Ab initio calculation of the 66 low-lying electronic states of HeH+: adiabatic and diabatic representations

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Abstract
Using the quantum chemistry package MOLPRO and an adapted basis set, we have calculated the adiabatic potential energy curves of the first 20 $^1\Sigma^+$, 19 $^3\Sigma^+$, 12 $^1\Pi$, 9 $^3\Pi$, 4 $^1\Delta$ and 2 $^3\Delta$ electronic states of the HeH$^+$ molecular ion in CASSCF and CI approaches. The results are compared with previous works. The radial and rotational non-adiabatic coupling matrix elements as well as the dipole moments are also calculated. The asymptotic behaviour of the potential energy curves and of the various couplings between the states is also studied. Using the radial couplings, the diabatic representation is defined and we present an example of our diabatization procedure on the $^1\Sigma^+$ states.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

HeH$^+$, or hydrohelium cation, is thought to be the first molecular species to appear in the Universe, its formation being due to radiative association between H$^+$ and He (Roberge and Dalgarno 1982). In addition, the high fractional abundance of HeH$^+$ should allow its detection in stars formed from primordial material such as the recently discovered very metal-poor stars HE1327$-$2326 and HE0107$-$5240 (Frebel et al 2005) or in He-rich environment as in the white dwarfs SDSS J133739+000142 and LHS 3250 (Harris et al 2004). The inclusion of HeH$^+$ in the existing atmospheric models of those objects could have serious implications. It should also be present in the planetary nebula NGC7027 but has eluded observation (Moorhead et al 1988). In fact, up to now, none of the several attempts to extraterrestrial observation of HeH$^+$ have been conclusive (Engel et al 1988). In fact, up to now, none of the several attempts to extraterrestrial observation of HeH$^+$ have been conclusive (Engel et al 2005). Considering that the excited states of HeH$^+$ are too shallow or unstable to support a visible or UV spectrum, those assessments have risen up a number of studies to obtain theoretically and experimentally the most accurate rotational spectrum of HeH$^+$ in the ground state, culminating with the recent work of Stanke et al (2006). In addition to extremely accurate knowledge of the spectroscopic properties of the hydrohelium cation, the various mechanisms leading to its formation or decay must be investigated to obtain a correct estimation of the population of the levels. In this context, the first experimental data for the photodissociation cross section in the far UV have been obtained recently using the free electron laser FLASH at Hambourg (Pedersen et al 2007), showing important disagreement with the previous theoretical works and motivating new calculations (Sodoga et al 2009, Dumitriu and Saenz 2009).

Despite the fact that its astrophysical observation is still questionable, HeH$^+$ is clearly present in helium–hydrogen laboratory plasmas. Indeed, since its first observation in mass spectrometry of discharges in mixtures of helium and hydrogen in 1925 (Hogness and Lunn 1925), HeH$^+$ has been found to be one of the major components in other He/H plasma sources such as high-voltage glow discharges, synchrotron
devices, inductively coupled plasma generators, capacitively
coupled RF discharges and magnetically confined plasmas,
the last one playing of course a very special role in today’s
development of thermonuclear fusion. Helium emission lines
have been proposed recently as a diagnostic tool for divertor
regions of the tokamak. However, to model the intensity of
these emission lines, knowledge of the cross sections of the
charge transfer processes which populate the emitting levels of
helium up to $n = 4$ is essential. At low or very low collisional
energy, the theoretical description of charge transfer requires
a molecular approach and the calculation of the excited states
of the HeH$^+$ quasi-molecule (Rosmej et al 2006).

From a theoretical point of view, the hydrohelium cation is
the simplest closed-shell heteronuclear molecule and therefore
a considerable amount of work has been dedicated to high-
precision calculations of its ground state, including accurate
description of relativistic and non-adiabatic effects (Stanke
et al 2008). In a lesser measure, the first excited states have
also been used to assess the efficiency of different ab initio
methods to describe states that are not the lowest of their
symmetry (Richings and Karadakov 2007) or to understand
and remedy the failure of time-dependent density functional
theory to provide accurate charge transfer excitation energies
(Giesbertz et al 2008). The most complete study of the excited
states of HeH$^+$ has been performed by Green et al in
a series of four articles (Green et al 1974a, 1974b, 1976,
1978). States up to $n = 3$ (where $n$ is the highest principal
quantum number in the dissociation configuration of hydrogen
or helium) have been calculated using a CI (configuration
interaction) method with a combination of Slater-type orbitals
and elliptoidal orbitals. Despite the fact that this exhaustive
study includes the calculation of dipole matrix elements and
radial non-adiabatic couplings, its accuracy has never been
assessed and the use of these results directly in quantum
molecular dynamics programs is problematic due to the lack
of data for medium or large internuclear distances.

While the first excited states of the neutral HeH molecule
emanate from the excitation of the hydrogen atom alone, the
first part of the electronic spectrum of HeH$^+$ results from a
mixing between states arising from single excitations of neutral
helium or hydrogen. The higher part of the spectrum is built
upon single excitations of the He$^+$ cation as well as double
excitations of neutral helium and of the ground state of the H$^-$
anion.

The purpose of this paper is to reexamine the first part of
the electronic spectrum of a HeH$^+$ molecule and to extend its
description up to $n = 4$ with high-level ab initio quantum
chemistry methods in order to provide adequate material
required for both spectroscopy and dynamical studies such
as charge transfer processes in excited states (Loreau et al
2010) or photodissociation in the far UV domain (Sodoga et al
2009). In addition, the diabatic representation of the potential
energy curves is investigated. The results of the present work
are compared to the corresponding data in the literature, when
available.

All the data described in this paper are accessible on
demand to the corresponding author of this paper.

2. One electron basis set and asymptotic atomic energy levels

One problem encountered in this work is the construction of
a reliable Gaussian basis set allowing the description of the
formation of the HeH$^+$ molecular ion from the first Rydberg
states of the H and He atoms up to $n = 4$. As mentioned above,
the first part of the electronic spectrum corresponds indeed
asymptotically to the excitation of both hydrogen and neutral
helium. Therefore, our basis set consists for each atom of the
aug-cc-pV5Z basis set (Dunning 1989; Woon and Dunning
1994) augmented by [3s, 3p, 2d, 1f] Gaussian-type orbitals
optimized to reproduce the spectroscopic orbitals of the He and
H excited states. A different atomic basis has been developed
up to $n = 4$ for He depending on whether the molecular
state under consideration is a singlet or a triplet state. Those
additional sets of orbitals have been obtained by fitting Slater-
type orbitals from calculations performed for each atomic state
using the AUTOSTRUCTURE package (Eissner et al 1974,
Badnell 1986, 1997). In total, a $[8s, 7p, 5d, 3f, 1g]$ basis set
has been used for both atoms. The additional orbitals and their
contraction coefficients are given in the appendix.

