

H_3^{++} MOLECULAR IONS CAN EXIST IN STRONG MAGNETIC FIELDS

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Submitted 6 May 1999

Using a variational method it is shown that for magnetic fields $B > 10^{11}$ G there can exist a molecular ion H_3^{++} .

PACS: 31.10.+z, 31.15.Pf, 32.60.+i, 97.10.Ld

Many years ago the formation of unusual chemical compounds in the presence of a strong magnetic field whose existence is impossible without strong magnetic fields was predicted by Kadomtsev and Kudryavtsev [1] and Ruderman [2] (for a recent advances and a review, see, for example, [3, 4] and references therein). In particular, using a semi-classical analysis it was shown that the influence of the strong magnetic field leads to the appearance of linear molecules (linear chains) situated along magnetic lines. The transverse size of such systems should be of the order of the cyclotron radius $\hat{\rho} \sim B^{-1/2}$ (a.u.), while the longitudinal size remains of a molecular (atomic) order. These systems are called needle-like. An important consequence of such a quasi-one-dimensionality of Coulombic systems is the possibility of effectively compensating the Coulombic repulsion of nuclei.

The goal of this Letter is to present the first quantitative study of the molecular ion H_3^{++} in a strong magnetic field which provides theoretical evidence that such a system can exist in magnetic field $B > 10^{11}$ G. Our study is limited to an exploration of the ground state. Throughout the present work it is assumed that the Born–Oppenheimer approximation holds which implies that the positions of protons are fixed. Exactly as for H_2^+ the configuration we consider corresponds to the case when the three protons are aligned with the magnetic field (linear chain, see above). Spin effects (linear Zeeman effect) are neglected. The magnetic field ranges from 0 up to 10^{13} G, where it is assumed that a contribution of relativistic corrections can still be neglected (for a discussion see, for instance, [4] and references therein). Finally, it is also demonstrated that the molecular ion H_2^+ is the most bound one-electron molecular system in a constant magnetic field.

The present calculation is carried out in the framework of a variational method using a *unique* simple trial function equally applicable to any value of the magnetic field strength. Very recently [5], this strategy was successfully applied to study the ground state of the molecular ion H_2^+ and a simple 10-parameter trial function allowed one to get the best (lowest) values of the ground state energy for magnetic fields from 0 up to 10^{13} G (except $B = 0$, where the relative accuracy was about 10^{-5} in comparison with the best calculations). It turned out that it was not only the best calculation in the region of accessible magnetic fields $0 - 10^{13}$ G but the only calculation which tackled the problem using a single approach. Since the key point of a successful study is a wise choice of trial

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functions, we give a detailed description of how to choose trial functions adequate to the problem in hand.

A constructive criterion for an adequate choice of trial function was formulated in [6] and further development was presented in [7, 8]. In its simplest form the criterion is the following. The trial function $\Psi_t(x)$ should contain all symmetry properties of the problem in hand. If the ground state is studied, the trial function should not vanish inside the domain where the problem is defined. The potential $V_t(x) = \nabla^2 \Psi_t / \Psi_t$, for which the trial function is an eigenfunction, should reproduce the original potential near singularities as well as its asymptotic behavior. The use of this simplest possible recipe has led to a unique one-parameter trial function, which in particular, made it possible to carry out the first qualitative study of the ground state of the hydrogen molecule H_2 in the region of both weak and strong magnetic fields [9]. Later a few-parameter trial function was proposed for a description of the hydrogen atom in an arbitrary magnetic field, which led, for the low-excited states, to an accuracy comparable with the best calculations [8, 10].

