The $H_2^+$ ion in a strong magnetic field.

Lowest excited states

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Abstract

As a continuation of our previous work (Phys. Rev. A 68, 012504 (2003)) an accurate study of the lowest $1\sigma_g$ and the low-lying excited $1\sigma_u$, $2\sigma_g$, $1\pi_{u,g}$, $1\delta_{g,u}$ electronic states of the molecular ion $H_2^+$ is made. Since the parallel configuration where the molecular axis coincides with the magnetic field direction is optimal, this is the only configuration which is considered. The variational method is applied and the same trial function is used for different magnetic fields. The magnetic field ranges from $10^9$ G to $4.414 \times 10^{13}$ G where non-relativistic considerations are justified. Particular attention is paid to the $1\sigma_u$ state which was studied for an arbitrary inclination. For this state a one-parameter vector potential is used which is then variationally optimized.

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I. INTRODUCTION

In our previous paper [1] (cited below as I) we carried out an accurate detailed study of the ground state $1_g$ of the molecular ion $H_2^+$ placed in a constant uniform magnetic field ranging from zero up to $4.414 \times 10^{13} \text{G}$ for all inclinations $0^\circ - 90^\circ$. The goal of that study was to investigate the domain of existence of the $H_2^+$ ion. We showed that for all magnetic fields studied the molecular ion $H_2^+$ exists for moderate (not very large) deviations of the molecular axis from the magnetic field direction (moderate inclinations). Furthermore it was found that for each magnetic field the most stable configuration of minimum total energy corresponded to zero inclination, where the molecular axis coincides with magnetic field direction. We called this configuration the ‘parallel configuration’. To this configuration the standard spectroscopic notation $1\sigma_g$ can be assigned. A major feature of this configuration is that with magnetic field growth the system becomes more and more bound (binding energy grows) and more and more compact (equilibrium distance decreases).

The aim of the present paper is to continue the study initiated in I and to explore several low-lying excited states. At first we re-examine the ground state for the parallel configuration $1\sigma_g$ in the region $10^9 - 4.414 \times 10^{13} \text{G}$. A detailed study of the $1\sigma_u$ state which is anti-bonding without a magnetic field is presented. Then the lowest states of different magnetic quantum numbers are investigated as well as the $2\sigma_g$ state.

Atomic units are used throughout ($\hbar=m_e=e=1$), although energies are expressed in Rydbergs (Ry). The magnetic field $B$ is given in a.u. with $B_0 = 2.35 \times 10^9 \text{G}$ [18].

II. GENERALITIES

The Hamiltonian which describes two infinitely heavy protons and one electron placed in a uniform constant magnetic field directed along the $z$–axis, $\mathbf{B} = (0, 0, B)$ is given by (see e.g. [2])

$$\mathcal{H} = \hat{p}^2 + \frac{2}{R} - \frac{2}{r_1} - \frac{2}{r_2} + (\hat{p}\mathcal{A} + \mathcal{A}\hat{p}) + \mathcal{A}^2,$$

(see Fig.1 for notations), where $\hat{p} = -i\nabla$ is the momentum, $\mathcal{A}$ is a vector potential which corresponds to the magnetic field $\mathbf{B}$ and is chosen in the symmetric gauge to be

$$\mathcal{A} = \frac{B}{2}(-y, x, 0).$$
Hence the total energy $E_T$ of $H_2^+$ is defined as the total electronic energy plus the Coulomb energy of proton repulsion. In turn, the binding energy is defined as an affinity to having the electron as well as both protons being infinitely separated, $E_b = B - E_T$. The dissociation energy is defined as an affinity to having one proton at infinity, $E_d = E_H - E_T$, where $E_H$ is the total energy of the hydrogen atom in a magnetic field $B$. Spin degrees of freedom can be separated out and their analysis is straightforward.

The problem is characterized by two integrals of motion: (i) angular momentum projection on the magnetic field direction (z-direction) and (ii) spatial parity $p$. Sometimes the parity $\sigma$ corresponding to interchange of charged centers $1 \leftrightarrow 2$ is used, which is connected with the magnetic quantum number and spatial parity, $p = \sigma(-1)^{|m|}$.

If the case $m$ is even, both parities coincide, $p = \sigma$. Thus, any eigenstate has two definite quantum numbers: the magnetic quantum number $m$ and the parity $p$ with respect $z \to -z$. Therefore the space of eigenstates is split into subspaces (sectors) each of them is characterized by definite $m$ and $\sigma$. Notation for the state we are going to use is based on the following convention: the first number corresponds to the number of excitation - "principal quantum number", e.g. the number 1 is assigned to the ground state, then a Greek letter $\sigma, \pi, \delta$ corresponds to $m = 0, -1, -2$, respectively, with subscript $g/u$ (gerade/ungerade) describing positive/negative parity with respect $z \to -z$.

Most of the excited states we study are the lowest states (of the type of the ground state) of the sectors with different magnetic quantum numbers $m$ and $p$. It is quite obvious from the physical point of view that the ground states of the sectors with $m > 0$ always have larger total energies than those with $m \leq 0$. Therefore we restrict our consideration to the states with $m = 0, -1, -2$.