For all values of $\ell$, this basis set reproduces the exact
non-relativistic atomic levels of hydrogen up to $n = 3$
in within 15 cm$^{-1}$. The electromegativity of H$^+$ deviates from
the experimental value from 37 cm$^{-1}$ in a full CI level of
approximation. Different Gaussian basis sets have already
been proposed in the literature mainly for the calculation of
the ground state of HeH$^+$ (Jurek et al 1995 and references
therein) or the ground and excited states of the neutral HeH
molecule which correspond asymptotically to excitations of
H up to $n = 3$ (van Hemert and Peyerimhoff 1990). Using
this last atomic basis set, the levels for the hydrogen atom are
reproduced within 20 cm$^{-1}$ for the $s$ and $p$ states and within
70 cm$^{-1}$ for the $d$ state.

In the non-relativistic approximation, the $1s\ell$ ($n = 1–3$)
levels of helium are described at a full CI level by our basis
set within 115 cm$^{-1}$ for $s$ states, 60 cm$^{-1}$ for $p$ states and
30 cm$^{-1}$ for $d$ states.

For both atoms, the $s$ states for $n = 4$ are more difficult to
reproduce, mainly due to the lack of upper states and the large
number of lower states, but are still in a reasonable agreement
(145 cm$^{-1}$ at most) with the exact values. The other $n = 4$
states are reproduced within 42 cm$^{-1}$ for both atoms.

In conclusion, although this basis set is rather small, it is
adapted to the HeH$^+$ system and will allow a correct description
of the potential energy curves as well as the determination
of the non-adiabatic couplings which, in our approach,
require CASSCF (complete active space self-consistent field)
calculations.

3. Potential energy curves

The Born–Oppenheimer adiabatic potential energy curves
(PEC) for the lowest molecular states corresponding
asymptotically to excitation in the $n = 1–4$ atomic shells
have been calculated as a function of the internuclear
distance $R$ using the MOLPRO molecular structure package
Table 1. $^3\Sigma^+$ states included in the calculations and their dissociation product. In this table, we use the notation $H(n\ell)$ or $He(1s n\ell^L L)$ to denote the electronic wavefunctions of the corresponding electronic states. Due to the He$^+$ charge, there is a Stark effect on the hydrogen levels (see the text). The mixing coefficients have been calculated by diagonalizing the perturbation matrix due to the electric field.

| $n$ | $m$ | Energy (hartree) at $R = 70$ au | Dissociative atomic wavefunctions |
|-----|-----|-----------------------------|--------------------------------|
| 1   | 1   | $-2.903 243.07$ He(1\$) | $H(1s)$ |
| 2   | 2   | $-2.499 955.02$ He(1\$) | $H(1s)$ |
| 2   | 3   | $-2.145 894.24$ He(1s) 2S | $\frac{1}{\sqrt{2}} H(2s) + \frac{1}{\sqrt{2}} H(2p)$ |
| 3   | 4   | $-2.125 564.99$ He(1s) 2P | $\frac{1}{\sqrt{2}} H(2s) + \frac{1}{\sqrt{2}} H(2p)$ |
| 5   | 5   | $-2.124 337.65$ He(1s) 2P | $\frac{1}{\sqrt{2}} H(2s) - \frac{1}{\sqrt{2}} H(2p)$ |
| 6   | 6   | $-2.123 740.55$ He(1s) 2P | $\frac{1}{\sqrt{2}} H(2s) - \frac{1}{\sqrt{2}} H(2p)$ |

Table 2. $^3\Sigma^+$ states included in the calculations and their dissociation product. In this table, we use the notation $H(n\ell)$ or $He(1s n\ell^L L)$ to denote the electronic wavefunctions of the corresponding electronic states. Due to the He$^+$ charge, there is a Stark effect on the hydrogen levels (see the text). The mixing coefficients have been calculated by diagonalizing the perturbation matrix due to the electric field.

| $n$ | $m$ | Energy (hartree) at $R = 70$ au | Dissociative atomic wavefunctions |
|-----|-----|-----------------------------|--------------------------------|
| 1   | 1   | $-2.499 960.40$ He(1s) | $H(1s)$ |
| 2   | 2   | $-2.175 134.28$ He(1s) 3S | $\frac{1}{\sqrt{3}} H(2s) + \frac{1}{\sqrt{3}} H(2p) + \frac{1}{\sqrt{3}} H(2d)$ |
| 3   | 3   | $-2.132 884.67$ He(1s) 3P | $\frac{1}{\sqrt{3}} H(2s) + \frac{1}{\sqrt{3}} H(2p) + \frac{1}{\sqrt{3}} H(2d)$ |
| 4   | 4   | $-2.125 570.46$ He(1s) 3P | $\frac{1}{\sqrt{3}} H(2s) + \frac{1}{\sqrt{3}} H(2p) + \frac{1}{\sqrt{3}} H(2d)$ |

$^a$ It is understood that $H(n\ell)$ is accompanied by He$^+(1s)$ and that $He(1s n\ell^L L)$ is accompanied by H$^+$. (Werner et al. 2006). This includes 20 $^1\Sigma^+$, 19 $^3\Sigma^+$, 12 $^1\Pi$, 9 $^3\Pi$, 4 $^1\Delta$ and 2 $^3\Delta$ states, which constitute a total of 66 electronic states. All these states, as well as their energy at $R = 70$ au and their dissociation products, are presented in tables 1–6. To obtain the PEC, we performed a state-averaged CASSCF (Werner and Knowles 1985, Knowles and Werner 1985) using the active spaces listed in table 7, followed by a full CI.

As we will not consider any spin-dependent interaction, the singlet and triplet states can be calculated separately.

3.1. Adiabatic $n = 1$ potential energy curves

The $n = 1$ states consist of two $^1\Sigma^+$ and one $^3\Sigma^+$ states and are shown in figure 1. All three are bound states that support a vibrational structure.

