H$_2^+$ ion in a strong magnetic field:

Lowest gerade and ungerade electronic states

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Abstract

In the framework of a variational method with a single trial function an accurate study of the lowest gerade $1_g$ and ungerade $1_u$ electronic states of the molecular ion $H_2^+$ in a magnetic field is performed. Magnetic field ranges from 0 to $4.414 \times 10^{13}$ G and orientations of the molecular axis with respect to the magnetic line $0^\circ \leq \theta \leq 90^\circ$ are considered. A one-parameter gauge dependent vector potential is used in the Hamiltonian, which is finally variationally optimized. A well pronounced minimum on the total energy surface of the (ppe) system in both $1_g$ and $1_u$ states is found for all magnetic fields and orientations studied. It is shown that for both states the parallel configuration ($\theta = 0$) at equilibrium always corresponds to the minimal total energy. It is found that for a given $\theta$ for both states the magnetic field growth is always accompanied by an increase in the total and binding energies as well as a shrinking of the equilibrium distance. We demonstrate that for $B \gtrsim 1.8 \times 10^{11}$ G the molecular ion can dissociate, $H_2^+ \rightarrow H + p$, over a certain range of orientations ($\theta_{cr} \leq \theta \leq 90^\circ$), where the minimal $\theta_{cr} \simeq 25^\circ$ occurs for the strongest magnetic field studied, $B = 4.414 \times 10^{13}$ G. For $B < 10^{12}$ G the ion $H_2^+$ in $1_g, 1_u$ states is the most compact, being in the perpendicular configuration ($\theta=90^\circ$), whereas for $B \gtrsim 10^{12}$ this occurs for an angle $< 90^\circ$. For the $1_g$ state in any orientation, with the magnetic field growth at $B \sim 10^{11}$ G, a two-peak electronic distribution changes to single-peak one.

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I. INTRODUCTION

There are theoretical qualitative indications that in the presence of a strong magnetic field
the physics of atoms and molecules gets a wealth of new, unexpected phenomena even for the
simplest systems [1, 2]. In practice, the atmosphere of neutron stars, which is characterized
by the existence of enormous magnetic fields $10^{12} - 10^{13}$ G, provides a valuable paradigm
where this physics could be realized.

One of the first general features observed in standard atomic and molecular systems
placed in a strong magnetic field is an increase in the binding energy, accompanied by a
drastic shrinking of the electron localization length. It leads to a decrease of the equilibrium
distance with magnetic field growth. This behavior can be considered as a consequence of the
fact that at large magnetic fields the electron cloud takes a needle-like form extended along
the magnetic field direction and the system becomes effectively quasi-one-dimensional. Fur-
thermore the phenomenon of quasi-one-dimensionality enhances the stability of standard
atomic and molecular systems. They become elongated along the magnetic line forming
molecules of the type of linear polymers (for details see review papers [3, 4]). It also hints
at the existence of exotic atomic and molecular systems which do not exist in the absence
of a magnetic field. Motivated by these simple observations it was shown in [5, 6] that
exotic one-electron molecular systems $H_3^{++}$ and $H_4^{+++}$ can exist in sufficiently strong mag-
netic fields in the form of linear polymers. However, the situation becomes much less clear
(and also much less investigated) when the nuclei are not aligned with the magnetic field
direction, thus not forming in general a linear system. Obviously, such a study would be
important for understanding the kinetics of a gas of molecules in the presence of a strong
magnetic field. As a first step towards such a study, even the simplest molecules in dif-
ferent spatial configurations deserve attention. The goal of the present work is to attempt
to make an extensive quantitative investigation of the lowest electronic states of $H_2^+$ in a
(near)equilibrium position in the framework of a single approach in its entire complexity:
wide range of magnetic field strengths ($0 - 4 \times 10^{13}$ G) and arbitrary orientation of the
molecular axis with respect to magnetic line.

It is well known that the molecular ion $H_2^+$ is the most stable one-electron molecular
system in the absence of a magnetic field. It remains so in the presence of a constant magnetic
field as well, but it turns out that for a magnetic field $B > 10^{13}$ G the exotic ion $H_3^{++}$ appears
to be the most bound (see [6]). The ion H\textsubscript{2}\textsuperscript{+} has been widely studied, both with and without the presence of a magnetic field, due to its importance in astrophysics, atomic and molecular physics, solid state and plasma physics (see [3-22] and references therein). The majority of the previously performed studies was focused on the case of the parallel configuration, when the angle between the molecular axis and the magnetic field direction was zero, $\theta = 0$, with an exception of [14], where a detailed quantitative analysis was performed for any $\theta$ but for $B = 1 a.u.$ Previous studies were based on various numerical techniques, most of all – different versions of the variational method, including the Thomas-Fermi approach. As a rule, in these studies the nuclear motion was separated from the electronic motion using the Born-Oppenheimer approximation at zero order – assuming protons as infinitely heavy charged centers. It was observed at a quantitative level that magnetic field growth is always accompanied by an increase in the total and binding energies, as well as shrinking of the equilibrium distance. As a consequence it led to a striking conclusion about the drastic increase in the probability of nuclear fusion for H\textsubscript{2}\textsuperscript{+} in the presence of a strong magnetic field [7].

In the present study we perform accurate calculations for the lowest $1_g$ and $1_u$ electronic states of H\textsubscript{2}\textsuperscript{+} in (near)equilibrium position for magnetic fields $B = 0 - 4.414 \times 10^{13}$ G and arbitrary orientation of the molecular axis towards the magnetic line. Since the Hamiltonian is gauge-dependent a choice of the form of the vector potential is one of the crucial points in our study. We construct state-of-the-art, ‘adequate’, trial functions with a variationally optimized gauge dependence consistent with the choice of vector potential. Although an appropriate position of the gauge origin [27] may be important (especially for large internuclear distances, this lies beyond the scope of the present article and will be discussed elsewhere) we place the gauge origin in the middle between the two nuclei (charged centers) and keep it fixed. For the parallel configuration the present work can be considered as an extension (and also an improvement) of previous work [20]. It is necessary to emphasize that we encountered several new physical phenomena which occur when the molecular axis deviates from the magnetic field direction. In particular, if the magnetic field is sufficiently strong, $B \approx 10^{11}$G the ion H\textsubscript{2}\textsuperscript{+} can dissociate to $H + p$ [28]. This means that even though the positive binding energy of H\textsubscript{2}\textsuperscript{+} in the optimal configuration ensures its existence, even under the high temperature conditions prevailing on the surface of neutron stars ($10 - 100 \ eV$), there is a certain probability of dissociation. The behavior of the equilibrium distance as a function
of \( \theta \) reveals another surprising feature: for magnetic fields \( B < 10^{12} \text{ G} \) the molecule is most compact in the perpendicular configuration, while for \( B \gtrsim 10^{12} \text{ G} \) this occurs for a certain angle \( \theta < 90^\circ \). We find that for the \( 1_g \) state at any orientation in the weak field regime the electronic distribution peaks at the positions of the protons, while at large magnetic fields the electronic distribution is characterized by one maximum which occurs at the midpoint between two protons. This change appears around \( B \sim 10^{10-11} \text{ G} \) with a slight dependence on the inclination angle \( \theta \). From a physical point of view the former means that the electron prefers to stay in the vicinity of a proton. It can be interpreted as a dominance of the \( H \)-atom plus proton interaction. The latter situation implies that the electron is ‘shared’ by both protons and hence a separation to \( H \)-atom plus proton cannot be done. Therefore, we can call the two-peak situation an ionic coupling, while the one-peak case is assigned to the covalent coupling, although this definition differs from the one widely accepted in textbooks (see for example [23]). Thus, we can conclude that a new phenomenon appears - as the magnetic field grows the type of coupling changes from ionic to covalent.

