The $^2\text{He}_2^{2+}$ molecular ion can exist in a magnetic field

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Abstract

A detailed study of the ground state of the Coulomb system ($\alpha\alpha ee$) which corresponds to the $^2\text{He}_2^{2+}$ molecular ion in a magnetic field $B = 0 - 4.414 \times 10^{13}$ G in parallel configuration (infinitely massive $\alpha$-particles are situated along a magnetic field line) is presented. The variational method is employed using a trial function which includes electronic correlation in the form $\exp(\gamma r_{12})$ where $\gamma$ is a variational parameter. It is shown that the quantum numbers of the lowest total energy state depend on the magnetic field strength. It evolves from the spin-singlet $^1\Sigma_g$ metastable state at $0 \leq B \lesssim 0.85$ a.u. to a repulsive spin-triplet $^3\Sigma_u$ state for $0.85 \lesssim B \lesssim 1100$ a.u. and, finally, to a strongly bound spin-triplet $^3\Pi_u$ state at stronger fields $B \gtrsim 1100$ a.u.

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I. INTRODUCTION

It is well-known that very strong magnetic fields may appear on the surface of white dwarfs, $B \approx 10^6 - 10^9$ G and neutron stars, $B \approx 10^{11} - 10^{13}$ G (for latter case they can be even stronger). It seems natural to expect that in a vicinity of the surface atomic and molecular systems can occur. For many years this assumption motivates a development of atomic-molecular physics in a strong magnetic field since it might lead to understanding of the spectra of these compact stars.

So far, a major attention was paid to a study of one-electron atomic and molecular systems (for a review see e.g. [1]). During the last years it was predicted the existence of many exotic, strongly bound one-electron molecular system. In turn, two-electron systems had explored very little being mostly focused to a study of atomic-type systems $H^-, He$ with the only exception of the $H_2$ molecule (see [8], [9] and references therein). Just recently, a first detailed study of the molecular ion $H_3^+$ was carried out [2]. It manifested quite surprising evolution of the ground state as a magnetic field increases. A goal of the present paper is to make a first study of the Coulomb system ($\alpha \alpha e e$) in a magnetic field and establish the existence of the molecular ion $He_2^{2+}$ and its excited states. It is worth mentioning that the molecular ion $He_2^{2+}$ exists in metastable state in field-free case (see e.g. [3]) being characterized by a well-pronounced potential well at a finite internuclear distance.

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

II. GENERALITIES

Let us consider the Coulomb system ($\alpha \alpha e e$) placed in a uniform constant magnetic field. We assume that the $\alpha$–particles are infinitely massive (Born-Oppenheimer approximation of zero order). They are situated along the magnetic field line (parallel configuration). The Hamiltonian which describes this system when the magnetic field is oriented along the $z$ direction, $B = (0, 0, B)$ is written as follows

$$\mathcal{H} = \sum_{\ell=1}^{2} \left( \hat{\mathbf{p}}_\ell + \mathbf{A}_\ell \right)^2 - \sum_{\kappa=\Lambda,B} \frac{4}{r_{1,\kappa}} + \frac{2}{r_{12}} - \frac{8}{R} + 2B \cdot \mathbf{S},$$

(1)
where  \( \hat{p}_\ell = -i \nabla_\ell \) is the 3-vector of the momentum of the \( \ell \)-th electron, the index \( \kappa \) runs over the \( \alpha \)-particles \( A \) and \( B \), \( r_{12} \) is the interelectron distance and \( S = \hat{s}_1 + \hat{s}_2 \) is the operator of the total spin. \( A_\ell \) is a vector potential which corresponds to the constant uniform magnetic field \( B \) chosen in the symmetric gauge,

\[
A_\ell = \frac{1}{2} (B \times r_\ell) = \frac{B}{2} (-y_\ell, x_\ell, 0) .
\]  

(2)

After substitution of (2) to (1) we arrive at the Hamiltonian in the form

\[
\mathcal{H} = \sum_{\ell=1}^{2} \left(-\nabla^2_\ell + \frac{B^2}{4} \rho^2_\ell\right) - \sum_{\ell,\kappa} \frac{4}{r_{\ell\kappa}} + \frac{2}{r_{12}} + \frac{8}{R} + B(\hat{L}_z + 2\hat{S}_z) ,
\]

(3)

where \( \hat{L}_z = \hat{l}_z + \hat{l}_z \) and \( \hat{S}_z = \hat{s}_z_1 + \hat{s}_z_2 \) are the z-components of the total angular momentum and total spin, respectively. The variable \( \rho_\ell = \sqrt{x^2_\ell + y^2_\ell} \) is the distance from \( \ell \)-th electron to \( z \)-axis.