Our calculations reproduce correctly the equilibrium distance of 1.463 au of the $X^1\Sigma^+$ state. The dissociation energy of the ground state calculated by Kolos and Peek (1976) is $D_e = 16 455.64$ cm$^{-1}$ and a more accurate value of

![Figure 1](image_url)
Table 3. \(^1\)T states included in the calculations and their dissociation product. In this table, we use the notation H(\(n\ell\)) or He(1sn\(\ell\)L) to denote the electronic wavefunctions of the corresponding electronic states. Due to the He\(^+\) charge, there is a Stark effect on the hydrogen levels (see the text). The mixing coefficients have been calculated by diagonalizing the perturbation matrix due to the electric field.

| \(m\) | Energy (hartree) at \(R = 70\) au | Dissociative atomic wavefunctions\(^a\) |
|---|---|---|
| \(n = 2\) | 1 \(-2.124 916 60\) | H(2p) |
| \(n = 3\) | 1 \(-2.056 398 37\) | He(1s2p\(^1\)P\(^o\)) |
| | 2 \(-2.056 164 25\) | He(1s2p\(^1\)D\(^o\)) |
| | 3 \(-2.054 563 33\) | He(1s3p\(^1\)P\(^o\)) |
| | 6 \(-2.054 198 37\) | He(1s3p\(^1\)D\(^o\)) |
| \(n = 4\) | 7 \(-2.033 794 03\) | \(\frac{1}{\sqrt{2}}\)H(4p) + \(\frac{1}{\sqrt{2}}\)H(4d) |
| | 8 \(-2.033 453 58\) | He(1s4f\(^1\)F\(^o\)) |
| | 9 \(-2.030 818 19\) | \(\frac{1}{\sqrt{2}}\)H(4p) + \(\frac{1}{\sqrt{2}}\)H(4f) |
| | 10 \(-2.030 657 50\) | He(1s4d\(^1\)D\(^o\)) |
| | 11 \(-2.028 925 58\) | \(\frac{1}{\sqrt{2}}\)H(4p) + \(\frac{1}{\sqrt{2}}\)H(4d) + \(\frac{1}{\sqrt{2}}\)H(4f) |
| | 12 \(-2.028 775 73\) | He(1s4p\(^1\)P\(^o\)) |

\(^a\) It is understood that H(\(n\ell\)) is accompanied by He\(^+\)(1s) and that He(1sn\(\ell\)L) is accompanied by H\(^+\).

Table 4. \(^3\)T states included in the calculations and their dissociation product. In this table, we use the notation H(\(n\ell\)) or He(1sn\(\ell\)L) to denote the electronic wavefunctions of the corresponding electronic states. Due to the He\(^+\) charge, there is a Stark effect on the hydrogen levels (see the text). The mixing coefficients have been calculated by diagonalizing the perturbation matrix due to the electric field.

| \(m\) | Energy (hartree) at \(R = 70\) au | Dissociative atomic wavefunctions\(^a\) |
|---|---|---|
| \(n = 2\) | 2 \(-2.124 825 25\) | He(1s2p\(^1\)P\(^o\)) |
| | 2 \(-2.124 918 45\) | H(2p) |
| \(n = 3\) | 1 \(-2.058 144 10\) | He(1s3p\(^1\)P\(^o\)) |
| | 4 \(-2.056 400 23\) | \(\frac{1}{\sqrt{2}}\)H(3p) + \(\frac{1}{\sqrt{2}}\)H(3d) |
| | 5 \(-2.055 261 05\) | He(1s3d\(^1\)D\(^o\)) |
| | 6 \(-2.054 565 18\) | \(\frac{1}{\sqrt{2}}\)H(3p) + \(\frac{1}{\sqrt{2}}\)H(3d) |
| \(n = 4\) | 7 \(-2.033 713 07\) | He(1s4p\(^1\)P\(^o\)) |
| | 8 \(-2.033 235 84\) | \(\frac{1}{\sqrt{2}}\)H(4p) - \(\frac{1}{\sqrt{2}}\)H(4d) + \(\frac{1}{\sqrt{2}}\)H(4f) |
| | 9 \(-2.030 816 42\) | \(\frac{1}{\sqrt{2}}\)H(4p) - \(\frac{1}{2}\)H(4f) |

\(^a\) It is understood that H(\(n\ell\)) is accompanied by He\(^+\)(1s) and that He(1sn\(\ell\)L) is accompanied by H\(^+\).

In addition, using a B-spline basis set method, we have resolved the vibrational nuclear equation for \(^4\)HeH\(^+\) and obtained 12 vibrational bound states, as was found in the recent paper of Stanke et al (2006).

The \(A\ 1\Sigma^+\) and the \(a\ 3\Sigma^+\) states have been studied by Kolos (1976) in the adiabatic approximation. They both present weakly attractive potential curves with a minimum at large internuclear distances, \(R_c = 5.53\) au and 4.47 au for the singlet and the triplet (respectively), to be compared with our values of 5.53 au and 4.45 au. We have determined the dissociation energies \(D_e = 849.71\) cm\(^{-1}\) for the A state and \(D_e = 379.70\) cm\(^{-1}\) for the a state. A study of the vibrational structure of the \(a\ 3\Sigma^+\) state of \(^4\)HeH\(^+\) has been performed by Chibisov et al (1996) using the potential energy curve of (Michels 1966) extended by an analytical expression in the asymptotic region. They found that this potential supports five bound vibrational levels, while our resolution of the vibrational motion produced six bound levels. However, the binding energy of the last level is less than 1 cm\(^{-1}\). The largest difference between our energy values and those of Chibisov et al is of 2 cm\(^{-1}\). It is also important to note that the non-adiabatic couplings between the \(3\Sigma^+\) states have been neglected in both calculations and could modify significantly the energy of the levels, as it has been shown already for the vibrational structure of the ground state (Stanke et al 2006). Finally, in our calculations, we found that four bound vibrational levels are supported by the \(A\ 1\Sigma^+\) state of \(^4\)HeH\(^+\).
The first category dissociated asymptotically into H+ and Dashed curves, states dissociating into He+ Dashed curves, states dissociating into He+ 2 and 3, respectively. In these figures, the states of the first category are plotted as solid curves while the states of the second category are plotted as dashed curves.

