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Binding energy and triplet-singlet splitting for the hydrogen molecule in ultrahigh magnetic fields

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The energy difference of triplet and singlet states due to exchange coupling, the energy levels, the ground binding state, and the wave functions is calculated for a hydrogen molecule in an ultrahigh magnetic field when the distance between the Landau levels $e\hbar H/mc$ exceeds the Coulomb unit (Rydberg) $me^4/2\hbar^2$. The results are asymptotically exact at the interatomic distance R, which is large compared with the atomic size and for high magnetic fields. It is shown here that the triplet electron term has a minimum at large interatomic distances corresponding to the formation of the ground state of a stable H_2 molecule. For the hydrogen molecule in an ultrahigh magnetic field, the energy of the singlet state also has a deep minimum at $R<1$, which is much higher than the triplet one and may be a metastable state only.

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I. INTRODUCTION

We will consider hydrogen atoms in an ultrahigh magnetic field H which exceeds the atomic magnitude $H_c=m^2e^3c/\hbar^3=2.35\times10^9$ Oe (in what follows the magnetic field H will be measured in precisely these units; other quantities will be expressed in atomic units). The atoms in such a field are elongated along the direction of the magnetic field and possess a large electric quadrupole moment. The forces of attraction acting between these quadrupole moments should lead to the formation of a hydrogen molecule. This problem was treated by Kadomtsev [1,2]. He obtained the solution using the Hartree-Thomas-Fermi approximation without taking into account the exchange coupling of the spins and the atomic interaction for a large interatomic distance. It was shown by Kadomtsev [1,2] that atoms in an ultrahigh magnetic field form dense molecules when the distances between protons are smaller than the atomic size. It is known that the energy difference of the singlet and triplet states of the hydrogen molecule measures the exchange coupling of the spins of the two atoms. For the hydrogen molecule without the magnetic field it was shown by Gor'kov and Pitaevskii [3] and by Herring and Flicker [4] that for the case of the large interatomic distance R, when the overlap of the wave functions of the different atoms is slight, the leading term in the expression for the energy difference of singlet and triplet states can be evaluated exactly.

In this paper we shall perform the explicit evaluation of the energy difference of the singlet and triplet states for the hydrogen molecule in an ultrahigh magnetic field which is large compared to the Coulomb binding energy. The solution shows that for an ultrahigh magnetic field the formation of a stable H_2 molecule occurs at an interatomic distance R, which is larger than the atomic unit of length if the magnetic field is not too high (≤ 1000). In the ground state the total spin of the hydrogen molecule in an ultrahigh magnetic field is one, $S=1$, i.e., the ground state is a triplet. In the singlet state ($S=0$), the energy has a minimum that may correspond to the formation of a metastable state of the H_2 molecule. The singlet energy level is much higher than the triplet ground one.

II. SCHRÖDINGER EQUATION: WAVE FUNCTIONS FOR THE HYDROGEN MOLECULE

Let us consider two hydrogen atoms in an ultrahigh magnetic field such that the following inequality holds:

$$m^2e^3c/\hbar^3H \ll 1 , \tag{1}$$

where m denotes the electron mass, H is the magnetic field, and all other designations are conventional. Since the atoms in an ultrahigh magnetic field possess a large electric quadrupole moment, their axis of symmetry need not coincide with the direction of the magnetic-field lines. Let us choose the coordinate system with the X axis directed along $\mathbf{H}$, and atoms 1 and 2 lying in the plane XZ. The coordinates of atoms 1 and 2 are

$$X_{1,2}\equiv\mp a=\mp\frac{R}{2}\cos\theta,\quad Z_{1,2}\equiv\mp b=\mp\frac{R}{2}\sin\theta ,$$

where R is the interatomic distance between atoms 1 and 2, and θ is the angle between axis of molecule and direction of the magnetic field.

