Nonadiabatic, Relativistic, and Leading-Order QED Corrections for Rovibrational Intervals of $^4\mathrm{He}_2^+$ $(X\,^2\Sigma_u^+)$

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The rovibrational intervals of the $^4\mathrm{He}_2^+$ molecular ion in its $X\,^2\Sigma_u^+$ ground electronic state are computed by including the nonadiabatic, 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, 70.937 589(23)$(60)_{\mathrm{sys}}$ cm^{-1} [L. Semeria *et al.*, Phys. Rev. Lett. **124**, 213001 (2020)].

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Few-electron molecules serve as benchmark systems for experimental and theoretical molecular physics and spectroscopy. Recent experimental and theoretical progress of H_2^+, 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.

This Letter joins this direction and focuses on the five-particle $^4\mathrm{He}_2^+$ molecular ion in its ground electronic state $(X\,^2\Sigma_u^+)$. In addition to testing fundamental aspects, precision spectroscopy of $^4\mathrm{He}_2^+$ in combination with accurate *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 $^4\mathrm{He}_2^+$, including the measurement of the spin-rotational fine structure [10] and the rotational and rovibrational intervals [9,11–13].

This Letter 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 experimental uncertainties of 0.0008 and 0.0012 cm^{-1}, respectively. The lowest-energy rotational interval is known more precisely to be 70.937 589(23) ± 0.000 060_{sys} cm^{-1} [9].

The most precise theoretical results for molecules can be obtained by including all electrons and nuclei in the nonrelativistic quantum mechanical treatment [2,16–20]. All bound rovibrational and several resonance states of H_2^+ treated as a three-particle system have been converged with an uncertainty in their nonrelativistic energy better than 10^{-7} cm^{-1} [17], and a similar precision has been achieved for selected states of H_2 treated as a four-particle system [21]. The fundamental vibration energy has been computed for $^3\mathrm{He}^4\mathrm{He}^+$ treated as a five-particle system [22], but the convergence error of this energy appears to be at least 2 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 nonadiabatic 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 nonadiabatic perturbation theory to perform well.

There is some evidence of the increasing importance of the nonadiabatic effects with a rotational excitation of $^4\mathrm{He}_2^+$ [12,15], but the nonadiabatic nonrelativistic computation of Ref. [15] was only partially able to account for the discrepancy between theory and experiment for the rotational series. Furthermore, the nonadiabatic 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].

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

First, we solved the electronic Schrödinger equation for $n = 3$ electrons and $N = 2$ fixed nuclei for the ϕ_0 ground electronic state (in Hartree atomic units)

$$
\begin{aligned}
&H_{\mathrm{el}}\phi_0(\boldsymbol{r},\boldsymbol{R}) = E_{\mathrm{el},0}(\boldsymbol{R})\phi_0(\boldsymbol{r},\boldsymbol{R}) \quad \text{with}\\
&\qquad H_{\mathrm{el}} = -\sum_{i=1}^{n}\frac{1}{2m_e}\Delta_{\boldsymbol{r}_i} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}\\
&\qquad\qquad -\sum_{i=1}^{n}\sum_{j=1}^{N}\frac{Z_j}{|\boldsymbol{r}_i-\boldsymbol{R}_j|}
\end{aligned}
\tag{1}
$$

using floating explicitly correlated Gaussian basis functions and the QUANTEN computer program [19,27].

The rovibrational Hamiltonian corresponding to the ground electronic ("0"th) state and accounting for nonadiabatic coupling up to the second-order terms in $\varepsilon = (m_e/m_{\mathrm{nuc}})^{(1/2)}$ is [23–27]

$$
H_0^{(2)} = \sum_{i,j=1}^{3N}\frac{1}{2}(-i\varepsilon\partial_{R_i})(\delta_{ij}-\varepsilon^2 M_{ij})(-i\varepsilon\partial_{R_i}) + E_{\mathrm{el},0} + \varepsilon^2 U_0,
\tag{2}
$$

where

$$
U = \frac{1}{2}\sum_{i=1}^{3N}\langle\partial_{R_i}\phi_0|\partial_{R_i}\phi_0\rangle
\tag{3}
$$

and

$$
\begin{aligned}
M_{ij} &= 2\langle\partial_{R_j}\phi_0|P_0^{\perp}(\hat{H}_{\mathrm{e}}-E_{\mathrm{el},0})^{-1}P_0^{\perp}|\partial_{R_i}\phi_0\rangle,\\
P_0^{\perp} &= 1-|\phi_0\rangle\langle\phi_0|
\end{aligned}
\tag{4}
$$