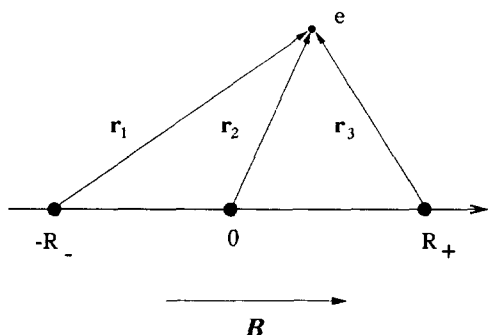


Fig.1. H_3^{++} in a magnetic field B . Explanation of the notation used

Now we wish to apply the above recipe to the ion H_3^{++} . Let us first introduce notation (see Fig.1). We consider three attractive identical centers of unit charge situated on the z -axis at origin and at a distance R_- , R_+ from the origin, respectively. The magnetic field of strength B is directed along the z axis and $r_{1,2,3}$ are the distances from the electron to the first (second, third) center, respectively. The quantity ρ is the distance from the electron to the z -axis. Through the paper the Rydberg is used as the energy unit. For the other quantities standard atomic units are used. The potential corresponding to the problem we study is given by

$$V = \frac{2}{R_-} + \frac{2}{R_+} + \frac{2}{R_- + R_+} - \frac{2}{r_1} - \frac{2}{r_2} - \frac{2}{r_3} + \frac{B^2 \rho^2}{4}, \quad (1)$$

where the first three terms have the meaning of the classical Coulomb energy of interaction of three charged centers. The recipe dictates that the trial functions should behave in a Coulomb-like way near the centers, correspond to two-dimensional oscillator behavior in the (x, y) plane at large distances and be permutationally-symmetric with respect to exchange of positions of the centers. It seems quite natural that the equilibrium configuration corresponding to minimal total energy of the system should appear at $R_- = R_+$.

One of the simplest functions satisfying the above recipe is the Heitler-London type function multiplied by the lowest Landau orbital:

$$\Psi_1 = \exp\{-\alpha_1(r_1 + r_2 + r_3) - \beta_1 B \rho^2 / 4\}, \quad (2)$$

(cf. Eq. (2.2) in [5]), where α_1, β_1 are variational parameters. It has a total of four variational parameters if the internuclear distances R_-, R_+ are taken as parameters. It is quite natural from a physical viewpoint to assume that a function of the Heitler–London type gives an adequate description of the system near the equilibrium position. The potential $V_1(x) = \nabla^2 \Psi_1 / \Psi_1$, corresponding to this function is:

$$V_1 = 3\alpha_1^2 - B\beta_1 - 2\alpha_1 \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) + \frac{\beta_1^2 B^2 \rho^2}{4} + 2\alpha_1^2 \left[\frac{1}{r_1 r_2} (\rho^2 + z(z + R_+)) + \frac{1}{r_2 r_3} (\rho^2 + z(z - R_-)) + \frac{1}{r_1 r_3} (\rho^2 + (z - R_-)(z + R_+)) \right] + \alpha_1 \beta_1 B \rho^2 \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right). \quad (3)$$

It is clear that this potential reproduces the original potential (1) near Coulomb singularities as well as at large distances, $|x, y| \rightarrow \infty$.

The Hund-Mulliken-type function multiplied by the lowest Landau orbital is another possible trial function:

$$\Psi_2 = [\exp(-\alpha_2 r_1) + \exp(-\alpha_2 r_2) + \exp(-\alpha_2 r_3)] \exp(-\beta_2 B \rho^2 / 4) \quad (4)$$

(cf. Eq.(2.4) in [5]), where α_2, β_2 are variational parameters. It is obvious that this function, in the absence of a magnetic field, gives an essential contribution to a description of the region of large internuclear distances. The calculations we have performed show that this property remains valid for all magnetic fields up to 10^{13} G. Like Eq.(2), the trial function (4) is characterized by four variational parameters. This function, when both internuclear distances are large, corresponds to a decay $H_3^{++} \rightarrow H + p + p$.