Atomic units are used throughout (\( \hbar = m_e = e = 1 \)) albeit energies are expressed in Rydbergs (Ry). In particular, the magnetic field \( B \) is given in a.u. with \( B_0 = 2.35 \times 10^9 \text{ G} \).

II. THEORY

The Hamiltonian which describes the \( H_2^+ \) molecular ion placed in a uniform constant magnetic field directed along the \( z \)-axis, \( \mathbf{B} = (0, 0, B) \) is given by (see, for example, [23])

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

(1)

(see Fig.1 for notations), where \( \hat{\mathbf{p}} = -i\nabla \) is the electron momentum, \( \mathbf{A} \) is a vector potential corresponding to the magnetic field \( \mathbf{B} \).

The vector potential is gauge-dependent and hence it is defined ambiguously. Therefore the Hamiltonian (1) is also explicitly gauge-dependent although the energies and other observables do not. Thus, when solving the eigenvalue problem corresponding to the above Hamiltonian within an approximate method, the energies (as well as other observables) will in general be gauge-dependent (only the exact ones would be gauge-independent). Hence, one can choose the form of the vector potential in a certain optimal way, for instance, which would lead to minimal approximate total energy of the ground state. In order to realize this
idea let us take a certain one-parametric family of vector potentials corresponding to the constant magnetic field \( B \) (e.g. see [9])

\[
\mathcal{A} = B((\xi - 1)y, \xi x, 0),
\]

where \( \xi \) is the parameter to be chosen in an optimal way. The well known symmetric (or circular) and asymmetric gauges are particular cases of (2) corresponding to \( \xi = 1/2 \) and \( \xi = 1 \), respectively (see, for instance, [23]). By substituting (2) into (1) we arrive at the Hamiltonian

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

(3)

The idea of choosing an optimal gauge is widely exploited in quantum field theory. Usually, the gauge is fixed following a certain convenience criterion or for technical simplicity. Regarding our present problem of \( \text{H}_2^+ \) in a magnetic field, there were also some attempts to discuss the gauge fixing (see, for instance, [14] and references therein). Perhaps the first constructive (and remarkable) attempt was realized by Larsen [4] in his study of the ground state. In particular, he explicitly showed that gauge dependence of the variational results can be quite significant and even an oversimplified optimization procedure improves drastically the accuracy of the numerical results.

It is rather evident that there exists a certain gauge for which the Hamiltonian (1) has the ground state eigenfunction given by a real function [23]. Thus, we can use real trial functions with explicit dependence on the gauge parameter \( \xi \). This parameter is fixed by performing a variational optimization of the energy. Therefore, as a result of the minimization we find
both a variational energy and a gauge for which the eigenfunction is real, as well as the corresponding Hamiltonian. One can show that for a system possessing axial (rotational) symmetry the optimal gauge is the symmetric one $\xi = 1/2$. It is precisely this gauge which was overwhelmingly used (without any explanations) in the majority of previously performed $\text{H}_2^+$ studies in the parallel configuration [3-22,25]. However, this is not the case if $\theta \neq 0^\circ$. For the symmetric gauge the exact eigenfunction now becomes complex, hence complex trial functions should be used. But we can avoid complexity by adjusting the gauge so as to continue with real eigenfunctions. This justifies the use of real trial functions. Our results (see Section 3) lead to the conclusion that for both studied states the optimal gauge parameter is $\xi \in [0.5, 1]$. In the limit $B \gg 1\text{a.u.}$, the parameter $\xi$ tends to one corresponding to asymmetric gauge. Likely, this tendency will continue for other excited states.

One can easily see that the expectation value of the term $\sim B$ in Eq.(3) vanishes when it is calculated with respect to any real normalizable function. Hence, without loss of generality, this term can be omitted in the Hamiltonian (1). It gives an essential simplification of the computational procedure. Our choice of variational trial function $\Psi_0$ can be formulated as follows [21]: we construct a real trial function for which the potential $V_0 = \nabla^2 \Psi_0$ reproduces the original potential near Coulomb singularities and its growing terms at large distances; it also supports all symmetries of the problem at hand and the gauge parameter $\xi$ is included into the trial function explicitly. This recipe (for symmetric gauge) was successfully exploited in the previous study of $\text{H}_2^+$ in strong magnetic fields in the parallel configuration [20]. This recipe was also used to construct trial functions when the question of the existence of the exotic ions $\text{H}_3^{++}$ and $\text{H}_4^{+++}$ is considered [5, 6].

The Hamiltonian (1) gives rise to different symmetry properties depending on the orientation of the magnetic field with respect to the internuclear axis. The most symmetric situation corresponds to $\theta = 0^\circ$, where invariance under permutation of the (identical) charged centers $P: (1 \leftrightarrow 2)$ together with $P_z: (z \rightarrow -z)$ symmetry hold. Since the angular momentum projection $\ell_z = m$ is conserved, $P_z$ accounts also for the degeneracy $m \rightarrow -m$. Thus, we classify the states as $1\sigma_{g,u}, 2\sigma_{g,u}, \ldots 1\pi_{g,u}, 2\pi_{g,u} \ldots 1\delta_{g,u}, 2\delta_{g,u} \ldots$, where the numbers $1, 2, \ldots$ refer to the electronic states in increasing order of energy. The labels $\sigma, \pi, \delta \ldots$ are used to denote $|m| = 0, 1, 2 \ldots$, respectively, the label $g$ ($u$) gerade (ungerade) is assigned to the states of even (odd) parity $P$ of the system. At $\theta = 90^\circ$ the Hamiltonian still remains invariant under the parity operations $P$ and $P_z$, while the angular momentum projection
is no longer conserved and \( m \) is no longer a quantum number. The classification in this case is \( 1_{g,u}^\pm, 2_{g,u}^\pm, \ldots \), where sign \(+(-)\) is reserved to denote even (odd) \( z\)-parity. Eventually, for arbitrary orientation the only parity under permutations \( P \) is conserved. In general, we refer to the lowest gerade and ungerade states in our study as \( 1_g \) and \( 1_u \). This is the only notation which make sense for all orientations \( 0^\circ \leq \theta \leq 90^\circ \).

