Non-adiabatic, relativistic, and leading-order QED corrections for rovibrational intervals of $^4\text{He}_2^+$ ($X^2\Sigma^+_u$)

Dávid Ferenc, Vladimir I. Korobov, and Edit Mátys

1Institute of Chemistry, ELTE, Eötvös Loránd University, Pázmány Péter sétány 1/A, Budapest, H-1117, Hungary
2Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia

(Dated: November 16, 2020)

Abstract

The rovibrational intervals of the $^4\text{He}_2^+$ molecular ion in its $X^2\Sigma^+_u$ ground electronic state are computed by including the non-adiabatic, relativistic, and leading-order quantum-electrodynamics corrections. Good agreement of theory and experiment is observed for the rotational excitation series of the vibrational ground state and the fundamental vibration. The lowest-energy rotational interval is computed to be 70.937 69(10) cm$^{-1}$ in agreement with the most recently reported experimental value, 70.937 58(23)(60) cm$^{-1}$ [L. Semeria, P. Jansen, G.-M. Camenisch, F. Mellini, H. Schmutz, and F. Merkt, Phys. Rev. Lett. 124, 213001 (2020)].
INTRODUCTION

Few-electron molecules serve as benchmark systems for experimental and theoretical molecular physics and spectroscopy. Recent experimental and theoretical progress of \( \text{H}_2^+ \), \( \text{H}_2 \), and their isotopologues \([1-3]\) is connected to proposals to test fundamental interactions \([4, 5]\) and to refine fundamental physical constants \([6, 7]\) using molecular spectroscopy.

The present work joins this direction and focuses on the five-particle \( ^4\text{He}_2^+ \) molecular ion in its ground electronic state \((X^2\Sigma_u^+)\). In addition to testing fundamental aspects, precision spectroscopy of \( ^4\text{He}_2^+ \) in combination with accurate \textit{ab initio} computations has been proposed as an alternative way to determine the polarizability of the helium atom \([8, 9]\). Precise knowledge of this quantity is necessary for a possible new definition of the pressure standard based on counting the number density of a sample of helium gas. There has been experimental progress in the precision spectroscopy of \( ^4\text{He}_2^+ \) including the measurement of the spin-rotational fine structure \([10]\) and the rotational and rovibrational intervals \([9, 11-13]\).

The present work is concerned with the rotational and rovibrational intervals for which disagreement was observed between the experimental results \([9, 11-13]\) and (lower-level) theoretical work \([14, 15]\). The experimental ‘dataset’ includes the rotational intervals for the vibrational ground state, \((0, N^+)-(0, 1)\) \((N^+ = 3, \ldots, 19)\) \([12]\) and the rovibrational intervals connecting the ground and the first excited vibrational state \((1, N^+)-(0, 1)\) \((N^+ = 1, \ldots, 13)\) \([13]\) with an experimental uncertainty of 0.0008 cm\(^{-1}\) and 0.0012 cm\(^{-1}\), respectively. The lowest-energy rotational interval is known more precisely to be 70.937 589(23) ± 0.000 060\(_{\text{sys}}\) cm\(^{-1}\) \([9]\).

The most precise theoretical results for molecules can be obtained by including all electrons and nuclei in the non-relativistic quantum mechanical treatment \([2, 16-20]\). All bound rovibrational and several resonance states of \( \text{H}_2^+ \) treated as a three-particle system have been converged with an uncertainty in their non-relativistic energy better than 10\(^{-7}\) cm\(^{-1}\) \([17]\), and a similar precision has been achieved for selected states of \( \text{H}_2 \) treated as a four-particle system \([21]\). The fundamental vibration energy has been computed for \( ^3\text{He}^4\text{He}^+ \) treated as a five-particle system \([22]\), but the convergence error of this energy appears to be at least two-orders of magnitude larger.
than the uncertainty of the currently available experimental value of the parent isotopologue.

To ensure a direct comparison with the experimental dataset, which includes high rotational angular momentum quantum numbers up to $N^+ = 19$, and a tight control of the numerical (convergence) error, we start out from the Born–Oppenheimer approximation and account for non-adiabatic corrections by perturbation theory [23–27]. The experimental dataset belongs to the ground ($X^2\Sigma_u^+$) electronic state that is well-separated from the electronically excited states over the relevant nuclear configuration range, hence we may expect non-adiabatic perturbation theory to perform well.

There is some evidence about the increasing importance of the non-adiabatic effects with rotational excitation of $^4\text{He}_2^+$ [12, 15], but the non-adiabatic non-relativistic computation of Ref. [15] was only partially able to account for the discrepancy between theory and experiment for the rotational series. Furthermore, the non-adiabatic corrections (without relativistic and QED effects) increased the deviation of theory and experiment for the fundamental vibration energy [13, 15] in comparison to the adiabatic result [14].

The present work reports a more complete theoretical treatment for the rovibrational intervals of $^4\text{He}_2^+$ ($X^2\Sigma_u^+$), and we account for the non-adiabatic, relativistic and leading-order QED corrections. The error balance of the computational procedure is analyzed and further contributions, neglected in this work, are discussed.