The n = 2 manifolds have a very similar behaviour in both singlet and triplet spin symmetries. However, for the singlet states an avoided crossing between the two highest states occurs at an internuclear distance of 50 au. This crossing is understandable once looking at the asymptotical behaviour of those two 1 Σ+ states, which is governed by the Stark effect. Indeed, at large internuclear distances, the system is composed of a neutral atom, perturbed by an ion. The atomic dissociative states are He(1s2p1P0) + H+ and He+(1s) + H(2s), respectively for the highest and the lowest state.

If we restrict the description to quadratic effects in the field, the helium state behaves asymptotically in the presence of the H+ charge as

\[ E(R) = E_{He(12p_{1/2})} - \frac{\alpha_{He(12p_{1/2})}}{2R^4} \]  

and the 2s state of H, under the electric field produced by He+, as

\[ E(R) = E_{He^*(1s) + H(2s)} + \frac{3}{R^2} - \frac{\alpha_{He(2s)}}{2R^4} \]

where \( E \) represent the atomic energies. In addition, the |2s⟩ state of hydrogen becomes \( \frac{1}{\sqrt{2}} |2s⟩ - \frac{1}{\sqrt{2}} |2p⟩ \).

The first-order Stark effect produces a term proportional to \( 1/R^2 \), which vanishes unless the atomic state is degenerate with a state of opposite parity (Goldman and Cassar 2005). The term proportional to \( 1/R^4 \) is due to the second-order Stark effect, and the constant \( \alpha \) is the dipole polarizability. The polarizabilities for the helium states can be found in (Yan 2000, 2002) while the polarizabilities for hydrogen are obtained analytically (Radzig and Smirnov 1985). The result is that while the helium state presents an almost flat asymptotic curve, the hydrogen state decreases to its atomic value, and a crossing occurs in the analytical model at \( R = 50 \) au, almost exactly as in the \( ab \) \( initio \) calculation.

From figure 4, we see that the asymptotic \( n = 2 \) states are correctly described using the Stark effect up to order 2. To a lesser extent, it is also the case of the \( n = 3 \) singlet states (see figure 5): for example, the analytical model reproduces the crossing which occurs at 90 au between the 11th and 12th states dissociating respectively into He*(1s) + H(3s) and He(1s3p 1P0) + H+ (see table 1).

In the Born–Oppenheimer approximation, in which the quantum chemical calculations are performed, these crossings are avoided. However, the large amplitude and the narrowness of the non-adiabatic couplings at those points indicate that a full diagonal diabatic representation at the crossing is perfectly justified.

It is clear from figures 2 and 3 that the number of avoided crossings increases strongly with \( n \) and that their positions are shifted to larger internuclear distances. Those avoided

| n value | 1 Σ+ | 3 Σ+ | 1 Π | 3 Π | 1,3 Δ |
|---------|------|------|------|------|--------|
| 1       | (6σ, 2π) (X1 Σ+) | (9σ, 4π, 1δ) (A1 Σ+) |
| 2       | (9σ, 4π, 1δ) | (9σ, 4π, 1δ) |
| 3       | (12σ, 6π, 4δ) | (12σ, 8π, 26) |
| 4       | (28σ, 25) | (28σ) |

The n = 2 states dissociating respectively into He+(1s) + H(2s), He+(1s) + H(3s) and He(1s3p 1P0) + H+. The n = 3 states are divided into two groups. The first category dissociated asymptotically into H+ and neutral He in an excited 1snt 1,3L state, while the second one dissociated into He+ in its 1s ground state and an excited nต state of H. Both categories of states alternated along the electronic spectrum resulting in a large number of avoided crossings leading to charge exchange dynamics. For the Σ symmetry, the total number of states up to \( n = 4 \) is 20 for the singlets and 19 for the triplets. They are shown in figures 2 and 3, respectively. In these figures, the states of the first category are plotted as solid curves while the states of the second category are plotted as dashed curves.

### Table 7. Active spaces used in state-averaged CASSCF calculations.

| n value | 1 Σ+ | 3 Σ+ | 1 Π | 3 Π | 1,3 Δ |
|---------|------|------|------|------|--------|
| 1       | (6σ, 2π) (X1 Σ+) | (9σ, 4π, 1δ) (A1 Σ+) |
| 2       | (9σ, 4π, 1δ) | (9σ, 4π, 1δ) |
| 3       | (12σ, 6π, 4δ) | (12σ, 8π, 26) |
| 4       | (28σ, 25) | (28σ) |
crossings mask partially the intrinsic oscillatory behaviour of the higher states that has been observed in previous calculations (Boutalib and Gadea 1992). This behaviour has been related to the nodal structure of the Rydberg orbitals which may start to be important in the \( n = 4 \) manifold and can be clearly seen in the last two \( \Sigma^+ \) states. The second observation is that the states belonging to different manifolds are very close in energy, especially at internuclear distances smaller than 10 au. In addition, well-defined avoided crossings couple the last state of a manifold to the first state of the next manifold at large internuclear distances (7 au between \( n = 2 \) and \( n = 3 \) and 18 au between \( n = 3 \) and \( n = 4 \) for the singlet symmetry).

Finally, due to the presence of the \( n = 5 \) states, very close in energy and not adequately described in our calculations, the representation of the highest \( n = 4 \) states is probably less accurate than for the other members of the Rydberg series.

The comparison can be made with the previous work of Green \textit{et al} (1974a, 1974b, 1976, 1978) for the \( n = 2 \) singlet and triplet states in the range \( R = 1–5 \) au and with the data of Klüner \textit{et al} (1999) for the three first singlet states in the range \( R = 1–10 \) au. The different sets of results are very similar for both spin symmetries, the present calculations being systematically more stable in energy.

We also note that Klüner \textit{et al} (1999) have associated, at short internuclear distances, the last state of the \( n = 2 \) manifold in their calculations as dissociating into \( \text{He}(1s2p^1P^+) + \text{H}^+ \) while due to the crossing involving this state at 50 au, it actually corresponds to \( \text{He}^+(1s) + \text{H} \) (\( n = 2 \)) (see table 1). This is very important since these authors are interested in the electron transfer mechanism and they have eliminated the last \( n = 2 \) state from their dynamical calculations.