One of the simplest trial functions for \( 1_g \) state which meets the requirements of our criterion of adequacy is

\[
\Psi_1 = e^{-\alpha_1(r_1+r_2)}e^{-B[\beta_{1x}\xi x^2+\beta_{1y}(1-\xi)y^2]}
\]  

(cf. [20, 22]), where \( \alpha_1, \beta_{1x} \) and \( \beta_{1y} \) are variational parameters and \( \xi \) is the parameter of the gauge (2). The first factor in this function, being symmetric under interchange of the charged centers \( r_1 \leftrightarrow r_2 \), and corresponding to the product of two 1s-Coulomb orbitals centered on each proton, is nothing but the celebrated Heitler-London approximation for the ground state \( 1\sigma_g \). The second one is the lowest Landau orbital corresponding to the vector potential of the form Eq. (2). So, the function (4) can be considered as a modification of the free field Heitler-London function. Following the experience gained in studies of \( \text{H}_2^+ \) without magnetic field it is natural to assume that Eq. (4) is adequate to describe internuclear distances near equilibrium. This assumption will be checked (and eventually confirmed) \textit{a posteriori}, after making concrete calculations (see Section 3).

The function (4) corresponds to an exact eigenfunction of the potential

\[
V_1 = \frac{\nabla^2 \Psi_1}{\Psi_1} = 2\alpha_1^2 - \frac{B}{2} [\beta_{1x}\xi + \beta_{1y}(1-\xi)] + \frac{B^2}{4} [\beta_{1x}^2\xi^2x^2 + \beta_{1y}^2(1-\xi)^2y^2] + 2\alpha_1^2(\hat{n}_1 \cdot \hat{n}_2)
\]

\[
+ \alpha_1 B \left[ \frac{\beta_{1x}\xi(x-x_1) + \beta_{1y}(1-\xi)y(y-y_1)}{r_1} + \frac{\beta_{1x}\xi(x-x_2) + \beta_{1y}(1-\xi)y(y-y_2)}{r_2} \right]
\]

\[
- 2\alpha_1 \left[ \frac{1}{r_1} + \frac{1}{r_2} \right].
\]

The potential \( V_1 \) reproduces the functional behaviour of the original potential (3) near Coulombic singularities and at large distances. These singularities are reproduced exactly when \( \beta_{1x} = \beta_{1y} = 1 \) and \( \alpha_1 = 1 \).

Another trial function meets the requirements of our criterion of adequacy as well

\[
\Psi_2 = \left( e^{-\alpha_2 r_1} + Pe^{-\alpha_2 r_2} \right) e^{-B[\beta_{2x}\xi x^2+\beta_{2y}(1-\xi)y^2]},
\]  

(5)
It is the celebrated Hund-Mulliken function of the free field case multiplied by the lowest Landau orbital, where $\alpha_2$, $\beta_{2x}$ and $\beta_{2y}$ are variational parameters. The parameter $P$ has the meaning of the parity, being equal to $+1$ for $1_g$ and $-1$ for $1_u$. From a physical point of view this function describes the interaction between a hydrogen atom and a proton (charged center), and also models the possible decay mode of $H_2^+$ into hydrogen atom plus proton. Thus, one can naturally expect that for sufficiently large internuclear distances $R$ this function prevails giving a dominant contribution. Again this assumption will be checked \textit{a posteriori}, by concrete calculations (see Section 3).

There are two natural ways to incorporate the behavior of the system both near equilibrium and at large distances into a single trial function. It is to make a linear or nonlinear interpolation. The linear interpolation is given by a linear superposition

$$\Psi_{3a} = A_1 \Psi_1 + A_2 \Psi_2 ,$$  \hspace{1cm} (6)

where $A_1$ or $A_2$ are parameters and one of them is kept fixed by a normalization condition. The function (6) makes sense for $1_g$ state only since the function (4) does not exist for $1_u$ state. Therefore, conditionally, for state $1_u$ we simply put the parameter $A_1 = 0$. In turn, the simplest nonlinear interpolation is of the form

$$\Psi_{3b} = \left( e^{-\alpha_3 r_1 - \alpha_4 r_2} + P e^{-\alpha_3 r_2 - \alpha_4 r_1} \right) e^{-B[\beta_{3x} \xi x^2 + \beta_{3y}(1-\xi) y^2]} ,$$  \hspace{1cm} (7)

(cf. [20, 22]), where $\alpha_3$, $\alpha_4$, $\beta_{3x}$ and $\beta_{3y}$ are variational parameters and $P = \pm 1$ is the parity of the state. This is a Guillemin-Zener function of the free field case multiplied by the lowest Landau orbital. If $\alpha_3 = \alpha_4$, the function (7) coincides with (4). If $\alpha_4 = 0$, the function (7) coincides with (5).

The most general Ansatz is a linear superposition of trial functions (3) and (7),

$$\Psi = A_1 \Psi_1 + A_2 \Psi_2 + A_3 \Psi_{3b} ,$$  \hspace{1cm} (8)

where we fix one of the $A$’s and let all other parameters vary. For the $1_u$ state we put the parameter $A_1 = 0$ since the function (4) does not exist for this state. Finally, the total number of variational parameters in (8), including $R$ and $\xi$, is fourteen for the $1_g$ state and ten for the $1_u$ state, respectively. For the parallel configuration, $\theta = 0^\circ$, the parameter $\xi = 0.5$ and hence $\beta_{1x} = \beta_{1y}$, $\beta_{2x} = \beta_{2y}$, $\beta_{3x} = \beta_{3y}$, and the number of free parameters is reduced to ten for the $1_g$ state and seven for the $1_u$ state, respectively. Finally, with the
function (8) we intend to describe the lowest (un)gerade state for all magnetic fields where non-relativistic consideration is valid for \( B \leq 4.414 \times 10^{13} \) G, and for all orientations of the molecular axes.

Our variational calculations were performed by using the minimization package MINUIT of CERN-LIB. Numerical integrations were carried out with relative accuracy \( \sim 10^{-7} \) by use of adaptive NAG-LIB (D01FCF) routine. All calculations were performed on a Pentium-III PC 750MHz.

III. RESULTS AND DISCUSSION

In this Section we present the results for the \( 1_g \) and the \( 1_u \) states of \( \text{H}_2^+ \) for magnetic fields ranging from \( B = 0 \) G through \( B = 4.414 \times 10^{13} \) G, where a non-relativistic consideration is relevant and relativistic corrections can be neglected (see [19] for discussion), and for orientations ranging from 0° (parallel configuration) to 90° (perpendicular configuration).

A. \( 1_g \) state

Before coming to a concrete quantitative consideration we must state that for all explored magnetic fields, \( B = 0 - 4.414 \times 10^{13} \) G, and all orientations we found that a well pronounced minimum in the total energy of the system \((ppe)\) appears at finite internuclear distance. This minimum always corresponds to positive binding energy \( E_b \) [31] and hence it implies the existence of the \( \text{H}_2^+ \) molecular ion for magnetic fields \( B = 0 - 4.414 \times 10^{13} \) G and any orientation of the molecular axis. This is at variance with the statement by Khersonskij [7] about the non-existence of a minimum at finite distances on the total energy surfaces at sufficiently strong magnetic fields for some, far from parallel orientations and therefore non-existence of the molecular ion \( \text{H}_2^+ \). Presumably, this statement of non-existence is an artifact arising from an inappropriate choice of trial functions and therefore a consequent loss of accuracy. It is worth emphasizing that the variational study in [7] was carried out with a trial function somewhat similar to that of Eq.(5), but which does not fulfill our criterion of adequacy in full. The potential corresponding to this function reproduces correctly the original potential near Coulomb singularities and \( \sim \rho^2\)-growth at large distances. However, it generates growing terms \( \sim \rho \) which implies a reduction in the rate of convergence of
a perturbation theory for which the variational energy represents the first two terms (see discussion in [24]).