The Schrödinger equation for the electrons will be (all quantities are expressed in atomic units)

$$\left[\tfrac{1}{2}(\mathbf{P}_1+\mathbf{A})^2+\tfrac{1}{2}(\mathbf{P}_2+\mathbf{A})^2-\sum_i\frac{1}{R_{1i}}-\sum_i\frac{1}{R_{2i}}+\frac{1}{r_{12}}+\frac{1}{R}+\tfrac{1}{2}\hat{\sigma}_1\mathbf{H}+\tfrac{1}{2}\hat{\sigma}_2\mathbf{H}\right]\psi=E\Psi , \tag{2}$$

where R_{1i} and R_{2i} denote the distances between the electrons with subscript i and proton 1 and 2, respectively, r_{12} is the distance between the electrons, $\hat{\sigma}_1$ and $\hat{\sigma}_2$ are Pauli matrices.

Let us choose the vector potential $\mathbf{A}$ in the form

$\mathbf{A}=\frac{1}{2}(\mathbf{H}\times\mathbf{r})$, so that Eq. (2) takes the form

$$[\mathcal{H}(1,2)+\tfrac{1}{2}\hat{\sigma}_1\mathbf{H}+\tfrac{1}{2}\hat{\sigma}_2\mathbf{H}]\Psi=E\Psi\ , \tag{3}$$

where

$$\mathcal{H}(1,2)=\left[-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2-\sum_i\frac{1}{R_{1i}}-\sum_i\frac{1}{R_{2i}}+\frac{1}{r_{12}}+\frac{1}{R}+\frac{\rho_1^2+\rho_2^2}{8\lambda^4}\right],$$

and $\rho_1^2=y_1^2+(b+z_1)^2$, $\rho_2^2=y_2^2+(b-z_2)^2$ are the coordinates of motion for the electrons 1 and 2 in the plane perpendicular to $\mathbf{H}$; $\lambda=\sqrt{c\hbar/eH}$ is the atomic size in the same plane, or using the atomic units ($\hbar=m=c=e=1$) $\lambda=\sqrt{1/H}$.

We will consider two energy levels, which are the singlet term and the triplet term. Let Ψ_s be the exact solution of the two-electron coordinate wave equation that is symmetrical in the coordinates of the two electrons. The singlet wave function is thus a product of Ψ_s and an appropriate spin function for the sum of the electron spins that is equal to zero, $S=0$. As a result of the Hamiltonian operator acting on the spin function, we obtain zero, i.e., the Pauli matrices disappear from the Hamiltonian. Thus, for the singlet wave function Ψ_s, the Schrödinger equation is

$$\mathcal{H}(1,2)\Psi_s=E_s\Psi_s\ . \tag{4}$$

The triplet wave function is the product of the exact solution of the two-electron wave function that is antisymmetrical in the coordinates of the two electrons and an appropriate spin function for the sum of the electron spins, $S=1$. The possible spin projections are $+1$, 0, -1, and the lowest energy level corresponds to spin projection equal to -1. Thus, the Schrödinger equation for the triplet term will be

$$\left[\mathcal{H}(1,2)-\frac{1}{2\lambda^2}-\frac{1}{2\lambda^2}\right]\Psi_a=E_a\Psi_a\ . \tag{5}$$

Using the new variable $E_{s1}=E_s-1/\lambda^2$, one can reduce Eq. (4) to the form identical to Eq. (5):

$$\left[\mathcal{H}(1,2)-\frac{1}{2\lambda^2}-\frac{1}{2\lambda^2}\right]\Psi_{s,a}=E_{s1,a}\Psi_{s,a}\ . \tag{6}$$