Another trial function supposedly describes a decay mode $H_3^{++} \rightarrow H_2^+ + p$ and could be taken to be of the form

$$\Psi_3 = [\exp(-\alpha_3(r_1 + r_2)) + \exp(-\alpha_3(r_1 + r_3)) + \exp(-\alpha_3(r_2 + r_3))] \exp(-\beta_3 B \rho^2 / 4), \quad (5)$$

where α_3, β_3 are variational parameters. Finally, it will become obvious that the function (5) does give the dominant contribution to the large internuclear distances. Eq.(5) also depends on four variational parameters.

To take into account both equilibrium and large distances, we use an interpolation of Eqs. (2), (4) and (5). There are three natural approaches to interpolate:

(i) a total non-linear superposition:

$$\Psi_{4-nl s-t} = \left[\exp(-\alpha_4 r_1 - \alpha_5 r_2 - \alpha_6 r_3) + \exp(-\alpha_5 r_1 - \alpha_4 r_2 - \alpha_6 r_3) + \exp(-\alpha_4 r_1 - \alpha_6 r_2 - \alpha_5 r_3) + \exp(-\alpha_6 r_1 - \alpha_4 r_2 - \alpha_5 r_3) + \exp(-\alpha_5 r_1 - \alpha_6 r_2 - \alpha_4 r_3) + \exp(-\alpha_6 r_1 - \alpha_5 r_2 - \alpha_4 r_3) \right] \exp(-\beta_4 B \rho^2 / 4), \quad (6)$$

(cf. Eq.(2.5) in [5]), where $\alpha_{4,5,6}, \beta_4$ are variational parameters. The function (6) is a three-center modification of the Guillemin–Zener type function used for the description of the molecular ion H_2^+ in a magnetic field [5]. If $\alpha_4 = \alpha_5 = \alpha_6 \equiv \alpha_1$, the function (6) reduces to Eq.(2). When $\alpha_4 \equiv \alpha_2, \alpha_5 = \alpha_6 = 0$, it coincides with Eq.(4). Finally, if $\alpha_4 = \alpha_5 \equiv \alpha_3, \alpha_6 = 0$, the function (6) reduces to Eq. (5). In total there are 6 variational parameters characterizing the trial function (6);

(ii) a partial non-linear superposition:

this appears if in Eq.(6) the two parameters are equal, for instance, $\alpha_4 = \alpha_5$:

$$\Psi_{4-nls-p} = \left[\exp(-\alpha_4(r_1 + r_2) - \alpha_6 r_3) + \exp(-\alpha_4(r_1 + r_3) - \alpha_6 r_2) + \exp(-\alpha_4(r_2 + r_3) - \alpha_6 r_1) \right] \exp(-\beta_4 B \rho^2 / 4). \quad (7)$$

This function can be considered as a non-linear interpolation between Eqs.(4) and (5);

(iii) a linear superposition of Eqs.(2), (4), (5)

$$\Psi_{4-ls} = A_1 \Psi_1 + A_2 \Psi_2 + A_3 \Psi_3, \quad (8)$$

where the relative weights of Eqs.(2), (4), (5) in Eq. (7) are taken as extra variational parameters. This is a 10-parameter trial function.

Of course, as a natural continuation of the above interpolation procedure one can take a linear superposition of all five functions (2), (4), (5), (6), (7):

$$\begin{aligned} \Psi_5 &= A_{4-nls-t} \Psi_{4-nls-t} + A_{4-nls-p} \Psi_{4-nls-p} + A_{4-ls} \Psi_{4-ls} = \\ &= A_{4-nls-t} \Psi_{4-nls-t} + A_{4-nls-p} \Psi_{4-nls-p} + A_1 \Psi_1 + A_2 \Psi_2 + A_3 \Psi_3 \end{aligned} \quad (9)$$

(cf. Eq. (2.7) in [5]), where again, as in the case of the function (8) the relative weights of different, "primary" trial functions are considered as variational parameters. In total, the trial function (9) is characterized by 17 variational parameters. However, only part of our calculation is carried out using this function. Usually, some particular cases of Eq. (9) are explored. The general case will be presented elsewhere. The minimization procedure is carried out using the standard minimization package MINUIT from CERN-LIB on a Pentium-Pro PC. All integrals were calculated using the CERN-LIB routine DGAUSS with relative accuracy $\leq 10^{-7}$.

