, where the endpoint of the tritium β-decay spectrum related to this mass difference is used to give limits on the neutrino mass.5 With the measurements reported here and in ref. 8, two of the three masses contributing to Δ_c have now been determined by our collaboration (LIONTRAP). Together with the remaining 3σ discrepancy in Δ_c, this provides motivation for an independent measurement of the mass of helium-3.

Online content

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Article

Methods

Additional information on the deuteron measurement

The data for the deuteron measurement campaign were obtained using two different AWGs for the excitations: AWG1 (Keysight 33600A, 80 MHz) and AWG2 (Agilent 33522A, 30 MHz). Because the excitations from two different AWGs will not be exactly equal in amplitude, we decided to treat this by taking both datasets separately. The data-fitting routine is described in the main text, and the fit for the first two ion pairs is shown in Fig. 3. In Extended Data Fig. 1a we show the residuals of the fit used for the next two pairs of ions.

Both fits give ratios extrapolated to zero-excitation amplitudes. To combine the two fits, which agree very well, a weighted average was used (the statistical ratio $R_{\text{stat}}$ given in the main text). The single-fit results are

$$R_{\text{stat}}(\text{AWG1}) = 1.0070527378313(86)$$

$$R_{\text{stat}}(\text{AWG2}) = 1.0070527378318(70).$$

The AWGs were exchanged because we noticed increased noise during the double-dip measurements, which might lead to heating. The PNA method is largely unaffected by this noise, because the excitation was on only for a very short time and was much weaker than for the double-dip measurements. We tried to induce a detectable effect by using excessively strong excitations for long times, but we did not detect any relevant heating. The values obtained with the two AWGs agree, indicating no systematic influence.

The temperatures of the ions were measured using standard methods. During the PNA measurements, electronic feedback was used to achieve a temperature of $T_{\text{FB}} = 1.2(5)$ K for both ions. During the dip measurement, no electronic feedback was used, and the temperature was $T_{\text{FB}} = 3.7(5)$ K.

Details on the HD$^+$ measurement

Here we present some more information on the direct measurement of the mass of HD$^+$. In principle, the measurement was very similar to the deuteron mass campaign. However, the charge-to-mass ratio for HD$^+$ and $^{12}$C$^+$ is $q/m = 1/e$, resulting in a reduced signal and a reduced cyclotron frequency of about 20 MHz. The trap voltage was adjusted so that approximately the same axial frequencies as in the deuteron measurement were used. The relatively low charge-to-mass ratio gave rise to an extremely narrow dip signal of about 0.35 Hz for HD$^+$. The data of the corresponding surface fit are shown in Extended Data Fig. 1b as for the $m_d$ fits.

Extended Data Table 1 summarizes the systematic shifts and uncertainties for the HD$^+$ measurement. These differ from the values given for $m_d$ because of the different frequencies and the different charge-to-mass ratio. The temperatures were equal to the temperature in the deuteron measurement.

Deuteron-to-proton mass ratio

In the main text, we give the deuteron-to-proton mass ratio

$$m_d/m_p(\text{LIONTRAP}) = 1.99900750(128)(59).$$

This ratio is taken from a least-squares adjustment using the measurements on $m_p$ (ref. 7), $m_d$ and $m(HD^+)$ (this work). This results in

$$m_p = 1.007276466595(29),$$

$$m_d = 2.013553212534(17),$$

with a correlation coefficient of $r(m_p, m_d) = -0.13$. The quotient of the above values gives the reported deuteron-to-proton mass ratio.

Deuteron nuclear binding energy

The nuclear binding energy of the deuteron was measured using Bragg spectroscopy. To translate the measured angle into a wavelength, the lattice constant of the silicon crystal used for the measurement is needed. This lattice constant (in the literature this crystal is referred to as $\text{IL}2.5$) was remeasured in 2006 and in 2017. In this section, we describe how the 2006 value is updated with the 2017 lattice constant.

The wavelength $\lambda$ extracted from the angle measurements in Bragg spectroscopy is proportional to the lattice constant $d$ (ref. 30). Therefore, to adjust the measured wavelength $\lambda_{\text{old}}$ to a new value $\lambda_{\text{new}}$ of the lattice constant, we use

$$\lambda_{\text{new}} = \frac{d_{\text{new}}}{d_{\text{old}}} \lambda_{\text{old}}.$$

Using $d_{\text{old}} = 192.0155721(64) \times 10^{-12}$ m (ref. 31), $d_{\text{new}} = 192.0155822(96)$ m and $\lambda_{\text{old}} = 0.5576713288(99) \times 10^{-12}$ m (ref. 31), one arrives at

$$\lambda_{\text{new}} = 0.557671299(97) \times 10^{-12} \text{ m},$$

corresponding to an energy of

$$E_{\text{meas}} = 2.223,248,69(39) \text{ eV}.$$

We note that the uncertainty is essentially unchanged because the lattice constant measurement was not the dominating contribution to the uncertainty. The measured energy was corrected for the nuclear recoil to obtain the nuclear binding energy $S_n$ (ref. 31)

$$S_n = E_{\text{meas}} \frac{(E_{\text{meas}}^2)}{2m_c^2}$$

$$= 2.224,566,35(39) \text{ eV}$$

$$= 2.38817008(42) \times 10^{-3} \text{ AMU},$$

Here, $m_c^2$ is the atomic mass of the deuteron expressed in electronvolts using the conversion factor (1 AMU)$^2 = 9.1349401242(28) \times 10^8$ eV (ref. 32), where $c$ is the speed of light in vacuum. We note that the discrepancies in $m_d$ and the conversion to electronvolts do not affect the level of precision needed for the recoil correction.

