Convergence of Experiment and Theory on the Pure Vibrational Spectrum of HeH$^+$

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Very accurate quantum mechanical calculations of the pure vibrational spectrum of the HeH$^+$ molecular ion are reported and compared with newly obtained pure vibrational transitions extracted from the available experimental data. The calculations are performed without assuming the Born-Oppenheimer approximation regarding separability of the nuclear and electronic motions and include the first order relativistic mass-velocity and Darwin corrections. For the two lowest transitions, whose experimental energies are established with the highest precision, the calculated and the experimental results show very good agreement.

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Modern gas phase measurements of molecular quantities such as rovibrational and electronic excitation energies, electron affinities, ionization potentials, bond dissociation, and atomization energies achieve nowadays the precision exceeding tens or even hundreds of a wave number. This presents a challenge to quantum mechanical calculations because in order to reach such an accuracy, not only the electronic component of the wave function has to be calculated with a very high precision, but also the component describing the motion of the nuclei (vibrational and rotational) and the component describing the coupling of the electronic and the nuclear motions has to be very accurately represented. Furthermore, even for small systems the relativistic effects need be taken into account.

In the present work we use the approach departing from the Born-Oppenheimer (BO) approximation whose development has been carried out for last several years in our research group [see [1–5] and references therein]. The main part of the development has been the use of correlated Gaussian functions that depend explicitly on the distances between the particles (nuclei and electrons) forming the molecule.

In this work we report the development and implementation of the algorithm for calculating electronic and nuclear mass velocity and Darwin corrections to the non-BO energy using an all-particle approach. To our knowledge, this is the first work where these relativistic corrections are computed for a molecular system with more than one electron within the non-BO framework. There have been very accurate calculations of molecular relativistic effects reported before [see, for example, Refs. [6,7]], but they only concerned the electronic corrections and all, except one on a single electron system [8], have been done within the BO approximation. The calculations presented in this work concern all bound states of the HeH$^+$ ion with zero total angular momentum. Such states are usually called “rovibrational states” although, if the Born-Openheimer approximation is not assumed, the vibrational motion of the nuclei is coupled with the electronic motion and, strictly speaking, the vibrational quantum number, $v$, is not a good quantum number.

The hydrohelium cation HeH$^+$, whose first laboratory observation dates back to 1925 [9], is relevant to astrochemistry [10] since hydrogen and helium are the two most abundant elements in the universe. Apart from our recent work [5], all previous vibrational calculations of HeH$^+$ in the electronic ground $^1\Sigma^+$ state have been based on the Born-Oppenheimer potential energy curve and they were summarized in the work of Bishop and Cheung [11]. Since HeH$^+$ has a relatively large permanent dipole moment, there have been some highly precise measurements of the vibration-rotational and pure rotational gas phase spectra of this system. We will refer to some of those measurements later in this work.

For several decades the most frequently used model system for testing the accuracy of high level quantum mechanical molecular calculations has been the hydrogen molecule. While the HeH$^+$ ion has been used less frequently in such tests, it is a useful model for high level calculations, particularly those that include some account of the relativistic effects. This is due to the simplicity of the HeH$^+$ electronic structure in the ground electronic state, which can be described as a helium atom slightly polarized by the proton. This polarization decreases with vibrational excitation. Our previous nonrelativistic non-BO calculations of HeH$^+$ [5] yielded the transition energies involving the first four pure vibrational states that systematically overestimated the corresponding experimental transition energies by about 0.07 cm$^{-1}$. These differences inspired the present work on the relativistic corrections with the main goal of reducing the remaining theoretical or experimental discrepancy. The two largest relativistic correc-
tions, i.e., the ones due to the mass-velocity and Darwin effects, have been included in the present calculations. The remaining corrections related to the spin-orbit, orbit-orbit, and spin-spin interactions are expected to be at least by 1 order of magnitude smaller [due to the He-like electron distribution in HeH\(^+\)]; this conclusion is based on the calculations of the relativistic effects in He performed by Mitdal and Aashamar [12] and have not been included.

We should also add that HeH\(^+\) is a system for which only a couple hundred rovibrational transitions have been assigned and no pure vibrational transitions have been measured. Thus, this important system is still “a work in progress” both in terms of the experimental and theoretical investigations. In this Letter we show how well these investigations are converging in determining the transition investigations. In this Letter we show how well these investigations are converging in determining the transition investigations.