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, (ρ,θ,ϕ), which leads to the solution of the radial equation [15,27]

$$
\begin{aligned}
&\left(-\frac{\partial}{\partial\rho}\frac{1}{m_{\mathrm{nuc}}}\left[1-\frac{\mathcal{M}^{\rho}{}_{\rho}}{m_{\mathrm{nuc}}}\right]\frac{\partial}{\partial\rho}\right.\\
&\left.+\frac{N^+(N^++1)}{\rho^2}\frac{1}{m_{\mathrm{nuc}}}\left[1-\frac{\mathcal{M}^{\Omega}{}_{\Omega}}{m_{\mathrm{nuc}}}\right]+U(\rho)+E_{\mathrm{el}}(\rho)\right)\chi_{N^+}(\rho)\\
&=E_{N^+}\chi_{N^+}(\rho).
\end{aligned}
\tag{5}
$$

$\mathcal{M}^{\rho}{}_{\rho}$ and $\mathcal{M}^{\Omega}{}_{\Omega}$ are the vibrational and rotational mass-correction functions corresponding to the curvilinear representation [27]. The equation is solved for each N^+ rotational angular momentum quantum number using a discrete variable representation [28].

We have computed the $E_{\mathrm{el}}(\rho)$ 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 Letter. As a result, the electronic energy at the equilibrium structure ($\rho_{\mathrm{eq}} = 2.042$ bohr) is within the 0.2 $\mu\mathrm{E_h}$ 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 $\mathrm{nE_h}$) at the equilibrium structure and by 0.034 cm^{-1} (155 $\mathrm{nE_h}$) 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 $\mathrm{nE_h}$.

The relativistic effects on the electronic motion are accounted for by incrementing the $E_{\mathrm{el}}+U$ 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]:

$$
E_{\mathrm{rel}}^{(2)} = \alpha^2\langle\phi_0|H_{\mathrm{rel}}^{(2)}|\phi_0\rangle,
\tag{6}
$$

where

$$
\begin{aligned}
H_{\mathrm{rel}}^{(2)} = &-\frac{1}{8}\sum_{i=1}^{n}\boldsymbol{p}_i^4 + \frac{\pi}{2}\sum_{i=1}^{n}\sum_{a=1}^{N}Z_a\delta(\boldsymbol{r}_{ia}) + \pi\sum_{i=1}^{n}\sum_{j>i}^{n}\delta(\boldsymbol{r}_{ij})\\
&-\frac{1}{2}\sum_{i=1}^{n}\sum_{j>i}^{n}\left[\frac{1}{r_{ij}}\boldsymbol{p}_i\cdot\boldsymbol{p}_j + \frac{1}{r_{ij}^3}\boldsymbol{r}_{ij}(\boldsymbol{r}_{ij}\cdot\boldsymbol{p}_i)\cdot\boldsymbol{p}_j\right].
\end{aligned}
\tag{7}
$$

In order to assess the uncertainty of the computations (Table I), we evaluated the expectation values "directly" for the $\boldsymbol{p}_i^4$ and $\pi\delta(\boldsymbol{r}_{ix}) = \frac{1}{4}\nabla_{\boldsymbol{r}_{ix}}^2(1/r_{ix})(x = j \text{ or } a)$ operators [31] and by using the integral-transformation technique [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 integral-transformation techniques are expected to have a lower uncertainty.