Conservation of the $z$-component of the angular momentum assumes the wave function of the electron (in cylindrical coordinates $(\rho, \varphi, z)$) can be taken in the representation:

$$
\Psi = e^{im\varphi} \rho^{|m|} \psi_m,
$$

where $m$ is magnetic quantum number. Let us gauge rotate the Hamiltonian (1),

$$
\begin{align*}
\mathcal{H}_m &= e^{-im\varphi} \rho^{-|m|} \mathcal{H} e^{im\varphi} \rho^{|m|} = \hat{p}_m^2 + \frac{2}{\rho} \frac{2}{r_1} - \frac{2}{r_2} + mB + \frac{B^2 \rho^2}{4},
\end{align*}
$$

(2)
FIG. 1: Geometrical setting for the \( H_2^+ \) ion placed in a magnetic field directed along the \( z \)-axis. The protons are situated in the \( y-z \) plane at a distance \( R \) from each other and marked by bullets.

where

\[
\hat{p}_m = e^{-im\varphi} \rho^{-|m|} \hat{p} e^{im\varphi} \rho^{|m|},
\]

is the gauge rotated momentum (covariant momentum). The constant term \( mB \) describes the linear Zeeman effect splitting. It can be absorbed to a definition of total energy. The representation (2) is rather convenient since each Hamiltonian for fixed \( m \) describes the family of eigenstates with quantum number \( m \) and can be treated independently of the states with \( m' \) different from \( m \). Now the Hamiltonian (2) has only the invariance corresponding to the spatial parity conservation.

We are going to use the variational method in a way similar to what was done in I. The recipe of choice of trial function is based on physical arguments and is described in full generality in [3] (see for details the article I). Eventually, the ground state trial function for fixed \( m \) and \( \sigma \) is chosen in a form

\[
\psi^{(trial)}_m = A_1 \psi_1 + A_2 \psi_2 + A_3 \psi_3,
\]
where

\[ \psi_1 = \begin{cases} e^{-\alpha_1 r_1} e^{-\beta_1 \rho^2}, & \text{if } \sigma = +1, \\ 0, & \text{if } \sigma = -1, \end{cases} \]

\[ \psi_2 = (e^{-\alpha_3 r_1 + \sigma e^{-\alpha_3 r_2}}) e^{-\beta_3 \rho^2}, \]

\[ \psi_3 = (e^{-\alpha_3 r_1 - \alpha_4 r_2 + \sigma e^{-\alpha_3 r_2 - \alpha_4 r_1}}) e^{-\beta_3 \rho^2}, \]

and \( \sigma = \pm 1, \ m = 0, \pm 1, \pm 2 \ldots \). Here \( A_{1,2,3} \) and \( \alpha_{1,2,3,4}, \beta_{1,2,3} \) as well as \( R \) are variational parameters, which are certainly different for different \( m \) [19]. The functions \( \psi_{1,2,3} \) carry a certain physical meaning. They describe coherent (incoherent) interaction of the electron with the protons as well as their non-linear interpolation, respectively. Calculations were performed using the minimization package MINUIT from CERN-LIB. Numerical integrations were carried out with a relative accuracy of \( \sim 10^{-9} \) by use of the adaptive NAG-LIB (D01FCF) routine. All calculations were performed on dual PC Pentium-4, with two processors of 2.8 GHz each. Every particular calculation of given eigenstate at fixed magnetic field including minimization has taken in total about an hour of CPU time. However, when the variational parameters are found it take a few seconds of CPU time to calculate the variational energy.

It is necessary to mention two technical difficulties we encountered. Calculation of two-dimensional integrals with high accuracy which appeared in the problem has required a development of a very sophisticated numerical technique. We created a ‘dynamical partitioning’ of the domain of integration, which depend on values of variational parameters similar to what was done in I. The domain partitioning was changed with a change of the parameters. Sometimes the number of sub-domains was around 50. Another technical problem is related with very complicated profile of variational energy as the function of variational parameters which is characterized by many local minima, saddle points and valleys. Localization of the global minimum numerically of such a complicated function with high accuracy is difficult technical problem which becomes even more difficult in the case of ten or more variational parameters. Examining the physical relevance of trial functions allows one to avoid spurious minima. The parameters obtained in [3] at every step of minimization were always examined from the physical point of view. Such considerations are always something of an art.
III. $m = 0$

The $m = 0$ subspace consists of two subspaces, $\sigma = 1$ (even states) and $\sigma = -1$ (odd states).

A. $1\sigma_g$ state ($\sigma = 1$)

The state $1_g$ was thoroughly investigated in the paper I for the whole range of inclinations $\theta = 0^\circ - 90^\circ$ (for settings see below Fig.2). At $\theta = 0^\circ$ this state becomes the state $1\sigma_g$ and our variational anzatz $\psi_{1\sigma_g}$ describing this state depends on ten parameters. As was mentioned above, the search for the global minimum numerically with high accuracy in the case of so many variational parameters is a difficult technical task. Although this state was thoroughly studied in [4] we decided to repeat the calculations using a more sophisticated strategy for localizing the minimum. The essential new element of the strategy was to impose an extra (natural) condition that the variational parameters change smoothly with $B$. Finally, it led to an improvement of the results in comparison to I and to previous calculations. It is worth mentioning that this recalculation is very important for calculation of the excited $2\sigma_g$ state, where the orthogonality condition on trial functions must be imposed, $(\psi_{1\sigma_g}, \psi_{2\sigma_g}) = 0$. It is evident that an intrinsic inaccuracy in $\psi_{1\sigma_g}$ due to the approximate nature of the trial function $\psi_{1\sigma_g}$ as a function of $x$ is a source of inaccuracy in the energy of the $\psi_{2\sigma_g}$ state. Thus, a reduction of this inaccuracy requires knowledge of the function $\psi_{1\sigma_g}$ as accurately as possible. The above-mentioned strategy allowed us to improve our previous results reported in [4] on total and binding energies (see Table I) and also on lowest rotational-vibrational energies (see Table II). Qualitative conclusions obtained in [4] remain unchanged.
TABLE I: Total $E_T$ and binding $E_b$ energies, and equilibrium distance $R_{eq}$ for the state $1\sigma_g$, which is the global ground state of the $H_2^+$ ion. Error bars for the equilibrium distance indicate a domain in $R$ where the value of binding energy remains the same within the indicated number of their digits shown in the table.

