Finite Hydrogenic molecular chain $H_3$ and ion $H_3^+$ exist in a strong magnetic field

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The existence and stability of the linear hydrogenic chain $H_3$ and $H_3^+$ in a strong magnetic field is established. Variational calculations for $H_3$ and $H_3^+$ are carried out in magnetic fields in the range $10^{11} \leq B \leq 10^{13}$ G with 17-parametric (14-parametric for $H_3^+$), physically adequate trial function. Protons are assumed infinitely massive, fixed along the magnetic line. States with total spin projection $S_z = -3/2$ and magnetic quantum numbers $M = -2, -3, -4$ are studied. It is shown that for both $H_3$ and $H_3^+$ the lowest energy state corresponds to $M = -3$ in the whole range of magnetic fields studied. As for a magnetic field $B \geq 10^{11}$ G both $H_3$ and $H_3^+$ exist, they become stable for $B \geq 1.9 \times 10^{11}$ G and for $B \geq 2.7 \times 10^{11}$ G, respectively.

Typical surface magnetic fields $B \sim 10^{11} - 10^{14}$ G exist for many neutron stars, while for magnetized white dwarfs the magnetic field can reach $B \sim 10^9$ G (see e.g. [1, 2]). Among these stars there are many which have atmosphere, which is mostly composed from electrons and protons while some heavy nucleus (e.g. a, O, Ne, C, Fe) can be also present. It is natural to assume that for surface temperatures of order of $10$ eV, electrons and protons can condense into hydrogenic species, forming Hydrogen atoms and Hydrogenic molecular ions.

These enormous magnetic fields modify dramatically the structure of atoms and molecules: as the strength of the magnetic field increases the atoms and molecules become more bound and more compact, their electronic clouds get pronounced cigar-type form and eventually the charged centers are aligned on a magnetic line. The Coulomb systems become quasi-one-dimensional. Such strong magnetic fields eventually lead to the appearance of exotic charged molecular and atomic systems which do not exist without a strong magnetic field (see e.g. [3] and references therein). In particular, the pioneering studies by Ruderman [4] and, independently, by Kadomtsev-Kudryavtsev [5, 6] predicted qualitatively that finite and supposedly even infinite neutral hydrogenic (linear) chains (and Wigner crystals) could exist if magnetic fields are sufficiently strong. In particular, accurate calculations have shown that in addition to the hydrogen atom $H$ and the $H^+_2$ molecular ion, which exist for any magnetic field, at magnetic fields $B \gtrsim 10^{11}$ G three protons situated along the magnetic line can be bound by single electron (!) forming the exotic molecular ion $H_3^{2+}$ in linear configuration [7]. Furthermore, $H_3^{2+}$ turns out to be the most bound one-electron hydrogenic system for magnetic fields $B \gtrsim 10^{11}$ G [8]. This discovery was used later to construct a model of the atmosphere of the isolated neutron star 1E1207.4-5209 (see [8]) to explain the origin of the absorption lines at $\sim 0.7$ and $1.4$ KeV detected by Chandra [9] and confirmed by XMM-Newton [10] X-ray observatories. It predicts the surface magnetic field of $(4 \pm 2) \times 10^{13}$ G.

For systems with two or more electrons it is known that in sufficiently strong magnetic fields the ground state appears in the configuration where all spins of electrons are antiparallel to the magnetic field direction, hence, the total spin takes its maximal value. In field free case the total spin usually does not takes the maximal value. It implies that the ground state type can evolve with magnetic field strength. This phenomenon was quantitatively observed for the first time for $H_2$ molecule, where it was shown that the ground state changes from spin-singlet state $^1\Sigma_g$ at zero and weak magnetic fields to triplet unbound (repulsive) state $^3\Sigma_u$ for intermediate fields $B \gtrsim 5 \times 10^8$ G while for larger magnetic fields $B \gtrsim 3 \times 10^{10}$ G the ground state is the spin-triplet state $^3\Pi_u$ [11]. As for the molecular ion $H_3^+$ in a strong magnetic field in linear parallel configuration (aligned with the magnetic field direction) the ground state of $H_3^+$ changes from spin-singlet $^1\Sigma_g$ state for weak magnetic fields $B \lesssim 5 \times 10^8$ G to a weakly-bound spin-triplet $^3\Sigma_u$ for intermediate fields and, eventually, to spin-triplet state $^3\Pi_u$ for magnetic fields $B \gtrsim 10^{10}$ G. The list of one-, two-electron hydrogenic systems, which can exist in a strong magnetic field being bound and stable, is given in [8, 12].

