The stability of the $1u$ state of H_2^+ in magnetic fields with arbitrary orientations

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The existence and stability of the van der Waals $1u$ state of the molecular ion H_2^+ with fixed centers (infinitely massive nuclei) in the presence of a magnetic field with arbitrary orientations in the range of strengths $0 \leq B \leq 10$ a.u. (1 a.u. $\equiv 2.35 \times 10^9$ G) is studied within the non-relativistic framework. The study is based on the variational method with physical relevant trial functions. A particular emphasis to the gauge optimization through variational parameters is incorporated. It is shown that, for all the magnetic fields studied, the potential energy curve has a pronounced minimum for finite internuclear distances and the optimal configuration of minimal total energy is realized when the molecular axis is oriented along the magnetic field lines (parallel configuration). We found a domain of magnetic fields $0 \leq B \lesssim 6.6$ a.u. where the $1u$ state in parallel configuration is stable towards dissociation $H_2^+ \nrightarrow H + p$. The maximal stability is found to be at magnetic field $B \sim 2$ a.u. where the potential well supports one vibrational state below the dissociation limit.

Keywords: H_2^+; magnetic field; variational; trial function.

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1. Introduction

The elucidation of the origin of the spectra coming from magnetic white dwarfs and neutron stars is only possible if we understand the behavior of simple atoms and molecules in the presence of strong magnetic fields. Chemistry of molecules in strong magnetic fields is quite different from traditional chemistry. For example, in strong magnetic fields, the presence of exotic species of atoms and molecules is possible (the case of one-two electron systems made out of protons and/or alpha particles is reviewed in [1] and [2] and references therein). Exotic molecules in strong magnetic fields were predicted by Ruderman [3,4] when he suggested that in strong magnetic fields linear chains of Hydrogen are formed along the magnetic field orientation. These predictions were motivated by the presumable existence of strong magnetic fields $B \sim 10^{12}$ G in neutron stars. Currently, such magnetic fields in neutron stars are confirmed by observations, and there is evidence [5] that even stronger magnetic fields can appear in magnetars ($B \sim 10^{14-15}$ G). Since then, the study of molecules and atoms in strong magnetic fields has gained relevance. In particular, from the observation by the Hubble Space Telescope of Helium atmospheres in magnetic white dwarfs [6] and more recently, from observations by Chandra X-Ray Observatory in 2002 when they detected a considerable amount of data of thermal emission showing clear signals of absorption features from the surface layer of the isolated neutron star 1E1207.4-5209 [7], which is characterized by an enormous magnetic field $B \gtrsim 10^{12}$ G. This conclusion was supported in 2003 by observations of XMM-Newton X-ray Observatory [8] (see also [9]). The origin of these absorption lines in spectra is not fully understood yet. Simple spectral models demonstrate that the atmosphere of the 1E1207 object cannot be Hydrogen or ionized Helium in ultra-strong magnetic fields, but leading to the extreme conclusion that the presence of oxygen or neon can possibly explain the absorption features (see for example [10]). Other possibilities led to the proposal of models based on the existence of simple exotic compounds like H_3^{++} (see [11] for example).

The simplest molecule H_2^+ has been widely and extensively studied by many authors with and without the presence of a magnetic field. In the absence of a magnetic field, the ground state ($1g$) is absolutely stable while the first excited state ($1u$), usually considered as unbound and purely repulsive, is characterized by a shallow Van der Waals minimum with a large inter-proton equilibrium distance ($\sim 12 - 13$ a.u.)[i]. Such minimum even supports the first vibrational level which remains stable towards dissociation [12]. This Van der Waals minimum remains stable even in the case of nuclei with finite masses (See [13]).

In the presence of a uniform magnetic field the ground state remains stable for any orientation of the magnetic field, and the well becomes deeper as the magnetic field increases. The parallel configuration realizes the optimal configuration of minimal total energy. For larger magnetic fields, the domain of inclinations where the H_2^+-ion exists (where the minimal total energy lies below the energy at the dissociation limit), reduces as the magnetic field increases and finally becomes 0-25° at $B = 4.414 \times 10^{13}$ G (see [1] and references therein).

The case of the $1u$ state in a magnetic field is by far, much less studied. The majority of studies were performed for the parallel configuration. Previous studies of this state in an arbitrarily oriented magnetic field only found stability when the molecular axis is oriented along the magnetic field lines and for relatively small strengths. In some cases, the accuracy of calculations has not allowed to make a definitive conclusion about the stability with respect dissociation and nuclear motion effects (see [1]).

The present study is focused to the $1u$ state of H_2^+ in presence of a uniform magnetic field in the range of strengths ($B = 0 - 10$ a.u.). Our goal is to confirm the stability of this excited state when the system is interacting with an arbitrarily oriented constant magnetic field. We are particularly interested in knowing the optimal configuration of minimal total energy. We developed a variational study with a physics recipe for choosing variational trial functions (described in full generality in [14]).

2. Hamitonian

The Hamiltonian which describes a system of two infinitely massive protons and one electron (ppe) (or H_2^+) placed in a uniform magnetic field $\mathbf{B}$, is given (in atomic units) by

$$\mathcal{H} = \frac{1}{2}\hat{p}^2 + \frac{1}{R} - \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{2}(\hat{p}\cdot\mathcal{A} + \mathcal{A}\cdot\hat{p}) + \frac{1}{2}\mathcal{A}^2, \quad (1)$$

where $\hat{p} = -i\nabla$ is the momentum of the electron, $\mathcal{A}$ is a vector potential corresponding to the magnetic field $\mathbf{B} = \nabla \times \mathcal{A}$, r_1, r_2 are the distances between the electron and each proton, and R is the internuclear distance. The total energy of this system is defined as the total electronic energy plus the classical Coulomb repulsion energy between the protons. We will consider the general situation where the molecular axis is oriented along the z-axis interacting with a uniform magnetic field arbitrarily oriented forming an angle θ with respect to the molecular axis