In our works concerning non-BO calculations on small diatomic molecular systems [3–5] we have shown that the explicitly correlated Gaussians (ECGs) involving functions with preexponential multipliers consisting of the internuclear distance, \( r_{1} \), raised to a non-negative even power, \( p_{k} \):

\[
\phi_{k} = r_{1}^{p_{k}} \exp[-r(A_{k} \otimes I_{3})r],
\]

with the non-BO wave function.

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\]

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The energy and the wave function for each state of \( \text{HeH}^+ \) were obtained by minimizing the Rayleigh quotient:

\[
E = \min c^jH(p_j, \{A_j\})c / c^jS(p_j, \{A_j\})c
\]  

(8)

with respect to the expansion coefficients of the wave function in terms of the basis functions, \( c_j \), the basis-function exponential parameters, \( \{A_j\} \), and the preexponential powers, \( \{p_j\} \). Here, \( H \) and \( S \) are the Hamiltonian and the overlap matrices. The optimization was done separately for each state using an algorithm based on analytical derivatives of the energy, \( E(c_j, \{p_j\}, \{A_j\}) \), with respect to the \( A_j \) parameters. To achieve high accuracy we used 5400 basis functions for each state [this is by 900 more than used in [5]]. We believe that with this many functions in the basis the energies were converged to the 8th–9th decimal figure. The range of the preexponential powers, \( \{p_j\} \), used was 0–250, and all the powers were partially optimized for each state.

After the wave functions for all 12 (\( v = 0, \ldots, 11 \)) states were generated, we calculated the expectation values of \( \hat{H}^j \) for each state and added them to the variational energies. Those values were used to calculate the transition energies. In the calculations we used the following values for the nuclear masses: \( m_{\text{He}} = 7294.299 536 3 m_e \), \( (\text{He isotope}) \), \( m_p = 1836.152 672 61 m_e \), taken from CODATA 2002. Here, \( m_e \) stands for the mass of the electron.

Based on the available experimental data, only the frequencies (\( \nu_\nu \)) of the lowest three pure vibrational transitions \( (J = 0) \), namely \( 1 \rightarrow 0, 2 \rightarrow 1, \) and \( 3 \rightarrow 2, \) of \( ^4\text{HeH}^+ \) can be estimated reliably. We used two independent estimation methods. The first one was based on fitting the microwave (MW) and infrared (IR) spectra of the four isotope variants of \( ^4\text{HeH}^+ \) to the radial parameters in the Herman-Ogilvie equation [14]:

\[
\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + V_{\nu_J}(x) - E_{\nu_J} \right|_{x_j} = 0,
\]

(9)

\[
U_{\nu_J}(x) = B_0 J(J+1)[1 + \alpha(x) - \beta(x)]
\]

(10)

\[
+ V(x)[1 - \beta(x)] + V(x)' + E_{\nu_J} \beta(x)
\]

including the adiabatic, \( V(x)' \), the nonadiabatic rotational, \( \alpha(x) \), and the vibrational, \( \beta(x) \), corrections to the BO energy levels, and then calculating \( \nu_{1-0}, \nu_{2-1}, \nu_{3-2}. \) The details of this method can be found in [5]. The results obtained are presented in Table I.

In the second method the vibrational frequencies were estimated by fitting the line positions of the separate bands \( 1 \rightarrow 0, 2 \rightarrow 1, \) and \( 3 \rightarrow 2 \) of \( ^4\text{HeH}^+ \), including \( R(J) \) and \( P(J) \) rovibrational transitions, to the Dunham’s energy formula [22,23]:

\[
E_{\nu_J} = \sum_{i,j} Y_{ij} \left( \nu + \frac{1}{2} \right) [J(J+1)]^j.
\]

(11)

In this approach the frequencies of the vibrational transitions \( n \rightarrow m \) are directly obtained from the relationship:

\[
\nu_{n \rightarrow m} = Y_{10}(\nu' \rightarrow \nu^m).
\]

(12)

The calculations were performed by using a weighted nonlinear least-squares routine with weights taken as the inverse squares of the uncertainties of the experimental data. To obtain the best set of the Dunham constants, \( Y_{ij} \), fitted from the spectra, we used as the criteria: the smallest number of the fitted parameters consistent with the minimum value of the normalized standard deviation, \( \sigma \), the maximum value of the \( F \) statistics, and the optimal values of the estimated standard error, \( \sigma_i \), of each fitted parameter \( i \) and of the coefficient, \( cc(i, j) \), correlating parameters \( i \) and \( j \). The results of these calculations are also presented in Table I. The uncertainty shown in parentheses is the estimated standard deviation in the units of the last quoted digit of the values of the fitted Dunham constants.