In general, it is known very little about atomic-molecular systems with three electrons in a strong magnetic field. In particular, the neutral hydrogenic chain $H_3$ was studied in [13] along with finite hydrogenic chains $H_n^+, n=2,3,4...$ in strong magnetic fields $B \geq 10^{11}$ G in sophisticated multiconfigurational Hartree-Fock method. The accuracy obtained was limited, grossly overestimated and in some cases the results were indicated as non-reliable (spurious), the question of the existence and stability was never discussed. We are not aware on any studies of negative hydrogenic molecular ion $H_3^-$. In present Letter the linear molecular chain $H_3$ is studied in a strong magnetic field being situated along a magnetic line (we call it the parallel configuration, see Fig. 1). Magnetic field is assumed strong enough to have minimal total spin projection $S_z = -3/2$, thus, we focus on states with total spin $3/2$, and total magnetic quantum numbers $M = -2, -3, -4$. We explore the magnetic fields $10^{11}$ G $\leq B \leq 10^{13}$ G, where a non-relativistic approach is still valid, see for discussion [13]. The study
is developed in the Born-Oppenheimer approximation of

\[
\mathcal{H} = -\sum_{i=1}^{3} \left( \frac{1}{2} \Delta_i + \sum_{\eta=A,B,C} \frac{Z_\eta}{r_{i\eta}} \right) + \sum_{i=1}^{3} \sum_{j>i}^{3} \frac{1}{r_{ij}} + B^2 \sum_{i=1}^{3} \rho_i^2 + \frac{B}{2} (L_z + 2S_z) + \frac{Z_A}{R_+} + \frac{Z_B}{R_-} + \frac{Z_C}{R_-},
\]

where \(\Delta_i\) is Laplacian for the \(i\)-th electron, \(i = 1, 2, 3\). \(Z_{A,B,C} = 1\) are the charges of the heavy centers, \(\eta = A, B, C\) (protons). The term \(-\frac{Z_\eta}{r_{i\eta}}\) corresponds to the Coulomb attractive potential between the electron \(i\) and the nuclei \(\eta\) with \(r_{i\eta}\) being the electron-nuclei distance. The term \(\frac{1}{r_{ij}}\) stands for the inter-electron repulsion between electrons \(i\) and \(j\), where \(r_{ij}\) is the distance between electrons. In turn, \(\frac{Z_i}{R_+}, \frac{Z_i}{R_-}\) are the classical Coulomb repulsion energy terms between the (fixed) \(A, B, C\) nuclei. The internuclear (classical) distances are \(R_+\) and \(R_-\) (see Fig 1). The Hamiltonian includes the Zeeman terms \(\frac{1}{2} B \cdot L = \frac{1}{2} B L_z\), and \(\frac{1}{2} B \cdot S = B S_z\) (with the g-factor, \(g = 2\)) and the diamagnetic terms \(\frac{\mu_B^2}{\hbar} \rho_i^2\), where \(\rho_i^2 = x_i^2 + y_i^2\), \(i = 1, 2, 3\) is the transverse distance (squared) between the \(i\)-th electron and the molecular axis. Putting \(Z_B = 0\) the Hamiltonian describes the 3-electron 2-center system in a magnetic field which may correspond to \(H_3^-\) molecule.

The equilibrium configuration was assumed symmet-

\[
\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \left( \prod_{k=1}^{3} \rho_k^{m_k} e^{-\alpha_k r_k - \alpha_k r_k - \alpha_k r_k} \right) \times e^{\alpha_{12} r_{12} + \alpha_{13} r_{13} + \alpha_{23} r_{23}},
\]

where \(\rho_k, \phi_k\) are the radial/angular cylindrical coordi-

zero order, i.e. the nuclei are considered to be infinitely

massive. The main goal of the study is to localize the

domain of stability and existence of \(H_3\) in strong mag-

netic fields. The lowest longitudinal vibrational states

around the equilibrium configuration of the ground state

are briefly studied. Similar study of negative hydrogen

molecular ion \(H_3^-\) is also carried.

Atomic units are used throughout (\(\hbar = m_e = e = 1\)).

For the magnetic field \(B\) given in a.u. the conversion \(B_0 = 1\) a.u. = \(2.35 \times 10^6\) G and as for the energy 1 a.u. = \(27.2 eV\) is used.