| $B$      | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | Ref. |
|----------|------------|------------|-----------------|------|
|          | 1.9971     | 1.20525    | -1.20525        |      |
|          | 1.923 ± 0.003 | 1.57623 | 1.15070         |      |
|          | 1.924      | 1.57625    | -1.15072        | Wille [5] |
|          | 1.752 ± 0.003 | 1.94992 | -0.94992        | Present |
|          | 1.752      | 1.9498     | -0.94642        | Larsen [6] |
|          | 1.76       | 1.94642    | -0.94642        | Kappes et al [7] |
| $10^9$ G | 1.246 ± 0.002 | 3.16488 | 1.09044         | Present |
|          | 1.246      | 3.16502    | 1.09031         | Wille [5] |
| $10^10$ G| 0.957 ± 0.002 | 4.34976 | 5.65024         | Present |
|          | 0.950      | 4.35       | -4.35           | Wille [5] |
|          | 0.958      | 4.35       | -4.3346         | Larsen [6] |
|          | 0.950      | 4.35       | -4.3346         | Vincke et al [8] |
| $10^11$ G| 0.593 ± 0.001 | 7.5100 | 35.0432         | Present |
|          | 0.593      | 7.5104     | 35.0428         | Wille [5] |
| $10^12$ G| 0.448 ± 0.001 | 10.2910 | 89.7090         | Present |
|          | 0.446      | 10.2892    | -10.2778        | Wille [5] |
|          | 0.448      | 10.270     | -10.2778        | Larsen [6] |
|          | 0.446      | 10.2778    | -10.2778        | Vincke et al [8] |
| $10^13$ G| 0.283 ± 0.001 | 17.1425 | 408.3894        | Present |
|          | 0.28       | 17.0588    | -17.0588        | Lai et al [9] |
| $10^14$ G| 0.2197 ± 0.0005 | 22.7786 | 977.2214        | Present |
|          | 0.219      | 22.7694    | -22.7694        | Vincke et al [8] |
| $10^15$ G| 0.1472 ± 0.0002 | 35.7539 | 4219.565        | Present |
|          | 0.15       | 35.74      | -35.74          | Lai et al [9] |
| $10^16$ G| 0.1183 ± 0.0002 | 45.7972 | 9954.203        | Present |
|          | 0.1016 ± 0.0002 | 54.5018 | 18728.477       | Present |
| $4.414 \times 10^{13}$ G | 0.1016 ± 0.0002 | 54.5018 | 18728.477       | Present |
TABLE II: Energies of the lowest vibrational ($E_{\text{vib}}$) and rotational ($E_{\text{rot}}$) electronic states associated with the $1\sigma_g$ state.

| $B$       | $E_{\text{vib}}$ (Ry) | $E_{\text{rot}}$ (Ry) | Reference          |
|-----------|------------------------|------------------------|--------------------|
| $10^9$ G  | 0.011                  | 0.0053                 | Present            |
|           | 0.011                  | 0.0038                 | Wille [10]         |
| 1 a.u.    | 0.014                  | 0.0110                 | Present            |
|           | 0.014                  | 0.0091                 | Larsen [6]         |
|           | 0.014                  | 0.0238                 | Le Guillou et al (b) [11] |
| $10^{10}$ G | 0.026                  | 0.0408                 | Present            |
|           | 0.026                  | 0.0308                 | Wille [10]         |
| 10 a.u.   | 0.040                  | 0.0790                 | Present            |
|           | 0.040                  | 0.133                  | Larsen[6]          |
|           | 0.040                  | 0.0844                 | Le Guillou et al (b) [11] |
| $10^{11}$ G | 0.085                  | 0.2151                 | Present            |
| 100 a.u.  | 0.132                  | 0.4128                 | Present            |
|           | 0.141                  | 0.365                  | Larsen[6]          |
|           | 0.13                   | —                      | Wunner et al [12]  |
|           | 0.132                  | 0.410                  | Le Guillou et al (b) [11] |
| $10^{12}$ G | 0.266                  | 1.0926                 | Present            |
|           | 0.198                  | 1.0375                 | Khersonskij [13]   |
| 1000 a.u. | 0.390                  | 1.9273                 | Present            |
|           | 0.38                   | 1.77                   | Larsen [6]         |
|           | 0.39                   | —                      | Wunner et al [12]  |
|           | 0.388                  | 1.916                  | Le Guillou et al (b) [11] |
| $10^{13}$ G | 0.714                  | 4.875                  | Present            |
|           | 0.592                  | 6.890                  | Khersonskij [13]   |
| 10000 a.u.| 0.993                  | —                      | Present            |
| $4.414 \times 10^{13}$ G | 1.248                  | 12.065                 | Present            |
B. $2\sigma_g$ state ($\sigma = 1$)

This is the first excited state in the family of states with quantum numbers $m = 0, \sigma = 1$. Here the trial function is taken in the form

$$\psi_{2\sigma_g} = \tilde{A}_1 \psi_1 + \tilde{A}_2 \psi_2 + \tilde{A}_3 \psi_3,$$

(4)

with

$$\psi_1 = (r_1 + r_2 - C_1) e^{-\tilde{a}_1(r_1+r_2)-\tilde{\beta}_1 B \rho^2/4},$$

$$\psi_2 = [(r_1 - C_2) e^{-\tilde{a}_2 r_1} + (r_2 - C_2) e^{-\tilde{a}_2 r_2}] e^{-\tilde{\beta}_2 B \rho^2/4},$$

$$\psi_3 = [(r_1 + ar_2 - C_3) e^{-\tilde{a}_3 r_1 - \tilde{\alpha}_4 r_2} + (r_2 + ar_1 - C_3) e^{-\tilde{a}_3 r_2 - \tilde{\alpha}_4 r_1}] e^{-\tilde{\beta}_3 B \rho^2/4},$$

(cf. (3)), where $\tilde{A}_{1,2,3}$ and $\tilde{a}_{1,2,3,4}, \tilde{\beta}_{1,2,3}, a, C_{1,2,3}$ as well as $R$ are variational parameters [20]. This eigenfunction should be orthogonal to the $\psi_{1\sigma_g}$ state trial function found in the previous Section. The total number of variational parameters in (4) is 13.