First, we solved the electronic Schrödinger equation for $n = 3$ electrons and $N = 2$ fixed nuclei for the $\phi_0$ ground electronic state (in Hartree atomic units)

\[
H_{el} \phi_0 (r, R) = E_{el,0} (R) \phi_0 (r, R) \quad \text{with}
\]

\[
H_{el} = - \sum_{i=1}^{n} \frac{1}{2m_e} \Delta_{r_i} + \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{|r_i - r_j|} + \sum_{i=1}^{n} \sum_{j=1}^{N} Z_j |r_i - R_j|
\]

using floating explicitly correlated Gaussian (fECG) basis functions and the QUANTEN computer program [19, 26].

The rovibrational Hamiltonian corresponding to the ground electronic (‘0’th) state and accounting for non-adiabatic coupling up to the second-order terms in
\[ \varepsilon = (m_e/m_{\text{nuc}})^{\frac{1}{2}}, \] is \[23, 24, 27\]

\[ H_0^{(2)} = \sum_{i,j=1}^{3N} \frac{1}{2} \left( -i\varepsilon \partial_{R_i} \right) (\delta_{ij} - \varepsilon^2 M_{ij}) \left( -i\varepsilon \partial_{R_i} \right) + E_{\text{el},0} + \varepsilon^2 U_0, \] \[ (2) \]

where

\[ U = \frac{1}{2} \sum_{i=1}^{3N} \langle \partial_{R_i} \phi_0 | \partial_{R_i} \phi_0 \rangle \] \[ (3) \]

and

\[ M_{ij} = 2 \langle \partial_{R_j} \phi_0 | P_0^\perp (\hat{H}_e - E_{\text{el},0})^{-1} P_0^\perp | \partial_{R_i} \phi_0 \rangle, \quad P_0^\perp = 1 - |\phi_0\rangle\langle\phi_0|, \] \[ (4) \]

are the diagonal Born–Oppenheimer correction (DBOC) and the mass-correction tensor, respectively.

Rotational-vibrational states of He\(_2^+\) are computed using this Hamiltonian written in spherical polar coordinates, \((\rho, \theta, \phi)\), which leads to the solution of the radial equation \[15, 26\]:

\[ \left( -\frac{\partial}{\partial \rho} \frac{1}{m_{\text{nuc}}} \left[ 1 - \frac{M^{\rho}_\rho}{m_{\text{nuc}}} \right] \frac{\partial}{\partial \rho} + \frac{N^+(N^+ + 1)}{\rho^2} \frac{1}{m_{\text{nuc}}} \left[ 1 - \frac{M^{\Omega}_\Omega}{m_{\text{nuc}}} \right] + U(\rho) + E_{\text{el}}(\rho) \right) \chi_{N^+}(\rho) = E_{N^+} \chi_{N^+}(\rho). \] \[ (5) \]

\(M^{\rho}_\rho\) and \(M^{\Omega}_\Omega\) are the vibrational and rotational mass correction functions corresponding to the curvilinear representation \[26\]. The equation is solved for each \(N^+\) rotational angular momentum quantum number using a discrete variable representation \[28\].

We have computed the \(E_{\text{el}}(\rho)\) potential energy curve over the \(\rho \in [0.992, 3.5]\) bohr interval of the internuclear separation that is necessary to converge the rovibrational states considered in this work. As a result, the electronic energy at the equilibrium structure \((\rho_{eq} = 2.042\) bohr\) is within the 0.2 \(\mu\)E\(_h\) error bar of the complete basis set limit estimate by Cencek et al. \[29\]. The newly computed part of the potential energy curve (PEC) improves the earlier PEC \[14\] by 0.012 cm\(^{-1}\) (59 nE\(_h\)) at the
TABLE I. Error balance of the rotational and (ro)vibrational intervals, in cm$^{-1}$, computed in the present work. The numerical uncertainty of the computed intervals is estimated based on the difference in the intervals obtained with two different datasets: \( ^{a} \) PEC (DBOC) curve from Ref. [14] and from the present work; \( ^{b} \) non-adiabatic mass computed in Ref. [15] and in the present work; \( ^{c} \) relativistic corrections obtained with the integral transformation technique [30] and the ‘direct’ method [31]; \( ^{d} \) effect of a hypothetical \( \pm 1\% \) change in \( \beta_{el} \); \( ^{e} \) \( \sigma \) is obtained as the sum of the absolute value of the terms; \( ^{f} \) the effect of the neglected higher-order QED corrections is estimated with the dominant term of \( E^{(4)} \), Eq. (11); \( ^{g} \) estimate for the coupling of the non-adiabatic and relativistic corrections, see also Ref. [32]; \( ^{h} \) estimate for the effect of the finite nuclear size [33]; * We use half of this value for the uncertainty estimate of the present results.

