Charged Hydrogenic, Helium and Helium-Hydrogenic Molecular Chains in a Strong Magnetic Field

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Abstract

A non-relativistic classification of charged molecular hydrogenic, helium and mixed helium-hydrogenic chains with one or two electrons which can exist in a strong magnetic field $B \lesssim 10^{16}$ G is given. It is shown that for both $1e−2e$ cases at the strongest studied magnetic fields the longest hydrogenic chain contains at most five protons indicating to the existence of the $H_5^{4+}$ and $H_5^{3+}$ ions, respectively. In the case of the helium chains the longest chains can exist at the strongest studied magnetic fields with three and four $\alpha$—particles for $1e−2e$ cases, respectively. For mixed helium-hydrogenic chains the number of heavy centers can reach five for highest magnetic fields studied. In general, for a fixed magnetic field two-electron chains are more bound than one-electron ones.

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I. INTRODUCTION

The behavior of atoms, molecules and ions placed in a strong magnetic field has attracted a significant attention during the last two decades (see, for example, the review papers [1–3]). It is motivated by both pure theoretical interest and by possible practical applications in astrophysics and solid state physics. From the point of theory, such studies would lead to a creation of a theory of atoms and molecules in a magnetic field similar to a standard atomic-molecular physics. In practice, even the basic elements of such a theory - a knowledge of the energy levels of the simplest Coulomb systems which can exist in a magnetic field - can be important for interpretation of the spectra of white dwarfs (where a surface magnetic field ranges in $B \approx 10^6 - 10^9$ G) and neutron stars where a surface magnetic field varies in $B \approx 10^{12} - 10^{13}$ G, and can be even $B \approx 10^{14} - 10^{16}$ G for the case of magnetars.

It was conjectured long ago [4, 5] that unusual chemical compounds can appear in a strong magnetic field. In particular, it was suggested by M Ruderman [5] and then developed by his followers (see [2] and references therein) that the presence of a strong magnetic field can lead to the formation of linear hydrogenic neutral molecules (linear chains) situated along magnetic lines. It was assumed that in the ground state all electrons are in the same spin state with all spins antiparallel to the magnetic field line. To avoid a contradiction with the Pauli principle it was further assumed that all electrons have different magnetic quantum numbers. It was considered as a characteristics of the ground state. It seems obviously correct in the case of atoms and atomic ions where the electrons are close to each other. However, it is not that obvious for the case of molecules where the electrons are situated in far distant places in space. All of them (or, at least, some of them) can be in the same quantum state, with the same spin projection and magnetic quantum number [6]. This situation was observed in H$_2$ [7] and H$_3^+$ [8], where in a domain of large magnetic fields the ground state was given by the state of the maximal total spin but with the electrons having the same zero magnetic quantum number (see a discussion below). In [5] qualitative arguments were presented that such chains can be of any length, thus, can contain arbitrary many protons. It seems that such a picture is oversimplified, it intrinsically assumes that the magnetic field is ”infinitely” strong. For instance, for any exotic chain (which does not exist in field-free case) there must be a certain threshold magnetic field since that it begins to exists. It can well happen that such a threshold magnetic field can be beyond of realistic
magnetic fields which occur in Nature. This phenomenon is absent in the qualitative theory [5]. Thus, some very general features of the Ruderman’s picture only, like growth of the binding energies, shrinking of the size of the molecules with a magnetic field increase and maximal total electronic spin can hold for realistic high magnetic fields.

It is well known that in absence of a magnetic field, in general, the hydrogenic linear chains (polymers) do not exist with the only exception of two shortest ones, \( \text{H}_2^+ \) and \( \text{H}_2 \) [20]. Therefore, for each other chain there must occur a threshold magnetic field from which the chain begins to exist if it is realized. It seems natural to assume that the threshold magnetic field grows with the length of the chain which is defined by a number of heavy particles therein. At the moment, only those \( \text{H}_2^+ \) and \( \text{H}_2 \) - the shortest chains - are studied in details, see e.g. [3] and [7], respectively. The results are far more sophisticated than those predicted in a simple qualitative picture in [5]. For example, the \( \text{H}_2 \)-molecule does not exist at a large domain of strong magnetic fields.

The aim of this article is to perform a detailed quantitative study of Hydrogen, Helium and also mixed, Helium-Hydrogen linear chains with one or two electrons making an emphasis of the domain of magnetic fields \( 10^2 \leq B \leq 10^7 \text{ a.u.} (= 2.35 \times 10^{16} \text{ G}) \). It is shown that in the one electron case depending on the magnetic field strength the hydrogenic systems \( \text{H}_2^+, \text{H}_3^+, \text{H}_4^+ \) and even \( \text{H}_5^+ \) can exist in linear geometry. It is also shown that, as the magnetic field is increased, the exotic helium-hydrogenic chains \( \text{He}_2^+, (\text{HeH})^2+, (\text{HHHe})^3+, (\text{HeHHHe})^4+ \) and \( \text{He}_3^+ \) begin to exist in linear geometry (see for a brief review [6]). For all magnetic fields the system \( \text{H}_2^+ \) is stable when the system \( \text{H}_3^+ \) becomes stable at \( B \gtrsim 10^{13} \text{ G} \). A detailed review of the current status of some one-electron hydrogenic molecular systems, both traditional and exotic, that might exist in a magnetic field \( B \geq 10^9 \text{ G} \) can be found in [3]. For two-electron case depending on the magnetic field strength the hydrogenic chains \( \text{H}_2, \text{H}_3^+, \text{H}_4^2+ \) and at most \( \text{H}_5^3+ \) can exist in linear geometry, as well as the two-electron Helium chains \( \text{He}_2^+, \text{He}_3^+ \) and \( \text{He}_4^6+ \), and the mixed Hydrogen-Helium chains \( (\text{HeH})^+, (\text{H} - \text{He} - \text{H})^2+, (\text{He} - \text{H} - \text{He})^3+, (\text{H} - \text{He} - \text{He} - \text{H})^4+, (\text{He} - \text{H} - \text{He} - \text{H})^4+, (\text{H} - \text{He} - \text{H} - \text{He} - \text{H})^5+ \text{ and } (\text{He} - \text{He} - \text{H} - \text{He} - \text{H})^7+. \)

Since our study is limited to the question of the existence of a particular Coulomb system the main attention is paid to an exploration of the ground state. Overall study is made in framework of non-relativistic consideration by solving the Schroedinger equation. It is also assumed that the Born-Oppenheimer approximation of zero order holds, which implies
that the positions of positively-charged heavy particles are kept fixed (they are assumed to be infinitely-massive). Relativistic corrections are always neglected assuming that the longitudinal motion of electrons is non-relativistic for magnetic field $\lesssim 10^{16}$ G while there are no relativistic corrections to the energies of transverse motion since the spectra of non-relativistic and relativistic harmonic oscillators coincide (we call it ‘the Duncan argument’, for a discussion see [9]). Some preliminary results were announced in [6].

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

II. ONE-ELECTRON HYDROGENIC CHAINS

A. Generalities

Let us consider the electron and $n$ infinitely-massive particles (protons) situated on a line which coincides to the magnetic line (see Fig. 1). We call this system a linear finite chain of the size $n$. If for such a system a bound state can be found it implies the existence of the ion $H_n^{(n-1)+}$ in linear geometry.

$$H_n^{(n-1)+}$$

FIG. 1: $H_n^{(n-1)+}$ linear molecular ion in parallel configuration with a magnetic field $B$ oriented along the $z$-axis.

The Hamiltonian which describes this system when the magnetic field is oriented along the $z$ direction, $B = (0, 0, B)$ is [21]

$$\mathcal{H}_n = (\hat{p} + A)^2 - 2 \sum_{i=1,n} \frac{Z_i}{r_i} + \sum_{i \neq j} \frac{Z_i Z_j}{R_{ij}} + 2B \cdot S ,$$

(see Fig. 1 for the geometrical setting and notations), where $Z_i = Z_j = 1$ in the case of protons, $\hat{p} = -i\nabla$ is the momentum of the electron and $S$ is the operator of the spin, $r_i$ is
the distance from the electron to the $i$th proton and $R_{ij}$ is the distance between the $i$th and $j$th protons. $A$ is a vector potential which corresponds to the constant uniform magnetic field $B$. It is chosen to be in the symmetric gauge,

$$A = \frac{1}{2}(B \times r) = \frac{B}{2}(-y, x, 0).$$

Finally, the Hamiltonian can be written as

$$\mathcal{H}_n = \left(-\nabla^2 + \frac{B^2}{4\rho^2}\right) - 2 \sum_{i=1}^{n} \frac{Z_i}{r_i} + \sum_{i \neq j}^{n} \frac{Z_iZ_j}{R_{ij}} + B(\hat{L}_z + 2\hat{S}_z),$$

where $\hat{L}_z$ and $\hat{S}_z$ are the $z$-components of the total angular momentum and total spin operators, respectively, and $\rho = \sqrt{x^2 + y^2}$. Both $\hat{L}_z$ and $\hat{S}_z$ are integrals of motion. Thus, the operators $\hat{L}_z$ and $\hat{S}_z$ in (3) can be replaced by their eigenvalues $m$ and $m_s$ respectively. Since we are interested by the ground state for which $m = 0$ and $m_s = -1/2$, the last term in (3) can be omitted and the reference point for energy becomes $(-B)$.