$$\mathbf{B} = B(\sin\theta, 0, \cos\theta)\,. \quad (2)$$

A 2-parameter vector potential corresponding to the magnetic field (2) is given by

$$\mathcal{A} = B(\lambda_1 y, (\cos\theta + \lambda_1)x + \lambda_2 z, (\sin\theta + \lambda_2)y)\,, \quad (3)$$

where λ_1 and λ_2 are two arbitrary parameters. Gauge (3) satisfies the Coulomb gauge ($\nabla \cdot \mathcal{A}(\mathbf{r}) = 0$). The symmetric gauge ($\mathcal{A} = (1/2)\mathbf{B} \times \mathbf{r}$) corresponds to the case $\lambda_1 = -(1/2)\cos\theta$ and $\lambda_2 = -(1/2)\sin\theta$. For a magnetic field oriented along the z-axis ($\theta = 0°$), the Landau gauge corresponds to $\lambda_1 = -1$ and $\lambda_2 = 0$. Gauge (3) includes a) the linear gauge $\mathcal{A} = ((1+\lambda_1)y, \lambda_1 x, 0)$ if $\lambda_2 = 0$ for a magnetic field oriented parallel to the z-axis, and b) the linear gauge $\mathcal{A} = (0, \lambda_2 z, (1+\lambda_2)y)$ if $\lambda_1 = 0$ for a magnetic field oriented parallel to the x-axis. The parameters λ_1 and λ_2 will be treated a priori as independent variational parameters in the present study.

Using the gauge (3) defined by 2 parameters, the Hamiltonian takes the form

$$\mathcal{H} = \frac{1}{2}\hat{p}^2 + \frac{1}{R} - \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + iB\left(\lambda_1 y\frac{\partial}{\partial x} + [(\cos\theta + \lambda_1)x + \lambda_2 z]\frac{\partial}{\partial y} + (\sin\theta + \lambda_2)y\frac{\partial}{\partial z}\right)$$
$$+ \frac{B^2}{2}\left([\lambda_1^2 + (\sin\theta + \lambda_2)^2]y^2 + (\cos\theta + \lambda_1)^2 x^2 + \lambda_2^2 z^2 + 2\lambda_2(\cos\theta + \lambda_1)xz\right). \quad (4)$$

In the parallel configuration, the problem is characterized by the quantum numbers corresponding to: (i) spatial parity p and (ii) the angular momentum projection m on the magnetic field direction (z-direction). In cases of arbitrary inclination of the magnetic field, axial symmetry around z-axis does not exist, therefore only spatial parity p characterizes the system. The notation we use for the different states 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, the number 2 to the first excited state, and then a subscript g/u (gerade/ungerade) corresponding to positive/negative eigenvalues of the parity operator.

3. Method

Since we used an approximate method for solving the Schrödinger equation with the Hamiltonian (1), our approximate energies can well be gauge-dependent (only the exact ones are gauge-independent). The present study is based on the variational method with the form of the vector potential chosen in a certain optimal way. The choice of trial functions is made according to the following recipe: As a first step, we construct an **adequate** variational real trial function Ψ_0 [14-17], for which the associated potential $V_0 \equiv (\Delta\Psi_0/\Psi_0)$ reproduces the original potential near Coulomb singularities and the harmonic oscillator behavior (transverse to the magnetic field direction) at large distances. The trial function should support the symmetries of the original problem. We then performed a minimization of the energy functional by treating the free parameters of the trial function and the parameters λ_1 and λ_2 defining the vector potential on the same footing. Such an approach enables us to find the *optimal* form of the Hamiltonian as a function of λ_1 and λ_2. It is worth to emphasize one important assumption in the present study. Namely, that for a fixed value of B and a given inclination, we can find a gauge for which the eigenfunction is real[ii]. This gauge optimization is nothing but a mechanism to justify the use of real trial functions. Therefore one can discard any imaginary term in the Hamiltonian. This prescription was used in [1] and led to adequate trial functions to study the two lowest states of H_2^+ in strong magnetic fields $B > 10^9$ G.

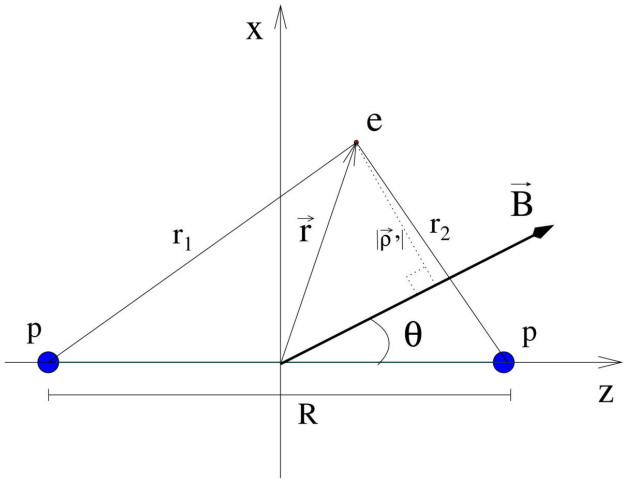

FIGURE 1. Geometrical setting for the H_2^+ molecular ion in presence of a magnetic field forming an angle θ with respect to the molecular axis and parallel to the x-z plane. The protons are situated along the z-axis separated by a distance R. The origin of coordinates coincides with the midpoint along the molecular axis, and it is chosen as the gauge origin.

A key point in the present study is based on the observation that in the Landau problem (one electron in a constant magnetic field) with the magnetic field given by (2) and the corresponding vector potential (3), the exact (real) eigenfunction for the ground state is given by

$$\Psi_0^{\rm Landau} = e^{-\frac{B}{4}|\vec{\rho}'|^2} = {\rm e}^{-\frac{B}{4}\left(\cos^2(\theta)\,x^2+y^2+\sin^2(\theta)\,z^2-2\sin(\theta)\cos(\theta)\,xz\right)}\,, \qquad (5)$$

where $|\vec{\rho}'|$ is the transverse distance between the electron position and the magnetic field line (see Fig. 1). For the parallel case ($\theta = 0^\circ$) the standard form, in the symmetric gauge, *i.e.* $\Psi_0^{\rm Landau} = e^{-(B/4)\rho^2}$, where ρ is the radial cylindrical coordinate, is recovered.