The results obtained are presented in Table III. This state is characterized by much smaller binding energy compared to the $1\sigma_g$ state and is much more extended. The binding energy displays a rather slow increase while the equilibrium distance decreases slowly as the magnetic field grows. This excited state is unstable with respect to dissociation to $H + p$. 

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TABLE III: Total $E_T$ and binding $E_b$ energies, and equilibrium distance $R_{eq}$ for the state $2\sigma_g$ ($m = 0, \sigma = 1$).

| $B$         | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | Reference                |
|-------------|------------|------------|-----------------|--------------------------|
| $B = 0$     | -0.350032  | 0.350032   | 8.8             | Present                  |
|             | -0.34936   | —          | 8.8             | Kappes [7]               |
|             | -0.350098  | —          | 8.834           | Peek-Katriel [14]        |
| $10^8$ G    | -0.121343  | 0.546875   | 7.55            | Present                  |
|             | -0.081824  | —          | 7.792           | Peek-Katriel [14]        |
| 1 a.u.      | 0.34912    | 0.65088    | 6.640           | Present                  |
|             | 0.34918    | 0.65082    | 6.632           | Alarcon et al [15]       |
|             | 0.34928    | —          | 6.64            | Kappes et al [7]         |
| $10^{10}$ G | 3.39938    | 0.85594    | 5.2             | Present                  |
| 10 a.u.     | 9.02452    | 0.97548    | 4.6             | Present                  |
| $10^{11}$ G | 41.4090    | 1.1442     | 3.91            | Present                  |
| 100 a.u.    | 98.7822    | 1.2178     | 3.65            | Present                  |
| $10^{12}$ G | 424.2277   | 1.3042     | 3.40            | Present                  |
| 1000 a.u.   | 998.6620   | 1.3380     | 3.30            | Present                  |
| $10^{13}$ G | 4253.937   | 1.382      | 3.21            | Present                  |
| 10000 a.u.  | 9998.608   | 1.392      | 3.145           | Present                  |
| $4.414 \times 10^{13}$ G | 18781.576 | 1.402      | 3.120           | Present                  |
C. $1\sigma_u$ state ($\sigma = -1$)

In the absence of a magnetic field the $1\sigma_u$ state ($m = 0, \sigma = -1$) is essentially repulsive and antibonding. However, in a strong magnetic field this state becomes bound. Due to this fact we want to study this state in full generality, for different magnetic fields and inclinations.

In the absence of a magnetic field, the $1\sigma_u$ state is characterized by a shallow minimum in the total energy situated at large internuclear distance (see, for example, [7](a), [14]). Also this state is a weakly bound state with respect to dissociation and it becomes even unbound if nuclear motion is taken into account. So far not many studies have been carried out for this state. Our major finding is that in the presence of a magnetic field of the magnitude $10^9 < B \lesssim 4.414 \times 10^{13}$ G the total energy surface of the system ($ppe$) in the state $1\sigma_u$ exhibits a well-pronounced minimum. Similar to the $1\sigma_g$ state, both total ($E_T$) and binding ($E_b$) energies of the $1\sigma_u$ state increase as the magnetic field grows, while the equilibrium distance decreases. However, the accuracy of our calculations does not allow us to make a definitive conclusion about the stability of the system in this state with respect to dissociation and nuclear motion effects. In the case of non-zero inclination $\theta \neq 0^\circ$ (for definition see Fig. 2) we denote this state as $1_u$ reflecting the fact that the only parity conservation exists. In I it was shown that for $B \gtrsim 10^{11}$ G and large inclinations the $1_g$ state disappears and hence the molecular ion $H_2^+$ does not exist. Thus, it seems it makes no sense to study the $1_u$ state in this domain. We checked a consistency of this statement verifying that always inequality $E_T^{1\sigma_g}(R) < E_T^{1\sigma_u}(R)$ holds.

To study the $1_u$ state we use the following form of the vector potential corresponding to a constant magnetic field $\mathbf{B} = (0, 0, B)$

$$\mathbf{A} = B((\xi - 1)y, \xi x, 0),$$

where $\xi$ is a parameter, which later will be considered as variational. If $\xi = 1/2$ we get the well-known and widely used gauge which is called symmetric or circular. If $\xi = 0$ or 1, we get the asymmetric or Landau gauge (see [2]). By substituting (5) into (1) we arrive at a Hamiltonian of the form

$$\mathcal{H} = -\nabla^2 + \frac{2}{R} - \frac{2}{r_1} - \frac{2}{r_2} - 2iB[(\xi - 1)y\partial_x + \xi x\partial_y] + B^2[\xi^2x^2 + (1 - \xi)^2y^2].$$

(6)
The trial function is chosen in the form

$$\psi_{1u} = A_1 \psi_1 + A_2 \psi_2 ,$$  \hspace{1cm} (7)

with

$$\psi_1 = (e^{-\alpha_1 r_1} - e^{-\alpha_1 r_2})e^{-B[\beta_{1x}\xi x^2 + \beta_{1y}(1-\xi)y^2]} ,$$

$$\psi_2 = (e^{-\alpha_2 r_1 - \alpha_3 r_2} - e^{-\alpha_2 r_2 - \alpha_3 r_1})e^{-B[\beta_{2x}\xi x^2 + \beta_{2y}(1-\xi)y^2]} ,$$

where $A_1, A_2$ are parameters and one of them is kept fixed by a normalization condition. All parameters $\alpha_{1,2,3}, \beta_{1x,1y,2x,2y}, A_1, A_2$ and $\xi$ are variational parameters. It is evident that if $\theta = 0^\circ$, the rotational invariance along $z$-axis exists and the vector potential should be taken in a form supporting this invariance. Hence the parameter $\xi$ in (5) takes value $\xi = 1/2$ and the parameters $\beta_{1x} = \beta_{1y}, \beta_{2x} = \beta_{2y}$.