Let us consider the functions $\Psi_1=(\Psi_s+\Psi_a)/2$ and $\Psi_2=(\Psi_s-\Psi_a)/2$, which will be large only when electron 1 is localized near proton a and electron 2 is near proton b. If the phases of Ψ_1 and Ψ_2 are properly chosen, the function $\Psi_1(r_1,r_2)$ for $r_1\to -R/2$, and $r_2\to R/2$ and $\Psi_2(r_1,r_2)$ for $r_1\to R/2$; $r_2\to -R/2$ will be the product of the two hydrogen single-atom wave functions in an ultrahigh magnetic field. To obtain the ground-state wave function of the hydrogen atom in the ultrahigh magnetic field one can consider the electron motion along $\mathbf{H}$ as a one-dimensional motion in the Coulomb field but in the plane (YZ) perpendicular to $\mathbf{H}$ it moves like a free electron in a magnetic field. Since electron motion along the X axis is limited by the length of order α, and in the plane perpendicular to H their motions are constrained by the cylindrical shell whose radius is of order of $\lambda \ll R$, then the above-mentioned approximation for the wave function is reasonable. According to results obtained in [5,6], we can write the ground-state wave function of the hydrogen atom in an ultrahigh magnetic field in the following form:

$$\Psi(\mathbf{r})=\phi(\rho)\psi(x)\ ,$$

where

$$\phi(\rho)=\frac{1}{\sqrt{2\pi}\lambda}\exp\left[-\frac{\rho^2}{4\lambda^2}\right]$$

is the wave function of the zeroth Landau level that corresponds to the motion in the plane perpendicular to the magnetic field ($\rho^2=y^2+z^2$), and for the function $\psi(x)$ we have the following expression:

$$\psi(x)=\frac{1}{\sqrt{\alpha}}W_{\alpha,1/2}\left[\frac{2}{\alpha}(x+\lambda)\right],$$

where $W_{\alpha,1/2}$ is the well-known Whittaker function. The main peculiarities of this solution compared to the wave function of the pure Coulomb field are due to the one-dimensional Coulomblike motion of the electron along the direction of the magnetic field.

The energy of the ground state, which is related to the quantity α, can be written with logarithmical accuracy in the following form [5–7]:

$$\varepsilon=-\frac{1}{2\alpha^2}\simeq-\tfrac{1}{2}\ln^2 H\ . \tag{7}$$

For the wave function $\psi(x)$ at large distances along the direction of the magnetic field in comparison with the atomic size α, we have the following asymptotic expression:

$$\psi(x)\simeq\frac{1}{\sqrt{\alpha}}\exp\left[-\frac{|x|}{\alpha}\right]. \tag{8}$$

Thus, we finally have the following expression for the ground-state wave function of the hydrogen atom in an ultrahigh magnetic field:

$$\Psi(\mathbf{r})=\frac{1}{\sqrt{\alpha}}\frac{1}{\sqrt{2\pi}\lambda}\exp\left[-\frac{\rho^2}{4\lambda^2}\right]W_{\alpha,1/2}\left[\frac{2}{\alpha}(x+\lambda)\right]. \tag{9}$$

We then seek the wave function Ψ_1 in the next form:

$$\Psi_1=B^2\chi_1\exp\left[-\frac{\rho_1^2+\rho_2^2}{4\lambda^2}\right]W_{\alpha,1/2}\left[\frac{2}{\alpha}(a+x_1+\lambda)\right]\times W_{\alpha,1/2}\left[\frac{2}{\alpha}(a-x_2+\lambda)\right], \tag{10}$$

where $B^2=(1/\alpha)(1/2\pi\lambda^2)$, and χ_1 is a slowly varying function compared with the exponential decay. Expression (10) is the product of the two hydrogen-atom wave functions, for the first electron being near the first proton and for the second electron near the second proton. Substituting expression (10) in Eq. (6) and after differentiation, taking into account the terms of zero-degree α only, we obtain the following equation for χ_1:

$$\left[\frac{1}{\alpha}\frac{\partial}{\partial x_1}-\frac{1}{\alpha}\frac{\partial}{\partial x_2}-\frac{1}{R_{12}}-\frac{1}{R_{12}}+\frac{1}{r_{12}}+\frac{1}{R}\right]\chi_1=0 . \tag{11}$$

For the derivation of Eq. (11) we do not take into account the terms that have the derivatives of χ_1 with respect to z_1, z_2, y_1, and y_2, because by substituting the expression (12a) written below for χ_1 into (11), one can see that, due to these derivatives, only terms of order α appear. They are smaller than the terms of order 1, which appear due to the derivatives χ_1 with respect to x_1 and x_2.