Motivated by the exact solution (5) for an electron in the presence of a constant magnetic field given by (2) we propose a trial function of the form

$$\Psi_{GZ} = \left(e^{-\alpha_3 r_1-\alpha_4 r_2} \pm e^{-\alpha_3 r_2-\alpha_4 r_1}\right) \times e^{-\frac{B}{4}[\beta_{3x}x^2+\beta_{3y}y^2+\beta_{3z}z^2-\beta_c xz]}\,, \qquad (6)$$

which is a (symmetric (gerade)/antisymmetric (ungerade)) function with respect to the interchange of the nuclei, of the Guillemin-Zener type multiplied by the Landau factor in the form (5). In (6) $\alpha_3, \alpha_4, \beta_{3x}, \beta_{3y}, \beta_{3z}$ and β_c are variational parameters. So, this function is characterized by 6 variational parameters. The function (6) is a modification of the Guillemin-Zenner type function used in [1]. Due to the symmetrization the trial function (9) can be separated in two terms $\psi_{GZ-a,b}$. Following a criterion of physical adequacy described in [14], the associated potential ($V = \Delta\Psi/\Psi$) corresponding to the first term ψ_{GZ-a} of the trial function (6) is

$$V_{GZ-a} = \frac{\alpha_3^2}{2} + \frac{\alpha_4^2}{2} - \frac{B}{4}(\beta_{3x}+\beta_{3y}+\beta_{3z}) - \frac{\alpha_3}{r_1} - \frac{\alpha_4}{r_2} + \frac{B^2}{8}\left(\beta_{3x}^2x^2+\beta_{3y}^2y^2+\beta_{3z}^2z^2-\beta_c(\beta_{3x}+\beta_{3z})xz + \frac{1}{4}\beta_c^2(x^2+z^2)\right) + \frac{B}{2}\left(\frac{\alpha_3}{r_1}+\frac{\alpha_4}{r_2}\right)\left(\beta_{3x}x^2+\beta_{3y}y^2 + \beta_{3z}z^2-\beta_c xz\right) + \frac{BR}{4}\left(\beta_{3z}z-\frac{1}{2}\beta_c x\right) \times\left(\frac{\alpha_3}{r_1}-\frac{\alpha_4}{r_2}\right) - \frac{\alpha_3\alpha_4}{4}\frac{[R^2-4r^2]}{r_1r_2}\,. \qquad (7)$$

The dominant terms in the associated potential V_{GZ-a} reproduce the terms of the original potential in (4), for the symmetric gauge, if $\alpha_3 = \alpha_4 = 1$, $\beta_{3x} = \cos^2\theta$, $\beta_{3y} = 1$, $\beta_{3z} = \sin^2\theta$, $\beta_c = 2\cos\theta\sin\theta$. The associated potential contains additional terms which are sub-dominant near Coulomb singularities and at large distances. It is important to mention that if the parameters $\beta_c = \beta_3 = 0$, then the associated potential reproduces the potential and, correspondingly, the trial function used in [1]. This situation occurs in the configurations of maximal symmetry 0° and 90°.

The Guillemin Zener type function (6) reduces to the particular cases of Heitler-London type, and Hund-Mulliken type functions, when $\alpha_3 = \alpha_4$ and $\alpha_3 = 0$, respectively.

3.1. Trial function

In order to describe the $1u$ state we consider in the present study a linear combination of three functions: two functions of the Guillemin-Zener type, each with its own variational parameters, and one Ansatz of the Hund-Mulliken type:

$$\psi_{\rm HM} = \left(e^{-\alpha_2 r_1} - e^{-\alpha_2 r_2}\right) \times e^{-\frac{B}{4}[\beta_{2x}x^2+\beta_{2y}y^2+\beta_{2z}z^2-\beta_{2c}xz]}\,. \qquad (8)$$

where α_2, β_{2x}, β_{2y}, β_{2xz}, β_c are variational parameters. The Hund-Mulliken type function describes adequately the physical situation of large internuclear distances. On the other hand, the Guillemin-Zener type function describes adequately the domain of intermediate and small internuclear distances. Thus, the complete trial function proposed in this study is the linear combination

$$\Psi = A_1\psi_{\rm HM} + A_2\psi_{\rm GZ-1} + A_3\psi_{\rm GZ-2}, \qquad (9)$$

where the coefficients A_1, A_2, A_3 are considered as variational parameters. One of these parameters can be chosen arbitrarily as a part of the normalization of the trial function. In general, the total number of variational parameters in (9) is 20 and the total number of parameters including R and the gauge parameters $\lambda_{1,2}$ is 23.

In the particular case of the parallel configuration, the system exhibits an azimuthal symmetry around the axis of

the magnetic field. This azimuthal symmetry reduces effectively the total number of parameters, because the parameters in front of the crossed terms xz, and in front of the z^2 terms in the Landau factor in (6) *i.e.* β_c and β_{3z}, must be zero in order to reproduce the corresponding magnetic field oriented along the z-axis. It is worth to mention that, in this parallel configuration, the trial function (9) coincides with that used in [1] with an additional second Ansatz of the Guillemin-Zener type.

3.2. The Hellman-Feynman theorem: Configurations of maximal symmetry

The configurations of maximal symmetry are especially relevant from a theoretical point of view. Some qualitative features of any system with an explicit dependence on a certain parameter can be predicted through the Hellman-Feynman theorem. For the particular system of H_2^+, the variation of the total energy as a function of the orientation θ of the magnetic field with respect to the molecular axis can be found by the relation

$$\frac{\partial E}{\partial \theta} = \langle \Psi | \frac{\partial \mathcal{H}}{\partial \theta} | \Psi \rangle \,, \tag{10}$$

where Ψ is the variational wave function (a stationary point for the Schrödinger functional) corresponding to the eigenvalue E, and $\mathcal{H}$ is the Hamiltonian of the system.