The spin-independent α^3-order QED correction to the adiabatic potential energy of a diatomic molecule is [34–36]

$$
\begin{aligned}
E_{\mathrm{rad}}^{(3)} = &\,\alpha^3\frac{4}{3}\sum_{i=1}^{n}\left(\ln\frac{1}{\alpha^2}-\beta_{\mathrm{el}}+\frac{19}{30}\right)\langle\phi_0|Z\delta(\boldsymbol{r}_{i1})+Z\delta(\boldsymbol{r}_{i2})|\phi_0\rangle\\
&+\alpha^3\sum_{i=1}^{n}\sum_{j>i}^{n}\left[\left(\frac{14}{3}\ln\alpha+\frac{164}{15}\right)\langle\phi_0|\delta(\boldsymbol{r}_{ij})|\phi_0\rangle-\frac{14}{3}Q_{\mathrm{el}}\right],
\end{aligned}
\tag{8}
$$

TABLE I. Error balance of the rotational and (ro)vibrational intervals, in cm^{-1}, computed in this Letter. The numerical uncertainty of the computed intervals is estimated based on the difference in the intervals obtained with two different datasets.

	Rotational intervals		(Ro)vibrational intervals	
	(0,3)–(0,1)	$\mathrm{RMSD}_{\rm rot}$	(1,0)–(0,0)	$\mathrm{RMSD}_{\rm rv}$
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
Relativistic[c]	−0.000 012	0.000 18	0.001 09	0.000 84
$\beta_{\rm el}$ ($\pm1\%$)[d]	−0.000 032	0.000 22	0.000 12	0.000 63
$\pm\sigma$[e]	±0.000 073	±0.001 09	±0.003 14	±0.003 59
Estimate for neglected theoretical terms ($\Delta_{\rm est}$):				
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
$\Delta_{\rm est}$	−0.000 010	−0.000 19	−0.000 16	−0.000 31

[a] PEC (DBOC) curve from Ref. [14] and from this Letter.
[b] Nonadiabatic mass computed in Ref. [15] and in this Letter.
[c] Relativistic corrections obtained with the integral transformation technique [30] and the "direct" method [31].
[d] Effect of a hypothetical ±1% change in $\beta_{\rm el}$.
[e] σ 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 nonadiabatic 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.

where

$$\beta_{\rm el} = \frac{\langle\phi_0|\boldsymbol{J}(H_0-E_0)\ln\left(2(H_0-E_0)/\mathrm{E_h}\right)\boldsymbol{J}\phi_0\rangle}{\langle\phi_0|[\boldsymbol{J},[H_0,\boldsymbol{J}]]/2\phi_0\rangle} \tag{9}$$

is the (nonrelativistic) Bethe logarithm, $\boldsymbol{J}=-\sum_{i=1}^{n}\boldsymbol{p}_i$ is the electric current density. A precise evaluation of $\beta_{\rm el}$ is a major numerical task, and values can be obtained if the wave function satisfies the electron-nucleus cusp condition [37,38]. The $Q_{\rm el}$ term [39,40],

$$Q_{\rm el} = \lim_{\epsilon\to0}\langle\phi_0|\left[\frac{\Theta(r_{ij}-\epsilon)}{4\pi r_{ij}^3}+(\ln\epsilon+\gamma_E)\delta(\boldsymbol{r}_{ij})\right]\phi_0\rangle, \tag{10}$$

has been evaluated for He_2^+ using the integral transformation technique [30] and the floating explicitly correlated Gaussian 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 and ions [41–45] to highlight the weak dependence of $\beta_{\rm el}$ 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 $\beta_{\rm el}(\rho)$ in the ground electronic state of the one-electron H_2^+ molecular ion and the two-electron H_2 molecule for selected values of the ρ internuclear distance. The $\beta_{\rm el}(\rho)$ values of H_2^+ and H_2 differ in the 4th and 5th significant digit.

These observations suggest that the Bethe logarithm of He_2^+ ($X\,{}^2\Sigma_u^+$) can be well approximated with the Bethe logarithm of the ground electronic state of 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 $\beta_{\mathrm{el,He}_2^+}(\rho)\approx\beta_{\mathrm{el,He}_2^{3+}}(\rho)$ approximation, which we use in this Letter, to be less than 1% over the relevant internuclear range $\rho\in[0.9,3.5]$ bohr (Table I).