The discrepancy \( \Delta \nu_{3-2} = 0.0452 \text{ cm}^{-1} \) in the values of the \( \nu_{3-2} \) vibrational frequency calculated by the two specified methods is due to a small number of available line positions (only 11) used in the calculation. Hence, in this case we can only specify the range for this frequency as \( \nu_{3-2} \in [2295.5340(61)–2295.5792]. \) The differences in the values of the remaining frequencies \( \Delta \nu_{1-0} = 0.0018 \text{ cm}^{-1} \) and \( \Delta \nu_{2-1} = 0.001 \text{ cm}^{-1} \) are less than the experimental uncertainties of the spectral data used in the calculations (0.002–0.003 cm\(^{-1}\)). The only exception is the data (7 lines) of Shy [20] obtained with the accuracy of 0.0006 cm\(^{-1}\).

| Table I. Dunham’s spectral parameters (in cm\(^{-1}\)) fitted to the \( ^4\text{HeH}^+ \) 0 \( \rightarrow \) 1, 1 \( \rightarrow \) 2, 2 \( \rightarrow \) 3 vibrational bands. |
|-----------------|--------|--------|--------|
| \( Y_{ij} \)    | \( \nu = 0 \rightarrow 1 \) | \( \nu = 1 \rightarrow 2 \) | \( \nu = 2 \rightarrow 3 \) |
| \( Y_{10} \)    | 2910.9572(7) | 2604.1482(12) | 2295.5340(61) |
| \( Y_{11} \)    | -2.718696(88) | -2.74063(34) | -2.79342(49) |
| \( Y_{12} \times 10^4 \) | 3.580(28) | 2.24(18) | -1.04(13) |
| \( Y_{13} \times 10^7 \) | -4.37(26) | -3.43(38) | 3.14(4) |
| \( Y_{14} \times 10^{10} \) | -1.29(47) | -0.565(52) |
| \( Y_{15} \times 10^{13} \) | -1.05(21) |
| \( Y_{01} \)    | 34.91777(13) | 34.95109(80) | 35.0828(15) |
| \( Y_{02} \times 10^{-2} \) | -1.63857(32) | -1.62631(37) | -1.5353(41) |
| \( Y_{03} \times 10^{-6} \) | 5.984(34) | 8.05(66) | 3.60(47) |
| \( Y_{04} \times 10^{-9} \) | -2.06(15) | -5.05(33) | 13.0(21) |
| \( Y_{05} \times 10^{-11} \) | -9.2(32) |
| \( Y_{06} \times 10^{-13} \) | 1.7(48) |
| \( \sigma \)     | 0.060   | 1.049   | 0.148   |
| \( J_{\text{min}} - J_{\text{max}} \) | 0–14    | 0–20    | 4–18    |

\( ^4\text{HeH}^+ \) frequencies obtained by fitting the MW and IR spectra of four isotopic variants of \( ^4\text{HeH}^+ \) to the radial parameters in the Eq. (9).
TABLE II. Total non-BO energies ($E_{\text{non-BO}}$), mass-velocity corrections (MV), Darwin corrections, $ν + 1 → ν$ vibrational frequencies calculated without ($ΔE_{\text{non-BO}}$) and with ($ΔE_{\text{non-BO+rel}}$) inclusion of relativistic corrections, and first three vibrational frequencies extracted from experimental data using two different methods of extrapolation ($ΔE_{\text{exp}}^{\text{BO}}$ and $ΔE_{\text{exp}}^{\text{rel}}$, respectively). The energies and corrections are given in a.u., the frequencies in cm$^{-1}$.