### Table 8. Location of the principal non-adiabatic radial couplings for the \( n = 1–3 \Sigma^+ \) states.

| \( \Sigma^+ \) states | \( R \) (a_0) |
|-----------------------|------------|
| \( 1 \Sigma^+ \) states |
| 3–4  | 3.9 |
| 4–5  | 3.1 |
| 5–6  | 4.5 |
| 6–7  | 7.0 |
| 7–8  | 2.9, 5.2 |
| 8–9  | 4.1 |
| 9–10 | 12.0 |
| 10–11| 4.0, 6.6, 12.2 |
| 11–12| 2.7, 5.4, 8.8, 25.0 |

| \( \Sigma^+ \) states | \( R \) (a_0) |
|-----------------------|------------|
| \( 2 \Sigma^+ \) states |
| 3–4  | 3.6 |
| 4–5  | 2.9 |
| 5–6  | 10.6 |
| 6–7  | 3.5, 6.8 |
| 7–8  | 5.5 |
| 8–9  | 4.5 |
| 9–10 | 10.8, 12.3, 28.0 |
| 10–11| 5.7, 8.8 |
| 11–12| 3.6, 12.1, 26.0 |

### Table 9. Location of the principal non-adiabatic radial couplings for the \( n = 1–3 \Pi \) states.

| \( \Pi \) states | \( R \) (a_0) |
|-----------------|------------|
| \( 1 \Pi \) states |
| 3–4  | 7.5 |
| 4–5  | 3.5, 18.8 |
| 5–6  | 18.1 |
| 6–7  | 4.5, 18.8 |
| 7–8  | 18.3 |

For the \( n = 3 \) manifold, only Green \textit{et al} provide a full set of results for both singlet and triplet states. The differences with our data are more important than for the \( n = 2 \) states in both spin multiplicities, especially for the highest states which undergo avoided crossings with the lowest \( n = 4 \) states. Tables 8 and 9 give the location of all the major avoided crossing points for singlet and triplet states which have been determined by an analysis of the calculated radial non-adiabatic couplings (see section 4.1).
presented in figures 6 and 7, respectively. The PEC have dissociating into $\text{He}^+$.

Figure 6. Adiabatic PEC of the $n = 2–4 \; ^1\Pi$ states. Solid curves, states dissociating into $\text{He}^+(1s\ell^1L) + \text{H}^+$. Dashed curves, states dissociating into $\text{He}^+(1s\ell) + \text{H}(n\ell)$.

Figure 7. Adiabatic PEC of the $n = 2–4 \; ^3\Pi$ states. Solid curves, states dissociating into $\text{He}^+(1s\ell^3L) + \text{H}^+$. Dashed curves, states dissociating into $\text{He}^+(1s\ell) + \text{H}(n\ell)$.

3.3. Adiabatic potential energy curves for the first Rydberg $^1\Pi$ and $^3\Delta$ states

The potential energy curves of the $^1\Pi$ and $^3\Pi$ states are presented in figures 6 and 7, respectively. The PEC have again a very similar behaviour for both spin multiplicities. Indeed, the first and the third state seem to present a shallow well, and we also see that an avoided crossing between the last three $n = 3$ states occurs at $R \approx 18$ au. Finally, the last $n = 3$ state and the first $n = 4$ state interact strongly at about 8 au.

Once again, the qualitative comparison with the results of Green et al for $n = 2–3$ is good but there are some differences. The avoided crossing mentioned above occurs at $R = 20$ au rather than at $R = 18$ au in our work, and we also see that the energy separation at the avoided crossing between the third and fourth state (internuclear distance of about 8 au) is larger in our calculation.

Finally, the PEC for the $\Delta$ states are presented in figure 8. They seem to be almost independent of the spin multiplicity. In the work of Green et al, the two $n = 4$ PEC present an avoided crossing, which is not the case in this work.

It should be noted that the calculation of the $\Delta$ states is more difficult than for the other symmetries. This is due to the fact that MOLPRO can only use Abelian groups, and the $C_2v$ subgroup of $C_{\infty v}$ is used for the diatomic molecules. In this group, the $\Sigma^+$ and $\Delta$ states are calculated within the same CI matrix diagonalization and it is sometimes difficult to separate the states of those symmetries. The same is true for the $\Phi$ states, which correspond to the same irreducible representations as the $\Pi$ states in $C_{2v}$.

4. Non-adiabatic corrections

We write the total Hamiltonian as the sum of an electronic part, $H^{\text{el}}$, and a nuclear kinetic part, $T^N$, which itself can be developed into a radial ($H^{\text{rad}}$) and a rotational ($H^{\text{rot}}$) part:

$$H = T^N + H^{\text{el}} = H^{\text{rad}} + H^{\text{rot}} + H^{\text{el}}.$$ 

In the electronic Hamiltonian, the mass polarization term has been neglected. Using the electronic wavefunctions $\zeta_{i,\Lambda}$, solutions of the electronic Schrödinger equation

$$H^{\text{el}}\zeta_{i,\Lambda}(\mathbf{r}; R) = U_i(R)\zeta_{i,\Lambda}(\mathbf{r}; R),$$

the total wavefunction is expressed as a product of an electronic and a nuclear wavefunction: $\Psi(\mathbf{r}, \mathbf{R}) = \sum_{i,\Lambda} \zeta_{i,\Lambda}(\mathbf{r}; R)\psi_{i,\Lambda}(\mathbf{R})$, where $\mathbf{R}$ and $\mathbf{r}$ stand for the electron and nuclear coordinates, respectively. $\Lambda$ is the quantum number associated with $L_z$, the projection of the electronic orbital angular momentum $\mathbf{L}$ onto the $z$ axis.

As the nuclear Hamiltonian is separable, the nuclear wavefunction is given by the product $\psi_l(R) = \psi_l(R) \langle K \Lambda \rangle$, where $\langle K \Lambda \rangle$ is an eigenfunction of the operators $K^2$ and $K_z$, and $K$ being the total angular momentum.