Numerical study for the $1_u$ state was carried out for different inclinations with the results at $0^\circ, 45^\circ$ and $90^\circ$ for magnetic fields $B = 0 - 4.414 \times 10^{13}$ G as shown in Tables IV-VI. The immediate conclusion is that

$$E_T(0^\circ) < E_T(45^\circ) < E_T(90^\circ)$$

for all magnetic fields, where this comparison makes sense (see below). Hence, similar to the $1_g$ state, the highest molecular stability of the $1_u$ state occurs for the parallel configuration, at $\theta = 0^\circ$ (see I). Also, the binding energy growth is maximal as a function of magnetic field for the parallel configuration. Therefore, the stability of $H_2^+$ in the parallel configuration in the $1_u$ state increases as the magnetic field grows, again similarly to what happens for the $1_g$ state. These results suggest the following picture for appearance of a bound state for
the $1\sigma_u$ state: for small magnetic fields the minimum in the total energy arises at very large internuclear distances \[21\], then, as the magnetic field grows, the position of the minimum moves to smaller and smaller internuclear distances.

Our results for $B > 0$ and $\theta = 0^\circ$ give the lowest total energies compared to other calculations. In general, they are in a good agreement with those by Kappes–Schmelcher \(1^{(a)}\) as well as by Peek–Katriel \(14\) for $B = 0, 10^9$ G, although for $B = 10^{10}$ G a certain disagreement is observed (see Table IV). However, for $\theta = 90^\circ$ our results are in striking, qualitative contrast with those by Wille \(5\), where even the optimal configuration is attached.

### TABLE IV: $1\sigma_u$ state in the parallel configuration, $\theta = 0^\circ$. Total ($E_T$) and binding ($E_b$) energies are in Ry and equilibrium distance $R_{eq}$ in a.u.

| $B$  | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | Source                |
|------|------------|------------|-----------------|-----------------------|
| $B = 0$ | -1.00010  | 1.00010    | 12.746          | Lopez et al [4]       |
|      | -1.00012  | 1.00012    | 12.55           | Peek-Katriel [14]     |
| $10^9$ G | -0.92103  | 1.34656    | 11.19           | Present               |
|      | -0.917134 | —          | 10.55           | Peek-Katriel [14]     |
| 1 a.u.| -0.66271  | 1.66271    | 9.73            | Present               |
|      | -0.66     | 1.66       | 9.6             | Kappes et al [7]      |
| $10^{10}$ G | 1.63989 | 2.61500    | 7.18            | Present               |
|      | 2.1294    | —          | 4.18            | Peek-Katriel [14]     |
| 10 a.u. | 6.52362  | 3.47638    | 6.336           | Present               |
| $10^{11}$ G | 36.8367 | 5.7165     | 4.629           | Present               |
| 100 a.u. | 92.4257  | 7.5743     | 3.976           | Present               |
| $10^{12}$ G | 413.6175 | 11.9144    | 3.209           | Present               |
| 1000 a.u. | 984.6852 | 15.3148    | 2.862           | Present               |
| $10^{13}$ G | 4232.554 | 22.765     | 2.360           | Present               |
| 10000 a.u. | 9971.727 | 28.273     | 2.134           | Present               |
| $4.414 \times 10^{13}$ G | 18750.07 | 32.912     | 2.021           | Present               |
TABLE V: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the $1_u$ state in the configuration $\theta = 45^\circ$. Optimal value for the gauge parameter $\xi$ is shown (see text).

| $B$          | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | $\xi$  |
|--------------|------------|------------|-----------------|--------|
| $10^9$ G     | -0.870391  | 1.295923   | 8.053           | 0.9308 |
| 1 a.u.       | -0.509041  | 1.509041   | 6.587           | 0.9406 |
| $10^{10}$ G  | 2.267998   | 1.987321   | 4.812           | 0.9671 |
| 10 a.u.      | 7.692812   | 2.307188   | 4.196           | 0.9808 |
| $10^{11}$ G  | 39.71061   | 2.84258    | 3.538           | 0.9935 |
| 100 a.u.     | 96.88464   | 3.11536    | 3.278           | 0.9968 |
| $10^{12}$ G  | 422.0074   | 3.5245     | 3.020           | 0.9991 |
| 1000 a.u.    | 996.3044   | 3.6956     | 2.894           | 0.9996 |

TABLE VI: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the $1_u$ state at $\theta = 90^\circ$. Optimal value for the gauge parameter $\xi$ is shown (see text).