<table>
<thead>
<tr>
<th>$ν$</th>
<th>$E_{\text{non-BO}}$</th>
<th>MV</th>
<th>Darwin</th>
<th>$ΔE_{\text{non-BO}}$</th>
<th>$ΔE_{\text{non-BO+rel}}$</th>
<th>$ΔE_{\text{exp}}^{\text{BO}}$</th>
<th>$ΔE_{\text{exp}}^{\text{rel}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$-2.9710784636$</td>
<td>5</td>
<td>$5.85088 × 10^{-4}$</td>
<td>$2911.0189$</td>
<td>$2910.9907$</td>
<td>2910.9597</td>
<td>2910.9597</td>
</tr>
<tr>
<td>1</td>
<td>$-2.9578148854$</td>
<td>5</td>
<td>$5.83300 × 10^{-4}$</td>
<td>$2604.2064$</td>
<td>$2604.1767$</td>
<td>2604.147</td>
<td>2604.148</td>
</tr>
<tr>
<td>2</td>
<td>$-2.9459492482$</td>
<td>5</td>
<td>$5.82058 × 10^{-4}$</td>
<td>$2295.6365$</td>
<td>$2295.5787$</td>
<td>2295.579</td>
<td>2295.534</td>
</tr>
<tr>
<td>4</td>
<td>$-2.9264582927$</td>
<td>5</td>
<td>$5.80981 × 10^{-4}$</td>
<td>$1660.4533$</td>
<td>$1660.3559$</td>
<td>1660.3559</td>
<td>1660.3559</td>
</tr>
<tr>
<td>5</td>
<td>$-2.9189272110$</td>
<td>5</td>
<td>$5.81152 × 10^{-4}$</td>
<td>$1327.9067$</td>
<td>$1327.7860$</td>
<td>1327.7860</td>
<td>1327.7860</td>
</tr>
<tr>
<td>6</td>
<td>$-2.9128423228$</td>
<td>5</td>
<td>$5.81981 × 10^{-4}$</td>
<td>$984.4980$</td>
<td>$984.3599$</td>
<td>984.3599</td>
<td>984.3599</td>
</tr>
<tr>
<td>7</td>
<td>$-2.9083566198$</td>
<td>5</td>
<td>$5.83609 × 10^{-4}$</td>
<td>$639.3467$</td>
<td>$639.1959$</td>
<td>639.1959</td>
<td>639.1959</td>
</tr>
<tr>
<td>8</td>
<td>$-2.9054435417$</td>
<td>5</td>
<td>$5.84625 × 10^{-4}$</td>
<td>$327.4922$</td>
<td>$327.3615$</td>
<td>327.3615</td>
<td>327.3615</td>
</tr>
<tr>
<td>10</td>
<td>$-2.9034218311$</td>
<td>5</td>
<td>$5.87166 × 10^{-4}$</td>
<td>$24.4368$</td>
<td>$24.4099$</td>
<td>24.4099</td>
<td>24.4099</td>
</tr>
<tr>
<td>11</td>
<td>$-2.9033104889$</td>
<td>5</td>
<td>$5.87541 × 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unbound</td>
<td>$-2.9033045565$</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

The total and transition energies for all 12 bound vibrational states of HeH$^{-1}$ with zero total angular momentum obtained in the non-BO calculations are presented in Table II. Both nonrelativistic results and results including the relativistic corrections are shown. All transition energies corrected for the relativistic effects are lower than their uncorrected counterparts. The largest shift of $\approx 0.1508$ cm$^{-1}$ due to the relativistic corrections occurs for the $8 → 7$ transition. It is clear that for all transitions the inclusion of relativistic corrections change the frequencies by much more than their respective experimental errors. The comparison between the calculated transition frequencies and the experimental results for the first three transitions is also shown in Table II. As mentioned, only for the first two transitions did the experimental results obtained using both estimation methods agree to high precision. For those two transitions the relativistic corrections bring the predicted frequencies noticeably closer to the experimental values. Although adding the relativistic correction to the third transition ($3 → 2$) also improves the result, there is a discrepancy between the two extrapolated experimental values, making this case less reliable.

In conclusion, it is clear from the results presented here that theoretical calculations with an approach that does not assume the BO approximation and includes some relativistic effects (of the order of $α^2$) are capable of generating results whose accuracy matches the accuracy of the experimental measurements. It is also clear that, while in the calculations all 11 pure vibrational transitions are predicted, only two lowest transitions are reliably established on the experimental side.

This work has been supported in part by the National Science Foundation. We would like to thank Professor Jacek Karwowski for many valuable discussions and suggestions concerning this work. Thanks are also due to Professor Jow-Tsong Shy for permission to use his unpublished HeH$^+$ spectral data.

[20] Unpublished data; it includes 6 lines of $ν = 1 → 0, 2 → 1, 3 → 2, 4HeH^+$ measured with the accuracy of 0.0006 cm$^{-1}$ by J.-T. Shy.