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

$$E_{\rm est}^{(4)}=\alpha^4\pi\left(\frac{427}{96}-2\ln2\right)\sum_{i=1}^{3}\sum_{a=1}^{2}Z_a\delta(\boldsymbol{r}_{ia}). \tag{11}$$

Table I collects the numerical uncertainty attributed to the rovibrational intervals within the described computational procedure. The present theoretical framework rests

TABLE II. Dependence of the $\beta_{\rm el}$ Bethe logarithm on the Z nuclear charge and on the n number of electrons in the ground state of atoms (ions). These data are compiled from Refs. [41–45].

	H	He	Li
$\beta_{\rm el}$ [$\mathrm{E_h}$]	$Z=1$	$Z=2$	$Z=3$
$n=1$	2.984 128	4.370 422	5.181 353
$n=2$	⋯	4.370 160	5.179 849
$n=3$	⋯	⋯	5.178 28

TABLE III. Comparison of the $\beta_{\mathrm{el}}(\rho)$ Bethe logarithm for selected ρ internuclear distances of the one-electron H_2^+ molecular ion [38] and the two-electron H_2 molecule [33] in the adiabatic approximation and in their ground electronic states.

ρ [bohr]	0.1	0.2	0.4	0.8	1.5	5.0
$\beta_{\mathrm{el}}(\rho)$ (H_2^+) [E_h] [38]	3.763 208	3.525 245	3.284 256	3.100 639	3.023 053	2.995 328
$\beta_{\mathrm{el}}(\rho)$ (H_2) [E_h] [33]	3.765	3.526	3.279	3.093 31	3.013 96	2.985 34

on two small parameters, the square root of the electron-to-nucleus mass ratio ε and the fine-structure constant α. The electron-nucleus (nonadiabatic) coupling is accounted for up to ε^2 order and higher-order contributions are neglected. Relativistic (α^2) and leading-order QED (α^3) corrections have been included, and an estimate for the α^4-order terms, Eq. (11), was also computed. We estimate the uncertainty of the rotational-vibrational intervals due to the missing part of α^4 and higher-order QED corrections by the (small) effect of the α^4 estimate (hQED in Table I). We have neglected the nonadiabatic-relativistic (and QED) coupling in this Letter that was found to be important in the 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 Letter are deposited in the Supplemental Material [47]).

The adiabatic description ("Ad") with the "empirical mass correction" using $m_{\mathrm{rot}} = m_{\mathrm{vib}} = m_\alpha + 1.5m_e$ [14] reproduces the fundamental vibration energy almost perfectly, while its deviation from experiment increases with increasing N^+. By including the rigorous nonadiabatic masses for the rotational and vibrational degrees of freedom [15], the error is reduced for the rotational excitations, but

TABLE IV. Rotational excitation energies of $^4\mathrm{He}_2^+$ ($X\,^2\Sigma_u^+$) in the vibrational ground state. $\tilde{\nu}_0$: Born–Oppenheimer description with nuclear masses. $\delta\tilde{\nu}_{\mathrm{DBOC}}$: The diagonal Born–Oppenheimer correction. $\delta\tilde{\nu}_{\mathrm{mveff}}$: Empirical mass $m_{\mathrm{rot}} = m_{\mathrm{vib}} = m_\alpha + 1.5m_e$. $\delta\tilde{\nu}_{\mathrm{Nad}}$: Rigorous nonadiabatic mass. $\delta\tilde{\nu}_{\mathrm{Rel}}$: Relativistic correction. $\delta\tilde{\nu}_{\mathrm{QED}}$: Leading-order QED correction. $\delta\tilde{\nu}_{\mathrm{hQED}}$: Estimate for higher-order QED corrections. For the derivation of the error estimates to the computed energies, see Table I.