In the equilibrium configuration the problem is characterized by two integrals of motion: (i) angular momentum projection $m$ on the magnetic field direction ($z$-direction) and (ii) spatial parity $p$. The problem for parallel symmetric configuration is characterized by the $z$-parity, $P_z(z \rightarrow -z)$ with eigenvalues $\sigma = \pm 1$. One can relate the magnetic quantum number $m$, spatial parity $p$ and $z$-parity $\sigma$,

$$p = \sigma(-1)^{|m|}.$$

In the case $m$ is even, both parities coincide, $p = \sigma$. Thus, any eigenstate has two definite quantum numbers: the magnetic quantum number $m$ and the parity $p$ with respect $\vec{r} \rightarrow -\vec{r}$. Therefore the space of eigenstates is split into subspaces (sectors) each of them is characterized by definite $m$ and $\sigma$, or $m$ and $p$. Notation for the 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, then a Greek letter $\sigma, \pi, \delta$ corresponds to $m = 0, -1, -2$, respectively, with subscript $g/u$ (gerade/ungerade) corresponding positive/negative eigenvalues of spacial parity operator $P$.
B. Method

The variational method is used for a study of the Hamiltonian (3). Trial functions are chosen following the physics relevance arguments [10]. Their explicit expression is a linear superposition of $K$ terms given by

$$\psi_{n,K}^{(\text{trial})} = \sum_{k=1}^{K} A_k \left\{ e^{-\sum_{i=1}^{n} \alpha_{k,i} r_i} \right\} e^{-B\beta_k R^2} ,$$  \hspace{1cm} (4)

(see [3]), where $A_k$ and $\alpha_{k,i},\beta_k$ are linear and non-linear parameters, respectively. Interproton distances $R$ are considered as variational parameters as well. Notation $\{\}$ means the symmetrization of identical nuclei of the expression inside the brackets. Usually, to each term in (4) a certain physical meaning is given. For example, one term had all $\alpha_{k,i}$ at $i = 1, \ldots, n$ equal being an analogue of the Heitler-London wavefunction for the $H^+_2$-ion - describing the coherent interaction of the electron with all protons. For another term all $\alpha_{k,i}$, except for one, vanish being an analogue of the Hund-Mulliken wavefunction - describing the incoherent interaction of the electron with all protons. All other terms are different non-linear superposition of these two being an analogue of Guillemin-Zener wavefunction for the $H^-_2$-ion. We call a term for which all $\alpha_{k,i}$ are different and unconstrained, the general term. Needless to mention that in each particular term in (4) the parameters are chosen in such a way to assure normalizability of this term as the overall function.

Calculations are performed using the minimization package MINUIT from CERN-LIB. Two-dimensional integration is carried out using a dynamical partitioning procedure: a domain of integration is manually divided into subdomains following an integrand profile with a localization of domains of large gradients of the integrand. Each subdomain is integrated (for details, see, e.g., [3]). Numerical integration of subdomains is done with a relative accuracy of $\sim 10^{-9} - 10^{-10}$ by use of the adaptive D01FCF routine from NAG-LIB.

$n = 1$. This case was considered for the sake of completeness. It is known that the hydrogen atom exists for any magnetic field strength. It is the least bound system among one-electron systems. The results for H-atom at $B = 10^6, 10^7$ a.u. are calculated with a ten-parametric variational trial function which is a modification of the function introduced in [10, 11]. It will be described elsewhere.

$n = 2$. The results for $H^+_2$-ion are found with 3-term trial function (4) which depends on the 10 free parameters including the interproton distance $R$, it is a linear superposition of the
Heitler-London, Hund-Mulliken and Guillemin-Zener (general term) wavefunctions. For $B \leq 10^4$ a.u. results are from [3].

$n = 3$. The results for $H_3^{2+}$-ion are found with a 3-term trial function (4) which depends on 22 free parameters including two interproton distances $R$’s, it is a linear superposition of the Heitler-London, Hund-Mulliken and a type of the Guillemin-Zener (general term) wavefunctions. For $B \leq 10^4$ a.u. results are from [3].

$n = 4$. Results for $H_4^{3+}$-ion are found with 1-term trial function (4) which depends on the 7 free parameters including three interproton distances $R$’s two of them are assumed to be equal (symmetric configuration). For $B \leq 10^4$ a.u. the results obtained with 3- and 7-term trial function (4) can be found in [3]. They lead to slightly better binding energies but do not change the qualitative picture.

$n = 5$. It is the first study of this system. The results for the $H_5^{4+}$-ion are obtained using a 2-term trial function (4) which depends on the 15 free parameters including four interproton distances $R$’s, two pairs of them are assumed to be equal (symmetric configuration). In fact, it implies that a linear superposition of two general terms is taken. It is worth noting that already 1-term trial function at $B = 10^7$ a.u. gives a clear indication to the existence of the $H_5^{4+}$-ion with binding energy $E_b = 206.11$ Ry and equilibrium distances $R_1 = 0.053$ a.u., $R_2 = 0.032$ a.u. The smallest magnetic field for which a minimum of the total energy surface in $R$’s was observed is $5 \times 10^6$ a.u. The $H_5^{4+}$-ion for these magnetic fields looks like $H_3^{2+}$-ion bound with a far-distant proton from each side.

$n = 6$. No indication to the existence of the $H_6^{5+}$-ion in the domain $B \leq 10^7$ a.u. is found.

C. Results

The results of the calculations are presented in Tables I-II. Two traditional for field-free case systems $H$ and $H_2^+$ exist for all studied magnetic fields $B \leq 10^7$ a.u. The first exotic molecular system $H_3^{2+}$ appears at $B \sim 10^2$ a.u. and exists for larger magnetic fields. Another exotic molecular system $H_4^{3+}$ appears at $B \sim 10^4$ a.u. and the last exotic molecular system $H_5^{4+}$ appears at $B \sim 5 \times 10^6$ a.u. No other one-electron molecular hydrogenic systems are
seen for $B \leq 10^7$ a.u. For $n > 1$ the optimal geometry of any molecular system is linear and aligned along magnetic field. Thus, such a system forms a finite chain. It is checked that the configuration is stable with respect to small deviations from linearity. All studied finite chains are characterized by two features: with a magnetic field growth (i) their total energies increase and (ii) their lengths decrease - each system becomes more bound and compact.

For all studied magnetic fields the systems H and $H_2^+$ are stable: the H-atom has no decay channels, where the total energy of the $H_2^+$-ion is always less than the total energy of the H-atom. Furthermore, for $B \lesssim 1.5 \times 10^4$ a.u. the $H_2^+$-ion has the smaller total energy then $H_3^{2+}$-ion when exists: these two finite chains are the only ones which exists in this domain. The $H_3^{2+}$-ion never dissociates to $H + 2p$ but it always dissociates to $H_2^+ + p$. For higher magnetic fields $B \gtrsim 1.5 \times 10^4$ a.u. the $H_3^{2+}$-ion becomes stable as well. It is characterized by the smallest total energy for these magnetic fields. Another exotic molecular system $H_4^{3+}$ never dissociates to $H + 3p$, but it dissociates to $H_2^+ + p$ for $10^4 < B < 10^6$ a.u. For magnetic fields $B \gtrsim 10^6$ a.u. the total energy of $H_4^{3+}$ is smaller than $H_2^+$ and the latter dissociation channel does not exist. For all studied magnetic fields $B \leq 10^7$ a.u. the system $H_4^{3+}$ can dissociate to $H_3^{2+}$, although the energy difference between such systems decreases gradually as the magnetic field increases. A smooth extrapolation indicates that at the magnetic $B \sim 2 \times 10^8$ a.u. there is a crossing for which the total energies of $H_3^{2+}$ and $H_4^{3+}$ become equal. The system $H_3^{1+}$ can dissociate to all finite chains except for single proton one: H-atom. Summarizing, one can state that there are two one-electron finite hydrogenic chains characterized by lowest total energy for different magnetic fields: it is the $H_2^+$-system at $0 \lesssim B \lesssim 1.5 \times 10^4$ a.u. and the $H_3^{2+}$-ion at $1.5 \times 10^4 \lesssim B \lesssim 10^7$ a.u.