The problem under study is characterized by three integrals of motion: (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 spin quantum number \( m_s \). Hence, to any eigenstate three explicit quantum numbers can be assigned: the magnetic quantum number \( m \), the parity \( p \) and the spin quantum number \( m_s \). Therefore, the space of eigenstates is split into subspaces (sectors) with each of them being characterized by definite values of \( m \), \( p \) and \( m_s \). It is worth noting the Hamiltonian \( \mathcal{H} \) is also invariant with respect to \( z_1 \to -z_1 \) and \( z_2 \to -z_2 \) (\( z \)-parity operator \( P_z \)) with quantum numbers \( \sigma_N = \pm 1 \) for positive/negative \( z \)-parity (this symmetry accounts for the interchange of the nuclei \( A \) and \( B \)).

Thus, to classify eigenstates we follow the convention widely accepted in molecular physics using the quantum numbers \( m, S \) and \( p \). In particular, the notation is \( 2S+1M_p \), where \( 2S + 1 \) is the spin multiplicity and corresponds to 1 for singlet \( (S = 0) \) and 3 for triplet \( (S = 1) \), for the label \( M \) Greek letters \( \Sigma, \Pi, \Delta \) are used that correspond to the states with \( |m| = 0, 1, 2, ..., \) respectively, and the subscript \( p \) (the spatial parity quantum number) will take gerade/ungerade(\( g/u \)) labels describing positive \( p = +1 \) and negative \( p = -1 \) parity states. However, there exists a relation between the quantum numbers corresponding to the
$z$-parity (interchange of nuclei A and B) and the spatial parity:

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

We restrict our consideration to the states with $m = 0, -1, -2$ because the ground state of a sector with $m > 0$ always has larger total energy than those with $m \leq 0$.

As a method to explore the problem the variational procedure is used. The recipe of choice of trial functions is based on arguments of physical relevance (see e.g. [5]). Eventually, a trial function for the state with magnetic quantum number $m$ is chosen in a form

$$\psi^{(\text{trial})} = (1 + \sigma_e P_{12})(1 + \sigma_N P_{AB}) \rho^m e^{im\phi_1} e^{-\alpha_1 r_{1A} - \alpha_2 r_{1B} - \alpha_3 r_{2A} - \alpha_4 r_{2B} + \gamma r_{12} - B \beta_1 \rho_1^2/4 - B \beta_2 \rho_2^2/4},$$

where $\sigma_e = 1, -1$ stands for spin singlet ($S = 0$) and triplet states ($S = 1$), respectively, when $\sigma_N = 1, -1$ stands for nuclear gerade and ungerade states, respectively. The $P_{12}$ is the operator which interchanges electrons (1 ↔ 2) and $P_{AB}$ is the operator which interchanges the two nuclei A and B. The parameters $\alpha_{1-4}, \beta_{1-2}$ and $\gamma$ are variational parameters. If the internuclear distance $R$ is taken into account as a variational parameter the trial function (4) depends on eight parameters.

Calculations were performed using the minimization package MINUIT from CERN-LIB. Multidimensional integration was carried out using a dynamical partitioning procedure: the domain of integration was divided into subdomains following an integrand profile and then each subdomain was integrated separately (for details see e.g. [2]). Numerical integration was done with a relative accuracy of $\sim 10^{-6} - 10^{-7}$ by use of the adaptive D01FCF routine from NAG-LIB. Computations were performed on a dual DELL PC with two Xeon processors of 2.8 GHz each (ICN), 54-node FENOMEC and 32-node TOCHITL clusters (UNAM) and DUKE dual DELL PC with two Xeon processors of 3.06 GHz each (CINVESTAV).
TABLE I: Total $E_T$, double ionization $E_I$ energies (in Ry) and equilibrium distance (in a.u.) of the $He_2^{2+}$ ion in the state $^1\Sigma_g$. Magnetic fields for which $He_2^{2+}$ does not exist (see text) are marked by (*). Total energy $E_T(He^+(1s_0) + He^+(1s_0))$ (in Ry) for zeroing total electron spin projection from [2] is shown for a comparison.