	$\tilde{\nu}(0,N^+)-\tilde{\nu}(0,1)$ [cm^{-1}]			
N^+:	3	5	7	9
$\tilde{\nu}_0$	70.960 61	198.427 8	381.954 3	620.898 1
$+\delta\tilde{\nu}_{\mathrm{DBOC}}$	−0.010 28	−0.028 7	−0.055 0	−0.089 1
$+\delta\tilde{\nu}_{\mathrm{mveff}}$	−0.014 46	−0.040 4	−0.077 6	−0.125 8
$+\delta\tilde{\nu}_{\mathrm{mvNad}}$	0.000 45	0.001 3	0.002 6	0.004 4
$+\delta\tilde{\nu}_{\mathrm{Rel}}$	0.002 16	0.006 0	0.011 5	0.018 7
$+\delta\tilde{\nu}_{\mathrm{QED}}$	−0.00078	−0.002 2	−0.004 2	−0.006 8
$+\delta\tilde{\nu}_{\mathrm{hQED}}$	0.000 01	0.000 0	0.000 0	−0.0001
$\tilde{\nu}_{\mathrm{calc}}$	70.937 68(10)	198.363 8(13)	381.831 6(13)	620.699 4(13)
$\tilde{\nu}_{\mathrm{expt}}$ [9,12]	70.937 589(23)(60)$_{\mathrm{sys}}$	198.364 7(8)	381.834 6(8)	620.702 1(9)
$\tilde{\nu}_{\mathrm{expt}}-\tilde{\nu}_{\mathrm{calc}}$	−0.00010	0.000 9	0.003 0	0.002 7

	$\tilde{\nu}(0,N^+)-\tilde{\nu}(0,1)$ [cm^{-1}]				
N^+:	11	13	15	17	19
$\tilde{\nu}_0$	914.426 5	1261.521 5	1660.986 0	2111.450 8	2611.382 6
$+\delta\tilde{\nu}_{\mathrm{DBOC}}$	−0.130 4	−0.178 8	−0.233 6	−0.294 4	−0.360 5
$+\delta\tilde{\nu}_{\mathrm{mveff}}$	−0.184 7	−0.253 8	−0.332 8	−0.420 9	−0.517 7
$+\delta\tilde{\nu}_{\mathrm{mvNad}}$	0.006 9	0.010 1	0.014 1	0.019 1	0.025 2
$+\delta\tilde{\nu}_{\mathrm{Rel}}$	0.027 3	0.037 3	0.048 6	0.061 1	0.074 5
$+\delta\tilde{\nu}_{\mathrm{QED}}$	−0.010 0	−0.013 8	−0.018 1	−0.023 0	−0.028 3
$+\delta\tilde{\nu}_{\mathrm{hQED}}$	−0.0001	−0.0001	−0.0002	−0.0002	−0.0003
$\tilde{\nu}_{\mathrm{calc}}$	914.135 4(13)	1261.122 3(13)	1660.464 0(13)	2110.792 5(13)	2610.575 5(15)
$\tilde{\nu}_{\mathrm{expt}}$ [12]	914.136 7(8)	1261.124 2(8)	1660.462 7(9)	2110.793 2(9)	2610.574 4(9)
$\tilde{\nu}_{\mathrm{expt}}-\tilde{\nu}_{\mathrm{calc}}$	0.001 3	0.001 9	−0.001 3	0.000 7	−0.001 1

TABLE V. Rovibrational excitation energies of ${}^4\mathrm{He}_2^+$ ($X\,{}^2\Sigma_u^+$) between the vibrational ground and first excited state. See also the caption to Table IV.