Generalities. The Hamiltonian describing the Coulomb system of three electrons and three aligned (infinitely) massive charged centers \(A, B, C\) subject to a constant uniform magnetic field, parallel to the molecular axis \(B = B \hat{e}_z\), is given by

\[
R_+ = R_- \equiv R\] it is confirmed by calculations. In this configuration the Hamiltonian is invariant under transformations \(z_1, z_2, z_3 \rightarrow -z_1, z_2, z_3\), and also invariant under rotation around the molecular axis. Thus, the conserved quantities we take into account are: the parity \((\pm)\) w.r.t. to \(z \rightarrow -z\), the \(z\)-component of the total angular momentum \(M_z\) (magnetic quantum number), the total electronic spin \(S\) and its projection \(S_z\) along the \(z\)-axis. These conserved quantities characterize the state of the system in the standard spectroscopic notation \(2S + 1(M_z)\).

The variational method is applied to find the energy of some low-lying states using a trial function based on physics relevance criteria. These trial functions allow us to reproduce both the Coulomb singularities and the correct asymptotic behavior of the potential at large distances (see, e.g. [14]).

Triiai Function. The orbital (spatial) part of the trial function is proposed as a product of nodeless screened Coulomb orbitals, Landau orbitals and exponential correlation factors:
number \(m_k, k = 1, 2, 3\). In turn, the parameters \(\alpha_{bij}, \alpha_{ij}\) with \(i < j = 1, 2, 3\), \(\eta = A, B, C\) are screened effective charges, \(\beta_{1,2,3}\) measure screening of the magnetic field, the classical internuclear distances \(R_{\pm}\) are taken as variational parameters. The total number of variational parameters in \(E\) is 17.

For states of total spin \(S = 3/2\) with projection \(S_z = -3/2\), the spin part of the trial function is \(\chi = \beta(1)\beta(2)\beta(3)\), where \(\beta(k), k = 1, 2, 3\) represents the \(S_z = 1/2\) spinor of the \(k\)-th electron with negative spin projection. Thus, the properly symmetrically total wave function is given by

\[
\Psi(r_1, r_2, r_3) = (1 + \sigma_N \hat{P}_{ac})\hat{A}[\psi(r_1, r_2, r_3)\chi],
\]

where \(\hat{P}_{ac}\) is the operator of permutation of the two end nuclei \(A\) and \(C\) (see Fig.1), and \(\sigma_N = \pm 1\) is z-parity. The operator \(\hat{A}\) is the three particle antisymmetrizer

\[
\hat{A} = 1 - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{231} + \hat{P}_{312},
\]

acting on the coordinates of the electrons. Here \(\hat{P}_{ij}\) is the operator of permutation of the electrons \(i \leftrightarrow j\), and \(\hat{P}_{ijk}\) stands for the permutation of (123) into (ijk).

Numerics for the calculation of the variational energy is described in [12]. Computations were performed in parallel using the cluster Karen (ICN-UNAM) with 120 Intel Xeon processors at \(\sim 2.70\) GHz.

**Results.** Variational calculations of the linear molecule \(H_3\) and \(H_2^+\) in parallel configuration for magnetic fields \(10^{11} G \leq B \leq 10^{13} G\) are carried out assuming the ground state is \(4(-3)^+\) as the first step. Later the states \(4(-4)^+\) and \(4(-2)^+\) were calculated. It was checked that minimal energy for \(H_3\) always corresponds to \(R_+ = R_-\). In Table I the total energy and the equilibrium internuclear distance \(R_{eq}\) are presented. From these results it is seen that both the total energy and the equilibrium internuclear distance of \(H_3\) and \(H_2^+\) decrease monotonously with the magnetic field increase, the systems become more bound and compact. Systematically, the total energies for \(H_3\) are smaller than ones calculated in [13], while equilibrium distances are comparable.

To study stability two main dissociation channels are considered for \(H_3\): (i) \(H_3 \rightarrow H_2 + H\), (ii) \(H_3 \rightarrow H_3^+ + e\) and for \(H_2^+\): (iii) \(H_2^+ \rightarrow H^- + H\) and (iv) \(H_2^+ \rightarrow H_2 + e\), while dissociation energies are defined accordingly,

\[
E_{\text{diss}}^{(i)} = E_{H_2^+ + H} - E_{H_3}, \quad E_{\text{diss}}^{(ii)} = E_{H_3^+ + e} - E_{H_3}
\]

and

\[
E_{\text{diss}}^{(iii)} = E_{H^- + H} - E_{H_2^+}, \quad E_{\text{diss}}^{(iv)} = E_{H_2^+ + e} - E_{H_2^+}.
\]

Note that writing about dissociation channels we ignore the conservation of total angular momentum projection due to possible presence of photon(s) in the final state and assume each of the final products is in the lowest energy state. The energy of a free electron in a magnetic field with \(S_z = -1/2\) is zero (see [12] for details).