| B(a.u.) | $E_T$   | $E_I$   | $R_{eq}$ | $2E_T(He^+(1s_0))$ |
|--------|---------|---------|----------|-------------------|
| 0      | -7.353  | 1.334   | -8.0     |                   |
|        | -7.363$^a$ | 1.33$^a$ |          |                   |
| 1(*)   | -7.137  | 9.137   | 1.278    | -7.764            |
| 10(*)  | 2.628   | 17.372  | 0.841    | 2.440             |
| 100(*) | 159.08  | 40.92   | 0.393    | 161.78            |
| 1000(*)| 1905.83 | 94.17   | 0.202    | 1919.20           |
| 10000  | 19799.3 | 200.7   | 0.094    | 19843.2           |

$^a$See Ref.[10]

III. RESULTS

It is known that in field-free case the $He_2^{2+}$ molecular ion exists in the state $^1\Sigma_g$ ($S = 0$, $\sigma_N = 1$ and $m = 0$) as a metastable state - it decays to $He^+ + He^+$ (see e.g. [10]). A natural goal is to check the existence of bound state of the system ($\alpha\alpha e e$) in parallel configuration in presence of the magnetic field ranging $B = 0 - 4.414 \times 10^{13}$ G. To carry out such a study the trial function (4) with $\sigma_e = 1$, $\sigma_N = 1$ and $m = 0$ is used, which depends on 8 variational parameters. The calculations indicate clearly the existence of a minimum in the total energy curve $E_T(R)$ for all magnetic fields $B \geq 0$. The concrete results for the $^1\Sigma_g$ state are presented in Table I. This state is a short-lived state for weak magnetic fields where its total energy curve lies above the total energy in the dissociation channel to two separate helium ions $E_T(He^+(1s_0) + He^+(1s_0))$, for which the spins of electrons in both $He^+$ are antiparallel to the magnetic field direction. In general, as the magnetic field strength grows, the total energy increases, the system becomes more bound - the double ionization energy $E_I = 2B - E_T$ increases and more compact (the internuclear equilibrium distance decreases).

As a next step a detailed study for the $^3\Sigma_u$ ($S = 1$, $\sigma_N = -1, m = 0$) state of the $He_2^{2+}$
molecular ion in parallel configuration in the domain of magnetic fields $0 \leq B \leq 4.414 \times 10^{13}$ G is carried out. For this state the variational trial function (4) is characterized by $\sigma_e = -1, \sigma_N = -1$ and $m = 0$, it depends on 8 variational parameters.

The performed variational calculations do not indicate to any minimum in the total energy curve $E_T(R)$ of the $(\alpha\alpha ee)$ system at finite internuclear distances for magnetic fields ranging $B = 0 - 4.414 \times 10^{13}$ G. Thus, the state $^3\Sigma_u$ is a repulsive state for all the range of studied magnetic fields, $0 \leq B \leq 4.414 \times 10^{13}$ G. One can state that this system ”exists” in a form of two Helium ions $He^+$ situated at infinitely large distance from each other.

However, it can be seen that at $B \approx 0.85$ a.u. the crossing occurs of the total energy curve at the equilibrium internuclear distance for the $^1\Sigma_g$ state and the (repulsive) total energy curve of the $^3\Sigma_u$ state. It means that the $He_2^{2+}$ molecular ion exists in the $^1\Sigma_g$ as a metastable state for $0 \leq B \leq 0.85$ a.u. However, for $0 \geq B \leq 0.85$ a.u. the $He_2^{2+}$ ion ceases to exist as a compact system characterized by a finite internuclear distance. But it does exist in a form of two separate Helium ions $He^+$ with each of them in $1s$ state with parallel electron spins. As an illustration we present on Fig.1-3 the plots of total energies of the $^1\Sigma_g$ and $^3\Sigma_u$ states for magnetic fields 0, 0.5 a.u. and 10 a.u.