	$\tilde{\nu}(v,N^+)'' - \tilde{\nu}(v,N^+)'$ [cm^{-1}]		
$(v,N^+)''$–$(v,N^+)'$:	(1,0)–(0,0)	(1,1)–(0,1)	(1,3)–(0,1)
$\tilde{\nu}_0$	1628.560 0	1628.108 1	1696.808 9
$\delta\tilde{\nu}_{\mathrm{DBOC}}$	−0.022 3	−0.022 2	−0.032 0
$\delta\tilde{\nu}_{\mathrm{mveff}}$	−0.160 2	−0.160 1	−0.173 9
$\delta\tilde{\nu}_{\mathrm{mvNad}}$	0.025 8	0.025 7	0.025 9
$\delta\tilde{\nu}_{\mathrm{Rel}}$	−0.010 2	−0.010 3	−0.008 3
$\delta\tilde{\nu}_{\mathrm{QED}}$	−0.012 0	−0.012 0	−0.012 8
$\delta\tilde{\nu}_{\mathrm{hQED}}$	−0.0001	−0.0001	−0.0001
$\tilde{\nu}_{\mathrm{calc}} = \tilde{\nu}_0 + \sum \delta\tilde{\nu}$	1628.380 9(33)	1627.929 1(39)	1696.607 7(39)
$\tilde{\nu}_{\mathrm{expt}}$ [13]	1628.383 2(12)	1627.931 8(12)	1696.609 6(12)
$\tilde{\nu}_{\mathrm{expt}} - \tilde{\nu}_{\mathrm{calc}}$	0.002 3	0.002 7	0.001 9

	$\tilde{\nu}(v,N^+)'' - \tilde{\nu}(v,N^+)'$ [cm^{-1}]		
$(v,N^+)''$–$(v,N^+)'$:	(1,7)–(0,1)	(1,11)–(0,1)	(1,13)–(0,1)
$\tilde{\nu}_0$	1997.857 8	2513.146 5	2848.931 6
$\delta\tilde{\nu}_{\mathrm{DBOC}}$	−0.074 4	−0.145 9	−0.191 6
$\delta\tilde{\nu}_{\mathrm{mveff}}$	−0.233 9	−0.335 7	−0.401 3
$\delta\tilde{\nu}_{\mathrm{mvNad}}$	0.026 9	0.029 3	0.031 2
$\delta\tilde{\nu}_{\mathrm{Rel}}$	0.000 2	0.014 3	0.023 3
$\delta\tilde{\nu}_{\mathrm{QED}}$	−0.016 1	−0.021 6	−0.025 2
$\delta\tilde{\nu}_{\mathrm{hQED}}$	−0.0002	−0.0002	−0.0003
$\tilde{\nu}_{\mathrm{calc}} = \tilde{\nu}_0 + \sum \delta\tilde{\nu}$	1997.560 4(39)	2512.686 7(39)	2848.367 8(39)
$\tilde{\nu}_{\mathrm{expt}}$ [13]	1997.563 3(12)	2512.687 1(12)	2848.369 0(12)
$\tilde{\nu}_{\mathrm{expt}} - \tilde{\nu}_{\mathrm{calc}}$	0.002 9	0.000 4	0.001 2

the fundamental vibration energy shows a large deviation from experiment. Adding the relativistic corrections to this nonadiabatic model reduces the deviation by a factor of two for the fundamental vibration, but it "overcorrects" 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 root-mean-squared deviations (RMSDs) of 0.001 7 and 0.0019 cm^{-1}, respectively. The experimental uncertainties of the rotational and rovibrational series is slightly smaller than these values [12,13]; they are 0.000 8 and 0.00012 cm^{-1}, respectively. The lowest-energy rotational interval, (0,3)–(0,1), has been recently measured more precisely, $70.937\,589(23) \pm 0.000\,06_{\mathrm{sys}}$ [9], and our theoretical value for this interval is $70.937\,69(10)$ cm^{-1}. For the fundamental vibration, our computational result is $1628.380\,9(33)$ cm^{-1}, which is in agreement with its value derived from experiments, $1628.383\,2(12)$ 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 3 times larger uncertainties than the experimental ones. We observe some discrepancies 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 I).