III. TWO-ELECTRON HYDROGENIC CHAINS

A. Generalities

Let us consider a system of two electrons and $n$ infinitely-massive protons situated on a line which coincides to the magnetic line (see Fig. 2). It is called $2e$-linear finite chain of the size $n$. If for such a system a bound state can be found it implies the existence of the ion $H_n^{(n-2)+}$ in linear geometry. Sometimes, we say that above system is “in the parallel configuration”. Also, it implies that the corresponding finite chain exists. It can be stable
\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
B (a.u.) & 0 & 1 & 10 & 10^2 & 10^4 & 10^6 & 10^7 \\
\hline
\text{System} & \hline
H & 1.0 & 1.662 & 3.495 & 7.564 & 27.10 & 73.96 & 108.86 \\
H_2^+ & 1.2053 & 1.9499 & 4.3498 & 10.291 & 45.799 & 139.91 & 217.75 \\
H_3^{2+} & \_ & \_ & \_ & 8.639 & 45.408 & 160.17 & 263.80 \\
H_4^{3+} & \_ & \_ & \_ & \_ & 34.922 & 142.75 & 251.71 \\
H_5^{4+} & \_ & \_ & \_ & \_ & \_ & \_ & 206.15 \\
\hline
\end{tabular}
\caption{Binding energies (in Ry) for the ground state 1σ_g of the one-electron hydrogenic linear systems (finite chains) in a magnetic field. Binding energies for the ground state 1s_0 of the H-atom at 0 \leq B \leq 10^2 \text{ a.u.} from [11].}
\end{table}

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
B (a.u.) & 0 & 1 & 10 & 10^2 & 10^4 & 10^6 \\
\hline
\text{System} & \hline
H_2^+ (R) & 1.997 & 1.752 & 0.957 & 0.448 & 0.118 & 0.045 \\
H_3^{2+} (R, R) & \_ & \_ & \_ & 0.579, - & 0.130, - & 0.044, - \\
H_4^{3+} (R_1, R_2, R_1) & \_ & \_ & \_ & \_ & 0.214, 0.138, - & 0.056, 0.044, - \\
H_5^{4+} (R_1, R_2, R_2, R_1) & \_ & \_ & \_ & \_ & \_ & 0.053, 0.032, - \\
\hline
\end{tabular}
\caption{Interproton equilibrium distances (in a.u.) for the ground state 1σ_g of the one-electron hydrogenic linear systems (finite chains) in a strong magnetic field. All configurations have center of symmetry, symmetric interproton distances are not displayed.}
\end{table}

The Hamiltonian which describes the system of two electrons and \( n \) protons when the magnetic field is oriented along the \( z \) direction, \( \mathbf{B} = (0, 0, B) \) is [19]
FIG. 2: $H_n^{(n-2)+}$ linear molecular ion in parallel configuration with a magnetic field $B$ oriented along the $z$-axis.

$$H_n = \sum_{\ell=1}^{2} \left( \hat{p}_\ell + A_\ell \right)^2 - 2 \sum_{\ell=1,2} Z_i r_{\ell i} + \frac{2}{r_{12}} + \sum_{i,j=1,n, i \neq j} Z_i Z_j \frac{1}{R_{ij}} + 2B \cdot S ,$$

(see Fig. 2 for the geometrical setting and notations), where $Z_i = Z_j = 1$ in the case of protons, $\hat{p}_\ell = -i \nabla_\ell$ is the momentum of the $\ell$th electron, $r_{\ell i}$ is the distance from the $\ell$th electron to the $i$th proton and $R_{ij}$ is the distance between $i$th and $j$th proton, $r_{12} = |\vec{r}_1 - \vec{r}_2|$ is the interelectron distance, where $\vec{r}_1 (\vec{r}_2)$ is the position from the center of the chain (mid-point with respect to the end-situated protons) of the first (second) electron and $S = S_1 + S_2$ is the operator of the total spin. $A_\ell$ is a vector potential which corresponds to the constant uniform magnetic field $B$ written in the symmetric gauge (2). Finally, the Hamiltonian can be written as

$$H_n = \sum_{\ell=1}^{2} \left( -\nabla_\ell^2 + \frac{B^2}{4 \rho_\ell^2} \right) - 2 \sum_{\ell=1,2} Z_i r_{\ell i} + \frac{2}{r_{12}} + \sum_{i,j=1,n, i \neq j} Z_i Z_j \frac{1}{R_{ij}} + B(\hat{L}_z + 2\hat{S}_z) ,$$

(6)

where $\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2}$ and $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$ are the $z$-components of the total angular momentum and total spin, respectively, and $\rho_\ell = \sqrt{x_\ell^2 + y_\ell^2}$. All performed calculations released a symmetry property of a chain: in the optimal geometry a chain has a center of symmetry. Hence, for any proton there is a partner situated symmetrically with respect to this center. We consider that property as intrinsic of any chain.

The problem under study is characterized by three conserved quantities: (i) the operator of the $z$-component of the total angular momentum (projection of the angular momentum on
the magnetic field direction) giving rise to the magnetic quantum number $m$, (ii) the spatial parity operator $P(\vec{r}_1 \to -\vec{r}_1, \vec{r}_2 \to -\vec{r}_2)$ which has eigenvalues $p = \pm 1$(gerade/ungerade) (iii) the operator of the $z$-component of the total spin (projection of the total spin on the magnetic field direction) giving rise to the total spin projection $m_s$. Hence, any eigenstate has three explicit quantum numbers assigned: the magnetic quantum number $m$, the total spin projection $m_s$ and the parity $p$. For the case of two electrons the total spin projection $m_s$ takes values $0, \pm 1$.

As a magnetic field increases a contribution from the Zeeman term (interaction of spin with magnetic field, $B \cdot S$) becomes more and more important. It seems natural to assume that for small magnetic fields a spin-singlet state is the state of lowest total energy, while for larger magnetic fields it should be a spin-triplet state with $m_s = -1$, where the electron spins are antiparallel to the magnetic field direction $B$. The total space of eigenstates is split into subspaces (sectors), each of them is characterized by definite values of $m$, $p$ and $m_s$. It is worth noting that the Hamiltonian $H_n$ is invariant with respect to reflections $P_z$: $z_1 \to -z_1$ and $z_2 \to -z_2$, with eigenvalues $\sigma_N = \pm 1$, for a symmetric chain.

In order to classify eigenstates we follow the convention widely accepted in molecular physics using the quantum numbers $m, p$ and the total spin $S$ without indication to the value of $m_s$. Eventually, the notation is $2S+1M_p$, where $2S+1$ is the spin multiplicity which is equal to 1 for spin-singlet state ($S = 0$) and 3 for spin-triplet ($S = 1$), as for the label $M$ we use Greek letters $\Sigma, \Pi, \Delta$ that mark the states with $|m| = 0, 1, 2, ..., $ respectively, but implying that $m$ takes negative values and the subscript $p$ (the spatial parity quantum number) takes gerade/ungerade($g/u$) labels describing positive $p = +1$ and negative $p = -1$ parity, respectively. There exists a relation between the quantum numbers corresponding to the $z$-parity and the spatial parity:

$$p = (-1)^{|m|} \sigma_N .$$

Present consideration is limited to the states with magnetic quantum numbers $m = 0, -1$ because the total energy of the lowest energy state in any sector with positive $m > 0$ is always larger than one with $m \leq 0$. A study of states with different $m$ is necessary to identify the state of lowest total energy. At large magnetic fields for all studied two-electron chains this state was characterized by $m = -1$ in agreement with Ruderman’s hypothesis.
B. Method

As a method to explore the problem we use the variational procedure. The recipe of choice of trial functions is based on physical arguments [10]. As a result the trial function for the lowest energy state with magnetic quantum number $m$ is chosen in the form

$$
\psi^{(\text{trial})} = (1 + \sigma_e P_{12}) \rho_1^{[m]} e^{i m \phi_1} \sum_{k=1}^{K} A_k \left\{ e^{-\sum_{l=1,2}^{n} a_{k,l} r_{1,l}} \right\} e^{\gamma_{k,12} - B \beta_{k,1} \rho_{1,2}^2 - B \beta_{k,2} \rho_{2,1}^2} \tag{7}
$$

where $\sigma_e = \pm 1$ stands for spin singlet (+) and triplet states (−), while $\{\}$ means the symmetrization of identical nuclei of the expression inside the brackets. The $P_{12}$ is the permutation operator for the electrons, $(1 \leftrightarrow 2)$. The $\alpha_{k,ij}, \beta_{k,1-2}$ and $\gamma_k$ as well as interproton distances $R_{ij} = R_{ji}$ are variational parameters. For each term with fixed $k$ their total number is $2n + 4$ including the linear parameter $A_k$. In addition, we have $n - 1$ interproton distances. It is worth emphasizing that in the trial function (7) the interelectron interaction is included explicitly in the exponential form $e^{\gamma_{12}}$.