| $B$          | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | $\xi$  |
|--------------|------------|------------|-----------------|--------|
| $10^9$ G     | -0.867234  | 1.292766   | 8.784           | 0.9692 Present |
| 1 a.u.       | -0.49963   | 1.49963    | 7.264           | 0.9737 Present |
|              | -0.65998   | 1.65998    | 5.45            | Kappes et al [7](b) |
| $10^{10}$ G  | 2.29365    | 1.96167    | 5.517           | 0.9866 Present |
| 10 a.u.      | 7.72998    | 2.27002    | 4.872           | 0.9923 Present |
| $10^{11}$ G  | 39.76500   | 2.78819    | 4.154           | 0.9975 Present |
| 100 a.u.     | 96.93497   | 3.06503    | 3.875           | 0.9988 Present |

to $\theta = 90^\circ$, contrary to our conclusion. For instance, at $B = 10^{10}$ G in [5] the values $E_b = 2.593$ Ry and $R_{eq} = 2.284$ a.u. are given, while our results are $E_b = 1.9617$ Ry and $R_{eq} = 5.517$ a.u., respectively (see Table VI). Similar, but less drastic disagreement, is observed with the results in [7](b). We can only guess this disagreement is due to the
shallow nature of the minimum, but a real explanation of this fact is missing. Independent calculations are needed in order to resolve this contradiction.

The analysis of Tables IV-VI shows that for $\theta > 0^\circ$ and fixed magnetic field the total energy of $H_2^+$ in the $1_u$ state is always larger than the total energy of the hydrogen atom [10]. It means that the $H_2^+$-ion in the $1_u$ state is unstable towards dissociation to $H + p$. For $\theta \sim 0^\circ$ the total energies presented for the $H_2^+$ ion and the most accurate results for the hydrogen atom [10] are comparable within the order of magnitude $10^{-4} - 10^{-5}$. We estimate that the accuracy of our calculations is of the same order of magnitude $10^{-4} - 10^{-5}$. This prevents us from making a conclusion about the stability of $H_2^+$ in the $1_u$ state with respect to dissociation. Thus, the only reliable conclusion can be drawn that the minimum is very shallow.

The $1_u$ state is much more extended than the $1_g$ state: for fixed magnetic field the equilibrium distance of the $1_g$ state is much smaller than that for the $1_u$ state. This picture remains the same for any inclination. It is quite impressive to observe the much lower rate of decrease of $R_{eq}$ in the range $B = 0 - 4.414 \times 10^{13}$ G with magnetic field growth. For example, in the case of the parallel configuration, $\theta = 0^\circ$, for the state $1_u$ the equilibrium distance falls $\sim 6$ times compared to the $1_g$ state, where it falls $\sim 20$ times.

The behavior of the equilibrium distance $R_{eq}$ of the $1_u$ state as a function of inclination is quite non-trivial (see Tables IV-VI). As in the $1_g$ state, the $H_2^+$-ion in the $1_u$ state for $B \lesssim 10^{12}$ G is most extended in the parallel configuration.

IV. $m = -1$

The subspace consists of two subspaces, $\sigma = 1$ (even states) and $\sigma = -1$ (odd states).

A. $1\pi_u$ state ($\sigma = 1$)

In order to study the $1\pi_u$ ($m = -1$ and $\sigma = 1$) state we take the trial function [8]. The results are presented in Table VII. In general, our results are more accurate than those obtained in other calculations giving lower total (and correspondingly, the higher binding) energies with the only exception of the magnetic field $B = 10$ a.u. where the result for binding energy from [8] is better in the fourth digit. The results for $B = 1$ a.u. obtained
TABLE VII: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the excited state $1\pi_u$ ($m = -1, \sigma = 1$).

| $B$        | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | Source           |
|------------|------------|------------|-----------------|------------------|
| $10^9$ G   | -0.293592  | 0.719123   | 4.940           | Present          |
| 1 a.u.     | -0.020150  | 1.020150   | 3.676           | Present          |
|            | -0.02014   | –          | 3.68            | Kappes et al [7] |
|            | -0.02011   | –          | 3.75            | Wille [5]        |
| $10^{10}$ G| 2.371845   | 1.883474   | 2.130           | Present          |
| 10 a.u.    | 7.29682    | 2.70318    | 1.526           | Present          |
|            |            |            | 2.6862          | Vincke-Baye [8]  |
|            |            |            | 2.7046          | Wille [5]        |
| $10^{11}$ G| 37.6490    | 4.9042     | 0.887           | Present          |
| 100 a.u.   | 93.1127    | 6.8873     | 0.651           | Present          |
|            |            |            | 6.8774          | Vincke-Baye [8]  |
|            |            |            | 6.8548          | Wille [5]        |
| $10^{12}$ G| 413.6306   | 11.902     | 0.395           | Present          |
| 1000 a.u.  | 983.874    | 16.126     | 0.301           | Present          |
| $10^{13}$ G| 4229.183   | 26.136     | 0.195           | Present          |
| 10000 a.u. | 9965.932   | 34.068     | 0.154           | Present          |
| $4.414 \times 10^{13}$ G | 18741.89 | 41.09 | 0.130 | Present |

In [5], are not very precise in $R_{eq}$ (see Table I therein), which explain their difference with the results by others. The binding energy at $B = 10$ and 100 a.u. in [5] is calculated for the same equilibrium distances as those found in [8] (see Table IV in Ref. [5]). Like for all studied states the binding energy grows steadily with magnetic field increase while the equilibrium distance shrinks in a quite drastic manner. If for small magnetic fields the equilibrium distance $R_{eq}$ is several times larger than this distance for the $1\sigma_g$ state, for large magnetic fields these equilibrium distances become comparable. Among $m = -1$ states the state $1\pi_u$ has the smallest total energy.
TABLE VIII: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the state $1\pi_g$ ($m = -1, \sigma = -1$).