As a next step the state $^3\Pi_u$ ($S = 1, \sigma_N = 1, m = -1$) of the $(\alpha\alpha ee)$ system in parallel

FIG. 1: $B = 0$: total energies of the $^1\Sigma_g (S = 0, \text{ground state})$ and $^3\Sigma_u (S = 1)$ states vs. the internuclear distance $R$. $^1\Sigma_g (S = 0)$ decays to two $He^+$ ions, their total energies are shown by dashed line.
configuration is studied in the domain of magnetic fields $2 \times 10^9 G \leq B \leq 4.414 \times 10^{13} G$. For this state the variational trial function (4) with $\sigma_e = -1$, $\sigma_N = 1$ and $m = -1$ depends on 8 variational parameters. Obtained results (see Table II) indicate to the existence of a clear minimum in the total energy curve $E_T(R)$ for magnetic fields $B \geq 10$ a.u. With an increase of the magnetic field strength the total energy at equilibrium position decreases, the system becomes more bound (in this case double ionization energy is equal to $E_I = -E_T$ and it grows) and more compact (the internuclear equilibrium distance decreases). Also, for magnetic fields $B \geq 10$ a.u. there exists at least one longitudinal vibrational state (see Table II). Table II also shows the total energies of the dissociation channels $(\alpha\alpha ee) \rightarrow He^+(1s_0) + He^+(2p_{-1})$, $(\alpha\alpha ee) \rightarrow He_2^{3+}(1\sigma_g) + e$ and $(\alpha\alpha ee) \rightarrow He(3(-1)^{-1}) + \alpha$ for different magnetic fields.

In Table II the total energy of two Helium ions $E_T(2) = 2E_T(He^+(1s_0))$ is shown in the case of parallel spins of electrons. This energy also corresponds to the lowest total energy of the $3\Sigma_u$ state (see above). The lowest total energies of the $3\Pi_u$ and $3\Sigma_u$ states cross at $B \approx 1100$ a.u. At larger magnetic fields the lowest total energy of the system $(\alpha\alpha ee)$ in the $3\Pi_u$ state is lower than the lowest total energy of the $3\Sigma_u$ state (which correspond to the separate ions $He^+$). Hence, the system $(\alpha\alpha ee)$ corresponds to the molecular ion
FIG. 3: $B = 10$: total energies of the $^1\Sigma_g (S = 0)$ and $^3\Sigma_u (S = 1,$ "ground state") states vs. the internuclear distance $R$. $^1\Sigma_g (S = 0)$ decays to two $He^+$ ions, their total energies for different total electronic spins are shown by dashed lines.

$He^2_2$ at $B \gtrsim 1100$ a.u. One can draw a conclusion that the molecular ion $He^2_2$ exists at $B \gtrsim 1100$ a.u. It is a stable system where its ground state is given by the $^3\Pi_u$ state. At smaller magnetic fields $0.85$ a.u. $\lesssim B \lesssim 1100$ a.u. the lowest total energy of the system $(\alpha\alpha ee)$ corresponds to the state $^3\Sigma_u$ at the infinite equilibrium distance. It means that the system $(\alpha\alpha ee)$ does not form a bound state, it does "exist" in a form of two separate Helium ions $He^+$.

If the system $(\alpha\alpha ee)$ can be kept externally in the $^3\Pi_u$ state, one can check a stability of the system towards dissociation channels. A comparison of the total energy of $(\alpha\alpha ee)$ in the $^3\Pi_u$ state and the total energy of the (dominant) channel of decay $(\alpha\alpha ee) \rightarrow He^+(1s_0) + He^+(2p_{-1})$ indicates that the $(\alpha\alpha ee)$ system in the $^3\Pi_u$ state becomes stable with respect to the possible channels of decay for $B \gtrsim 100$ a.u. The dissociation energy increases monotonously with a magnetic field growth.

To complete a study of the existence of the $He^2_2$ ion we carried out calculations of the energy for the state $^3\Delta_g (S = 1, \sigma_N = 1, m = -2)$ of the system $(\alpha\alpha ee)$ in parallel configuration in the domain of magnetic fields $1$ a.u. $\leq B \leq 4.414 \times 10^{13}$ G. For this state
TABLE II: The state $^3\Pi_u$: total $E_T$, lowest longitudinal vibrational $E_{vib}$ energies (in Ry) and equilibrium distance $R_{eq}$ (in a.u.) of the $He_2^{2+}$ ion as a function of the magnetic field. Magnetic fields for which $He_2^{2+}$ does not exist (see text) are marked by ($^*$). Total energy of two Helium ions $He^+(1s_0) + He^+(2p_{-1})$ with electron spins antiparallel to magnetic field (from [2]) is denoted as $E_T(1)$, also the total energy of two Helium ions both in $1s$-state, $He^+(1s_0)$ each of them with electron spin antiparallel to magnetic field from [2] is denoted as $E_T(2)$ for comparison as well as total energy of the system $He_2^{3+}(1\sigma_g) + e$ from [2]. Total energy $E_T(He(*)$) for He atom in $3(-1)^{-1}$-state was taken from [7].