Calculations are performed using the minimization package MINUIT from CERN-LIB. Multidimensional integration is carried out using a dynamical partitioning procedure: a domain of integration is manually divided into subdomains following an integrand profile with a localization of domains of large gradients of the integrand. Each subdomain is integrated separately using parallelization procedure (for details, see, e.g., [3]). Numerical integration of subdomains is done with a relative accuracy of $\sim 10^{-6} - 10^{-7}$ by use of the adaptive D01FCF routine from NAG-LIB. A process of minimization for each given magnetic field and for any particular state was quite time-consuming due to a complicated profile of the total energy surface in the parameter space but when a minimum is found it takes several seconds of CPU time to compute a variational energy.

$n = 1$. This case corresponds to the negative hydrogen ion $H^-$ and is mentioned for the sake of completeness. It is known that the negative hydrogen ion $H^-$ exists for any magnetic field strength [12]. At zero and small magnetic fields $B < 5 \times 10^{-2}$ a.u. the spin-singlet state $^10$ is the ground state. If $B > 5 \times 10^{-2}$ a.u. the spin-triplet state $^3(-1)$ which does not exist in the absence of a magnetic field becomes bound and the ground state. Although this result is checked quantitatively for magnetic fields up to 4000 a.u. [12, 13] it is quite likely that it holds for higher magnetic fields. It is the least bound
TABLE III: Double ionization energies \( E_I \) in Ry (\( E_T = -E_I \)) for the ground state \( ^3\Pi_u \) of the two-electron hydrogenic systems (finite chains) in a strong magnetic field. \(^a\) from [7]. Energy in brackets means that the state \( ^3\Pi_u \) is bound but the ground state corresponds to an unbound state. The magnetic field \( B_{Schwinger} = 4.414 \times 10^{13} \text{ G} = 1.878 \times 10^4 \text{ a.u.} \) corresponds to the so called non-relativistic threshold for which the electron cyclotron energy equals the electron rest mass.

In a domain of non ultra-high magnetic fields the \( \text{H}_2 \)-molecule was studied in details in [7]. It was shown that the lowest total energy state depends on the magnetic field strength. It evolves from the spin-singlet \( ^1\Sigma_g \) state at \( 0 \leq B \lesssim 0.18 \text{ a.u.} \) to a repulsive spin-triplet \( ^3\Sigma_u \) state (unbound state) for \( 0.18 \text{ a.u.} \lesssim B \lesssim 12.3 \text{ a.u.} \) and, finally, to a strongly bound spin-triplet \( ^3\Pi_u \) state. Hence, there exists quite large domain of magnetic fields where the \( \text{H}_2 \)-molecule is unbound being represented by two hydrogen atoms in the same electron spin state but situated at infinite distance from each other. The optimal geometry of the \( \text{H}_2 \)-molecule (when exists) corresponds always to the elongation along a magnetic line for the \( ^1\Sigma_g \) state thus forming a finite chain. It is assumed that the chain in the \( ^3\Pi_u \) state is stable towards the deviation from linearity. This assumption seems well justified from physics point of view at large magnetic fields: any deviation from linearity leads to a sharp increase in total energy due to non-vanishing rotational energy. This chain is stable (when exists) for all studied
| System                  | $B$ (a.u.) | $10^2$ | $10^3$ | $10^4$ | $4.414 \times 10^{13}$ G | $10^6$ | $10^7$ |
|------------------------|-----------|-------|-------|-------|------------------------|-------|-------|
| $H_2$ $(R)$            |           |       |       |       |                        |       |       |
| $H_3^+$ $(R, R)$       |           |       |       |       |                        |       |       |
| $H_4^{2+}$ $(R_1, R_2, R_1)$ |       |       |       |       |                        |       |       |
| $H_5^{3+}$ $(R_1, R_2, R_2, R_1)$ |   |       |       |       |                        |       |       |

TABLE IV: Interproton equilibrium distances (in a.u.) for the ground state $^3\Pi_u$ of the two-electron hydrogenic linear systems (finite chains) in a strong magnetic field. All configurations have center of symmetry and symmetric interproton distances are not displayed. * from [7]. Distances in brackets mean that the state $^3\Pi_u$ is bound but the ground state corresponds to an unbound state.
magnetic fields. However, this chain always has the total energy higher than the H$_3^+$ chain (see below) and thus less preferable energetically. Calculations for the $^3\Pi_u$ state of H$_2$ using a single function of the form (7) for which all $\alpha$ parameters are different (general term) are presented in Tables III-IV.

**n = 3.** In [8] it is shown that the H$_3^+$ molecular ion exists in a magnetic field as a bound state. For $B \gtrsim 0.2$ a.u. the ground state geometry is realized in the linear, parallel to the magnetic field line configuration. Thus, the three-proton finite chain occurs. In the domain $0.2 \lesssim B \lesssim 20$ a.u. the ground state is realized by $^3\Sigma_u$ state and it is weakly bound. However, at $B > 20$ a.u. the ground state $^3\Pi_u$ state is strongly bound and the chain is stable.

**n = 4.** In field-free case the system (4p2e) does not display any binding. However, for magnetic fields $B \gtrsim 2000$ a.u. it becomes bound in the linear configuration aligned along the magnetic line with the $^3\Pi_u$ state as the ground state. Hence, the molecular ion H$_4^{2+}$ begins to exist. Its total energy is lower systematically than the total energy of H$_3^+$. Hence, the molecular ion H$_4^{2+}$ is stable. With an increase of the magnetic field strength, the total energy at the equilibrium position decreases, the system becomes more bound (in this case, the double ionization energy is $E_I = -E_T$, it increases with $B$) and more compact (the internuclear equilibrium distance decreases with $B$). Eventually, we state that the finite chain H$_4^{2+}$ is always stable. For magnetic fields $1 \lesssim B \lesssim 2000$ a.u. the state $^3\Pi_u$ is bound but the ground state corresponds to an unbound system in the repulsive $^3\Sigma_u$ state: It consists of two H$_2^+$ ions at infinite distance from each other.

**n = 5.** In field-free case the system (5p2e) does not display any binding. However, for magnetic fields $B \gtrsim 5000$ a.u. it becomes bound in the linear configuration aligned along the magnetic line with the $^3\Pi_u$ state as the ground state; hence, the molecular ion H$_5^{3+}$ begins to exist. For $5000 \lesssim B \lesssim 10^6$ a.u. the H$_5^{3+}$ molecular ion decays to H$_4^{2+} + \text{p}$. At magnetic fields $B \gtrsim 10^6$ a.u. the molecular ion H$_5^{3+}$ becomes stable.

**n = 6.** It is not found an indication to the bound state of the (6p2e)-system even for the highest magnetic field studied.
C. Results

The results of the calculations are presented in Tables III-IV. Three traditional for
the field-free case systems $\text{H}^{-}$, $\text{H}_{2}$ and $\text{H}_{3}^{+}$ continue to exist at magnetic fields $10^{2}\text{a.u.} \leq B \leq 10^{7}\text{a.u.}$. The first exotic molecular system $\text{H}_{4}^{2+}$ appears at $\sim 2 \times 10^{3}\text{a.u.}$ in linear
configuration and exists for all larger magnetic fields. Another exotic molecular system $\text{H}_{5}^{3+}$
appears at slightly larger magnetic field $\sim 5 \times 10^{3}\text{a.u.}$ No other two-electron molecular
hydrogenic system is seen in the domain $B \leq 10^{7}\text{a.u.}$ At large magnetic fields the ground
state of all studied systems is the spin-triplet state with spin projection $m_{s} = -1$ and total
magnetic quantum number $m = -1$ in agreement with Ruderman hypothesis. For $n > 1$
the optimal geometry of the molecular system is linear, and the system is aligned along
magnetic field. Thus, each molecular system forms a finite chain. It is checked that such a
linear configuration is stable with respect to small vibrations and its vibrational energies can
be calculated. However, we were not able to check stability of the configuration with respect
to small deviations from linearity and to calculate the rotational energies. All studied finite
chains are characterized by two features: with a magnetic field growth (i) their binding
energies increase and (ii) their longitudinal lengths decrease - each system becomes more
bound and compact. For all studied magnetic fields $B \gtrsim 10^{2}\text{a.u.}$ the systems $\text{H}^{-}$ and
$\text{H}_{2}$ are stable. They are characterized by much smaller binding energies in comparison with
other systems. Thus, their significance for a thermodynamics at a fixed magnetic field seems
limited.