Using this development, the Schrödinger equation can be expressed as

$$\sum_{j,\Lambda} \langle \zeta_{j,\Lambda} | H^{\text{rad}} + H^{\text{rot}} | \psi_{j,\Lambda} \rangle \psi_{j,\Lambda} + (U_j - E)\psi_{j,\Lambda} = 0,$$
are known as ‘Landau–Zener couplings’ (Zener 1932). The cross at those points upon diabatization. These couplings the $\Sigma_1$ states and in table 8 for the $\Pi_1$ states which are isolated in energy. The PEC will cross at those points upon diabatization. These couplings are known as ‘Landau–Zener couplings’ (Zener 1932).

where

$$H^{\text{rad}} = -\frac{1}{2\mu} \partial^2_R$$

and

$$H^{\text{rot}} = \frac{1}{2\mu R^2} \mathbf{N}^2$$

$$= \frac{1}{2\mu R^2} [K^2 + L^2 - 2K_z L_z - K_+ L_+ - K_- L_-]$$

(3)

where $\mathbf{N}$ is the nuclear angular momentum.

4.1. Radial couplings

Using the orthonormality of the electronic wavefunctions, the matrix elements of the radial Hamiltonian are given by

$$\langle \zeta_i, \Lambda | -\frac{1}{2\mu} \partial^2_R | \zeta_j, \Lambda' \rangle$$

$$= -\frac{1}{2\mu} [\partial^2_R \delta_{ji} + 2\langle \zeta_i, \Lambda | \partial_R | \zeta_j, \Lambda' \rangle \partial_R + \langle \zeta_i, \Lambda | \partial^2_R | \zeta_j, \Lambda' \rangle] \delta_{\Lambda, \Lambda'}$$

$$= -\frac{1}{2\mu} [\partial^2_R \delta_{ji} + 2F_{i, j, \Lambda' \Lambda} \partial_R + G_{i, j, \Lambda' \Lambda}] \delta_{\Lambda, \Lambda'}.$$

Since it can be shown that in matrix form $\mathcal{G} = \mathbb{F}^2 + \partial_R \mathbb{F}$ (Baer 2006), we only need to calculate the elements of $\mathbb{F}$, which is block diagonal in $\Lambda$. These couplings were calculated using a three-point central difference method implemented in the DDR programme of MOLPRO with a displacement parameter $dR = 0.01$ au.

For the analysis of the radial couplings, we will focus on the $n = 2$ states since all the $k(k-1)/2$ couplings (where $k$ is the number of states for a given $\Lambda$) cannot be shown here. We note that the dominant couplings are systematically those connecting two adjacent states (i.e. the couplings $F_{i, i+1}$), as shown in figure 9 for the $n = 2$ states. This implies that states of different values of $n$ can interact at the exception of the two $n = 1$ states which are isolated in energy. The dominant couplings are narrow and their maxima correspond to the positions of the avoided crossings given in table 8 for the $\Sigma$ states and in table 9 for the $\Pi$ states. The PEC will cross at those points upon diabatization. These couplings are known as ‘Landau–Zener couplings’ (Zener 1932).

radial couplings presented in figure 9 are of this type. On other hand, some couplings are wider and do not correspond to clear avoided crossings; instead, the PEC are parallel in the coupling region. These couplings arise mainly at large internuclear distances. The dynamics around these couplings is described by the Rosen–Zener theory (Rosen and Zener 1932). Both types of couplings will give rise to very different dynamical behaviours. As an example, we will consider the case of the coupling $F_{34}$ (shown in figure 10), which can be separated in a Landau–Zener coupling (centred around $R \sim 4$ au) and a Rosen–Zener coupling, centred at $R \sim 17$ au. The position and the shape of the long-range coupling are invariant under changes in the level of electron correlation or in the atomic basis set used in the calculation, as illustrated in figure 10.

We observed that some of the radial couplings tend asymptotically to a constant which differ from zero. This behaviour is expected for the couplings between two molecular states of the same symmetry degenerated at infinity when the calculations of the couplings are done using an origin of the electronic coordinates at the centre of the nuclear mass (Belyaev et al. 2001).

As the final goal of this work is the study of non-adiabatic dynamics involving those couplings, we should note here that a number of authors demonstrated the importance of electron translation factors at high and intermediate energies and proposed different methods to take them into account (Thorson and Delos 1978, Errea et al. 1994). It was also established that these factors are linked to the choice of the origin of the electronic coordinates (Bransden and McDowell 1992). As we noted the quasi-invariance of the radial couplings under a translation of the origin of the electronic coordinates along the internuclear axis (see figure 11), it appears that the inclusion of translation factors in dynamical simulations will not be necessary.

4.2. Rotational couplings

From equation (3), we can obtain the matrix elements of the rotational Hamiltonian between the electronic and rotational...
nuclear functions. They are given by
\[ H_{\mu K,\mu' K'} = \langle K|L_2^{(2)}|\mu\rangle \delta_{\mu\mu'} + \langle K,\mu|L_2^{(2)}|\mu' K'\rangle \delta_{\mu,\mu'} + 2\langle K,\mu|L_2^{(2)}|\mu' K'\rangle \delta_{\mu',\mu'} \delta_{\Lambda,\Lambda'} + 2\langle K,\mu|L_2^{(2)}|\mu' K'\rangle \delta_{\mu',\mu} \delta_{\Lambda',\Lambda} \delta_{\Lambda,\Lambda'} \] (4)

We see from the formula above that \[ L_2^{(2)} \] is an interaction between states of the same \[ \Lambda \] value. In particular, the diagonal part \( (L_2^{(2)} + L_2^{(2)})_{\mu\mu} \) modifies the energies of the states. This contribution can be evaluated using MOLPRO at the CASSCF level, but we will not report it here since it was shown by Bishop and Cheung (1979) that for the ground state it is of the same order of magnitude as the effect of the mass polarization term, which we have neglected. The same conclusion was reached by Bunker (1968) for \( \text{H}_2 \). We only mention the fact that asymptotically, these matrix elements behave as \( R^2 \), so the corrections to the energies are constants (see equation (4)) when the internuclear distance is large.

The operator \( L_{2\gamma}, \) on the other hand, connects states with \( \Delta\Lambda = \pm 1 \) and cannot be neglected. Note that the calculation of the matrix elements of \( L_{2\gamma} \) necessitates the simultaneous determination of electronic states of different values of \( \Lambda \) in the same calculation.

The rotational couplings between the \( n = 2 \ ^1\Pi \) and \( ^1\Sigma^+ \) states are presented in figure 12. Asymptotically, the couplings between states that dissociate into the same atomic species and into the same \( \Lambda \) manifold are constant. Some rotational couplings between states dissociating into different \( \Lambda \) manifolds make an exception and behave asymptotically as \( R \), as indicated by Belyaev et al (2001). All the couplings between states dissociating into different atomic species tend to zero at large internuclear distances.