| B(a.u.) | $E_T$    | $R_{eq}$ | $E_{vib}$ | $E_T(1)$ | $E_T(He^{3+}(1\sigma_g) + e)$ | $E_T(He(*))$ | $E_T(2)$ |
|--------|----------|----------|-----------|----------|--------------------------------|----------------|----------|
| $10^1$ | -13.7694 | 1.100    | 0.03      | -14.018  | -11.67895                      | -17.560        |          |
| $100^1$| -33.983  | 0.463    | 0.12      | -31.843  | -16.516                        | -26.210        | -38.217  |
| $1000^1$| -80.492  | 0.212    | 0.40      | -69.150  | -39.268                        | -80.801        |          |
| 10000  | -174.51  | 0.106    | 1.16      | -137.26  | -86.23                         | -156.86        |          |
|        | $B = 4.414 \times 10^{13}$ G | -212.14 | 0.0902    | 1.69     | -162.84                        | -105.121       | -185.06  |

TABLE III: The state $^3\Delta_g$: total energy $E_T$ in Ry and equilibrium distance $R_{eq}$ in a.u. of the $He_2^{2+}$ ion. Magnetic fields for which $He_2^{2+}$ does not exist (see text) are marked by ($^*$).

| B(a.u.) | $E_T$    | $R_{eq}$ |
|--------|----------|----------|
| $10^1$ | -12.3118 | 1.278    |
| $100^1$| -30.607  | 0.517    |
| $1000^1$| -73.125  | 0.230    |
| 10000  | -160.64  | 0.113    |
|        | $B = 4.414 \times 10^{13}$ G | -195.87 | 0.099 |

the variational trial function (4) is used with $\sigma_e = -1$, $\sigma_N = 1$ and $m = -2$, it depends on 8 variational parameters.

There exists a clear minimum in the total energy surface $E_T(R)$ of ($\alpha aee$) for magnetic fields $B \geq 10$ a.u. It is found that with an increase of the magnetic field strength the total energies decrease, the system becomes more bound (double ionization energies increase, $E_I = -E_T$, for triplet states) and more compact (the internuclear equilibrium distance decreases) (see Table III). At $B \approx 7000$ a.u. the crossing between the total energy curves of the $^3\Sigma_u$ and $^3\Delta_g$ state occurs. The $^3\Delta_g$ state becomes the lowest-lying excited state for $B \geq 7000$ a.u. until the Schwinger limit.
IV. CONCLUSION

The existence of the $He^{2+}_2$ molecular ion and its low-lying excited states in a magnetic field ranging from zero to $4.414 \times 10^{13}$ G in parallel configuration are studied in the Born-Oppenheimer approximation using the variational method. It is found that the quantum numbers of the state of lowest total energy depend on the magnetic field strength. The ground state evolves from the spin-singlet $^1\Sigma_g$ state which is a metastable state for weak magnetic fields $B \lesssim 0.85$ a.u. to the unbound (repulsive) spin-triplet $^3\Sigma_u$ for intermediate fields $0.85 \lesssim B \lesssim 1100$ a.u. and eventually to a strongly bound spin-triplet $^3\Pi_u$ state for strong magnetic fields $B \gtrsim 1100$ a.u. It manifests the existence of the stable $He^{2+}_2$ molecular ion at $B \gtrsim 1100$ a.u.

In the domain $1100 \lesssim B \lesssim 7000$ a.u. where the state $^3\Pi_u$ becomes the ground state, the lowest-lying excited state is the repulsive $^3\Sigma_u$ state. The next excited state is the ”bound” $^3\Delta_g$ state (having a clear minimum in the total energy curve) lies above the $^3\Sigma_u$ state. One can state that the $He^{2+}_2$ molecular ion does not have excited states in a traditional sense in this domain of magnetic fields. At larger magnetic fields $B \gtrsim 7000$ a.u. up to the Schwinger limit the lowest-lying excited state is $^3\Delta_g$, while the next excited state is the repulsive $^3\Sigma_u$ state.

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