It is worth emphasizing that among two-electron hydrogenic finite chains the system $\text{H}_{3}^{+}$
has the lowest total energy in the domain $10^{2} \lesssim B \lesssim 2 \times 10^{3}\text{a.u.}$, at larger magnetic fields
$2 \times 10^{3} \lesssim B \lesssim 10^{6}\text{a.u.}$ the finite chain $\text{H}_{4}^{2+}$ gets the lowest total energy and, eventually, at
$B \gtrsim 10^{6}\text{a.u.}$ the molecular ion $\text{H}_{5}^{3+}$ (the longest hydrogenic chain) is characterized by the
lowest total energy. Interestingly, in the domain $10^{6} \lesssim B \lesssim 10^{7}\text{a.u.}$ all two-electron finite
Hydrogen chains are stable.
IV. ONE-ELECTRON HELIUM AND HELIUM-HYDROGEN CHAINS

A. Generalities

Let us consider now molecular systems composed of one electron and a finite number $n$ of infinitely-massive protons and/or $\alpha$-particles as charged centers, situated on a line which coincides to the direction of an homogeneous magnetic field. The geometrical arrangement is similar to that depicted in Figure 1, except for the fact that charged centers can be either protons or $\alpha$ particles. If found, bound states of such systems are called one-electron helium or helium-hydrogen chains. In the present review only one-electron helium or helium-hydrogen chains with $n = 1, 2, 3$ were included.

Following similar considerations as for the case of hydrogenic chains (see section II), the Hamiltonian which describes the one-electron helium (helium-hydrogen) chains in a magnetic field oriented along the $z$ direction, $\mathbf{B} = (0, 0, B)$ is given by the Hamiltonian (3) with $Z_i, Z_j = 1$ or 2, depending on each particular system. Since we are interested by the ground state for which $m = 0$ and $m_s = -1/2$, the last term in (3) can be omitted and the reference point for energy becomes equal to $(-B)$.

B. Method

The variational method is used for a study of the helium (helium-hydrogen) chains described by the Hamiltonian (3). Trial functions are chosen following physics relevance arguments [10]. Their explicit expressions are linear superpositions of $K$ terms given by functions of the class (4), where $A_k$ and $\alpha_k, \beta_k$ are linear and non-linear parameters, respectively. Internuclear distances $R$ are considered as variational parameters as well. In this case the notation $\{\}$ in (4) means the symmetrization of the expression inside the brackets with respect to the permutations of the identical charged centers (for example for the system $(\text{HHeH})^{3+}$ it means permutation with respect to the external protons. As for the case of hydrogenic chains, each term in (4) has a certain physical meaning (see section II). In the following we describe the different chains studied.

$n = 1. (\alpha e)$. This case corresponds to the simplest one electron helium system. It is known that the positive atomic ion of helium exists for any magnetic field strength. Fur-
Thermore, it is the only one electron helium system which exists for magnetic fields of strength $B \lesssim 10$ a.u. The results presented below for the ground state $1s_0$ of the He$^+$ atomic ion (see Table V) were obtained with a seven-parametric variational trial function introduced in [11] for a study of the H-atom.

$n = 2$. (i) ($\alpha\alpha\alpha\epsilon$). Accurate variational calculations in equilibrium configuration (parallel to the magnetic field) for the ground state $1\sigma_g$ of the system He$_2^{3+}$ were carried out in details in [3, 17] for the range of magnetic fields $10^2 \lesssim B \lesssim B_{\text{Schwinger}}$. A 3-term trial function of the form (4) which depends on ten free parameters including the internuclear distance $R$ is used in the calculations. It is the same linear superposition of the Heitler-London, Hund-Mulliken and Guillemin-Zener wavefunctions which was used to study the H$_2^+$ molecular ion (see section II above). It is found that for magnetic fields $10^2 \lesssim B \lesssim 10^3$ a.u. the system He$_2^{3+}$ is unstable towards the decay to He$^+ + \alpha$. Nonetheless, at $B \gtrsim 10^4$ a.u. this compound becomes the system with the lowest total energy among the one electron helium (helium-hydrogen) chains. In [17] lowest vibrational and rotational energies for this system were also calculated.

(ii) ($\alpha\rho\epsilon$). The first indication about the existence of the hybrid system (HeH)$_2^{2+}$, for magnetic fields $B \gtrsim 10^4$ a.u., was established in [3, 17], where accurate variational calculations for the ground state $1\sigma$ of the system (HeH)$_2^{2+}$ were carried out. Variational calculations are done with a 3-term trial function of the type (4). In [3, 17] it was also demonstrated that the equilibrium configuration corresponds to the situation when the molecular axis (the line connecting the proton and the $\alpha$ particle) is parallel to the magnetic field. For the narrow range of magnetic fields $10^4$ a.u. $\lesssim B \lesssim B_{\text{Schwinger}}$ the system (HeH)$_2^{2+}$ is found to be a long-living metastable state decaying to He$^+ + p$. For magnetic fields larger than $B_{\text{Schwinger}}$ the system becomes stable towards the decay to He$^+ + p$.

$n = 3$. (i) ($\alpha\alpha\alpha\epsilon\epsilon$). It seems it is for the first time we see an indication to the possible existence of the exotic molecular ion He$_3^{5+}$ for magnetic fields $B \gtrsim 10^6$ a.u. For this system a 3-term trial function of the form (4) is used for its variational study. It depends on 22 free parameters including two internuclear distances $R_{1,2}$. This function is the same linear superposition of the Heitler-London, Hund-Mulliken
and a type of the Guillemin-Zener wavefunctions which was used to study the H$_3^{2+}$ molecular ion (see section II above). It is found that the system (αααe) begins to exist as a bound state (i.e. displays a minimum in the corresponding potential energy surface for finite internuclear distances) at magnetic fields $B \gtrsim 10^6$ a.u. in the linear symmetric configuration (for which the two internuclear distances are equal, $R_1 = R_2$) parallel to the magnetic field direction. Ground state is 1σ$_g$.

(ii) (pαpe). First indications on the existence of the exotic trilinear molecular ion (H – He – H)$^{3+}$ for magnetic fields $B \gtrsim B_{\text{Schwinger}}$, were given in [3, 17]. For this system a 3-term trial function of the form (4) which depends on 14 free parameters including two $R_{1,2}$ is used in the variational calculations. The results clearly show the appearance of a minimum in the potential energy surface of the (αppe) system for the symmetric configuration of the charged centers ($p – α – p$) with $R_1 = R_2$. Ground state is the type 1σ$_g$. It was not seen an indication to the existence of non-symmetric configuration ($α – p – p$).

(iii) (αpαe). First indications on the existence of the exotic trilinear molecular ion (He – H – He)$^{4+}$ for magnetic fields $B \gtrsim B_{\text{Schwinger}}$ were given in [3, 17]. For this system a 3-term trial function (4) which depends on 14 free parameters including two internuclear distances $R_1, R_2$ is used in the variational calculations. The results show the appearance of a minimum in the potential energy surface of the (ααpe) system for the symmetric configuration of the charged centers ($α – p – α$) with $R_1 = R_2$. Ground state is 1σ$_g$. It was not seen an indication to the existence of non-symmetric configuration ($α – α – p$).

n = 4. No binding is detected for systems (ααααe), (αppαe), (pααpe) even for the highest studied magnetic field $\sim 10^7$ a.u.