In Tables I, II and III the results for the total energy ($E_T$), binding energy ($E_b$) and equilibrium distance ($R_{eq}$) are shown for $\theta=0^\circ$, $45^\circ$ and $90^\circ$, respectively. As seen in Table I, our results for $\theta = 0^\circ$ lead to the largest binding energies for $B > 10^{11}$ in comparison with other calculations. As for $B \lesssim 10^{11}$ G, our binding energies for the parallel configuration appear to be very close (of the order of $\lesssim 10^{-4}\,\text{--}\,5$ in relative deviation) to the variational results at Wille [12], which are the most accurate so far in this region of magnetic field strengths. They are based on a trial function in the form of a linear superposition of $\lesssim 500$ Hylleraas type functions. It is quite amazing that our simple trial function (8) with ten variational parameters gives comparable (for $B \lesssim 10^{11}$ G) or even better (for $B > 10^{11}$ G) accuracy. It is important to state the reason why the trial function [12] fails being, increasingly inaccurate as a function of magnetic field growth for $B > 10^{11}$ G. An explanation of this inaccuracy is related to the fact that in the $(x,y)$- directions the exact wave function decays asymptotically as a Gaussian function, unlike Hylleraas functions which decay like the exponential of a linear function. The potential corresponding to the function [12] reproduces correctly the original potential near Coulomb singularities but fails to reproduce $\sim \rho^2$-growth at large distances. It implies a zero radius of convergence of the perturbation theory for which the variational energy represents the first two terms (see discussion in [24]).

A failure to adequately reproduce the asymptotic behavior of the wave functions leads to a failure in the proper description of the electronic cloud shrinking in transversal to magnetic line directions which become more and more essential with magnetic field growth. The origin of this shrinking is the Lorentz force action. The above drawback can easily be fixed by modifying the Hylleraas function by multiplication on the lowest Landau orbital. Nevertheless, it is worth emphasizing that it is quite surprising that a linear superposition of Hylleraas type functions, which form a natural basis for the free-field case, still allows one to get high accuracy results for magnetic fields $B \lesssim 10^{11}$ G. Implicitly, it indicates that the ground state wave function for these magnetic fields does not deviate drastically from free-field behavior. It is obvious that taking the above-mentioned modified Hylleraas functions in the analysis made by Wille [12] would allow us to reach the same accuracies but with a much smaller basis. We can treat the results by Larsen [9] as an explicit demonstration that an insertion of the Landau orbitals (multiplied by a Gaussian in $z$ function) in the
TABLE I: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the state $1_g$ in parallel configuration, $\theta = 0^\circ$. † This value is taken from [20].

| $B$       | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | Source       |
|-----------|------------|------------|-----------------|--------------|
| $B = 0$   | -1.20525   | —          | 1.9971          | Present†     |
|           | -1.20527   | —          | 1.997           | Wille [12]  |
| $10^9$G   | -1.15070   | 1.57623    | 1.924           | Present      |
|           | -1.15072   | 1.57625    | 1.924           | Wille [12]  |
| 1 a.u.    | -0.94991   | 1.94991    | 1.752           | Present      |
|           | —          | 1.9498     | 1.752           | Larsen [9]  |
|           | -0.94642   | 1.94642    | 1.76            | Kappes et al [14] |
| $10^{10}$G| 1.09044    | 3.16488    | 1.246           | Present      |
|           | 1.09031    | 3.16502    | 1.246           | Wille [12]  |
| 10 a.u    | 5.65024    | 4.34976    | 0.957           | Present      |
|           | —          | 4.35       | 0.950           | Wille [12]  |
|           | —          | 4.35       | 0.958           | Larsen [9]  |
|           | —          | 4.3346     | 0.950           | Vincze et al [10] |
| $10^{11}$G| 35.0434    | 7.50975    | 0.593           | Present      |
|           | 35.0428    | 7.5104     | 0.593           | Wille [12]  |
|           | —          | 7.34559    | 0.61            | Lai et al [18] |
| 100 a.u.  | 89.7096    | 10.2904    | 0.448           | Present      |
|           | —          | 10.2892    | 0.446           | Wille [12]  |
|           | —          | 10.1577    | 0.455           | Wunner et al [21] |
|           | —          | 10.270     | 0.448           | Larsen [9]  |
|           | —          | 10.2778    | 0.446           | Vincze et al [10] |
| $10^{12}$G| 408.3894   | 17.1425    | 0.283           | Present      |
|           | —          | 17.0588    | 0.28            | Lai et al [18] |
|           | —          | 16.966     | 0.278           | Wille [12]  |
| 1000 a.u. | 977.2219   | 22.7781    | 0.220           | Present      |
|           | —          | 21.6688    | 0.219           | Wille [12]  |
|           | —          | 22.7069    | 0.221           | Wunner et al [21] |
|           | —          | 22.67      | 0.222           | Larsen [9]  |
|           | —          | 22.7694    | 0.219           | Vincze et al [10] |
| $10^{13}$G| 4219.565   | 35.7539    | 0.147           | Present      |
|           | 4231.82    | 23.52      | 0.125           | Wille [12]  |
|           | —          | 35.74      | 0.15            | Lai et al [18] |
| $4.414 \times 10^{13}$G | 18728.48 | 54.4992 | 0.101 | Present |

Trial function (hence not in a fully adequate way as follows from our recipe) together with an optimization of the gauge dependence (in a different manner than what we propose) leads to rather accurate results. Finally, it is worth mentioning that in the domain of very strong magnetic fields, $B \gtrsim 10^{12}$ G, our results are more accurate than those obtained by the Thomas-Fermi method [18].
Table II: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the $1_g$ state at $\theta = 45^\circ$.

Optimal value of the gauge parameter $\xi$ is given (see text).

| $B$     | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | $\xi$ |
|---------|------------|------------|-----------------|------|
| $10^9$ G | -1.14248   | 1.56801    | 1.891           | 0.5806 |
| 1 a.u.  | -0.918334  | 1.91833    | 1.667           | 0.5846 |
| $10^{10}$ G | 1.26195  | 2.99337    | 1.103           | 0.5958 |
| 10 a.u. | 6.02330    | 3.97670    | 0.812           | 0.6044 |
| $10^{11}$ G | 36.15638 | 6.39681    | 0.466           | 0.6249 |
| 100 a.u. | 91.70480   | 8.29520    | 0.337           | 0.6424 |
| $10^{12}$ G | 413.2988  | 12.2331    | 0.198           | 0.6894 |
| 1000 a.u. | 985.1956   | 14.8044    | 0.147           | 0.7151 |
| $10^{13}$ G | 4236.342   | 18.9769    | 0.097           | 0.8277 |
| $4.414 \times 10^{13}$ G | 18760.77  | 22.2047    | 0.073           | 0.9276 |

The results for $\theta = 45^\circ$ are shown in Table II, where a gradual shortening of the equilibrium distance is accompanied by an increase of total and binding energies with magnetic field growth. It is worth noting that the parameter $\xi$ evolves from about 0.5 to 0.93 with magnetic field growth, thus changing from symmetric gauge for weak fields to an almost asymmetric one for strong ones. This phenomenon takes place for all orientations $\theta \neq 0$, becoming more and more pronounced with the inclination angle growth (see below). We are unaware of any other calculations for $\theta = 45^\circ$ to compare with.