Introducing the new variables $\xi=(x_1+x_2)/2$ and $\eta=x_1-x_2$, we can write the solution of Eq. (11) in the following form:

$$\chi_1=\left[C(\xi,z_1,z_2,y_1,y_2)\exp\left[-\frac{(x_1-x_2)}{R}\right]\right]^{\alpha} G , \tag{12a}$$

where

$$G=\left[\frac{x_2-x_1+[(x_2-x_1)^2+(z_2-z_1)^2+(y_2-y_1)^2]^{1/2}}{\{a+x_2+[(a+x_2)^2+(b+z_2)^2]^{1/2}\}^2}\frac{1}{\{a-x_1+[(a-x_1)^2+(b-z_1)^2]^{1/2}\}^2}\right]^{\alpha/2} , \tag{12b}$$

and where $C(\xi,z_1,z_2,y_1,y_2)$ is an arbitrary function of variables ξ, z_1, z_2, y_1, and y_2. To determine this function we can use the condition that χ_1 tends to 1 for $x_1\to -a$ and $z_1\to -b$, or for $x_2\to a$ and $z_2\to b$. That is, after some calculations, we finally have the following expression for the wave function:

$$\Psi_1(\mathbf{r}_1,\mathbf{r}_2)=\Gamma\exp\left[-\frac{\rho_1^2+\rho_2^2}{4\lambda^2}\right]W_{\alpha,1/2}\left[\frac{2}{\alpha}(a+x_1+\lambda)\right]W_{\alpha,1/2}\left[\frac{2}{\alpha}(a-x_2+\lambda)\right]FG , \tag{13a}$$

where

$$F=\left[\frac{\{2a+x_1+x_2+[(2a+x_1+x_2)^2+(2b+z_1+z_2)^2]^{1/2}\}^2}{2a+x_1+x_2+[(2a+x_1+x_2)^2+(2b+z_1+z_2)^2+y_{21}^2]^{1/2}}\right]^{\alpha/2}\exp\left[-\frac{\alpha(a+x_1)}{(a^2+b^2)^{1/2}}\right] \tag{13b}$$

for $x_1+x_2<0$ and $z_1+z_2<0$,

$$F=\left[\frac{\{2a-x_1-x_2+[(2a-x_1-x_2)^2+(2b-z_1-z_2)^2]^{1/2}\}^2}{2a-x_1-x_2+[(2a-x_1-x_2)^2+(2b-z_1-z_2)^2+y_2^2]^{1/2}}\right]^{\alpha/2}\exp\left[-\frac{\alpha(a-x_2)}{2(a^2+b^2)^{1/2}}\right] \tag{13c}$$

for $x_1+x_2>0$ and $z_1+z_2>0$. Here $\Gamma=B^2\{2[a+(a^2+b^2)^{1/2}]\}^{\alpha}$, and $y_{21}=y_2-y_1$. Function Ψ_2 follows from the expression for Ψ_1 by replacing the variable 1 by 2.

III. THE BINDING ENERGY AND TERMS SPLITTING

We are now ready to evaluate the singlet-triplet energy difference. Let us introduce a coordinate system that is the result of a rotation through the angle θ about the Y axis:

$$x=x'\cos\theta-z'\sin\theta,\quad z=x'\sin\theta+z'\cos\theta .$$

(We will omit designations by hatch in what follows.)

It was shown by Gor'kov and Pitaevskii [3] that the singlet-triplet energy splitting due to the exchange coupling of the spins for the hydrogen molecule can be represented with the exponential accuracy in the following form:

$$E_{s1}-E_a=2\oint_S(\Psi_2\nabla_1\Psi_1-\Psi_1\nabla_1\Psi_2)d\mathbf{S} , \tag{14}$$

where S is the hyperplane $(x_1=x_2)$ in the six-dimensional space $\{\mathbf{r}_1,\mathbf{r}_2\}$. The scalar product in Eq. (14) will reduce to differentiation with respect to the variable x_1 only, since the gradients in (14) are projected on the direction of the hyperplane $d\mathbf{S}$.