|               | Rotational intervals | (Ro)vibrational intervals |
|---------------|----------------------|---------------------------|
|               | (0,3)–(0,1) RMSD$_{\text{rot}}$ | (1,0)–(0,0) RMSD$_{\text{rv}}$ |
| Numerical uncertainty estimate for the computed terms (\( \pm \sigma \)) | | |
| PEC$^{a}$     | $-0.000 \, 002$ | $0.000 \, 15$ | $-0.003 \, 28^*$ | $0.003 \, 37^*$ |
| DBOC$^{a}$    | $-0.000 \, 010$ | $0.000 \, 18$ | $-0.000 \, 16$ | $0.000 \, 19$ |
| Nadm$^{b}$    | $-0.000 \, 018$ | $0.000 \, 36$ | $-0.000 \, 13$ | $0.000 \, 24$ |
| Rel.$^{c}$    | $-0.000 \, 012$ | $0.000 \, 18$ | $0.001 \, 09$ | $0.000 \, 84$ |
| \( \beta_{el} \) (\( \pm 1\% \))$^{d}$ | $-0.000 \, 032$ | $0.000 \, 22$ | $0.000 \, 12$ | $0.000 \, 63$ |
| \( \pm \sigma \)$^{e}$ | $\pm 0.000 \, 073$ | $\pm 0.001 \, 09$ | $\pm 0.003 \, 14$ | $\pm 0.003 \, 59$ |

|               | Estimate for neglected theoretical terms (\( \Delta_{\text{est}} \)) |
|---------------|-------------------------------------------------------------|
| hQED$^{f}$    | $-0.000 \, 008$ | $-0.000 \, 15$ | $-0.000 \, 13$ | $-0.000 \, 25$ |
| Nad&Rel$^{g}$ | $-0.000 \, 001$ | $-0.000 \, 02$ | $-0.000 \, 01$ | $-0.000 \, 03$ |
| Fsn$^{h}$     | $-0.000 \, 001$ | $-0.000 \, 02$ | $-0.000 \, 02$ | $-0.000 \, 04$ |
| \( \Delta_{\text{est}} \) | $-0.000 \, 010$ | $-0.000 \, 19$ | $-0.000 \, 16$ | $-0.000 \, 31$ |

Equilibrium structure and by 0.034 cm$^{-1}$ (155 n$E_{\text{h}}$) at \( \rho = 3.5 \) bohr.

Table I collects the calculated change in the energy intervals using the newly computed and the earlier curves. As a (conservative) estimate for the remaining error due to uncertainties of the PEC, we used the half of the observed change. We think that the uncertainty of the rovibrational intervals due to the uncertainty of the PEC is within a few n$E_{\text{h}}$.

The relativistic effects on the electronic motion are accounted for by incrementing the \( E_{el} + U \) adiabatic potential energy curve with the expectation value of the spin-independent part of the Breit–Pauli Hamiltonian, including the mass-velocity term, the Darwin terms and the spin-spin coupling, as well as the orbit-orbit term [34]:

\[
E_{\text{rel}}^{(2)} = \alpha^2 \langle \phi_0 | H_{\text{rel}}^{(2)} | \phi_0 \rangle ,
\]
where

\[ H_{\text{rel}}^{(2)} = -\frac{1}{8} \sum_{i=1}^{n} \mathbf{p}_i^4 + \frac{\pi}{2} \sum_{i=1}^{n} \sum_{a=1}^{N} Z_a \delta(r_{ia}) + \pi \sum_{i=1}^{n} \sum_{j>i}^{n} \delta(r_{ij}) \]

\[ -\frac{1}{2} \sum_{i=1}^{n} \sum_{j>i}^{n} \left( \frac{1}{r_{ij}} \mathbf{p}_i \cdot \mathbf{p}_j + \frac{1}{r_{ij}^3} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \mathbf{p}_i) \cdot \mathbf{p}_j \right). \]  

(7)

In order to assess the uncertainty of the computations (Table I), we evaluated the expectation values 'directly' for the \( p_i^4 \) and \( \pi \delta(r_{ix}) = \frac{1}{4} \nabla^2 r_{ix} \cdot \frac{1}{r_{ix}} (x = j \text{ or } a) \) operators \[31\] and by using the integral-transformation technique (IT) \[30\]. Since we have accurate electronic wave functions, we expect that the two routes give very similar rovibrational intervals, still the results obtained with the IT integrals are expected to have a lower uncertainty.

The spin-independent \( \alpha^3 \)-order QED corrections to the adiabatic potential energy of a diatomic molecule is \[34-36\]:

\[ E_{\text{rad}}^{(3)} = \alpha^3 \frac{4}{3} \sum_{i=1}^{n} \left( \ln \frac{1}{\alpha^2} - \beta_{\text{el}} + \frac{19}{30} \right) \langle \phi_0 | Z \delta(r_{i1}) + Z \delta(r_{i2}) | \phi_0 \rangle \]

\[ + \alpha^3 \sum_{i=1}^{n} \sum_{j>i}^{n} \left[ \left( \frac{14}{3} \ln \alpha + \frac{164}{15} \right) \langle \phi_0 | \delta(r_{ij}) | \phi_0 \rangle - \frac{14}{3} Q_{\text{el}} \right], \]  

(8)

where

\[ \beta_{\text{el}} = \frac{\langle \phi_0 | J (H_0 - E_0) \ln (2(H_0 - E_0)/E_\text{h}) J | \phi_0 \rangle}{\langle \phi_0 | [J, [H_0, J]]/2 | \phi_0 \rangle} \]  

(9)

is the (non-relativistic) Bethe logarithm including the \( J = -\sum_{i=1}^{n} p_i \) electric current density. A precise evaluation of \( \beta_{\text{el}} \) is a major numerical task and values can be obtained if the wave function satisfies the electron-nucleus cusp condition \[37, 38\]. The \( Q_{\text{el}} \) term was introduced by Araki and Sucher \[39, 40\]:

\[ Q_{\text{el}} = \lim_{\epsilon \to 0} \left\langle \phi_0 \left| \frac{\Theta(r_{ij} - \epsilon)}{4\pi r_{ij}^3} + (\ln \epsilon + \gamma_E) \delta(r_{ij}) \right| \phi_0 \right\rangle \]  

(10)

that is evaluated for \( \text{He}_2^+ \) using the integral transformation technique \[30\] and the fECG basis representation.