C. Results

The results of the ground state calculations are presented in Tables V-VI. The positive atomic ion of helium He$^+$ is the only system which exists for all studied magnetic fields $0 \leq B \leq 10^7$ a.u. At $B \sim 10^2$ a.u. the first exotic molecular system He$_2^{3+}$ appears being unstable towards decay to He$^+ + α$ in the range of magnetic fields $10^2$ a.u. $\lesssim B \lesssim 2 \times 10^4$ a.u.
For larger magnetic fields \( B \gtrsim 2 \times 10^4 \text{a.u.} \) the system \( \text{He}_2^{3+} \) becomes the most bound one-electron system among the systems made out from protons and/or \( \alpha \)-particles and it is stable. Two exotic molecular systems begin to exist at about the same magnetic field \( B \sim 10^4 \text{a.u.} \). Namely, the hybrid molecular ion \((\text{HeH})^{2+}\), followed by the trilinear symmetric molecular system \((\text{H} - \text{He} - \text{H})^{3+}\), being unstable towards decay to \( \text{He}^+ + p \) and \( \text{He}^+ + 2p \), respectively. Remarkably, the system \((\text{HeH})^{2+}\) rapidly becomes stable for magnetic fields \( B \gtrsim 2 \times 10^4 \text{a.u.} \). The system \((\text{H} - \text{He} - \text{H})^{3+}\) becomes more bound than \( \text{He}^+ \) for magnetic fields \( B \gtrsim 5 \times 10^5 \text{a.u.} \) but remains unstable towards decay to \((\text{HeH})^{2+} + p\) in the range of magnetic fields \( 5 \times 10^5 \lesssim B \leq 10^7 \text{a.u.} \). It never dissociates to \( \text{H}_2^+ + \alpha \). Another exotic symmetric molecular system \((\text{He} - \text{H} - \text{He})^{4+}\) appears at \( B \sim B_{\text{Schwinger}} \), being unstable towards decay to \((\text{HeH})^{2+} + \alpha\) for magnetic fields \( B_{\text{Schwinger}} \lesssim B \lesssim 6.5 \times 10^6 \text{a.u.} \), as well as towards decay to \( \text{He}_2^{3+} + p \) for all magnetic fields studied. It is worth noting that, in spite of the greater Coulomb repulsion, the system \((\text{He} - \text{H} - \text{He})^{4+}\) becomes more bound than \((\text{H} - \text{He} - \text{H})^{3+}\) for magnetic fields \( B \gtrsim 1.8 \times 10^6 \text{a.u.} \). The last exotic molecular system \( \text{He}_3^{5+} \) appears at \( B \gtrsim 10^6 \text{a.u.} \). This system is unstable with respect to decay into \( \text{He}_2^{3+} + \alpha \). Present level of available computational resources does allow to draw a reliable conclusion about this molecular system at larger magnetic fields. No more one-electron helium-hydrogenic system is seen for the range of magnetic fields studied \( B \leq 10^7 \text{a.u.} \).

Concrete variational calculations for the chains \( \text{He}_2^{3+} \) and \((\text{HeH})^{2+}\) demonstrate that the optimal geometry of the molecular systems is linear and aligned along magnetic field, being stable with respect to small deviations from linearity. This is understood with simple arguments since any slight deviation from the magnetic field direction leads to a large increase in the rotational energy. So, it is natural to assume that all other studied linear chains are also stable with respect to small deviations from linearity.

All studied finite chains are characterized by two features: with a magnetic field growth (i) their total energies increase and (ii) their equilibrium size decreases - each system becomes more bound and compact.

Summarizing, one can state that among the one-electron helium-hydrogen chains there are two helium systems characterized by the lowest total energy for different magnetic fields: it is the \( \text{He}^+ \) ion at \( 0 \lesssim B \lesssim 2 \times 10^3 \text{a.u.} \) and the \( \text{He}_2^{3+}\)-chain at \( 2 \times 10^3 \lesssim B \lesssim 10^7 \text{a.u.} \).
| $B$ (a.u.) | $1$ | $10$ | $10^2$ | $10^4$ | $4.414 \times 10^{13}$ G | $10^6$ | $10^7$ |
|------------|-----|------|--------|--------|----------------------|-------|-------|
| He$^+$     | 4.8820 | 8.7801 | 19.109 | 78.426 | 92.528 | 226.66 | 345.17 |
| He$^3_2^+$ | – – | 16.516 | 86.233 | 105.121 | 305.11 | 507.31 |
| He$^5_3^+$ | – – – | – | – | 227.83 | 417.15 |
| (HeH)$^{2+}$ | – – – | 77.303 | 92.858 | 251.32 | 402.10 |
| (HHeH)$^{3+}$ | – – – | 64.747 | 79.69 | 233.71 | 392.47 |
| (HeHHe)$^{4+}$ | – – – – | 70.76 | 230.38 | 408.58 |

TABLE V: Binding energies (in Ry) for the ground state $1\sigma_g$ of the one-electron helium and helium-hydrogenic linear systems (finite chains) in a magnetic field (the ground state for (HeH)$^{2+}$ is $1\sigma$). For He$^{5+}_3$: $E_b = 86.76$ Ry, $R_{eq} = 0.202$ a.u. at $B = 10^{14}$ G, while for $B_{Schwinger}$ there is no minimum.

V. TWO-ELECTRON HELIUM AND HELIUM-HYDROGEN CHAINS

A. Generalities

Let us consider systems of two electrons and $n$ infinitely-massive $\alpha$-particles situated on a line which coincides to the magnetic line. If a bound state is found the system is called $2e$-linear Helium chain of the length $n$ indicating the existence of the ion He$^{(2n-2)+}_n$ in linear geometry.

The Hamiltonian which describes systems of two electrons and a number of $\alpha$ particles with a magnetic field oriented along the $z$ direction, $\mathbf{B} = (0, 0, B)$ is given by the Hamiltonian (6) with $Z_i = Z_j = 2$.

All performed calculations show that in the optimal geometry the chain possesses a symmetry property similar to two-electron hydrogenic chains: for any $\alpha$-particle there is a partner situated symmetrically with respect to the center of the chain.

Another type of systems we study are mixed ones: out of $n$ heavy centers some of them have the charge two ($\alpha$-particles) and some have the charge one (protons). If a bound state
TABLE VI: Internuclear equilibrium distances (in a.u.) for the ground state $1\sigma_g$ of the one-electron helium and helium-hydrogenic linear systems (finite chains) in a strong magnetic field (the ground state for $(\text{HeH})^2^+$ is $1\sigma$). For all configurations which have center of symmetry, symmetric internuclear distances are not displayed.

is found the system is called $2e$-linear Helium-Hydrogen chain of the length $n$.

B. Method

For these systems we follow similar consideration as for the case of two-electron hydrogenic chains. The variational procedure is used to explore the problem. Physical relevance arguments are followed to choose the trial function (see, e.g. [10]) which is given by the function (7).

$n = 1. \ (\alpha ee)$

This case is only mentioned for the sake of completeness. It is known that the helium atom exists for any magnetic field strength [14]. At zero field and as well as for small magnetic fields $B \lesssim 0.75$ a.u. the spin-singlet state $1^10^+$ is the ground state. For $B \gtrsim 0.75$ a.u. the spin-triplet state $1^3(−1)^+$ becomes the ground state. Neutral Helium atom is the least bound system among two-electron Coulomb systems made from $\alpha$-particles.

$n = 2. \ (i) \ (\alpha\alpha ee)$
| $B \, (\text{a.u.})$ System | $10^2$ | $10^3$ | $10^4$ | $4.414 \times 10^{13} \, \text{G}$ | $10^5$ | $10^6$ | $10^7$ |
|------------------------|-------|-------|-------|------------------|-------|-------|-------|
| He                    | 25.65 | 54.37 | 106.4 | 126.0            | 191.4 | 319.7 | 494.3 |
| He$_{2}^{2+}$         | 33.98 | 80.49 | 174.51| 212.14           | 343.47| 616.68| 1016.75|
| He$_{3}^{4+}$         | 26.58 | 68.93 | 163.90| 202.60           | 352.50| 684.19| 1212.40|
| He$_{4}^{6+}$         | –     | –     | –     | –               | 272.07| 576.85| 1089.89|
| HeH$^{+}$             | 28.36 | 64.24 | 133.49| 160.50           | 253.22| 440.24| 709.65 |
| (H – He – H)$_{2}^{2+}$| –     | –     | 142.40| 172.58           | 279.39| 509.99| 843.38 |
| (He – H – He)$_{3}^{3+}$| –     | –     | 153.62| 190.22           | 320.63| 603.91| 1029.95|
| (H – He – He – H)$_{4}^{4+}$| –     | –     | –     | –               | 275.00| 585.00| 979.10 |
| (He – H – H – He)$_{4}^{4+}$| –     | –     | –     | –               | 223.00| 510.40| 885.20 |

TABLE VII: Double ionization energies $E_{I}$ in Ry for the ground state $^3\Pi_u$ of the two-electron helium and helium-hydrogenic linear systems (finite chains) in a strong magnetic field (the ground state for (HeH)$^{+}$ is $^3\Pi$).