| $B$  | $E_T$ (Ry)  | $E_b$ (Ry)  | $R_{eq}$ (a.u.) | Reference    |
|------|-------------|-------------|-----------------|--------------|
| $10^9$ G | -0.232060  | 0.65759    | 20.10           | Present      |
| 1 a.u. | 0.086868   | 0.91313    | 14.05           | Present      |
|       | 0.0866     | 13.5       |                 | Kappes et al [7] |
| $10^{10}$ G | 2.641122  | 1.61420    | 9.370           | Present      |
| 10 a.u. | 7.749819   | 2.25018    | 7.622           | Present      |
| $10^{11}$ G | 38.67642   | 3.87677    | 5.622           | Present      |
| 100 a.u. | 94.73386   | 5.26614    | 4.791           | Present      |
| $10^{12}$ G | 416.9354   | 8.59654    | 3.767           | Present      |
| 1000 a.u. | 988.7286   | 11.2714    | 3.321           | Present      |
| $10^{13}$ G | 4238.038   | 17.2810    | 2.708           | Present      |
| 10000 a.u. | 9978.175   | 21.8254    | 2.420           | Present      |
| $4.414 \times 10^{13}$ G | 18757.273 | 25.7054    | 2.237           | Present      |

B. $1\pi_g$ state ($\sigma = -1$)

In order to study the $1\pi_g$ state ($m = -1$ and $\sigma = -1$) we take the trial function [5]. The results are presented in Table VIII. For $B = 1$ a.u. our total energy deviates from [7] in the third digit and an independent calculation would be desirable.
V.  \( m = -2 \)

The subspace consists of two subspaces, \( \sigma = 1 \) (even states) and \( \sigma = -1 \) (odd states).

A.  1\( \delta_g \) state \( (\sigma = 1) \)

In order to study the 1\( \delta_g \) state \( (m = -2 \text{ and } \sigma = 1) \) we take the trial function (3). The results are presented in Table IX. In [5] for \( B = 1 \) a.u. the equilibrium distance is simply placed equal to 5.0 a.u. (see Table I therein). For \( B = 10, 100 \) a.u. the energies computed in [8] were calculated for the same equilibrium distances as those found in [8] (see Table IV in [8]). Among \( m = -2 \) states the 1\( \delta_g \) state has the smallest total energy. It is worth mentioning a drastic decrease of \( R_{eq} \) with magnetic field growth similar to what appears for 1\( \sigma_g \) and 1\( \pi_u \) states.
TABLE IX: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the state $1\delta_g$ ($m = -2, \sigma = +1$).

| $B$     | $E_T$ (Ry)   | $E_b$ (Ry)  | $R_{eq}$ (a.u.) |
|---------|--------------|-------------|----------------|
| $10^9$ G | -0.107945    | 0.533477    | 6.865 Present  |
| 1 a.u.  | 0.221163     | 0.778837    | 4.872 Present  |
|         | 0.22112      | 4.87        | Kappes et al [7] |
|         | 0.22126      | 5.0         | Wille [5]      |
| $10^{10}$ G | 2.77538  | 1.47994     | 2.694 Present  |
| 10 a.u. | 7.85113      | 2.14887     | 1.907 Present  |
|         | 2.1306       | 1.880       | Vincke-Baye [8] |
|         | 2.1496       | 1.880       | Wille [5]      |
| $10^{11}$ G | 38.58470 | 3.9685      | 1.080 Present  |
| 100 a.u.| 94.38093     | 5.6191      | 0.782 Present  |
|         | 5.6058       | 0.778       | Vincke-Baye [8] |
|         | 5.510        | 0.778       | Wille [5]      |
| $10^{12}$ G | 415.6710 | 9.8609      | 0.470 Present  |
| 1000 a.u.| 986.5119     | 13.4881     | 0.353 Present  |
| $10^{13}$ G | 4233.125 | 22.194      | 0.225 Present  |
| 10000 a.u.| 9970.802    | 29.198      | 0.176 Present  |
| $4.414 \times 10^{13}$ G | 18747.572 |
|         | 35.407       | 0.148       | Present        |
TABLE X: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the state 1$\delta_u$ ($m = -2, \sigma = -1$).

| $B$   | $E_T$ (Ry)   | $E_b$ (Ry) | $R_{eq}$ (a.u.) | Reference       |
|-------|--------------|------------|-----------------|-----------------|
| $10^9$ G | -0.06873     | 0.49426    | 23.902          | Present         |
| 1 a.u. | 0.29410      | 0.70590    | 16.377          | Present         |
|       | 0.2936       | —          | 16.0            | Kappes et al [7]|
| $10^{10}$ G | 2.97742      | 1.27790    | 11.475          | Present         |
| 10 a.u.| 8.19892      | 1.80108    | 9.458           | Present         |
| $10^{11}$ G | 39.40596     | 3.14723    | 6.858           | Present         |
| 100 a.u.| 95.69542     | 4.30458    | 5.619           | Present         |
| $10^{12}$ G | 418.4335     | 7.0984     | 4.071           | Present         |
| 1000 a.u.| 990.6416     | 9.3584     | 3.406           | Present         |
| $10^{13}$ G | 4240.834     | 14.485     | 2.625           | Present         |
| 10000 a.u.| 9981.587     | 18.413     | 2.391           | Present         |
| $4.414 \times 10^{13}$ G | 18761.18     | 21.80      | 2.230           | Present         |

B. 1$\delta_u$ state ($\sigma = -1$)

In order to study the 1$\delta_u$ state ($m = -2$ and $\sigma = -1$) we take the trial function [3]. The results are presented in Table X.
VI. DISCUSSION

In Table XI a summary of total energies of eigenstates explored in this article for magnetic fields ranging from $10^9$ G to $4.414 \times 10^{13}$ G is presented. An analysis of Table IX allows to draw a certain immediate conclusions:

1. The state $1\sigma_g$ is the global ground state for all magnetic fields. It is rather evident that this statement remains valid in general, when even the states other than studied are taken into account (Perron theorem);