Considering that the trial function (9) is real, the extremals of the total energy as a function of the inclination angle θ, are found by the relation

$$\langle \Psi | \frac{\partial \mathcal{H}}{\partial \theta} | \Psi \rangle = \langle \Psi | \frac{\partial \mathcal{A}^2}{\partial \theta} | \Psi \rangle = 0 \,, \tag{11}$$

where

$$\frac{\partial \mathcal{A}^2}{\partial \theta} = B^2[-2(\cos\theta + \lambda_1)\sin\theta x^2 + 2(\sin\theta + \lambda_2)\cos\theta y^2 - 2\lambda_2 \sin\theta xz] \,. \tag{12}$$

Thus, using the variational results (see *e.g.* Table V) we verify that Eq. (11) is satisfied in the configurations of maximal symmetry

$$\frac{\partial E(\theta = 0^\circ)}{\partial \theta} = \frac{\partial E(\theta = 90^\circ)}{\partial \theta} = 0 \,. \tag{13}$$

This relation should be gauge invariant. A similar analysis was done in [18] where the symmetric gauge was used leading to the same conclusion. It is also worth to notice, that in the case when the magnetic field is chosen along the z-axis and the molecular axis is inclined (as it was done in [1]) there is no explicit dependence on the inclination angle in the Hamiltonian, and the Hellman-Feynman theorem cannot be applied.

4. Results

We carried out a variational study of the $1u$ state of the system (ppe) with infinitely heavy nuclei, interacting with a magnetic field $0 < B \leq 10$ a.u. in inclined configuration $0^\circ \leq \theta \leq 90^\circ$ with respect to the molecular axis. In this range of magnetic fields the total energy of the $1u$ state presents a pronounced minimum. Our variational results indicate that there exist some critical fields and critical inclinations where the $1u$ becomes unstable towards dissociation $H_2^+ \rightarrow H + p$. This is described in more details below.

The numerical calculation was developed using subroutines D01FCF of NAG-LIB [19] for the 2(3) dimensional integrations (depending to the symmetry of the configuration) and the package MINUIT of CERN-LIB [20] to minimize the energy functional. In order to reach a higher (and stable) accuracy, the (finite) domain of integration was manually and conveniently subdivided following the profile of the integrand. Usually, the domain of integration along each coordinate was subdivided into 3 or more subregions. The variational results are presented with an estimated relative accuracy of 10^{-6}.

4.1. Configurations of maximal symmetry

The results of our variational calculations with the trial function (9) for the $1u$ state of H_2^+ in the presence of a uni form magnetic field, in maximal symmetry configurations $\theta = 0^\circ, 90^\circ$, are presented in Table I and Table II, respectively.

TABLE I. Total, E_T, binding, $E_b = E_e - E_T$, energies and equilibrium distance R_{eq} for the state $1u$ as a function of magnetic field B in the parallel configuration $\theta = 0^\circ$ which becomes $1\sigma_u$. This state represents the first excited state or the ground of state of negative parity. The optimal gauge is found to correspond to the symmetric gauge ($\lambda_1 = -1/2, \lambda_2 = 0$) for all magnetic fields. The ground state of energy of the Hydrogen atom $1s_0$ [27] is presented in the last column for comparison. The horizontal line divides the fields where the $1u$ is stable/unstable.

B (a.u.)	E_T (a.u.)	R_{eq} (a.u.)	E_b (a.u.)	E_H (a.u.)
0	−0.500049	12.77	0.500049	−0.500000
0.1	−0.497583	12.43	0.547583	−0.497526
0.5	−0.447348	10.80	0.697348	−0.447211
1	−0.331403	9.57	0.831403	−0.331169
	−0.331355†	9.73†		
	−0.330000*	9.6*		
	−0.331436•	9.58•		
2	−0.022474	8.29	1.022474	−0.022214
	−0.022638•	8.34•		
5	1.119484	6.90	1.380516	1.119601
6	1.531709	6.68	1.468291	1.531754
8	2.380879	6.31	1.619122	2.380615
10	3.252534	6.04	1.747466	3.252203
	3.261810†	6.34†		

† results from [1].

* results from [24].

• results from [25].

TABLE II. Total, E_T, binding, E_b, energies and equilibrium distance R_{eq} for the state $1u$ as a function of magnetic field B in the perpendicular configuration $\theta = 90^\circ$. This state represents the first excited state or the ground of state of negative parity. The optimal gauge is found to correspond to $\sim$ Landau gauge $(\lambda_1 = 0, \lambda_2 = -0.08)$ for all magnetic fields. The ground state of energy of the Hydrogen atom $1s_0$ [27] is presented in the last column for comparison. The horizontal line divides the fields where the $1u$ is stable/unstable.

B (a.u.)	E_T (a.u.)	R_{eq} (a.u.)	E_b (a.u.)	E_H (a.u.)
0	-0.500049	12.77	0.500049	-0.5000000
0.1	-0.495345	11.17	0.545195	-0.497526
0.5	-0.413423	8.51	0.663423	-0.447211
1	-0.249852	7.28	0.749818	-0.331169
	$-0.249815^\dagger$	$7.26^\dagger$		
2	0.145674	6.32	0.854326	-0.022214
5	1.487704	5.39	1.012296	1.119601
6	1.954286	5.23	1.045714	1.531754
8	2.901345	5.02	1.098655	2.380615
10	3.859941	4.87	1.140059	3.252203
	$3.864990^\dagger$	$4.87^\dagger$		

† Results from [1].