For the perpendicular configuration ($\theta = 90^\circ$) the results are presented in Table III. Similar to what appeared for the parallel configuration (see above) our results are again slightly less accurate than those of Wille for $B \lesssim 10^{10}$ G becoming the most accurate for stronger fields. In particular, it indicates that a domain of applicability of the trial function, taken in the form of a superposition of Hylleraas type functions, reduces when the inclination grows. The results reported by Larsen [8] and by Kappes-Schmelcher [14] are slightly worse than ours although the difference is very small. The evolution of the gauge parameter follows
TABLE III: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the $1_g$ state in perpendicular configuration, $\theta = 90^\circ$. Optimal value of the gauge parameter $\xi$ is given (see text).

| $B$     | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) | $\xi$      |
|---------|------------|------------|-----------------|------------|
| $10^9$ G | -1.137342  | 1.56287    | 1.875           | 0.6380     | Present    |
|         |            | 1.56384    | 1.879           |            | Present    |
|         | -0.89911   | 1.89911    | 1.636           | 0.6448     | Present    |
|         |            | 1.8988     | 1.634           |            | Present    |
|         | -0.89774   | 1.8977     | 1.65            |            | Present    |
| $10^{10}$ G | 1.36207    | 2.89324    | 1.059           | 0.6621     | Present    |
|         |            | 2.8992     | 1.067           |            | Present    |
| 1 a.u.  | 6.23170    | 3.76830    | 0.772           | 0.6752     | Present    |
|         |            | 3.7620     | 0.772           |            | Present    |
| $10^{11}$ G | 36.7687    | 5.78445    | 0.442           | 0.7064     | Present    |
|         |            | 5.6818     | 0.428           |            | Present    |
| 10 a.u. | 92.7346    | 7.26543    | 0.320           | 0.7329     | Present    |
|         |            | 7.229      | 0.320           |            | Present    |
| $10^{12}$ G | 415.5621   | 9.96986    | 0.196           | 0.8034     | Present    |
|         |            | 4.558      | 0.148           |            | Present    |
| 100 a.u.| 988.3082   | 11.6918    | 0.151           | 0.8520     | Present    |
|         |            | 11.58      | 0.1578          |            | Present    |
| $10^{13}$ G | 4241.470   | 13.8490    | 0.113           | 0.9359     | Present    |
|         |            | 15.4700    | 0.0937          | 0.9795     | Present    |

a similar trend as was observed at $\theta = 45^\circ$, varying from $\xi = 0.64$ to $\xi = 0.98$ with magnetic field growth from $B = 10^9$ G to $B = 4.414 \times 10^{13}$ G [12].

The total energy dependence of $H_2^+$ as a function of the inclination angle $\theta$ for different magnetic fields is shown in Fig.2. The dotted line corresponds to the $H$-atom total energy in the magnetic field. For weak magnetic fields the hydrogen atom total energy is higher than that of the $H_2^+$-ion one. However, for $B \gtrsim 1.8 \times 10^{11}$ G the total energy of the $H$-atom becomes lower than the total energy of the $H_2^+$-ion for some angles $\theta_{cr} < \theta < 90^\circ$. It implies
that one proton in the $H_2^+$ system can go to infinity. Thus, it manifests the appearance of a \textit{dissociation} channel $H_2^+ \to H + p$. At first, the dissociation occurs at $\theta = 90^\circ$. Afterward the domain of inclinations with allowed dissociation widens with the magnetic field growth reaching $25^\circ \lesssim \theta \lesssim 90^\circ$ for $B = 4.414 \times 10^{13}$ G. The dependence of the critical angle $\theta_{cr}$ on the magnetic field is shown in Fig.3. Naively, it looks like the rate of dissociation is maximal at $\theta = 90^\circ$. However, a precise conclusion depends on the form of the barrier or, in other words, on the form of the potential surface in $\theta, R$. The rate of dissociation as a function of inclination angle and magnetic field is not studied in detail in present work and will be published elsewhere.

We observe that for fixed value of the magnetic field strength $B$ the binding energy $E_b$ as a function of $\theta$ always decreases when changing from the parallel to the perpendicular configuration (see Fig.2). A similar picture holds for all studied values of the magnetic field strength. Thus, we can draw the conclusion that the molecular ion becomes less and less stable monotonically as a function of inclination angle growth. It confirms the statement \textit{[7, 9, 12, 14]}, that the \textit{highest molecular stability of the $1_g$ state occurs for the parallel configuration}. We extend its validity to magnetic field strengths $B \lesssim 4.414 \times 10^{13}$ G. It is worth emphasizing that the rate of increase of binding energy with magnetic field growth depends on the inclination – it slows down with inclination increase. This effect means that $H_2^+$ in the parallel configuration becomes more and more stable towards rotations – the energy of the lowest rotational state should increase rapidly with magnetic field (see Table V and discussion there).

Regarding the internuclear equilibrium distance $R_{eq}$, one would straightforwardly expect that it will always decrease with inclination growth. Indeed, for all studied magnetic fields we observe that $R_{eq}$ at $\theta = 0^\circ$ is larger than $R_{eq}$ at $\theta = 90^\circ$ (cf. Tables I,III). This can be explained as a consequence of the much more drastic shrinking of the electronic cloud in the direction transverse to the magnetic field than in the longitudinal one. Actually, for magnetic fields $B \lesssim 10^{12}$ G the equilibrium distance $R_{eq}$ decreases monotonically with inclination growth, as seen in Fig.4. However, this trend breaks down for higher magnetic fields where the shortest equilibrium distances occur for orientations $\theta_{min} < 90^\circ$ (!). Furthermore, as the magnetic field grows the molecular ion becomes the most compact for smaller angles, being $\theta_{min} \sim 60^\circ$ for $B \lesssim 10^{12}$ G and then going down to $\theta_{min} \sim 30^\circ$ for $B = 4.414 \times 10^{13}$ G. The minimal value of $R_{eq}$ also deepens in comparison with $R_{eq}$ at $\theta = 90^\circ$. For example,
FIG. 2: \( \Pi_2^+ \) total energy (\( E_T \)) for the ground state 1\(_g\) as function of the inclination angle \( \theta \) for different magnetic fields. The dotted lines correspond to the H-atom total energy taken from [18].

for \( B = 4.414 \times 10^{13} \) G it becomes almost twice as small as \( R_{eq} \) at \( \theta = 90^\circ \). All these irregularities appear when at the same time the binding energy decreases monotonically as inclination grows (see Fig.2). We do not have a physical explanation of this phenomenon yet.
Fig. 3: \( H_2^+ \): domains of dissociation ↔ non-dissociation for the 1\(_g\) state.