The He$_{2}^{2+}$-molecule was studied in details in [15] in a magnetic field $B = 0 – 4.414 \times 10^{13} \, \text{G}$. It was shown that the lowest total energy state depends on the magnetic field strength. Similarly to the case of $ppee$, it evolves from the spin-singlet $^1\Sigma_g$ metastable state at $0 \leq B \lesssim 0.85 \, \text{a.u.}$ to a repulsive spin-triplet $^3\Sigma_u$ state (unbound state) for $0.85 \, \text{a.u.} \lesssim B \lesssim 1100 \, \text{a.u.}$ and, finally, to a strongly bound spin-triplet $^3\Pi_u$ state. Hence, there exists quite large domain of magnetic fields where the He$_{2}^{2+}$-molecule is unbound being represented by two atomic helium ions in the same electron spin state but situated at the infinite distance from each other. The optimal geometry of the He$_{2}^{2+}$-molecule (when exists) corresponds always to the elongation along a magnetic line forming a finite chain. It is assumed that the chain in the $^3\Pi_u$ state is stable towards the deviation from linearity. This chain is stable (or metastable) for all studied
| $B$ (a.u.) | $10^2$ | $10^3$ | $10^4$ | $4.414 \times 10^{13}$ G | $10^5$ | $10^6$ | $10^7$ |
|------------|--------|--------|--------|----------------------|--------|--------|--------|
| He$_2^{2+}$ ($R$) | 0.463  | 0.212  | 0.106  | 0.0902               | 0.060  | 0.0353 | 0.023  |
| He$_3^{4+}$ ($R, R$) | 0.67, - | 0.27, - | 0.122, - | 0.116, -           | 0.063, - | 0.0358, - | 0.023, - |
| He$_4^{6+}$ ($R_1, R_2, R_1$) | -      | -      | -      | 0.089, 0.060, -    | 0.047, 0.037, - | 0.030, 0.023, - |
| HeH$^+$      | 0.440  | 0.203  | 0.104  | 0.092               | 0.0585 | 0.0356 | 0.0238 |
| (H – He – H)$_2^{2+}$ ($R_1, R_1$) | -      | -      | 0.105, - | 0.092, -           | 0.059, - | 0.035, - | 0.022, - |
| (He – H – He)$_3^{3+}$ ($R_1, R_1$) | -      | -      | 0.095, - | 0.081, -           | 0.051, - | 0.030, - | 0.018, - |
| (H – He – He – H)$_4^{4+}$ ($R_1, R_2, R_1$) | -      | -      | -      | 0.07, 0.10, -      | 0.047, 0.030, - | 0.027, 0.015, - |
| (He – H – H – He)$_4^{4+}$ ($R_1, R_2, R_1$) | -      | -      | -      | 0.08, 0.12, -     | 0.041, 0.025, - | 0.025, 0.019, - |

TABLE VIII: Internuclear equilibrium distances (in a.u.) for the ground state $^3\Pi_u$ of the two-electron helium linear systems (finite chains) in a strong magnetic field (the ground state for (HeH)$_2^+$ is the $^3\Pi$ state). All configurations (except for (HeH)$_2^+$) have center of symmetry and symmetric interproton distances are not displayed.

magnetic fields. However, this chain has the total energy higher than the He$_3^{4+}$ chain (see below) for $B \gtrsim 3 \times 10^4$ a.u. and thus less preferable energetically.

(ii) (apee)

It is the simplest 2e mixed helium-hydrogen system. A detailed study of the low-lying electronic states $^1\Sigma, ^3\Sigma, ^3\Pi, ^3\Delta$ of the HeH$^+$ ion was carried out in [16]. The ground state evolves from the spin-singlet $^1\Sigma$ state for small magnetic fields $B \lesssim 0.5$ a.u. to the spin-triplet $^3\Sigma$ (unbound or weakly bound) state for intermediate fields and to the spin-triplet strongly bound $^3\Pi$ state for $B \gtrsim 15$ a.u. When the HeH$^+$ molecular ion exists, it is stable with respect to a dissociation. In the domain $B \gtrsim 15$ a.u. the optimal geometry is linear and parallel: the ion is elongated along a magnetic line. Hence, the chain is formed. With a magnetic field increase the chain gets more bound and more compact. At magnetic fields
$B < 10^4 \text{a.u.}$ the double ionization energy $E_I$ of the HeH$^+$ ion is smaller but comparable with one of the He$_2^{2+}$ ion. However, for $B > 10^4 \text{a.u.}$ $E_I$ gets, in fact, the smallest value among $2e$ Helium-contained molecular ions.

$n = 3$. (i) $(\alpha\alpha\alphaee)$

In field-free case the system $(\alpha\alpha\alphaee)$ does not display any binding. However, for magnetic fields $B \gtrsim 100$ a.u. the He$_3^{4+}$-molecule becomes bound in the linear configuration aligned along the magnetic line. For $100$ a.u. $\lesssim B \lesssim 1000$ a.u. the $^3\Sigma_u$ state is the ground state [18]. This state is a metastable state for any magnetic field, its total energy lies above the total energies of its lowest dissociation channel. For $B \gtrsim 1000$ a.u. the state $^3\Pi_u$ is the ground state. For magnetic fields $1000$ a.u. $\lesssim B \lesssim 3 \times 10^4$ a.u. the total energy of the dominant dissociation channel He$_3^{4+} \rightarrow$ He$_2^{2+}(^3\Pi_u) + \alpha$ is lower than the total energy of the He$_3^{4+}$ ion in the $^3\Pi_u$ state. Thus, in this range of magnetic fields, the ion He$_3^{4+}(^3\Pi_u)$ is a metastable state towards the lowest channel of decay. Hence, for magnetic fields $B \gtrsim 3 \times 10^4$ a.u. the molecular ion He$_3^{4+}$ ion in the $^3\Pi_u$-state is stable. With an increase of the magnetic field strength, the total energy at the equilibrium position decreases, the system becomes more bound (in this case, the double ionization energy is $E_I = -E_T$, it increases with $B$) and more compact (the internuclear equilibrium distance decreases with $B$).

(ii) $(p\alpha pee)$

In field-free case the system $(p\alpha pee)$ does not display any binding. However, for magnetic fields $B \gtrsim 10^4$ a.u. the $(\text{H} - \text{He} - \text{H})^{2+}$-ion becomes bound in the linear configuration aligned along the magnetic line with the $^3\Pi_u$ state as the ground state. This ion is stable.

(iii) $(\alpha p\alpha ee)$

In field-free case the system $(\alpha p\alpha ee)$ does not display any binding. However, for magnetic fields $B \gtrsim 10^4$ a.u. the $(\text{He} - \text{H} - \text{He})^{3+}$-ion becomes bound in the linear configuration aligned along the magnetic line with the $^3\Pi_u$ state as the ground state. This ion is unstable towards a decay to He$_2^{2+}(^3\Pi_u) + p$, however, at $B > 10^6$ a.u. the ion $(\text{He} - \text{H} - \text{He})^{3+}$ becomes stable.
(i) \( (4\alpha 2e) \)

In field-free case the system \((4\alpha 2e)\) does not display any binding. However, for magnetic fields \(B \gtrsim 10^5\) a.u. the He\(_{4}^{6+}\)-molecule becomes bound in the linear configuration aligned along the magnetic line with the \(^3\Pi_u\) state as the ground state. With an increase of the magnetic field strength, the total energy at the equilibrium position decreases, the system becomes more bound (in this case, the double ionization energy is \(E_I = -E_T\), it increases with \(B\)) and more compact (the internuclear equilibrium distance decreases with \(B\)). For magnetic fields \(B \gtrsim 10^5\) a.u. the total energy of the dominant dissociation channel \(\text{He}_3^{4+}(^3\Pi_u) + \alpha\) is lower than the total energy of the \(\text{He}_4^{6+}(^3\Pi_u)\) ion. Thus, the ion \(\text{He}_4^{6+}(^3\Pi_u)\) is a metastable state toward the lowest channel of decay. It is also unstable towards decay to \(\text{He}_2^{2+}(^3\Pi_u) + 2\alpha\) for magnetic fields \(10^5 \lesssim B \lesssim 2 \times 10^6\) a.u.

(ii) \( (p\alpha\alpha p2e) \)

In field-free case the system \((p\alpha\alpha p2e)\) does not display any binding. However, for magnetic fields \(B > 10^5\) a.u. the \((\text{H} - \text{He} - \text{He} - \text{H})^{4+}\)-molecule becomes bound in the linear configuration aligned along the magnetic line with the \(^3\Pi_u\) state as the ground state. With an increase of the magnetic field strength, the system becomes more bound (the double ionization energy increases with \(B\)) and more compact, i.e. both, the internuclear equilibrium distance \(R_1\) between a proton and the closest \(\alpha\) particle, and the distance \(R_2\) between the two \(\alpha\) particles, decrease with \(B\). For magnetic fields \(B \gtrsim 10^5\) a.u. the total energy of the dominant dissociation channel \(\text{He}_2^{2+}(^3\Pi_u) + 2p\) is lower than the total energy of the \((\text{H} - \text{He} - \text{He} - \text{H})^{4+}\) ion. Thus, the ion \((\text{H} - \text{He} - \text{He} - \text{H})^{4+}\) is a metastable state toward the lowest channel of decay.