In the parallel configuration our results for the total energy of the $1u$ state are in excellent agreement with the best results [21-25]. For example, for $B = 1$ a.u. the difference with respect to the best known results existing in the literature [25] is beyond 10^{-5} a.u. Qualitatively, we observed a monotonous increase in the total E_T and binding[iii] energy E_B, accompanied by a monotonous decrease in the equilibrium internuclear distance R_{eq} as a function of magnetic field ($0 \leq B \leq 10$ a.u.) It is worth emphasizing that in this particular configuration, our results improve slightly the results from [1] with a simple addition of one Guillemin-Zener type function (the improvement was $\sim 10^{-5}$ for $B = 1$ a.u.). However, such a small difference may be enough to confirm or discard stability in some cases. The fact that we obtained a small improvement in the total energy, even adding one more Guillemin-Zener term to the trial function (*i.e.* 5 more variational parameters), can be interpreted as a manifestation of the convergence of the trial function. However, the obtained equilibrium distance $R_{eq} = 9.57$ a.u. at $B = 1$ a.u. shows a better agreement with results in [24,25] (see Table I).

The $1u$ state in the perpendicular configuration has received less attention in the literature. The only exceptions are references [24-26][iv]. In the perpendicular configuration, the system also exhibits an increasing behavior of the total and binding energies as a function of the magnetic field, accompanied by a monotonous decrease in the equilibrium internuclear distance (see Table II). For all the magnetic fields considered, the total energy for the $1u$ state in the perpendicular configuration is always larger compared with the energy in the parallel configuration. Also, for all magnetic fields studied, we observe that in perpendicular configuration the system is more compact (the internuclear equilibrium distance is smaller) in comparison to the parallel configuration (*e.g.* by ~ 2.3 a.u. at $B = 1$ a.u.)

One of the main goals of the present study is to find the optimal configuration (of lowest total energy) for this state. From our variational results, we confirm the conjecture that the parallel configuration realizes the configuration of minimal total energy of the H_2^+ molecular ion in the $1u$ state for all magnetic fields considered in the present study (see Tables I and II). In particular, for $B = 1$ a.u. the minimal total energy in the parallel configuration is in agreement with adiabatic potential energy calculations carried out in [24] where a basis set of ~ 360 generalized optimized atomic orbitals was used. It is worth to notice that for the optimal (parallel) configuration our 20-parameter trial function (9) provides a better (lower) total energy (by $\sim 1.4 \times 10^{-3}$ a.u.) in comparison to [24].

The difference between the energies of maximal symmetry configurations increases as a function of the magnetic field ($\Delta E = E_T(90^\circ) - E_T(0^\circ) = 0.8$ a.u for $B = 1$ a.u.), such behavior is interpreted as the $1u$ state becomes more rigid towards rotations as the magnetic field increases.

4.2. Stability of $1u$ state: Critical Fields

One can observe from Table I and Table II that the $1u$ state is not stable for all the magnetic fields. First of all, it is important to emphasize that a high accuracy was required in order to analyze the stability the $1u$ state, since it is a weakly bound state and the potential well is very shallow. The present variational results show that the energy of the $1s$ ground state of Hydrogen atom and the total energy of the $1u$ state of H_2^+ in the parallel configuration are very close. Therefore, it is necessary to analyze the dissociation energy (see Fig. 2).

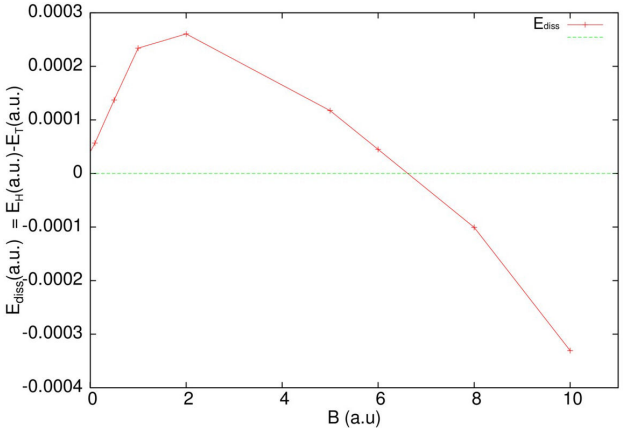

FIGURE 2. Dissociation energy $E_{diss} = E_H - E_T$ of the $1u$ state of H_2^+ at equilibrium as a function of the magnetic field B in the parallel configuration ($\theta = 0^\circ$). The curve E_{diss} vs B exhibits a domain of magnetic fields where the $1u$ state of H_2^+ is stable with respect to dissociation to Hydrogen atom plus proton (positive dissociation energy). The range of this domain goes from $B = 0$ a.u to $B_{cr} \sim 6.6$ a.u.

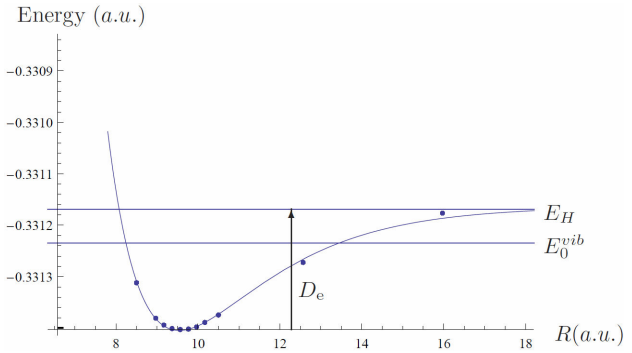

FIGURE 3. Total energy (dots) of the $1u$ state of H_2^+ as a function of the internuclear distance R at the magnetic field $B = 1$ a.u. in the parallel configuration $\theta = 0°$. The curve represents the Morse fit to the variational results. The upper horizontal line represents the asymptotic energy i.e. the total energy of the ground state $1s_0$ of Hydrogen atom $E_H = -0.331169$ a.u. at $B = 1$ a.u. (see [27]). The horizontal line below the asymptotic energy represents the first vibrational state ($E_0^{vib} = 0.00014$ a.u. with respect to the equilibrium energy). The total energy at equilibrium is $E_T = -0.331403$ a.u. at $R_{eq} = 9.57$ a.u.