5. Adiabatic dipole moments
There are \( k(k + 1)/2 \) (where \( k \) is the number of states) dipole matrix elements and we will again restrict our discussion to the \( ^1\Sigma^+ \) states. The permanent dipole moments of the \( n = 1 \) and \( 2 \ ^1\Sigma^+ \) states are represented in figure 13, while the transition dipole moments of the \( n = 2 \ ^1\Sigma^+ \) states are represented in figure 14.
In a given \( \Lambda \) subspace, the dipole interaction occurs only through the \( z \) component. As there is no ambiguity, we will thus write the dipole moment between two states \( i \) and \( j \) as \( \mu_{ij} \) instead of \( \mu_{i,j} \).

The behaviour of the dipole moments is consistent with the calculation of the radial couplings, illustrating the relation between the two operators (Macías and Riera 1978) which allows the use of the dipole moment rather than the radial couplings to find a diabatic representation. For example, the crossing between the dipoles \( \mu_{55} \) and \( \mu_{66} \) at \( R = 12.75 \) au corresponds to the sharp radial coupling seen in figure 9 at the same internuclear distance, and is reflected on the transition dipole moment between the two states, \( \mu_{56} \), which presents a sharp peak in the crossing region. Conversely, when two permanent dipoles have a peak of opposite value, as do \( \mu_{44} \) and \( \mu_{55} \) at \( R = 3.1 \) au, the sign of the transition dipole \( \mu_{45} \) changes abruptly. Again, this is linked to an avoided crossing between the fourth and fifth states at the same internuclear distance.

As can be seen from figure 13, all the permanent dipole moments \( \mu_{ii} \) behave asymptotically as \( R \), since the origin of the coordinates is at the nuclear centre of mass and not on one of the atoms. As the reduced mass of \( ^4\text{HeH}^+ \) is \( \mu = 0.805 \) amu, the helium and the hydrogen nuclei are situated approximatively at \( -0.2R \) and \( 0.8R \) of the origin, respectively. The permanent dipole moment can then be divided into a nuclear and an electronic part. The nuclear contribution is of \( 0.4R \) and is identical for all states, while the electronic contribution is of \( 0.4R \) for the He(\( 1\text{sn}\ell^1L \)) + H\(^+\) states and of \( -0.6R \) for the He\(^+\)(\( 1\text{s} \)) + H(\( n\ell \)) states. For the latter, there is an additional contribution from the interaction between the helium \( 1s \) electron and the hydrogen \( n\ell \) electron which explains that the permanent dipole moments for these states do not tend to the same asymptotic value.

6. Diabatic representation of the Rydberg states

The diabatic representation is defined so as to cancel the \( F \) matrix, which is the case if the adiabatic-to-diabatic transformation matrix \( D \) satisfies the matrix equation

\[
\partial_R D + F \cdot D = 0.
\]

The diabatic potential energy curves are then given as the diagonal elements of the transformed matrix \( D^U = D^{-1} \cdot U \cdot D \). We solve equation (5) by continuity using a grid of 2000 points, starting from \( R = 60 \) au where we require that the adiabatic and diabatic representations are identical (so that \( D \equiv 1 \)). It should also be noted that, as we calculate the non-adiabatic radial coupling at the CASSCF level, we also use the CASSCF energies, which differ slightly from the CI energies presented in section 3.

In our diabatization procedure, we will not consider the complete \( F \) matrix, keeping only the couplings \( F_{i,i+1} \) and putting all the other couplings to zero. This approximation, which amounts to a succession of two-states cases, is used for various reasons. The first one is that, as was shown in section 4.1, those couplings are systematically the most important ones. Secondly, it has been shown by Zhu and Nakamura (1997) that this approximation gives correct results in dynamical calculations even for low energies, which is confirmed by our calculations of the electron-transfer cross sections in the \( n = 2 \) manifold (Loreau et al 2010). Thirdly, some of the couplings which we neglect remain non-zero at large internuclear distance. This phenomenon is known and has been discussed in detail by Belyaev et al (2001), but raises a problem in our diabatization method. Indeed, our procedure is based on the fact that the adiabatic and diabatic representations coincide at \( R = \infty \), which is not the case if the couplings do not vanish. As a consequence, these residual couplings, although small, influence the diabatic PEC at large \( R \), a feature which is of course undesirable.

We will consider the \( ^1\Sigma^+ \) states as an example of the diabatization procedure. The result of the diabatization for these states up to \( n = 3 \) is given as an example in figure 15.

It is clear that the diabatization alters considerably the shape of the ground state. From figure 16, we see that this is essentially due to the coupling \( F_{1,2} \) since the same behaviour is observed when the \( n = 1 \) states are diabatized independently.
The first excited state also changes dramatically, crossing the entire \( n = 2 \) manifold in the diabatic representation, which is due to the coupling \( F_{23} \) (see figure 16). However, one must remember that the non-adiabatic coupling between the two first \( ^1\Sigma^+ \) states is of the Rosen–Zener type, and that therefore the diabatic representation of those states has little physical significance. Likewise, the influence of the two first \( ^1\Sigma^+ \) states on the diabatic representation of the \( n = 2 \) states is very important but has little effect on the non-adiabatic dynamics in the \( n = 2 \) manifold, as has been observed in the calculation of charge exchange cross section between He* and H at low energies (Loreau et al. 2010). To our knowledge, the only other work on the diabatic representation of the PEC of the HeH* ion has been done by Klüner et al. (1999) using the quasi-diabatization procedure proposed by Pacher et al. (1988). These authors compare a 3-state (the three lowest \( n = 2 \) states) and a 4-state (adding the second \( n = 1 \) state) diabatization in a small interval of internuclear distances (0.8 au \( \leq R \leq 5.4 \) au). It is concluded that the inclusion of the \( n = 1 \) state does not modify the diabatic PEC of the \( n = 2 \) manifold, and this state is therefore neglected in wavepacket simulations of charge exchange processes involving \( n = 2 \) states. Although we arrive at the same conclusion regarding the dynamics, our method gives significantly different diagonal as well as non-diagonal matrix elements of the electronic Hamiltonian in the diabatic representation.