Concerning the Bethe logarithm, we start with a few numerical observations. Table II presents a compilation of the Bethe logarithm values for the lightest atoms.
TABLE II. Dependence of the $\beta_{el}$ Bethe logarithm on the $Z$ nuclear charge and on the $n$ number of electrons in the ground state of atoms (ions). The data is compiled from Refs. [41–45].

| $\beta_{el}$ | H  | He | Li  |
|--------------|----|----|-----|
| $[E_h]$      | $Z = 1$ | $Z = 2$ | $Z = 3$ |
| $n = 1$      | 2.984128 | 4.370422 | 5.181353 |
| $n = 2$      | – | 4.370160 | 5.179849 |
| $n = 3$      | – | – | 5.17828 |

TABLE III. Comparison of the $\beta_{el}(\rho)$ Bethe logarithm for selected $\rho$ internuclear distances of the one-electron $\text{H}_2^+$ molecular ion [38] and the two-electron $\text{H}_2$ molecule [33] in the adiabatic approximation and in their ground electronic states.

| $\rho$ [bohr] | 0.1 | 0.2 | 0.4 | 0.8 | 1.5 | 5.0 |
|---------------|-----|-----|-----|-----|-----|-----|
| $\beta_{el}(\rho)(\text{H}_2^+)$ $[E_h]$ [38] | 3.763208 | 3.525245 | 3.284256 | 3.100639 | 3.023053 | 2.995328 |
| $\beta_{el}(\rho)(\text{H}_2)$ $[E_h]$ [33] | 3.765 | 3.526 | 3.279 | 3.09331 | 3.01396 | 2.98534 |

and ions [41–45] to highlight the weak dependence of $\beta_{el}$ on the number of electrons, but its strong dependence on the nuclear charge, $Z$. A similar observation applies for molecules described within the adiabatic approximation. Table [III] shows the value of $\beta_{el}(\rho)$ in the ground electronic state of the one-electron $\text{H}_2^+$ molecular ion and the two-electron $\text{H}_2$ molecule for selected values of the $\rho$ internuclear distance. The $\beta_{el}(\rho)$ values of $\text{H}_2^+$ and $\text{H}_2$ differ in the 4-5th significant digit.

These observations suggest that the Bethe logarithm of $\text{He}_2^+$ ($X^2\Sigma_u^+$) can be well approximated with the Bethe logarithm of the ground electronic state of $\text{He}_2^{3+}$. The Bethe logarithm for this one-electron two-center problem was computed using the procedure of Ref. [38]. We estimate the error introduced by the $\beta_{el,\text{He}_2^+}(\rho) \approx \beta_{el,\text{He}_2^{3+}}(\rho)$ approximation, which we use in this work, to be less than 1 % over the relevant internuclear range, $\rho \in [0.9, 3.5]$ bohr (Table [II]).

The effect of higher-order QED corrections is estimated as in Refs. [33, 46]:

$$E^{(4)}_{\text{est}} = \alpha^4 \pi \left( \frac{427}{96} - 2 \ln 2 \right) \sum_{i=1}^{3} \sum_{a=1}^{2} Z_a \delta(r_{ia}) .$$ (11)

Table II collects the numerical uncertainty attributed to the rovibrational intervals within the described computational procedure. The present theoretical framework rests on two small parameters, the square root of the electron-to-nucleus mass ratio,
$\varepsilon$, and the fine-structure constant, $\alpha$. The electron-nucleus (non-adiabatic) coupling is accounted for up to $\varepsilon^2$ order and higher-order contributions are neglected. Relativistic ($\alpha^2$) and leading-order QED ($\alpha^3$) corrections have been included, and an estimate for the $\alpha^4$-order terms, Eq. (11), was also computed. We estimate the uncertainty of the rotational-vibrational intervals due to the missing part of $\alpha^4$ and higher-order QED corrections by the (small) effect of the $\alpha^4$ estimate (hQED in Table I). We have neglected the non-adiabatic-relativistic (and QED) coupling in the present work that was found to be important in the $\text{H}_2$ molecule [32]. An elaborate theoretical and computational study of this coupling for the present system will require further work, but we give an estimate for its magnitude (Nad&Rel in Table I). The estimated effect of the finite nuclear size is also shown in Table I. We used the CODATA18 recommendations for the physical constants and conversion factors throughout the computations.

The computed rotational and (ro)vibrational intervals and corrections are listed in Tables IV and V. Figure 1 visualizes the results and reveals a fine interplay of the various corrections. (The potential energy points and all corrections computed and used in this work are deposited in the Supplementary Material.)