Our variational results show that in the parallel configuration the $1u$ state is stable towards dissociation $H_2^+ \rightarrow H + p$ for $B < 8$ a.u. In Fig. 2 the dissociation energy is plotted as a function of the magnetic field. In such plot we can see that there is a critical value of the magnetic field where the $1u$ state becomes unstable towards dissociation (the dissociation energy turns negative), such critical field is estimated at ~ 6.6 a.u. by a simple interpolation. This critical field defines a domain of magnetic fields where the $1u$ state remains stable towards dissociation.

As for the parallel configuration we can do a similar analysis for the perpendicular case. In this configuration the $1u$ state is only stable for magnetic fields $B < 0.1$ a.u. Thus, the domain of stability in the perpendicular configuration is quite smaller compared with that of the parallel configuration. The critical magnetic field is estimated at $B = 2 \times 10^{-3}$ a.u.

In both configurations, for all the magnetic fields considered, the $1u$ state exhibits a pronounced minimum in the potential energy curve, but only in those magnetic fields for which the global minimum of energy at finite R_{eq} is below the total energy of the Hydrogen atom in the ground state (see Fig. 3 for example for $B = 1$ a.u) the system is considered to be stable. The deepest well in the parallel configuration occurs for a uniform magnetic field of ~ 2 a.u. that represents the maximal stability of the system (maximum of dissociation energy as a function of the magnetic field) (see Fig. 2).

4.3. Vibrational states

A natural question concerning the stability of molecular systems is related to the existence of at least one nuclear vibrational state. In order to answer this question, for $B = 1$ a.u. we carried out variational calculations for different fixed values of the internuclear distance R and built the potential curve corresponding to the $1u$ state. In Fig. 3 we show that such potential curve fits reasonably well a Morse potential. Using this fit, we computed the energy of the first vibrational state obtaining $E_0^{vib} = 0.00014$ a.u. with respect to the energy at equilibrium. Therefore, the H_2^+ molecular ion in the $1u$ state in the first vibrational state of the nuclei is still stable towards dissociation $H_2^+ \rightarrow H + p$. For this magnetic field, the first vibrational state is more stable with respect dissociation than in absence of magnetic field [12].

5. Inclined Configurations

5.1. Stability of $1u$ state: Critical Angles

In the present study, we also considered the analysis of inclined configurations $0° < \theta < 90°$ using the trial function (9). It is important to mention that for arbitrary inclinations of the magnetic field there are almost no references in the literature. The only exception is [26] where the qualitative description is very different from the behavior obtained in the present study. We consider that such differences do not allow for a direct comparison with the present results[v] and that independent calculations are needed in order to resolve this disagreement.

Our variational results are presented in Tables III and IV for the magnetic fields $B = 0.1$ a.u. and $B = 1$ a.u. respectively.

As we expected the maximal symmetry configurations are found to correspond to the extremals of energy: the parallel configuration is the optimal configuration of total energy, while the perpendicular configuration corresponds to the maximum of total energy (though it also corresponds to the most compact configuration).

The behavior of the total energy of $1u$ state of (ppe)-system for both representative magnetic fields is monotonously increasing as a function of the inclination angle θ of the magnetic field, while the equilibrium distance R_{eq} decreases monotonically (see Tables III, IV and Figs. 4, 5).

TABLE III. Total energy E_T, and equilibrium distance R_{eq} for the state $1u$ at different orientations θ of the magnetic field with respect to the molecular axis for the magnetic field $B = 0.1$ a.u. We estimate that the uncertainty in R_{eq} is $\Delta \simeq 0.05$ a.u. due to the fact that the potential well is too flat. The total energy of the ground state of Hydrogen atom at $B = 0.1$ a.u. is -0.497527 a.u.

θ (deg)	E_T (a.u.)	R_{eq} (a.u.)	$E_T^{\dagger}$ (a.u.)
$0°$	-0.497583	12.43	$-0.497583^{\dagger}$
$10°$	-0.497517	12.22	$-0.496800^{\dagger}$
$30°$	-0.497014	12.18	$-0.495668^{\dagger}$
$45°$	-0.496444	11.97	$-0.495459^{\dagger}$
$60°$	-0.495884	11.90	$-0.495383^{\dagger}$
$80°$	-0.495498	11.45	
$90°$	-0.495435	11.20	$-0.495345^{\dagger}$

† results from [1].

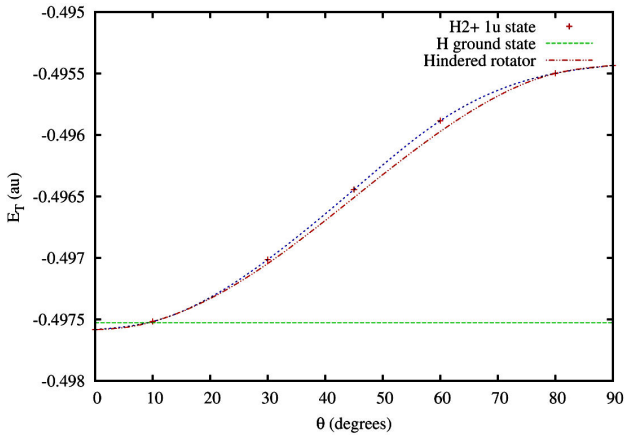

FIGURE 4. Total energy E_T of the $1u$ state of H_2^+ at equilibrium as a function of orientation θ at a magnetic field $B = 0.1$ a.u. The horizontal line represents total energy of the separate system $H + p$ (*i.e.* the energy of the Hydrogen atom at $B = 0.1$ a.u.). The orange curve represents the Hindered Rotor Model. The curve exhibits a domain of orientations where the $1u$ state of H_2^+ system is stable with respect to dissociation. The critical angle for which the system becomes unstable is estimated at $\theta_{cr} \sim 9^\circ$.