Fig. 5 illustrates the above-mentioned non-monotonic behaviour of the internuclear distances near the equilibrium position, \( R \lesssim 0.3 \) a.u., for different orientations at \( B = 10^{13} \) G. For all values of \( \theta \) a clear minimum in \( R \) develops. For certain orientations (\( \theta \gtrsim 45^\circ \)) the potential energy curves are situated above the \( H \)-atom total energy. The total energy curves lie at increasingly higher energies as inclination grows. Hence, one can draw the conclusion that the growth of the inclination angle leads to an excitation of the \( H_2^+ \) system. It is quite interesting to make a comparison of the present situation with what appears in chemistry. The typical situation for the behaviour of molecular electronic excitations of standard chemical systems (in the absence of a magnetic field) is characterized by an increase of equilibrium distance with energy growth. This is explained either by enhancement of the antibonding character or suppression of the bonding character. Our situation is the opposite – in general the antibonding character is suppressed or, equivalently, the bonding character is enhanced. However, for strong magnetic fields \( B > 10^{12} \) G, where an abnormal behavior of the equilibrium distance is seen (see Fig. 4), the situation is reminiscent of the chemical one. Starting from \( \theta_{cr} \) the growth of inclination leads to an increase in the equilibrium distance. We do not know if this analogy makes physical sense or it is simply a coincidence.

In order to characterize the electronic distribution for different orientations we have calculated the expectation values of the transversal \(< \rho >\) and longitudinal \(< |z| >\) sizes of the electronic cloud (see Table IV). The ratio
\[
\frac{< \rho >}{< |z| >} < 1,
\]
quickly decreases with magnetic field growth, especially for small inclination angles. It reflects the fact that the electronic cloud has a more and more pronounced needle-like form, oriented along the magnetic line as was predicted in [1-2]. The behaviour of \( < \rho > \) itself does not display any unusual properties, smoothly decreasing with magnetic field, quickly approaching the cyclotron radius for small inclinations at large magnetic fields. On the
contrary, the $\langle |z| \rangle$ behaviour reveals some surprising features. At the beginning, at small magnetic fields, the $\langle |z| \rangle$ expectation value monotonically decreases with inclination, but then after some irregular behavior at $10^{12} \lesssim B \lesssim 10^{13}$, it begins a monotonic increase with inclination. It is quite striking that there is a domain of magnetic fields where $\langle |z| \rangle$ has almost no dependence on inclination.

As a result of our analysis the parallel configuration turned out to be optimal for all studied magnetic fields. Therefore, it makes sense to perform a study of the lowest vibrational state and also the lowest rotational state (see Table V). In order to do this we separate the nuclear motion along the molecular axis near equilibrium in the parallel configuration (vibrational motion) and deviation in $\theta$ of the molecular axis from $\theta = 0^\circ$ (rotational motion). The vicinity of the minimum of the potential surface $E(\theta, R)$ at $\theta = 0^\circ$, $R = R_{eq}$ is approximated by a quadratic potential and hence we arrive at a two-dimensional harmonic oscillator problem in $(R, \theta)$. Corresponding curvatures near the minimum define the vibrational and rotational energies (for precise definitions and discussion see, for example,
TABLE IV: $1_g$ state: Expectation values of the transversal $<\rho>$ and longitudinal $<|z|>$ sizes of the electron distribution in $H_2^+$ in a.u. at different orientations and magnetic field strengths. At $\theta = 0^\circ$ the expectation value $<\rho>$ almost coincides to the cyclotron radius of electron.

| $B$       | $<\rho>$ | $<|z|>$ |
|-----------|----------|----------|
|           | $0^\circ$| $45^\circ$| $90^\circ$| $0^\circ$| $45^\circ$| $90^\circ$|
| $10^9$ G  | 0.909    | 1.002    | 1.084    | 1.666    | 1.440    | 1.180    |
| 1 a.u.    | 0.801    | 0.866    | 0.929    | 1.534    | 1.313    | 1.090    |
| $10^{10}$ G | 0.511    | 0.538    | 0.569    | 1.144    | 0.972    | 0.848    |
| 10 a.u.   | 0.359    | 0.375    | 0.396    | 0.918    | 0.787    | 0.708    |
| $10^{11}$ G | 0.185    | 0.193    | 0.205    | 0.624    | 0.542    | 0.514    |
| 100 a.u.  | 0.123    | 0.129    | 0.139    | 0.499    | 0.443    | 0.431    |
| $10^{12}$ G | 0.060    | 0.065    | 0.074    | 0.351    | 0.324    | 0.340    |
| 1000 a.u. | 0.039    | 0.043    | 0.054    | 0.289    | 0.275    | 0.290    |
| $10^{13}$ G | 0.019    | 0.025    | 0.037    | 0.215    | 0.221    | 0.256    |
| $4.414 \times 10^{13}$ G | 0.009    | 0.017    | 0.030    | 0.164    | 0.191    | 0.232    |

We did not carry out a detailed numerical analysis, making rough estimates of the order of 20%. For example, at $B= 10^{12}$ G we obtain $E_{vib} = 0.276$ Ry in comparison with $E_{vib} = 0.259$ Ry given in [6], where a detailed variational analysis of the potential electronic curves was performed. Our estimates for the energy, $E_{vib}$, of the lowest vibrational state are in reasonable agreement with previous studies. In particular, we confirm a general trend of the considerable increase of vibrational frequency viz. growth of $B$ indicated for the first time by Larsen [9]. The energy dependence on the magnetic field is much more pronounced for the lowest rotational state – it grows much faster than the vibrational one with magnetic field increase. It implies that the $H_2^+$ in parallel configuration becomes more stable for larger magnetic fields. From a quantitative point of view the results obtained by different authors are not in good agreement. It is worth mentioning that our results agree for large magnetic fields $\gtrsim 10 a.u.$ with results by Le Guillou et al. [13], obtained in the framework of the so called ‘improved static approximation’, but deviate drastically at $B = 1 a.u.$, being quite close to the results of Larsen [9] and Wille [11]. As for the energy of the lowest rotational state our results are in good agreement with those obtained by other authors (see Table V).
TABLE V: Energies of the lowest vibrational \((E_{\text{vib}})\) and rotational \((E_{\text{rot}})\) electronic states associated with \(1_g\) state at \(\theta = 0^\circ\). The indexes in Le Guillou et al [13] correspond to the ‘improved adiabatic approximation’ (a), and to the ‘improved static approximation’ (b).