The adiabatic description (‘Ad’) with the ‘empirical mass correction’ using $m_{\text{rot}} = m_{\text{vib}} = m_\alpha + 1.5m_e$ [14] reproduces the fundamental vibration energy almost perfect, while its deviation from experiment increases with increasing $N^+$. By including the rigorous non-adiabatic masses for the rotational and vibrational degrees of freedom [15], the error is reduced for the rotational excitations, but the fundamental vibration energy shows a large deviation from experiment. Adding the relativistic corrections to this non-adiabatic model reduces the deviation to the half for the fundamental vibration, but it ‘over-corrects’ the rotational excitation energies. By including also the leading-order QED corrections in the theoretical treatment both the fundamental vibration energy, the rotational and the rovibrational excitation energies come in agreement with experiment with a root-mean-squared deviation (RMSD) of 0.0017 and 0.0019 cm$^{-1}$, respectively. The experimental uncertainty of the rotational and rovibrational series is slightly smaller than these values [12, 13], they are 0.0008 and 0.00012 cm$^{-1}$, respectively. The lowest-energy rotational interval, (0, 3)–(0, 1), has been recently measured more precisely, 70.937 589(23) ± 0.000 06$_{\text{sys}}$ [9], and our
theoretical value for this interval is 70.93769(10) cm\(^{-1}\). For the fundamental vibration, our computational result is 1628.3809(33) cm\(^{-1}\), which is in agreement with its value derived from experiments, 1628.3832(12) cm\(^{-1}\) [13].

All the rovibrational intervals (Table V) are in agreement with the experimental results within the given uncertainties, although the computational results have almost three times larger uncertainties than the experimental ones. We observe some discrepancy for the rotational intervals with intermediate \(N^+\) values (especially, \(N^+ = 7, 9\) and 13). We note that the pure rotational intervals have a smaller uncertainty than the rovibrational ones, since they were much less affected by the PEC improvement (Table II).

We finish the discussion with observations regarding the interplay of the computed corrections (Tables IV and V). First, we point out that \(\delta \tilde{\nu}_{\text{mveff}}\) and \(\delta \tilde{\nu}_{\text{mvNad}}\) together account for the non-adiabatic mass effect. \(\delta \tilde{\nu}_{\text{mveff}}\) is a simple, intuitive, constant mass model \((m_{\text{rot}} = m_{\text{vib}} = m_{\alpha} + 1.5m_e)\) and \(\delta \tilde{\nu}_{\text{mvNad}}\) labels the value, which corrects this empirical model to arrive at the rigorous second-order non-adiabatic result. It is interesting to observe, at least for the present example, that \(\delta \tilde{\nu}_{\text{mvNad}}\) has the same order of magnitude but opposite sign as the leading-order QED correction, \(\delta \tilde{\nu}_{\text{QED}}\). The interplay of the corrections changes for the different types of motions, i.e., the relativistic correction has a different sign for the rotational and for the vibrational excitation, whereas the QED contribution is positive in both cases. This interplay of the higher-order correction terms—that we explicitly compute in the present work—had resulted in cancellation of errors in the lower-order calculations [14] and a seemingly good agreement with the experimental result [13] for this interval.
FIG. 1. Deviation of the rotational and (ro)vibrational excitation energies of the $^4$He$_2^+$ molecular ion ($X\ 3\Sigma^+_u$) from experiment [9, 12, 13]. ($v, N^+$) labels the $v$th vibrational state with the $N^+$ rotational quantum number. □: adiabatic with the $m_{\text{vib}} = m_{\text{rot}} = m_\alpha + 1.5m_e$ empirical mass in the kinetic energy operator; ■: non-adiabatic, i.e., with rigorous rotational and vibrational masses; ○: non-adiabatic and relativistic corrections; ●: non-adiabatic, relativistic, and leading-order QED corrections; ×: non-adiabatic, relativistic, leading-order QED with estimates for higher-order QED corrections.
TABLE IV. Rotational excitation energies of $^4$He$_2^+$ ($X \ ^2\Sigma_u^+$) in the vibrational ground state. $\tilde{\nu}_0$: Born–Oppenheimer description with nuclear masses; $\delta \nu_{\text{DBOC}}$: the diagonal Born–Oppenheimer correction; $\delta \nu_{\text{mvNad}}$: empirical mass; $m_{\text{rot}} = m_{\text{vib}} = m_\alpha + 1.5m_e$; $\delta \nu_{\text{Nad}}$: rigorous non-adiabatic mass; $\delta \nu_{\text{Rel}}$: relativistic correction; $\delta \nu_{\text{QED}}$: leading-order QED correction; $\delta \nu_{\text{QED}}$: estimate for higher-order QED corrections. For the derivation of the error estimates to the computed energies see Table I.

| $N^+$: | $\tilde{\nu}(0, N^+)$ $-$ $\tilde{\nu}(0, 1)$ [cm$^{-1}$] | 3       | 5      | 7      | 9     |
|-------|-------------------------------------------------------|--------|--------|--------|-------|
| $\tilde{\nu}_0$ | 70.96061 | 198.4278 | 381.9543 | 620.8981 |
| $+\delta \tilde{\nu}_{\text{DBOC}}$ | $-$0.01028 | $-$0.0287 | $-$0.0550 | $-$0.0891 |
| $+\delta \nu_{\text{mvNad}}$ | $-$0.01446 | $-$0.0404 | $-$0.0776 | $-$0.1258 |
| $+\delta \nu_{\text{Rel}}$ | 0.00045 | 0.0013 | 0.0026 | 0.0044 |
| $+\delta \nu_{\text{QED}}$ | 0.00216 | 0.0060 | 0.0115 | 0.0187 |
| $+\delta \nu_{\text{QED}}$ | $-$0.00078 | $-$0.0022 | $-$0.0042 | $-$0.0068 |
| $\nu_{\text{calc}}$ | 70.93768(10) | 198.3638(13) | 381.8316(13) | 620.6994(13) |
| $\tilde{\nu}_{\text{expt}}$ $-$ $\nu_{\text{calc}}$ | $-$0.00010 | 0.0009 | 0.0030 | 0.0027 |