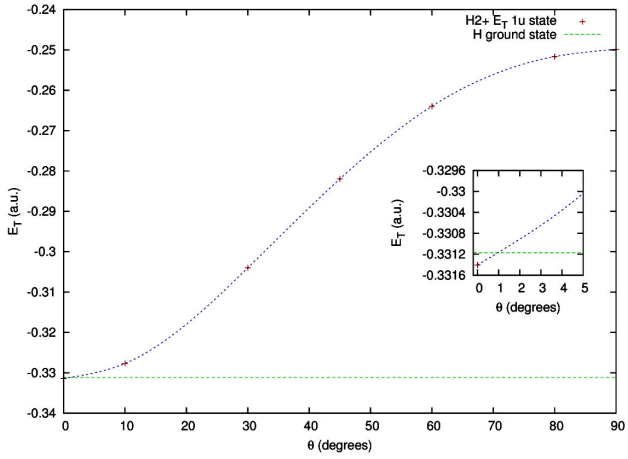

FIGURE 5. Total energy E_T of the $1u$ state of H_2^+ as a function of orientation θ with respect to the molecular axis for the magnetic field $B = 1$ a.u. The horizontal line represents total energy of the separate system $H + p$ (*i.e.* the energy of the Hydrogen atom at $B = 1$ a.u.). The curve exhibits a domain of orientations where the $1u$ state of H_2^+ system is stable with respect to dissociation. The critical angle for which the system becomes unstable is estimated at $\theta_{cr} \sim 1^\circ$.

For both magnetic fields, the $1u$ state of the (ppe)-system becomes unstable towards dissociation $H_2^+ \rightarrow H + p$ from a certain critical orientation (see Figs. 4 and 5). Critical angles were found at $\theta_{cr} \sim 9$ for $B = 0.1$ a.u and $\theta_{cr} \sim 1$ for $B = 1$ a.u. This non-negligible decreasing of θ_{cr} as a function of the magnetic field corresponds to the increase in the total energy difference between the maximal symmetry configurations. Though the improvement to the total energy using the trial function (9) is relatively small in comparison to the total energy found in [1], the change in the critical angle

TABLE IV. Total energy E_T, and equilibrium distance R_{eq} for the state $1u$ at different orientations θ of the magnetic field with respect to the molecular axis for the magnetic field $B = 1$ a.u. We estimate that the uncertainty in R_{eq} is $\Delta \simeq 0.05$ a.u. due to the fact that the potential well is too flat. The total energy of the ground state of Hydrogen atom at $B = 1$ a.u. is -0.331169 a.u.

θ (deg)	E_T (a.u.)	R_{eq} (a.u.)	$E_T^\dagger$ (a.u.)
0°	-0.331403	9.57	-0.331355†
10°	-0.327681	9.05	
30°	-0.304002	8.60	
45°	-0.281976	8.10	$-0.254521^\dagger$
60°	-0.264042	7.50	
80°	-0.251663	7.35	
90°	-0.249852	7.28	$-0.249815^\dagger$

† results from [1].

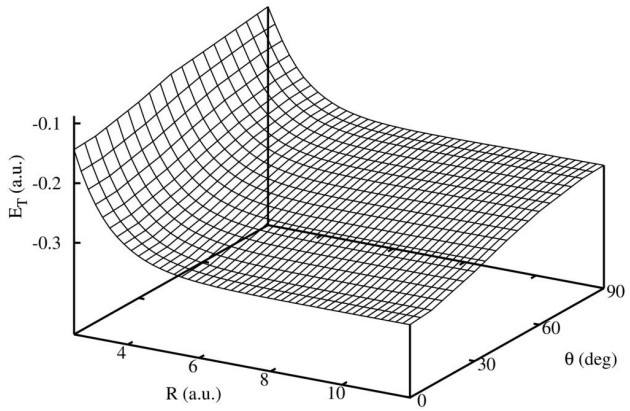

FIGURE 6. Total energy E_T (in a.u.) of the $1u$ state of H_2^+ as a function of the internuclear distance R (in a.u.) and the orientation θ (in degrees) with respect to the molecular axis at the magnetic field $B = 1$ a.u. The potential surface exhibits a global minimum at $R = 9.56$ a.u. and $\theta = 0^\circ$, and shows that the configurations of maximal symmetry correspond to the extremals of energy.

is quite significant. This qualitatively different result implies that the $1u$ state is more stable towards rotations.

It is worth to observe from Fig. 4 that our variational results as a function of the inclination angle θ fit well at a hindered rotator model

$$V(R,\theta) = V(R,0) + \Delta V(R)\sin^2\theta\,, \qquad (14)$$

where $\Delta V(R) = V(R,90^\circ) - V(R,0^\circ)$ is the barrier height for a given value of R. Such behavior would allow us to make a similar rotational analysis as it was done in [28] for the ground state $1g$ (this will be done elsewhere).

Using our variational results, it is possible to construct a surface of energy as a function of the molecular distance R and the magnetic field orientation θ (see Fig. 6 for $B = 1$ a.u). The potential energy surface appears smooth and without indications to any other local minimum.

Additionally, we made an analysis of the behavior of the expectation values $\langle x^2\rangle$, $\langle y^2\rangle$, $\langle xz\rangle$ as well the gauge param-

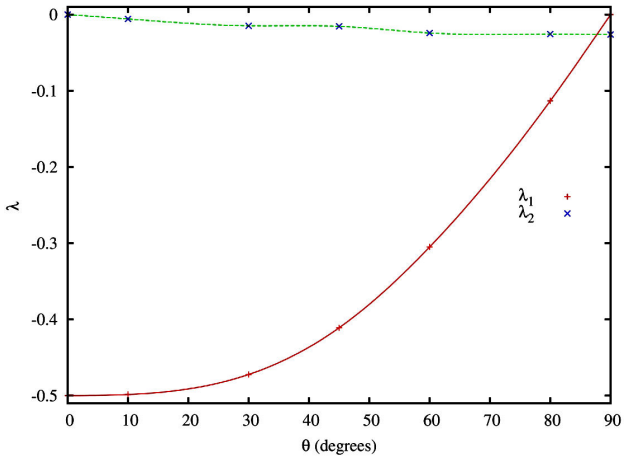

FIGURE 7. Optimal gauge variational parameters λ as a function of the orientation θ for the magnetic field $B = 1$ a.u. In the parallel configuration ($\theta = 0^\circ$) the optimal gauge corresponds to the symmetric gauge ($\lambda_1 = -1/2$, $\lambda_2 = 0$). In the perpendicular configuration ($\theta = 90^\circ$) the optimal gauge is very close to the Landau gauge ($\lambda_1 = 0$, $\lambda_2 = -0.08$).