Since we are interested in the systems with the large interatomic distance between two protons in the hydrogen molecule in comparison with the atomic size $\sim\alpha$, we use the asymptotic expression (8) for the wave function $\psi(x)$. After the differentiation of the exponent factor in the expression (10) with respect to x_1, we can reduce Eq. (14) to the following form:

$$E_{s1}-E_a=-4\left[\frac{2\cos\theta}{\alpha}+\frac{b\sin\theta}{\lambda^2}\right]\times\int_0^{R/2}dx\int\int\int_{-\infty}^{+\infty}\int dy_1dy_2dz_1dz_2\times(\Psi_1\Psi_2)_{\substack{x_1+x_2>0\\ x_1=x_2}} . \tag{15}$$

Substituting the expression Ψ_1 and Ψ_2 in Eq. (15) and using the condition $0<\alpha\ll 1$, we obtain the following expression, if θ is in the range $0\le\theta<\pi/2-\epsilon$ (where $\epsilon\sim\alpha$):

$$E_{s1}-E_a=-\frac{2R}{\alpha^2\cos^2\theta}\left[\frac{2\cos\theta}{\alpha}+\frac{R\sin^2\theta}{2\lambda^2}\right]$$
$$\times\exp\left[-R\left[\frac{2\cos\theta}{\alpha}+\frac{R\sin^2\theta}{4\lambda^2}\right]\right] . \qquad (16)$$

Thus, for the part of the energy difference ΔE between the singlet and triplet states due to the exchange coupling of the spins of two atoms, we have the following expression (in atomic units):

$$\begin{aligned}\Delta E&=(E_S-H)-E_a\\&=-\frac{2R\ln^2 H}{\cos^2\theta}(2\ln H\cos\theta+\tfrac{1}{2}RH\sin^2\theta)\\&\quad\times\exp[-R(2\ln H\cos\theta+\tfrac{1}{4}RH\sin^2\theta)] . \qquad (17)\end{aligned}$$

Calculations are similar to the above for the case $\theta=\pi/2$, which gives the following expression:

$$E_{s1}-E_a=-\frac{R}{2\sqrt{\pi}\lambda^3}\exp\left[-\frac{R^2}{4\lambda^2}\right] .$$

For large distances R between the two hydrogen atoms in an ultrahigh magnetic field, the atoms interact like two quadrupoles. Since the electron density distribution is $\Psi^2(x)$, and the quadrupole moment for the atoms is equal to $Q=2\langle x^2\rangle=\alpha^2/2$, the energy of interaction of the two quadrupoles at large distance R is therefore

$$U_{qq}=\tfrac{9}{8}\frac{1}{\ln^4 H}\frac{1}{R^5}P_4(\cos\theta) , \qquad (18)$$

where

$$P_4(\cos\theta)=\tfrac{1}{8}(35\cos^4\theta-30\cos^2\theta+3)$$

is the Legendre polynomial.

Taking into account the quadrupole interaction as well as the exchange coupling of the spins as the singlet-triplet splitting, we can write the final expression for the energy levels of the hydrogen molecule [with the condition $R\gg(\langle x^2\rangle^{1/2}\sim\alpha]$.

For the singlet term

$$U_s=E_s-E_0=-\tfrac{1}{2}\Delta E+H+Uqq . \qquad (19)$$

For the triplet term

$$U_s=E_a-E_0=+\tfrac{1}{2}\Delta E+U_{qq} , \qquad (20)$$

where E_0 is the ground-state energy of the two isolated hydrogen atoms.