Constants

Where not stated otherwise, the values given by CODATA 2018 have been used. In Extended Data Table 2 some of the most important constants used in this work are summarized for convenience.

Data availability

The datasets analysed for this study are available from the corresponding author on reasonable request. Source data are provided with this paper.

Code availability

The analysis codes are available from the corresponding author on reasonable request.

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Author contributions The experiment was performed by S.R., F.K.-L. and S. Sasidharan. The data were analysed by S.R, F.K.-L. and S. Sturm. The manuscript was written by S.R. The deuterated target was prepared by R.H., D.R. and C.E.D. All authors discussed and approved the data as well as the manuscript.

Competing interests The authors declare no competing interests.

Additional information Correspondence and requests for materials should be addressed to S.R.

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Extended Data Fig. 1 | Averages of cyclotron frequency ratios. a, b. Averages of cyclotron frequency ratios with equal parameters, after correction to zero-excitation amplitude using the fit described in the main text, for the data obtained with AWG2 for the deuteron campaign (a) and for HD+ (b). Each point corresponds to a setting used in the PNA method. On the x axis, the corresponding cyclotron radii of the deuteron (rd) and carbon (rc) and the number of cyclotron ratios N are given. The error bars denote the standard error of the mean and are estimated from the standard deviations divided by the square root of N. The grey band with dashed borders denotes 1σ uncertainty for the fitted frequency ratio.
## Extended Data Table 1 | Systematic effects in the HD$^+$ measurement

| Effect                      | Shift of $v_1$ for HD$^+$ | Correction to $a^{\text{ref}}$ | Uncertainty |
|-----------------------------|---------------------------|---------------------------------|-------------|
| Image charge                | -24.9                     | -98.7                           | 73.8        | 3.7         |
| Special relativity (thermal)| -1.5                      | -0.4                            | -1.1        | 0.5         |
| Magnetic inhomogeneity      | 0.2                       | 0.1                             | 0.2         | 0.3         |
| Electrostatic anharmonicity | 0                         | 0                               | <0.1        | 0.4         |
| Dip lineshape               | 0                         | 0                               | 0           | 6.8         |
| Magnetron frequency         | 0                         | 0                               | 0           | 2.1         |
| Polarization                | -18.4                     | 0                               | -18.5       | <0.1        |
| **Total**                   | **-44.6**                 | **-99.0**                       | **54.3**    | **8.1**     |

Systematic shifts and their uncertainties after extrapolation to zero-excitation amplitude for HD$^+$. All values are relative and expressed in parts per trillion.
Extended Data Table 2 | Constants used in this work

| constant [reference]                        | value                           |
|--------------------------------------------|---------------------------------|
| electron mass [7]                          | 5.485 799 090 65 (16) × 10⁻⁴ u  |
| atomic mass unit – electron volt conversion| 9.314 941 0242 (28) × 10⁸ eV    |
| inverse meter - atomic mass unit           | 1.331 025 050 10 (40) × 10⁻¹⁵ u |
| ionization energy C I [16]                 | 11.260 288 0 (11) eV            |
| ionization energy C II                     | 24.383 154 (16) eV              |
| ionization energy C III                    | 47.887 78 (25) eV               |
| ionization energy C IV                     | 64.493 52 (19) eV               |
| ionization energy C V                      | 392.090 515 (25) eV             |
| ionization energy C VI                     | 489.993 194 (7) eV              |
| ionization energy D a                      | 13.602 134 52 (8) eV            |
| ionization energy of HD⁺ [4]               | 131.224.684 165 0 (6) × 10⁻⁷ cm⁻³|
| ground-state polarizability HD⁺ [26]       | 395.31 (4) b                    |
| conversion polarizability in atomic units to SI [7] | 1.648 78 × 10⁻⁴ kgT⁻² |

When no uncertainty is given, the precision of the value is much better than needed for this work. When multiple values are taken from the same reference, the reference is cited only with the first value.

*aTo be updated for new values of the Rydberg constant. However, this does not affect the value on the level of precision needed in this work.

*bError of about 1 × 10⁻¹⁴ because this is a nonrelativistic calculation. Value in atomic units (1 atomic unit = 4πε₀a₀², where ε₀ is the vacuum electric permittivity and a₀ is the Bohr radius; both values from ref. 7).