On the other hand, the effect of the interaction between the \( n = 2 \) and \( n = 3 \) manifolds through the \( F_{67} \) matrix element is relatively small, as shown in figure 17.

Finally, the description of the diabatic \( n = 3 \) states necessitates to take some higher-lying states into account, since the highest diabatic state undergoes an avoided crossing around \( R = 20 \) (as can be seen in figure 2) with the first \( n = 4 \) state. The inclusion of the first two \( n = 4 \) states in the diabatization, while leaving the first five \( n = 3 \) states unaltered, clearly influences the sixth state by shifting the position of the avoided crossing to smaller values of \( R \), as illustrated in figure 18. Therefore, a more correct description of the last \( n = 3 \) diabatic state should include more \( n = 4 \) states, even though we are only considering the couplings between adjacent states.

### 7. Conclusions

We present an accurate description of 66 low-lying adiabatic states of HeH*. Using the MOLPRO package and a large adapted basis set, the potential energy curves of the \( n = 1–3 \) as well as most of the \( n = 4 \) states of the molecular ion have been obtained and compared to previous theoretical works. The radial and rotational non-adiabatic coupling matrix elements, as well as the dipole matrix elements, have been calculated for all the \( n = 1–3 \) states. The radial couplings allow us to switch to the diabatic representation which is used to treat dynamical processes involving the ion. This material has been used to calculate the cross section of the photodissociation of the ion (Sodoga et al. 2009) and the cross sections for the charge transfer processes He*(1s) + H(n\ell) \rightarrow He(1s\ell'1\Sigma) + H* at low energy (Loreau et al. 2010).

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### Appendix. Basis set

Tables A1, A2 and A3 list additional basis sets for hydrogen and for the singlet and triplet states of helium.
Table A1. Additional basis functions for hydrogen.

| Coefficient | Exponent | Coefficient | Exponent |
|-------------|----------|-------------|----------|
| 2s          | 0.000 144 | 19.907 407  | 3p       | 0.024 590 | 0.986 107  |
| −0.005 010  | 8.988 620  | 0.260 387   | 1.081 062 |
| −0.059 868  | 0.645 915  | 0.903 505   | 0.051 409 |
| −0.123 387  | 0.071 221  | −1.874 014  | 0.007 783 |
| 0.891 720   | 0.242 689  | −0.287 393  | 0.003 281 |
| 3s          | 0.017 083 | 1.000 840   | 4p       | 0.015 685 | 1.015 267  |
| 0.120 859   | 0.272 819  | 0.170 182   | 1.006 800 |
| 0.381 641   | 0.093 336  | 0.625 077   | 0.035 622 |
| 0.782 727   | 0.023 846  | −0.204 089  | 0.009 383 |
| −2.036 422  | 0.019 287  | 2.535 609   | 0.002 477 |
| 1.594 513   | 0.004 250  |                        |           |
|              | 3d        | 0.050 502   | 0.199 534 |

Table A3. Additional basis functions for the triplet states of helium.

| Coefficient | Exponent | Coefficient | Exponent |
|-------------|----------|-------------|----------|
| 2s          | 0.006 837 | 99.181 525  | 3p       | 0.002 497 | 4.675 067  |
| 0.067 529   | 10.551 100 | 0.035 791   | 0.789 129 |
| 0.269 982   | 2.355 836  | 0.247 261   | 0.205 234 |
| 0.759 139   | 0.643 556  | 0.833 266   | 0.065 732 |
| −3.666 553  | 0.037 246  | −2.061 784  | 0.007 542 |
| 3s          | −0.000 849 | 99.836 273  | 4p       | 0.013 260 | 1.567 909  |
| 0.012 336   | 49.044 874 | 0.137 119   | 0.284 565 |
| 0.156 413   | 3.473 103  | 0.208 845   | 0.076 404 |
| 0.448 487   | 0.589 924  | 3.155 372   | 0.015 570 |
| −3.036 160  | 0.043 579  | −7.946 015  | 0.013 266 |
| 4.329 233   | 0.006 971  | 3.796 480   | 0.002 506 |

Table A2. Additional basis functions for the singlet states of helium.

| Coefficient | Exponent | Coefficient | Exponent |
|-------------|----------|-------------|----------|
| 2s          | 0.006 700 | 99.181 545  | 3p       | 0.002 929 | 4.673 075  |
| 0.030 509   | 10.536 516 | 0.037 026   | 0.848 515 |
| 0.196 191   | 1.095 592  | 0.244 477   | 0.027 656 |
| 0.775 469   | 0.424 822  | 0.806 379   | 0.070 757 |
| −3.722 470  | 0.029 920  | −2.050 784  | 0.007 911 |
| 3s          | −0.001 952 | 99.838 262  | 4p       | 0.002 547 | 4.629 236  |
| 0.012 286   | 49.068 205 | 0.076 795   | 0.396 874 |
| 0.151 694   | 2.653 277  | 0.488 599   | 0.081 760 |
| 0.516 699   | 0.309 173  | 3.304 293   | 0.017 020 |
| −3.156 883  | 0.038 398  | −4.482 362  | 0.013 667 |
| 4.383 564   | 0.006 064  | 2.305 609   | 0.002 825 |
| 4s          | −0.004 235 | 99.861 298  | 3d       | 0.062 634 | 0.102 716  |
| 0.011 613   | 49.188 130 | 0.430 990   | 0.026 362 |
| 0.316 811   | 0.732 304  | 0.551 594   | 0.008 950 |
| −2.495 917  | 0.035 479  |                        |           |
| 4.534 324   | 0.009 221  | 0.077 839   | 0.082 347 |
| 4.267 928   | 0.001 472  | 0.445 447   | 0.021 503 |
| −0.894 818  | 0.003 283  |                        |           |
| 2p          | 0.000 152  | 19.984 152  | 4f       | 0.026 447 | 0.033 780  |
| 0.002 135   | 4.719 990  | 0.026 447   | 0.033 780 |
| 0.025 319   | 1.021 806  | 0.170 021   | 0.010 582 |
| 0.160 069   | 0.292 204  | 0.204 038   | 0.004 106 |
| 0.592 704   | 0.101 345  |                        |           |
| 1.066 547   | 0.039 590  |                        |           |
| 0.527 114   | 0.016 351  |                        |           |

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