TABLE V. Expectation values, optimal gauge parameters $\lambda_{1,2}$, and the variation of the total energy (10) as a function of the orientation θ corresponding to the trial function (9) for the magnetic field $B = 1$ a.u.

θ (deg)	$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle xz\rangle$	λ_1	λ_2	$\frac{\partial E}{\partial \theta}$
0°	0.5360	0.5360	0.0	-0.5	0.0	0.0
10°	0.5390	0.5299	0.0847	-0.4985	-0.0058	0.0827
30°	0.5612	0.4620	0.1424	-0.4723	-0.0148	0.1703
45°	0.5956	0.4235	0.0975	-0.4110	-0.0155	0.1669
60°	0.6328	0.3962	0.1122	-0.3050	-0.0242	0.1244
80°	0.7175	0.3727	0.0481	-0.1133	-0.0256	0.0412
90°	0.7250	0.3705	0.0	0.0	-0.0262	0.0

eters $\lambda_{1,2}$, with respect to the orientation angle θ for a magnetic field $B = 1$ a.u. (see Fig. 7 and Table V) as obtained with the trial function (9). From these values, we can compute the variation of the total energy of the $1u$ state through Eq. (10). Both expectation values $\langle x^2\rangle$ and $\langle y^2\rangle$ increase/decrease monotonously as a function of the inclination angle. On the other side, the expectation value $\langle xz\rangle$ vanishes in the configurations $\theta = 0^\circ, 90^\circ$ due to the symmetry $z \to -z$. This corroborates the result predicted by the Hellman-Feynman theorem, *i.e.* the variation of the total energy becomes zero only in the configurations of maximal symmetry. The analysis also confirms that the optimal gauge for the parallel configuration $\theta = 0^\circ$ corresponds to the symmetric gauge, while for the perpendicular configuration $\theta = 90^\circ$, the Landau Gauge seems to be more adequate.

6. Conclusions

We found a range of magnetic fields where the $1u$ state of H_2^+ with infinitely massive protons is stable in both ($\theta = 0^\circ$ and 90°) configurations of maximal symmetry. With the improved trial function (6) proposed in this study we found in the parallel configuration a domain of stability for magnetic fields $0 \leq B \lesssim 6.6$ a.u. This range of magnetic fields overlaps with the range of magnetic fields typically present in magnetic white dwarfs. The maximal stability for this state is realized at $B \sim 2$ a.u. Up to magnetic fields $B = 1$ a.u. the first vibrational state remains stable towards dissociation. Additionally, the trial function (6) describes a larger range of stable orientations θ for two representative magnetic fields: $\theta_{cr} \simeq 9^\circ$ for $B = 0.1$ a.u. and $\theta_{cr} \simeq 1^\circ$ for $B = 1$ a.u. From the optimization of the vector potential, we confirm that both gauge parameters $\lambda_{1,2}$ are relevant to obtain the minimal energy in configurations of arbitrary orientation of the magnetic field, despite the fact that λ_2 is relatively small. We confirmed the theoretical predictions by Hellman-Feynman theorem that the energy extrema correspond to the configuration of maximal symmetry: the minimum corresponds to 0° and the maximum corresponds to 90°.

From an astrophysics point of view, the stability of the $1u$ state can be of relevance for the analysis of the spectra of white dwarfs. For example, in the magnetic field $B = 1$ a.u. the energy corresponding to the transition between the two lowest states of H_2^+ is 3.9 eV.

7. Note added in proof

While this manuscript was under consideration the authors performed an analysis for the ground state $1g$ in magnetic fields $0.1\,\text{a.u.} \leq B \leq 1$ a.u., using a linear superposition of three functions of the type (6) and found an improvement in the variational energy (for intermediate angles $0^\circ < \theta < 90^\circ$) which is in excellent agreement with the hindered rotor model approximation (14) used in the reference [28]. It is worth to mention that the agreement between the hindered rotor model and the variational results using the functions of the type (6) is much better in the case of the ground state $1g$. This results will be reported elsewhere.

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i. The well is presumably deeper in presence of a magnetic field [1].

ii. If one assumes that the eigenfunction is a complex function $\psi(\mathbf{r}) = \varrho(\mathbf{r})e^{i\,\varphi(\mathbf{r})}$, where $\varrho(\mathbf{r}) = (\psi_{\rm Re}^2 + \psi_{\rm Im}^2)^{1/2}$, and $\varphi(\mathbf{r}) = \tan^{-1}(\psi_{\rm Im}/\psi_{\rm Re})$, then, by a gauge transformation, we can have a real function by gauging the phase.

iii. Binding energy represents the difference between the total energy of the system and the energy of each component (only the energy of the electron E_e contributes).

iv. The results in Ref. 26 show a very different qualitative behavior. A comparison with those results might be misleading and therefore we prefer not to include them in the Tables.

v. Despite the fact that the studies in [26] present in general lower total energies than the total energies of the present study, they obtained arbitrary inclinations as optimal configurations of minimal total energy for some magnetic fields in contradiction to the Hellman-Feynman theorem. For example, for $B = 0.1$ a.u., they obtained $E_T(0^\circ) = -0.497590$ a.u. at $R_{eq} = 12.38$ a.u. and $E_T(90^\circ) = -0.497602$ a.u. at $R_{eq} = 11.49$ a.u. On the other hand at $B = 10^{10}$ G they found the optimal configuration at $\theta = 30^\circ$.

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