(iii) \( (\alpha p\alpha 2e) \)

In field-free case the system \((\alpha p\alpha 2e)\) does not display any binding. However, for magnetic fields \(B > 10^5\) a.u. the \((\text{He} - \text{H} - \text{He})^{4+}\)-molecular ion becomes bound in the linear configuration aligned along the magnetic line with the \(^3\Pi_u\) state as the ground state. With an increase of the magnetic field strength, the system becomes more bound (the double ionization energy increases with \(B\)) and more compact, i.e. both, the internuclear equilibrium distance \(R_1\) between a
proton and the closest α particle, and the distance $R_2$ between the two protons, decrease with $B$. For magnetic fields $B \gtrsim 10^5$ a.u. the total energy of the dominant dissociation channel $\text{He}_2^{2+}(3\Pi_u) + 2p$ is lower than the total energy of the $(\text{He} - \text{H} - \text{H} - \text{He})^{4+}$-molecular ion, thus being a metastable state toward the lowest channel of decay.

$n = 5$. The results of the analysis of 5-center, 2-electron systems is shown in Table IX. It is not found an indication to binding of the proton-free systems ($5\alpha 2e$) for the whole domain of studied magnetic fields, while ($4\alpha p 2e$) gets bound at $B \sim 10^7$ a.u. being unstable decaying towards many different finite chains. The system ($3\alpha 2p 2e$) is unbound although a particular configuration ($\alpha p \alpha p 2e$) displays a minimum in the potential curve. The two α-contained system are bound in both symmetric configuration - ($p\alpha p \alpha p 2e$) and ($a\alpha p p \alpha p 2e$) - while the latter one is more bound even for magnetic field $B \sim 10^6$ a.u. This system is unstable with dominant decay mode to ($\alpha p \alpha 2e$). One α-contained system ($p p \alpha p p 2e$) is bound at $\sim 10^7$ a.u. and it is stable(!). It is worth noting that the system $5p 2e$ is bound for magnetic fields $B \gtrsim 10^4$ a.u. (see Table III and a discussion on p.15).

$n = 6$. It is not found an indication to the bound state of any 6-center system even for the highest magnetic field studied.

C. Results

The results of the calculations are presented in Tables VII-IX. Three traditional systems He, $\text{He}_2^{2+}$ and $\text{HeH}^+$ exist for all studied magnetic fields $10^2 \leq B \leq 10^7$ a.u. The first exotic molecular system $\text{He}_3^{4+}$ appears at $\sim 100$ a.u. in linear configuration and exists for larger magnetic fields. For $100 \lesssim B \lesssim 5 \times 10^4$ a.u. the $\text{He}_3^{4+}$ ground state is a metastable state with respect to its lowest dissociation channel. For magnetic fields $B > 5 \times 10^4$ a.u. the ground state of the system $\text{He}_3^{4+}$ becomes a strongly bound state. Another exotic molecular system $\text{He}_4^{6+}$ appears at $\sim 10^5$ a.u. as a metastable state. No other two-electron molecular helium systems are seen for $B \leq 10^7$ a.u. At large magnetic field the ground state of all studied systems is the spin-triplet state with spin projection $m_s = -1$ and total magnetic quantum number $m = -1$. For $n > 1$ the optimal geometry of the molecular system is linear, and the
| Composition | Configuration | \( E_T = -E_I \) (Ry) |
|-------------|---------------|----------------------|
| \( 1-\alpha \ 4-p \) | H-H-He-H-H | Unbound \quad \text{Bound} \quad \sim -450 \quad -866.0 \quad (R_1 = 0.0228, R_2 = 0.0203 \text{ a.u.}) |
| \( 2-\alpha \ 3-p \) | He-H-H-He | Bound \quad \text{Bound} \quad -414.5 \quad -792.6 |
| \quad | H-He-H-He-H | Bound \quad \text{Bound} \quad -485.3 \quad -873.9 \quad (R_1 = 0.0306, R_2 = 0.0189 \text{ a.u.}) |
| \( 3-\alpha \ 2-p \) | He-H-He-H-He | Unbound \quad \text{“Bound”} \quad \sim -420 \quad -860.0 \quad (R_1 = 0.023, R_2 = 0.018 \text{ a.u.}) |
| \quad | H-He-He-He-H | Unbound \quad \text{Unbound} \quad \sim -620 \quad \sim -1055 |
| \( 4-\alpha \ 1-p \) | He-He-He-He-He | Unbound \quad \text{Bound} \quad \sim -380 \quad -862.4 \quad (R_1 = 0.0356, R_2 = 0.0195 \text{ a.u.}) |

**TABLE IX:** 2-electron 5-center molecular ions (finite chains) in a magnetic field in \( ^3\Pi_u \) state - symmetric, spin-triplet configuration parallel to the magnetic field direction. \( E_T, E_I \) is total and double ionization energy, respectively. For unbound states a characteristic total energy indicated.
system is aligned along magnetic field. Thus, each molecular system forms a finite chain. It is checked that such a linear configuration is stable with respect to small vibrations and its vibrational energies can be calculated. However, we were not able to check stability of the configuration with respect to small deviations from linearity and to calculate the rotational energies. All studied finite chains are characterized by two features: with a magnetic field growth (i) their binding energies increase and (ii) their longitudinal lengths decrease - each system becomes more bound and compact.

It is worth noting that among two-electron helium finite chains the system $\text{He}_2^{2+}$ in triplet $^3\Pi_u$ state has the lowest total energy in the domain $10^2 \lesssim B \lesssim 3 \times 10^4$ a.u., whereas at larger magnetic fields $3 \times 10^4 \lesssim B \lesssim 10^7$ a.u. the finite chain $\text{He}_3^{4+}$ in triplet $^3\Pi_u$ state acquires the lowest total energy. In the domain $2 \times 10^6 \lesssim B \lesssim 10^7$ a.u. all studied two electron finite helium chains become stable with the only exception of $\text{He}_4^{6+}$.

**Conclusions**

A complete non-relativistic classification of one-two electron finite molecular chains (polymers) made out of protons/$\alpha$–particles in a strong magnetic field is presented. It is naturally assumed that the ground state of any one-electron chain is $1\sigma_g$ (or $1\sigma$ for non-symmetric systems), while for any two-electron chain is spin-triplet $^3\Pi_u$ (or $^3\Pi$ for non-symmetric systems). All calculations were carried out in variational methods with state-of-the-art trial functions. Protons and $\alpha$–particles are assumed to be infinitely-massive and situated along a magnetic line.

It is clearly seen the existence of three magnetic field thresholds [22],

$$B_t^{(1)} \sim 10^2 a.u., \quad B_t^{(2)} \sim 10^4 a.u., \quad B_t^{(3)} \sim 10^6 a.u.$$  

At magnetic fields $B \lesssim 10^2$ a.u. the only traditional ions, atoms and molecules may exist, the chains are not well-pronounced, they are very short containing at most two heavy particles. However, at $10^2 < B < 10^4$ a.u. several new exotic ions appear in addition to traditional ones. All ions immediately form strongly bound linear chains aligned along a magnetic field. At $B \sim 10^4$ a.u. several more new exotic ions appear quickly forming linear chains. Then similar appearance of new exotic ions happens at $B \sim 10^6$ a.u. It is quite interesting that the ions which already appeared (existed) below some magnetic field threshold, above of the

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threshold they become stable. It is worth noting that for fixed magnetic field the neutral systems are always the least bound ones.

Concluding we present a list of 1-2e proton-oparticle contained ions for which a certain magnetic fields exist where they are stable,

\[
\begin{align*}
H, H_2^+, H_3^{2+}, He^+, He_2^{3+}, (HeH)^{2+}, \\
H^-, H_2, H_3^+, H_4^{2+}, H_5^{3+}, He, He_2^+, He_3^{4+}, (HeH)^+, (HHeH)^{2+}, (HeHHe)^{3+}, (HHHeHH)^{4+},
\end{align*}
\]

among the 25 Coulomb 1-2e systems which (can) exist in a magnetic field (see Tables I-IX).

All presented results are obtained in non-relativistic way with an assumption that masses of heavy particles are infinite. They can be considered as an indication to a new atom-molecular physics in magnetic fields \( B \gtrsim 10^2 \) a.u. It encourages us to an exploration of finite mass effects in a magnetic field. This issue looks quite complicated technically due to absence of a separation of variables, especially, in the case of more than two particles and non-zero total charge of the system. Those two cases are exactly ones which are the most important from the point of view of obtained results: the most bound systems contain usually more than two bodies and charged. Another important issue is related to relativistic corrections to our non-relativistic results. Although in our understanding the Duncan qualitative argument [9] sounds physically, it needs to be checked quantitatively. Present authors plan to study both issues in near future.

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