	$B = 0$		$B = 10^{11} \text{ G}$			$B = 10^{12} \text{ G}$			$B = 10^{13} \text{ G}$		
	E (Ry)	R_{eq} (a.u.)	E (Ry)	R_{eq} (a.u.)	$\langle z \rangle$ (a.u.)	E (Ry)	R_{eq} (a.u.)	$\langle z \rangle$ (a.u.)	E (Ry)	R_{eq} (a.u.)	$\langle z \rangle$ (a.u.)
H	-1.000	-	36.929	-	-	413.57	-	-	4231.6	-	-
H_2^+	-1.205	1.997	35.036	0.593	0.312	408.300	0.283	0.174	4218.662	0.147	0.107
H_3^{++}	-	-	36.429	0.803	0.432	410.296	0.346	0.219	4220.090	0.165	0.121

Data for the ground state of H_3^{++} and a comparison with data for other one-electron systems, H, H_2^+ . Total energy E is in Rydbergs, the equilibrium distance $R_{eq} \equiv R_{+eq} = R_{-eq}$ (see text) and the average value of the longitudinal size of the system $\langle z \rangle$ in a.u. Total energy for hydrogen atom from [11]; data for H_2^+ from [5].

In Table the results of our variational calculations are presented. It is quite remarkable that for magnetic field strengths $> 10^{11} \text{ G}$ there exists a minimum of total energy in the (R_+, R_-) plane. Furthermore, for such magnetic fields the value of the energy at the minimum correspondent to the total energy of H_3^{++} is always lower than the total energy of the hydrogen atom but higher than that of H_2^+ . Hence the decay mode $H_3^{++} \rightarrow H + p + p$ is forbidden. However, H_3^{++} is unstable with respect to the decay $H_3^{++} \rightarrow H_2^+ + p$. It seems natural to assume that even if one-electron systems like H_4^{+++} , H_5^{++++} etc. would be bounded, their total energies will be larger than the total energy for H_3^{++} . This

assumption and comparison of the total energies of H , H_2^+ , H_3^{++} (see Table) allows one to conclude that H_2^+ is the most stable one-electron system in a constant magnetic field oriented along the magnetic field. The equilibrium distances for H_3^{++} decrease with the growth of the magnetic field: the ion H_3^{++} , like H_2^+ , becomes more and more compact. It is worth noting that for both H_2^+ and H_3^{++} the average value $\langle z \rangle$ is much smaller than a "natural" size of a system determined by the positions of the centers: R_{eq} for H_2^+ and $(R_{+eq} + R_{-eq})$ for H_3^{++} (see Fig.1). In other words this means that the localization length of electron is much smaller than the "natural" size of the system.

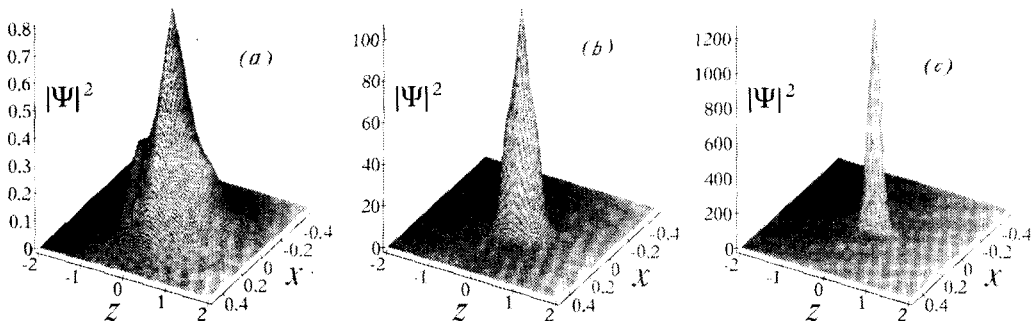


Fig.2. Electronic distribution for various magnetic fields: 10^{11} G (a), 10^{12} G (b) and 10^{13} G (c). It peaks more and more sharply at origin with growth of magnetic field.