| \(B\) | \(E_T\) (Ry) | \(E_{\text{vib}}\) (Ry) | \(E_{\text{rot}}\) (Ry) | 
|------|-------------|----------------|----------------|------|
| \(10^9\) G | -1.15070 | 0.013 | 0.0053 | Present |
| | — | 0.011 | 0.0038 | Wille [11] |
| 1 a.u. | -0.94991 | 0.015 | 0.0110 | Present |
| | — | — | 0.0086 | Wille [11] |
| | — | 0.014 | 0.0091 | Larsen [9] |
| | — | 0.013 | — | Le Guillou et al (a) [13] |
| | — | 0.014 | 0.0238 | Le Guillou et al (b) [13] |
| \(10^{10}\) G | 1.09044 | 0.028 | 0.0408 | Present |
| | — | 0.026 | 0.0308 | Wille [11] |
| 10 a.u | 5.65024 | 0.045 | 0.0790 | Present |
| | — | 0.040 | 0.133 | Larsen [9] |
| | — | 0.039 | — | Le Guillou et al (a) [13] |
| | — | 0.040 | 0.0844 | Le Guillou et al (b) [13] |
| \(10^{11}\) G | 35.0434 | 0.087 | 0.2151 | Present |
| 100 a.u | 89.7096 | 0.133 | 0.4128 | Present |
| | — | 0.141 | 0.365 | Larsen [11] |
| | — | 0.13 | — | Wunner et al [21] |
| | — | 0.128 | — | Le Guillou et al (a) [13] |
| | — | 0.132 | 0.410 | Le Guillou et al (b) [13] |
| \(10^{12}\) G | 408.389 | 0.276 | 1.0926 | Present |
| | — | 0.198 | 1.0375 | Khersonskij [8] |
| 1000 a.u | 977.222 | 0.402 | 1.9273 | Present |
| | — | 0.38 | 1.77 | Larsen [11] |
| | — | 0.39 | — | Wunner et al [21] |
| | — | 0.366 | — | Le Guillou et al (a) [13] |
| | — | 0.388 | 1.916 | Le Guillou et al (b) [13] |
| \(10^{13}\) G | 4219.565 | 0.717 | 4.875 | Present |
| | — | 0.592 | 6.890 | Khersonskij [8] |
| \(4.414 \times 10^{13}\)G | 18728.48 | 1.249 | 12.065 | Present |

We show the electronic distributions \(|\psi(x, z)|^2\), integrated over \(y\) and normalized to one for magnetic fields \(10^9, 10^{10}, 10^{11}, 10^{12}\) G and different orientations in Fig.6. It was already found [21] that there is a change from ionic (two-peak electronic distribution) to covalent coupling (single-peak distribution) at \(\theta = 0^\circ\). If for \(B = 10^9\) G, all electronic distributions are characterized by two peaks, then for \(10^{12}\) G all distributions have a sharp single peak. Fig.6 demonstrates also how the change of the type of coupling appears for different inclinations. It is quite natural that for the perpendicular configuration \(\theta = 90^\circ\), where the equilibrium...
distance is the smallest, this change appears for smaller magnetic field.

To complete the study of the \(1_g\) state we show in Fig.7 the behavior of the variational parameters of (8) as a function of the magnetic field strength for the optimal (parallel) configuration, \(\theta = 0\). In general, the behavior of the parameters is rather smooth and very slow-changing even though the magnetic field changes by several orders of magnitude. In our opinion it reflects the level of adequacy (or, in other words, the level of quality) of our trial function. In practice, the parameters can be approximated by splain method and then can be used to study any magnetic field strength other than presented here.

B. \(1_u\) state

In the absence of a magnetic field the \(1_u\) state [33] is essentially repulsive, antibonding and characterized by shallow minimum in the total energy situated at large internuclear distance (see, for example, [17], [14]). It is a weakly bound state with respect to dissociation and it becomes unbound if nuclear motion is taken into account. There are not many studies of this state. Our major finding is that the total energy surface of the system (ppe) in the state \(1_u\) exhibits a well-pronounced minimum for \(0 < B < 4.414 \times 10^{13}\) G and for all inclinations. Similar to the \(1_g\) state, both total (\(E_T\)) and binding (\(E_b\)) energies of the \(1_u\) state increase as the magnetic field grows, while the equilibrium distance shortens. However, the accuracy of our calculations do not allow us to make a definitive conclusion about the stability of the system with respect to dissociation and nuclear motion effects.

Variational results for the \(1_u\) state at 0°, 45° and 90° for magnetic fields \(B = 0 - 4.414 \times 10^{13}\) G are shown in Tables VI-VIII. The immediate conclusion is that \(E_T(0°) < E_T(45°) < E_T(90°)\) for all magnetic fields. Hence, as for the \(1_g\) state, the highest molecular stability of the \(1_u\) state occurs for the parallel configuration. 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 even increases as the magnetic field grows, similarly to what happens for the \(1_g\) state. These results suggest the following picture for appearance of bound state: for small magnetic fields the minimum in the total energy arises at very large internuclear distances [34], then, as the magnetic field grows, the position of the minimum moves to smaller and smaller internuclear distances.

Our results for \(B > 0\) and \(\theta = 0°\) give the lowest total energies compared to other
$B = 10^9 \text{G}$

$\theta = 0^\circ$

$\theta = 45^\circ$

$\theta = 90^\circ$

$B = 10^{10} \text{G}$

$\theta = 0^\circ$

$\theta = 45^\circ$

$\theta = 90^\circ$

$B = 10^{11} \text{G}$

$\theta = 0^\circ$

$\theta = 45^\circ$

$\theta = 90^\circ$

$B = 10^{12} \text{G}$

$\theta = 0^\circ$

$\theta = 45^\circ$

$\theta = 90^\circ$

FIG. 6: $H_2^+$ electronic distributions $|\psi(x, z)|^2$ (normalized to one) for the $1_g$ state for different magnetic fields and inclinations.
FIG. 7: Variational parameters of the trial function (8) as function of the magnetic field strength $B$ for the $1_g$ state in parallel configuration, $\theta = 0^\circ$. The parameter $A_3$ is fixed being equal to 1 (see text). The error bars correspond to relative deviation in the variational energy in the region $\Delta E_T \equiv \frac{E_T}{E_{var}} \lesssim 10^{-5}$. 

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TABLE VI: Total $E_T$, binding $E_b$ energies and equilibrium distance $R_{eq}$ for the $1_u$ state in the parallel configuration, $\theta = 0^\circ$. †This value is taken from [20].

| $B$       | $E_T$ (Ry) | $E_b$ (Ry) | $R_{eq}$ (a.u.) |
|-----------|------------|------------|----------------|
| $B = 0$   | -1.00010   | 1.00010    | 12.746         |
|           | -1.00012   | 1.00012    | 12.55          |
| $10^9$ G  | -0.92103   | 1.34656    | 11.19          |
|           | -0.917134  | —          | 10.55          |
| 1 a.u.    | -0.66271   | 1.66271    | 9.732          |
|           | -0.66      | 1.66       | 9.6            |
| $10^{10}$ G | 1.63989   | 2.61500    | 7.180          |
|           | 2.1294     | —          | 4.18           |
| 10 a.u.   | 6.52362    | 3.47638    | 6.336          |
| $10^{11}$ G | 36.83671  | 5.71649    | 4.629          |
| 100 a.u.  | 92.42566   | 7.57434    | 3.976          |
| $10^{12}$ G | 413.6175  | 11.9144    | 3.209          |
| 1000 a.u. | 984.6852   | 15.3148    | 2.862          |
| $10^{13}$ G | 4232.554  | 22.7648    | 2.360          |
| $4.414 \times 10^{13}$ G | 18750.07  | 32.9104    | 1.794          |

calculations. They are in good agreement with those by Kappes–Schmelcher [14] as well as by Peek–Katriel [17] for $B = 0, 10^9$ G, although for $B = 10^{10}$ G a certain disagreement is observed (see Table VI). However, for $\theta = 90^\circ$ our results are in striking contrast with those by Wille [12], where even the optimal configuration is attached to $\theta = 90^\circ$, contrary to our conclusion. For instance, at $B = 10^{10}$ G in [12] 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 VIII). Similar, but less drastic disagreement, is the observed with the results in [14] (b).