2. For the states with fixed $m$ the lowest total energy corresponds to the state of positive parity $\sigma = +1$. We guess that this statement remains correct in general;

3. For the same parity $\sigma$ ground states are ordered following the value of $m$,

$$E_T^{1\sigma_g} < E_T^{1\pi_u} < E_T^{1\delta_g},$$

$$E_T^{1\sigma_u} < E_T^{1\pi_g} < E_T^{1\delta_u}.$$  

4. There exist several true level crossings,

- For $B \lesssim 10^{12}$ G

$$E_T^{1\sigma_u} < E_T^{1\pi_u},$$

while for $B > 10^{12}$ G

$$E_T^{1\sigma_u} > E_T^{1\pi_u},$$

- For $B \lesssim 10000$ a.u.

$$E_T^{1\sigma_u} < E_T^{1\delta_g},$$

while for $B > 10000$ a.u.

$$E_T^{1\sigma_u} > E_T^{1\delta_g},$$

- For $B \lesssim 10$ a.u.

$$E_T^{1\pi_g} < E_T^{1\delta_g},$$

while for $B > 10$ a.u.

$$E_T^{1\pi_g} > E_T^{1\delta_g},$$
For $B \lesssim 1$ a.u.

$$E_T^{1\delta_g} \geq E_T^{2\sigma_g},$$

while for $B > 1$ a.u.

$$E_T^{1\delta_g} < E_T^{2\sigma_g},$$

For $B \lesssim 1$ a.u.

$$E_T^{1\delta_u} \geq E_T^{2\sigma_u},$$

while for $B > 1$ a.u.

$$E_T^{1\delta_u} < E_T^{2\sigma_u}.$$

**TABLE XI:** Comparison of the total energies $E_T$ (in Rydbergs) for the low-lying states of the $H_2^+$ molecular ion for magnetic fields $10^9$ G - $4.414 \times 10^{13}$ G.

| $B$      | $1\sigma_g$ | $1\sigma_u$ | $1\pi_u$ | $1\pi_g$ | $1\delta_g$ | $1\delta_u$ | $2\sigma_g$ |
|----------|-------------|-------------|----------|----------|-------------|-------------|-------------|
| $10^9$ G | -1.15070    | -0.92103    | -0.29359 | -0.232060| -0.107945   | -0.068727   | -0.121343   |
| 1 a.u.   | -0.94992    | -0.66271    | -0.20150 | 0.086868 | 0.22117     | 0.29410     | 0.34912     |
| $10^{10}$G | 1.09044    | 1.63989     | 2.371845 | 2.641122 | 2.77538     | 2.977418    | 3.39938     |
| 10 a.u.  | 5.65024     | 6.52362     | 7.296816 | 7.749819 | 7.85113     | 8.198922    | 9.02452     |
| $10^{11}$G | 35.04320   | 36.83671    | 37.64895 | 38.67642 | 38.58470    | 39.40596    | 41.4090     |
| 100 a.u. | 89.7090     | 92.4257     | 93.11267 | 94.7339  | 94.38093    | 95.69542    | 98.7822     |
| $10^{12}$G | 408.3894   | 413.6175    | 413.6306 | 416.9354 | 415.6710    | 418.4335    | 424.2278    |
| 1000 a.u.| 977.2214    | 984.685     | 983.874  | 988.7286 | 986.5119    | 990.6416    | 998.662     |
| $10^{13}$G | 4219.565   | 4232.554    | 4229.183 | 4238.038 | 4233.126    | 4240.834    | 4253.937    |
| 10000 a.u.| 9954.203    | 9971.727    | 9965.932 | 9978.175 | 9970.802    | 9981.587    | 9998.608    |
| $4.414 \times 10^{13}$G | 18728.477   | 18750.070   | 18741.889 | 18757.273 | 18747.572   | 18761.180   | 18781.576    |
VII. CONCLUSION

We have carried out an accurate, non-relativistic calculation in the Born-Oppenheimer approximation for the low-lying states of the $H_2^+$ molecular ion in the parallel configuration at equilibrium in the framework of a unique computational approach. The $1\sigma_u$ state is considered in full generality for all inclinations of the molecular axis vs. magnetic field direction. We studied constant uniform magnetic fields ranging from $B = 10^9 G$ up to $B = 4.414 \times 10^{13} G$, where non-relativistic considerations hold, although our method can be naturally applied to study the domain $B < 10^9 G$. We used a variational method with a very simple trial function with a few variational parameters inspired by the underlying physics of the problem. Thus our trial function can be easily analyzed and in contrast to other approaches our results can be easily reproduced. The trial function (3) can be easily modified to explore other excited states.

The present study of several low-lying excited states complements a study of the ground state performed in I. Usually the total, binding, dissociation and transition energies grow with increase in the magnetic field, reaching values of several hundred eV at magnetic fields of $10^{12} - 10^{13} G$. These results can be used to construct a model of the atmosphere of an isolated neutron star 1E1207.4-5209 (see [17]). This will be done elsewhere.

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[18] In the absence of convention, majority of results presented in literature are obtained for $B_0 = 2.35 \times 10^9$ G, although sometimes another convention is used $B_0 = 2.3505 \times 10^9$ G. Thus, in making a comparison of the high accuracy results obtained by different authors especially for high magnetic fields this fact should be taken into account

[19] Due to normalization of wave function one of $A$’s should be kept fixed. Usually, we put $A_3 = 1$

[20] Due to normalization of wave function one of $\tilde{A}$’s can be kept fixed. Usually, we put $\tilde{A}_3 = 1$
[21] It is natural to assume that for $B = 0$ a minimum exists at infinite (or almost infinite) internuclear distance.