For \(B \gtrsim 10^{11}\) G we assume that the molecule \(H_3\) and \(H_2^+\) ion are in linear parallel configuration as optimal and all electron spins are antiparallel to the magnetic field direction, hence, it corresponds to total spin \(3/2\). Thus, we have to find the lowest energy state among the states with different total magnetic quantum number \(M = m_1 + m_2 + m_3\). Among these states there is one with \(M = -3\) when the magnetic quantum numbers of the electrons correspond to Landau orbitals with \(m_1 = 0, m_2 = -1, m_3 = -2\) and, being in agreement to the Pauli principle, it guarantees zero Pauli force. Taking trial function \(E\) with \(m_1 = 0, m_2 = -1, m_3 = -2\) we calculated total energy and equilibrium distance, see Table II. Taking different \(m_i\) with \(M = -3\) in \(E\) does not lead to better energies.

We have carried out similar calculations for the states \(4(-2)^+\) with \(M = -2\) and \(4(-4)^+\) with \(M = -4\). The total energies and the equilibrium distances \(R_+ = R_-\) are also presented in Table I. As well as for the state \(4(-3)^+\), both the total energy and the equilibrium distance for these states decrease as the magnetic field increase. The state with the lowest energy is always realized by the state \(4(-3)^+\), hence this state is the ground state in the whole range of magnetic fields studied. Note that the smallest equilibrium internuclear distance also corresponds to this ground state. Similar analysis was made for \(H_2^+\) where the ground state was also the state \(4(-3)^+\), see Table II.

The stability of the linear molecule \(H_3\) was checked towards longitudinal symmetric vibrations (s), \(R_+ \neq R_-\) and antisymmetric vibrations (a) \(R_+ \neq R_-\). The lowest vibrational energy of the symmetric mode \(E_{\text{vib}}^{(s)}\) are always smaller than those of the antisymmetric mode \(E_{\text{vib}}^{(a)}\). Both energies increase with the magnetic field growth, see Table I. For \(B \gtrsim 5 \times 10^{11}\) G the dissociation energies are always larger than the sum of the lowest vibrational energies, hence, the potential energy surface contains, at least, one vibrational state. As for \(H_2^+\) ion the longitudinal vibrational mode was calculated with similar conclusions: the lowest vibrational energy increases with the magnetic field growth and the potential energy surface contains, at least, one vibrational state.

For \(B \gtrsim 10^{11}\) G the molecule \(H_3\) is always stable towards the dissociation \(H_3^+ + e\), see Table II. However, as for the channel \(H_3 \rightarrow H_2 + H\) there is a critical magnetic field when dissociation energy vanishes

\[
B_c \sim 80 \text{ a.u.} \sim 1.9 \times 10^{11} \text{ G},
\]

see Table I. It indicates that the linear molecular chain \(H_3\) becomes stable at \(B > B_c\) being unstable for smaller magnetic fields.

As for the ion \(H_2^+\) for \(B \gtrsim 10^{11}\) G it is unstable towards both channels (iii) \(H_2^+ \rightarrow H^- + H\) and (iv) \(H_2^+ \rightarrow H_2 + e\). However, at the magnetic field \(B \sim 100\) a.u. the dissociation (iii) gets forbidden while the channel (iv) is still open. With magnetic field increase at

\[
B_c \sim 116 \text{ a.u.} \sim 2.7 \times 10^{11} \text{ G},
\]

(5)
Table I. H$_3$: Total energy $E_T$ and equilibrium distance $R_{eq}$ (= $R_+ = R_-$) for the states $^4(-3)^+$ (ground state) and $^4(-2)^+$, $^4(-4)^+$ vs magnetic field \( B \). Results $^\dagger$ marked by $\dagger$. Lowest longitudinal vibrational energies for symmetrical ($s$) and antisymmetrical ($a$) modes presented.

This channel gets forbidden as well and H$_3^-$ becomes stable.

Conclusions. We have shown that trihydrogen molecule H$_3$ in the form of linear chain exists for \( B \geq 10^{11} \) G with the ground state $^4(-3)^+$ and it becomes stable towards all possible dissociation channels for magnetic fields larger than the critical magnetic field \( B_c \simeq 1.9 \times 10^{11} \) G and remains stable towards small longitudinal vibrations. It excludes a qualitative prediction [4] about existence of infinite hydrogenic chain (and Wigner crystal) for magnetic fields $B < B_c$. For any available strong magnetic field the absorption due dissociation of H$_3$ occurs at less than 100 eV, hence, could not be detected by Chandra or XMM X-ray observatories. Dihydrogen negative molecular ion H$_2^-$ with the ground state $^4(-3)^+$ is stable for \( B_c \simeq 2.7 \times 10^{11} \) G. Both molecular systems can be present in the magnetized neutron star atmosphere at large surface magnetic field but with not very hot surface temperature.

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