| $N^+$: | $\tilde{\nu}(0, N^+)$ $-$ $\tilde{\nu}(0, 1)$ [cm$^{-1}$] | 11     | 13     | 15     | 17    | 19    |
|-------|-------------------------------------------------------|--------|--------|--------|-------|-------|
| $\tilde{\nu}_0$ | 914.4265 | 1261.5215 | 1660.9860 | 2111.4508 | 2611.3826 |
| $+\delta \tilde{\nu}_{\text{DBOC}}$ | $-$0.1304 | $-$0.1788 | $-$0.2336 | $-$0.2944 | $-$0.3605 |
| $+\delta \nu_{\text{mvNad}}$ | $-$0.1847 | $-$0.2538 | $-$0.3328 | $-$0.4209 | $-$0.5177 |
| $+\delta \nu_{\text{Rel}}$ | 0.0069 | 0.0101 | 0.0141 | 0.0191 | 0.0252 |
| $+\delta \nu_{\text{QED}}$ | 0.0273 | 0.0373 | 0.0486 | 0.0611 | 0.0745 |
| $+\delta \nu_{\text{QED}}$ | $-$0.0100 | $-$0.0138 | $-$0.0181 | $-$0.0230 | $-$0.0283 |
| $+\delta \nu_{\text{QED}}$ | $-$0.0001 | $-$0.0001 | $-$0.0002 | $-$0.0002 | $-$0.0003 |
| $\nu_{\text{calc}}$ | 914.1354(13) | 1261.1223(13) | 1660.4640(13) | 2110.7925(13) | 2610.5755(15) |
| $\tilde{\nu}_{\text{expt}}$ $-$ $\nu_{\text{calc}}$ | 0.0013 | 0.0019 | $-$0.0013 | 0.0007 | $-$0.0011 |
TABLE V. Rovibrational excitation energies of $^4\text{He}_2^+$ ($X^2\Sigma^+_u$) between the vibrational ground and first excited state. See also the caption to Table [IV].

| $(v, N^+)^{\prime\prime} - (v, N^+)^{\prime}$ | $\tilde{\nu}(v, N^+)^{\prime\prime} - \tilde{\nu}(v, N^+)^{\prime}$ [cm$^{-1}$] |
|---------------------------------------------|----------------------------------|
| $(v, N^+)^{\prime\prime} - (v, N^+)^{\prime}$ | (1, 0)--(0, 0) | (1, 1)--(0, 1) | (1, 3)--(0, 1) |
| $\tilde{\nu}_0$ | 1628.5600 | 1628.1081 | 1696.8089 |
| $\delta \tilde{\nu}_{\text{DBOC}}$ | -0.0223 | -0.0222 | -0.0320 |
| $\delta \tilde{\nu}_{\text{mv eff}}$ | -0.1602 | -0.1601 | -0.1739 |
| $\delta \tilde{\nu}_{\text{mvNad}}$ | 0.0258 | 0.0257 | 0.0259 |
| $\delta \tilde{\nu}_{\text{Rel}}$ | -0.0102 | -0.0103 | -0.0083 |
| $\delta \tilde{\nu}_{\text{QED}}$ | -0.0120 | -0.0120 | -0.0128 |
| $\delta \tilde{\nu}_{\text{mvNad}}$ | -0.0001 | -0.0001 | -0.0001 |
| $\tilde{\nu}_{\text{calc}} = \tilde{\nu}_0 + \sum \delta \tilde{\nu}$ | 1628.3809(33) | 1627.9291(39) | 1696.6077(39) |
| $\tilde{\nu}_{\text{expt}}$ | 1628.3832(12) | 1627.9318(12) | 1696.6096(12) |
| $\tilde{\nu}_{\text{expt}} - \tilde{\nu}_{\text{calc}}$ | 0.0023 | 0.0027 | 0.0019 |