We finish the discussion with observations regarding the interplay of the computed corrections (Tables IV and V). First, we point out that $\delta\tilde{\nu}_{\mathrm{mveff}}$ and $\delta\tilde{\nu}_{\mathrm{mvNad}}$ together account for the nonadiabatic mass effect. $\delta\tilde{\nu}_{\mathrm{mveff}}$ is a simple, intuitive, constant mass model ($m_{\mathrm{rot}} = m_{\mathrm{vib}} = m_\alpha + 1.5 m_e$), and $\delta\tilde{\nu}_{\mathrm{mvNad}}$ labels the value, which corrects this empirical model to arrive at the rigorous second-order nonadiabatic result. It is interesting to observe, at least for the present example, that $\delta\tilde{\nu}_{\mathrm{mvNad}}$ has the same order of magnitude but opposite sign as the leading-order QED correction $\delta\tilde{\nu}_{\mathrm{QED}}$. 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—which we explicitly compute in this Letter—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.

Rotational and (ro)vibrational intervals have been reported for the three-electron ${}^4\mathrm{He}_2^+$ ($X\,{}^2\Sigma_u^+$) molecular ion on a newly computed potential energy curve with nonadiabatic, relativistic, and QED corrections. The computed rotational-vibrational intervals are in good agreement with recent precision

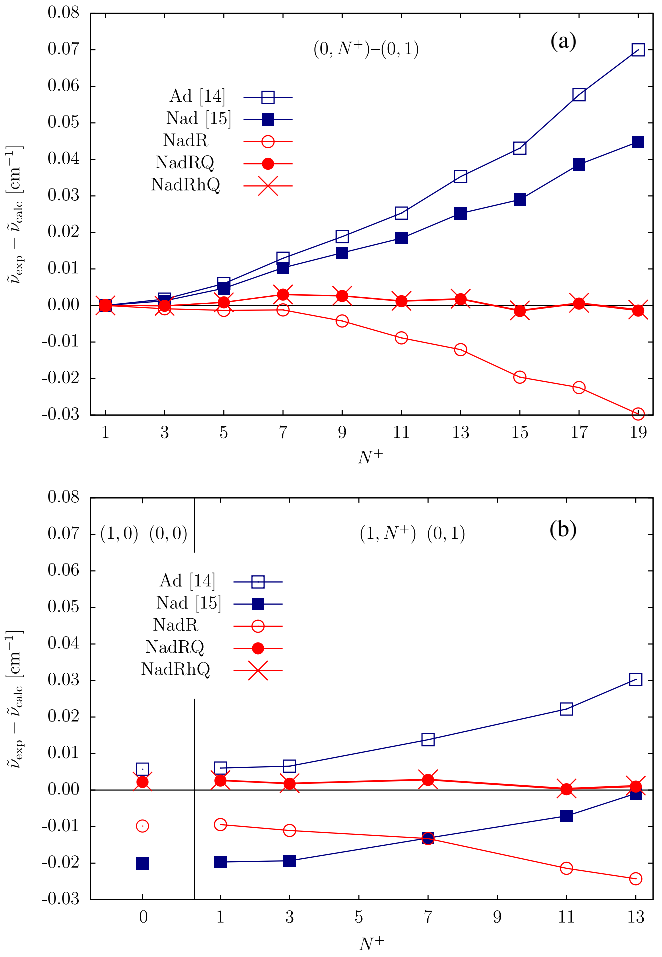

FIG. 1. Deviation of the rotational and (ro)vibrational excitation energies of the $^4\mathrm{He}_2^+$ molecular ion ($X\,^2\Sigma_u^+$) from experiment [9,12,13]. (v, N^+) labels the vth vibrational state with the N^+ rotational quantum number. Square: Adiabatic with the $m_{\mathrm{vib}} = m_{\mathrm{rot}} = m_\alpha + 1.5 m_e$ empirical mass in the kinetic energy operator. Filled square: Nonadiabatic, i.e., with rigorous rotational and vibrational masses. Circle: Nonadiabatic and relativistic corrections. Filled circle: Nonadiabatic, relativistic, and leading-order QED corrections. Cross: Nonadiabatic, relativistic, leading-order QED with estimates for higher-order QED corrections.

spectroscopy measurements. Further developments, most importantly, a detailed study of the relativistic-nonadiabatic coupling and the extension of the potential energy curve with parts-per-billion uncertainty over large internuclear distances, will challenge precision spectroscopy experiments and contribute to the establishment of primary pressure standards.

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