Fig.2 shows the electronic density distribution as a function of magnetic field. For a magnetic field $B \simeq 10^{11}$ G the distribution has three clear maxima corresponding to the positions of the centers, but the electron is situated preferably near the central proton. The situation changes drastically with an increase of magnetic field: the electron is localized near $z = 0$, having almost no memory of the two centers on either side. It is important to investigate paths of possible tunneling. There are two explicitly pronounced (symmetric with respect to $R_+ \leftrightarrow R_-$) valleys in the electronic potential energy surfaces, $E_{total}(R_+, R_-)$ (see, Fig.3a):

They vary from the position of the H_3^{++} minimum to infinity which corresponds to the $H_2^+ + p$ dissociation: $(R_{+eq}, R_{-eq}) \rightarrow (\infty, R_{H_2^+}^{eq})$ and $(R_{+eq}, R_{-eq}) \rightarrow (R_{H_2^+}^{eq}, \infty)$, where $R_{H_2^+}^{eq}$ is the equilibrium distance for the H_2^+ ion. In Fig.3b one can see the profile of the valley as a function of magnetic field. Calculating the Gauss curvatures in the H_3^{++} minimum one can estimate the position of the ground state energy level and answer the question of whether the well is deep enough to hold an energy level. It is always delicate to answer this question starting from what 'depth' of the well the level exists. Usually, it requires special analysis. We made an estimate and obtained the result that for a magnetic field of 10^{11} G, the situation is not certain, the well is probably still too shallow to hold the ground state energy level. However, the well undoubtedly becomes sufficiently deep for 10^{12-13} G. From the form of the profile (see Fig. 3b) it is quite obvious that for 10^{12-13} G the barrier is rather high and the probability of tunneling should be small.

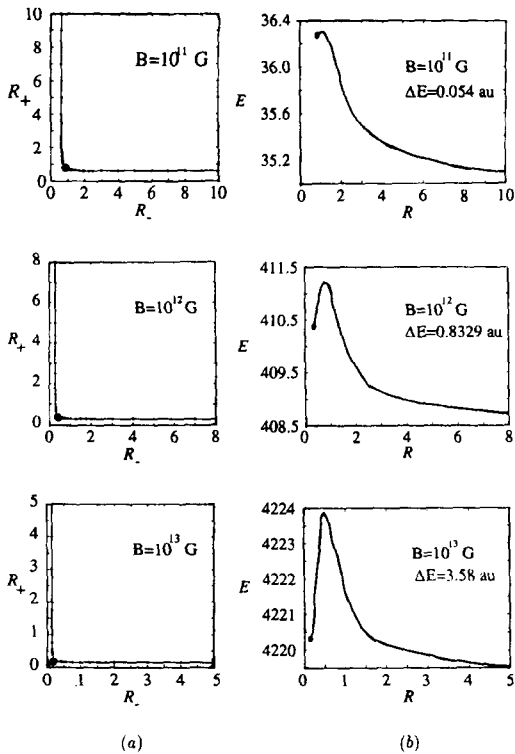


Fig.3. Valleys in the electronic potential energy surfaces, $E_{total}(R_+, R_-)$, (a) and their profiles (b) for various magnetic fields. The position of the minimum is indicated by a bullet, and ΔE denotes the depth of the well: the distance between top of the barrier and the value of minimum

The authors wish to thank K.G. Boreskov (Moscow) for useful discussions. A.T. thanks L.Cederbaum (Heidelberg) for a valuable comment. Fruitful discussions with P.O.Hess (México) in the early stage of the work are gratefully acknowledged.

This work is supported in part by DGAPA grant IN105296 (México).

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