| $(v, N^+)^{\prime\prime} - (v, N^+)^{\prime}$ | $\tilde{\nu}(v, N^+)^{\prime\prime} - \tilde{\nu}(v, N^+)^{\prime}$ [cm$^{-1}$] |
|---------------------------------------------|----------------------------------|
| $(v, N^+)^{\prime\prime} - (v, N^+)^{\prime}$ | (1, 7)--(0, 1) | (1, 11)--(0, 1) | (1, 13)--(0, 1) |
| $\tilde{\nu}_0$ | 1997.8578 | 2513.1465 | 2848.9316 |
| $\delta \tilde{\nu}_{\text{DBOC}}$ | -0.0744 | -0.1459 | -0.1916 |
| $\delta \tilde{\nu}_{\text{mv eff}}$ | -0.2339 | -0.3357 | -0.4013 |
| $\delta \tilde{\nu}_{\text{mvNad}}$ | 0.0269 | 0.0293 | 0.0312 |
| $\delta \tilde{\nu}_{\text{Rel}}$ | 0.0002 | 0.0143 | 0.0233 |
| $\delta \tilde{\nu}_{\text{QED}}$ | -0.0161 | -0.0216 | -0.0252 |
| $\delta \tilde{\nu}_{\text{mvNad}}$ | -0.0002 | -0.0002 | -0.0003 |
| $\tilde{\nu}_{\text{calc}} = \tilde{\nu}_0 + \sum \delta \tilde{\nu}$ | 1997.5604(39) | 2512.6867(39) | 2848.3678(39) |
| $\tilde{\nu}_{\text{expt}}$ | 1997.5633(12) | 2512.6871(12) | 2848.3690(12) |
| $\tilde{\nu}_{\text{expt}} - \tilde{\nu}_{\text{calc}}$ | 0.0029 | 0.0004 | 0.0012 |
Rotational and (ro)vibrational intervals have been reported for the three-electron $^4\text{He}_2^+$ ($X^2\Sigma^+$) molecular ion on a newly computed potential energy curve with non-adiabatic, relativistic, and QED corrections. The computed rotational-vibrational intervals are in good agreement with recent precision spectroscopy measurements. Further developments, most importantly, a detailed study of the relativistic-non-adiabatic coupling and the extension of the potential energy curve with ppb uncertainty over large internuclear distances, will challenge precision spectroscopy experiments and contribute to the establishment of primary pressure standards.

DF acknowledges the support from the ÚNKP-19-3 New National Excellence Program of the Ministry for Innovation and Technology (ÚNKP-19-3-I-ELTE-24). EM and DF acknowledge the financial support of the Swiss National Science Foundation (PROMYS Grant, No. IZ11Z0_166525) at the beginning of this work and the European Research Council (Starting Grant, No. 851421). EM thanks Frédéric Merkt for discussions. V.I.K. acknowledges support from the Russian Foundation for Basic Research under Grant No. 19-02-00058-a.

*korobov@theor.jinr.ru
†matyus@chem.elte.hu

[1] N. Hölsc, 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).

[2] 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).

[3] 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 581, 152 (2020).

[4] R. K. Altmann, L. S. Dreissen, E. J. Salumbides, W. Ubachs, and K. S. E. Eikema, Deep-ultraviolet frequency metrology of H$_2$ for tests of molecular quantum theory, Phys. Rev. Lett. 120, 043204 (2018).
[5] M. S. Safronova, D. Budker, D. DeMille, D. F. J. Kimball, A. Derevianko, and C. W. Clark, Search for new physics with atoms and molecules, Rev. Mod. Phys. 90, 025008 (2018).

[6] J.-P. Karr, L. Hilico, J. C. J. Koelemeij, and V. I. Korobov, Hydrogen molecular ions for improved determination of fundamental constants, Phys. Rev. A 94, 050501(R) (2016).

[7] S. Alighanbari, M. G. Hansen, V. I. Korobov, and S. Schiller, Rotational spectroscopy of cold and trapped molecular ions in the Lamb–Dicke regime, Nature Phys. 14, 555 (2018).

[8] M. Puchalski, K. Pisztaszowski, J. Komasa, B. Jezierski, and K. Szalewicz, Theoretical determination of the polarizability dispersion and the refractive index of helium, Phys. Rev. A 93, 032515 (2016).

[9] L. Semeria, P. Jansen, G.-M. Camenisch, F. Mellini, H. Schmutz, and F. Merkt, Precision measurement in few-electron molecules: The ionization energy of metastable $^4$He$_2$ and the first rotational interval in $^4$He$_2^+$, Phys. Rev. Lett. 124, 213001 (2020).

[10] P. Jansen, L. Semeria, and F. Merkt, Determination of the spin-rotation fine structure of He$_2^+$, Phys. Rev. Lett. 120, 043001 (2018).

[11] P. Jansen, L. Semeria, and F. Merkt, High-resolution spectroscopy of He$_2^+$ using Rydberg-series extrapolation and Zeeman-decelerated supersonic beams of metastable He$_2$, J. Mol. Spectrosc. 322, 9 (2016).

[12] L. Semeria, P. Jansen, and F. Merkt, Precision measurement of the rotational energy-level structure of the three-electron molecule He$_2^+$, J. Chem. Phys. 145, 204301 (2016).

[13] P. Jansen, L. Semeria, and F. Merkt, Fundamental vibration frequency and rotational structure of the first excited vibrational level of the molecular helium ion (He$_2^+$), J. Chem. Phys. 149, 154302 (2018).

[14] W.-C. Tung, M. Pavanello, and L. Adamowicz, Very accurate potential energy curve of the He$_2^+$ ion, J. Chem. Phys. 136, 104309 (2012).

[15] E. Mátyus, Non-adiabatic mass-correction functions and rovibrational states of $^4$He$_2^+$ ($X^2Σ^+_u^+$), J. Chem. Phys. 149, 194112 (2018).

[16] S. Bubin, M. Pavanello, W.-C. Tung, K. L. Sharkey, and L. Adamowicz, Born–Oppenheimer and Non-Born–Oppenheimer, atomic and molecular calculations with
explicitly correlated Gaussians, Chem. Rev. 113, 36 (2013).

[17] V. I. Korobov, Ro-vibrational states of $\text{H}_2^+$, variational calculations, Mol. Phys. 116, 93 (2018).