We can guess this disagreement is due to the shallow nature of the minimum, but a real explanation of this effect is missing.
TABLE VII: 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|
| $10^{13}$G | 4251.409    | 3.9103      | 2.790           | 0.9999|
| $4.414 \times 10^{13}$G | 18778.95    | 4.0330      | 2.746           | 0.9999|

The analysis of Tables VI-VIII 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 $[25]$. 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 present total energies of the $H_2^+$ ion and the most accurate results for the hydrogen atom $[25]$ are comparable within the order of magnitude $10^{-4} - 10^{-5}$. At the same time we estimate that the accuracy of our calculations is of the same order of magnitude. It prevents us from making a conclusion about the stability of $H_2^+$ in the $1_u$ state with respect to dissociation. The only conclusion can be drawn is 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 striking to see the much lower rate of decrease of $R_{eq}$ in the range $B = 0 - 4.414 \times 10^{13}$ G: for the state $1_u$ it falls $\sim 3$ 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
TABLE VIII: 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            | 0.9866| Present |
| $10^{10}$ G | 2.29365   | 1.96167    | 5.517           | 0.9737| 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 |
| $10^{12}$ G | 422.0834  | 3.44848    | 3.594           | 0.9997| Present |
| 1000 a.u.| 996.3807   | 3.61935    | 3.460           | 0.9998| Present |
| $10^{13}$ G | 4251.497  | 3.82238    | 3.340           | 0.9999| Present |
| $4.414 \times 10^{13}$ G | 18779.04  | 3.9409     | 3.306           | 0.9999| Present |

is quite non-trivial (see Tables VI-VIII). 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, while being most compact at $\theta \simeq 45^\circ$. For $B \sim 10^{12}$ G the equilibrium distance is almost independent of the inclination, while for $B > 10^{12}$ G the most compact configuration corresponds to $\theta = 0^\circ$, in contrast to the $1_g$ state.

IV. CONCLUSION

We carried out accurate non-relativistic calculations in the Bohr-Oppenheimer approximation for the lowest states of the $H_2^+$ molecular ion of even parity, $1_g$, and odd parity, $1_u$, for different orientations of the magnetic field with respect to the molecular axis. We studied constant magnetic fields ranging up to $B = 4.414 \times 10^{13}$ G, where a non-relativistic consideration is valid.

For all studied magnetic fields and orientations a well-pronounced minimum in the total
energy surface for both $1_g$ and $1_u$ states was found. This makes manifest the existence of $H_2^+$ in both states for magnetic fields $B = 0 - 4.414 \times 10^{13}$ G. The smallest total energy was always found to correspond to the parallel configuration $\theta = 0^\circ$. The total energy increased while the binding energy decreased steadily as the inclination angle grew from $0^\circ$ to $90^\circ$ for both states. The rate of the total energy increase as well as the binding energy decrease was seen to be always maximal for the parallel configuration for both states.

However, the equilibrium distance exhibited quite non-trivial behavior as a function of the orientation angle $\theta$. In the case of the $1_g$ state, the shortest equilibrium distance always corresponded to the perpendicular configuration for magnetic fields $B \lesssim 10^{12}$ G, whereas for $B \gtrsim 10^{12}$ it occurred for some angle $\theta < 90^\circ$. On the contrary for the $1_u$ state the shortest equilibrium distance always corresponded to orientations $\theta < 90^\circ$ for all magnetic fields considered. In particular, for $B > 10^{12}$ G, it begins to correspond to the parallel configuration. As for the largest equilibrium distances – they were found to always correspond to the parallel configuration for both the $1_g$ state for all studied magnetic fields and for the $1_u$ state for $B \lesssim 10^{12}$. However, for larger magnetic fields $B \gtrsim 10^{12}$ the largest equilibrium distance for the $1_u$ state was seen to correspond to the perpendicular configuration (!).

Confirming the previous qualitative observations made by Larsen [9] and Khersonskij [7] for the $1_g$ state we demonstrated that the $H_2^+$ ion in the lowest energy state can dissociate to $H + p$ for a certain range of orientations starting from magnetic fields $B \gtrsim 1.8 \times 10^{11}$ G. As the magnetic field increases the region where dissociation is allowed was seen to steadily broaden, reaching $25^\circ \lesssim \theta \lesssim 90^\circ$ for $B = 4.414 \times 10^{13}$ G.

The electronic distributions were found to be qualitatively different for weak and large magnetic fields. In the domain $B < 10^{10}$ G the electronic distribution for any inclination peaks near the position of the protons. On the contrary for $B > 10^{11}$ G the electronic distribution is always peaked near the midpoint between the protons for any inclination. It implies physically different structure of the ground state - for weak fields the ground state can be modeled as a combination of hydrogen atom and proton while for strong fields such modeling is irrelevant.

Combining all the above-mentioned observations we conclude that for magnetic fields of the order of magnitude $B \sim 10^{11}$ G some qualitative changes in the behavior of the $H_2^+$ take place. The behavior of the variational parameters also favors this conclusion. It looks like as appearance of a new scale in the problem. It might be interpreted as a signal of a
transition to the domain of developed quantum chaos [26].

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[27] where the vector potential vanishes, see Section 2
[28] It confirms and extends a prediction made by Larsen [9] about the possible instability of H$_2^+$ in
    the perpendicular configuration for magnetic fields $B \gtrsim 1.6 \times 10^{11}$ G. The same phenomenon
was mentioned by Khersonskij [7] for $B \gtrsim 10^{12} \text{G}$. An accurate study of this phenomenon was carried out in Ref. [22].

\[29\] Similar statement is correct for any other given eigenfunction. In general, reality of the eigenfunctions corresponds to different values of gauge parameter.

\[30\] This is the case whenever the magnetic line is directed alongside the molecular axis (parallel configuration).

\[31\] The binding energy is defined as the affinity to keep the electron bound, $E_b = B - E_T$. $B$ is given in $\text{Ry}$ and thus has the meaning of the energy of a free electron in a magnetic field.

\[32\] $\xi = 0.5$ at $B = 0$

\[33\] $2p\sigma_u$ in standard spectroscopic notation

\[34\] It is natural to assume that for $B = 0$ a minimum exists at infinite (or almost infinite) internuclear distance.