[18] L. M. Wang and Z.-C. Yan, Relativistic corrections to the ground state of H$_2$ calculated without using the Born–Oppenheimer approximation, Phys. Rev. A 97, 060501(R) (2018).

[19] E. Mátyus, Pre-Born–Oppenheimer molecular structure theory, Mol. Phys. 117, 590 (2019).

[20] D. Ferenc and E. Mátyus, Computation of rovibronic resonances of molecular hydrogen: $\text{EF} \ 1\Sigma_g^+$ inner-well rotational states, Phys. Rev. A 100, 020501(R) (2019).

[21] K. Pachucki and J. Komasa, Nonadiabatic rotational states of the hydrogen molecule, Phys. Chem. Chem. Phys. 20, 247 (2018).

[22] M. Stanke, S. Bubin, and L. Adamowicz, Fundamental vibrational transitions of the $^3\text{He}^4\text{He}^+$ and $^7\text{LiH}^+$ ions calculated without assuming the Born–Oppenheimer approximation and with including leading relativistic corrections, Phys. Rev. A 79, 060501(R) (2009).

[23] S. Teufel, Adiabatic perturbation theory in quantum dynamics, Lecture Notes in Mathematics (Springer, 2003).

[24] G. Panati, H. Spohn, and S. Teufel, The time-dependent Born–Oppenheimer approximation, ESAIM: Mathematical Modelling and Numerical Analysis 41, 297 (2007).

[25] K. Pachucki and J. Komasa, Nonadiabatic corrections to rovibrational levels of H$_2$, J. Chem. Phys. 130, 164113 (2009).

[26] E. Mátyus, Non-adiabatic mass correction to the rovibrational states of molecules. numerical application for the H$_2^+$ molecular ion, J. Chem. Phys. 149, 194111 (2018).

[27] E. Matyus and S. Teufel, Effective non-adiabatic Hamiltonians for the quantum nuclear motion over coupled electronic states, J. Chem. Phys. 151, 014113 (2019).

[28] J. C. Light and T. Carrington Jr., Discrete-variable representations and their utilization, in Advances in Chemical Physics (John Wiley & Sons, Ltd, 2000) pp. 263–310.

[29] W. Cencek and J. Rychlewski, Benchmark calculations for He$_2^+$ and LiH molecules using explicitly correlated Gaussian functions, Chem. Phys. Lett. 320, 549 (2000).

[30] K. Pachucki, W. Cencek, and J. Komasa, On the acceleration of the convergence of
singular operators in Gaussian basis sets, J. Chem. Phys. 122, 184101 (2005).

[31] M. Stanke, E. Palikot, and L. Adamowicz, Algorithms for calculating mass-velocity and Darwin relativistic corrections with \( n \)-electron explicitly correlated Gaussians with shifted centers, J. Chem. Phys. 144, 174101 (2016).

[32] P. Czachorowski, M. Puchalski, J. Komasa, and K. Pachucki, Nonadiabatic relativistic correction in \( H_2, D_2 \), and HD, Phys. Rev. A 98, 052506 (2018).

[33] K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, Theoretical determination of the dissociation energy of molecular hydrogen, J. Chem. Theory Comput. 5, 3039 (2009).

[34] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Plenum Publishing Co., New York, 1977).

[35] K. Pachucki, Simple derivation of helium Lamb shift, J. Phys. B 31, 5123 (1998).

[36] K. Pachucki and J. Komasa, Rovibrational levels of HD, Phys. Chem. Chem. Phys. 12, 9188 (2010).

[37] R. Bukowski, B. Jeziorski, R. Moszynski, and W. Kolos, Bethe logarithm and Lamb shift for the hydrogen molecular ion, Int. J. Quant. Chem. 42, 287 (1992).

[38] V. I. Korobov, L. Hilico, and J.-P. Karr, Calculation of the relativistic Bethe logarithm in the two-center problem, Phys. Rev. A 87, 062506 (2013).

[39] H. Araki, Quantum-electrodynamical corrections to energy-level of helium, Prog. Theor. Phys. 17, 619 (1957).

[40] J. Sucher, Energy levels of the two-electron atom to order \( \alpha^3 \)Ry; Ionization energy of helium, Phys. Rev. 109, 1010 (1958).

[41] G. W. F. Drake and S. P. Goldman, Bethe logarithms for \( Ps^- \), \( H^- \), and heliumlike atoms, Can. J. Phys. 77, 835 (1999).

[42] V. A. Yerokhin and K. Pachucki, Theoretical energies of low-lying states of light helium-like ions, Phys. Rev. A 81, 022507 (2010).

[43] V. I. Korobov, Calculation of the nonrelativistic Bethe logarithm in the velocity gauge, Phys. Rev. A 85, 042514 (2012).

[44] K. Pachucki and J. Komasa, Bethe logarithm for the lithium atom from exponentially correlated Gaussian functions, Phys. Rev. A 68, 042507 (2003).

[45] Z.-C. Yan, W. Nórtersháuser, and G. W. F. Drake, High precision atomic theory for
Li and Be$^+$: QED shifts and isotope shifts, Phys. Rev. Lett. 100, 243002 (2008).

[46] M. Puchalski, J. Komasa, P. Czachorowski, and K. Pachucki, Complete $ma^6$ corrections to the ground state of H$_2$, Phys. Rev. Lett. 117, 263002 (2016).