Since the energy of the quadrupole interaction has a deep negative minimum for $\theta\simeq 49°$, binding states are possible for both singlet and triplet states. However, for the condition $H\gg 1$, the triplet energy level lies much deeper than the singlet level, which means that the triplet is the ground state for the hydrogen molecule in an ultrahigh magnetic field.

The results of the numerical calculation according to Eqs. (19) and (20) are shown in Fig. 1. The curves in the figure correspond to the singlet level (Fig. 1, top) and the triplet level (Fig. 1, bottom), respectively, where the numbering 1, 2, and 3 on the curves corresponds to the different values of the magnetic field, 20, 50, and 100, respectively, for $\theta\simeq 49°$. All the values are in atomic units. At a very small distance $R\leq\alpha$ the quadrupole interaction U_{qq} is replaced by the Coulomb repulsion. For the distance $\alpha\ll R\cong 1$ the interaction energy has a deep minimum for both singlet and triplet terms, which may be the ground or exited states of the hydrogen molecule. In any case the triplet level lies below the singlet one; i.e., the triplet state is the ground state of the hydrogen molecule in an ultrahigh magnetic field. As one can see from Fig. 1, the depths of the potential wells for the two terms are increasing with increasing magnetic field. For example, the binding energy for the ground state varies from

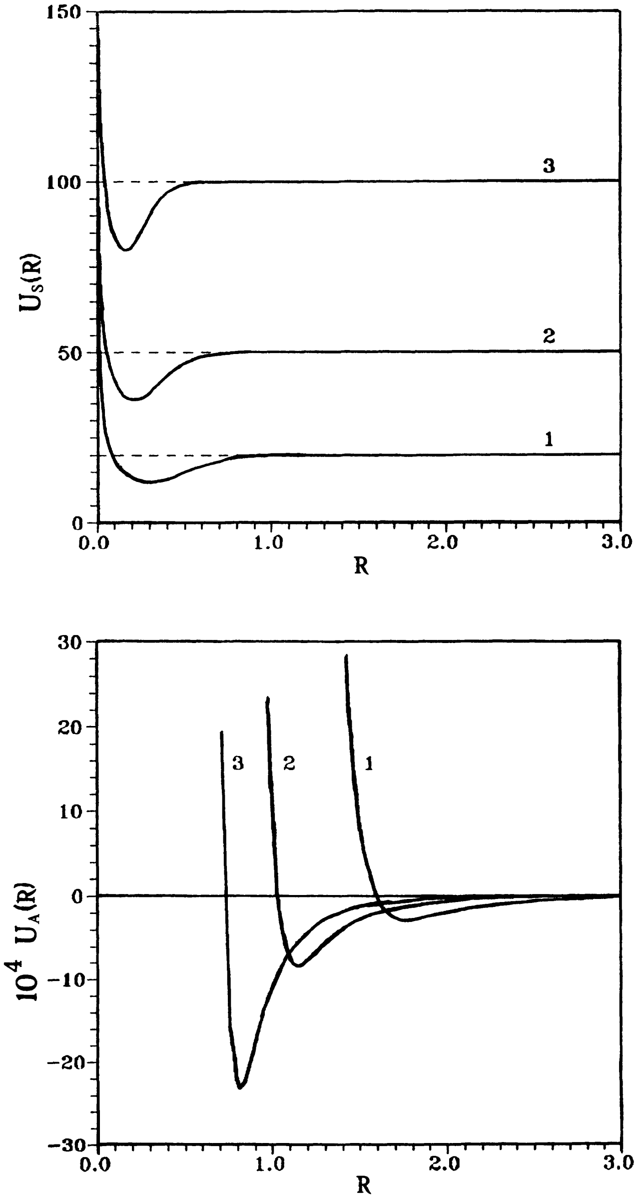

FIG. 1. The potential energy in the singlet state $^1\Sigma$ (top) and the triplet state $^3\Sigma$ (bottom). Curves 1, 2, and 3 correspond to magnetic fields 20, 50, and 100, respectively. All quantities are expressed in atomic units.

$\varepsilon_t = 2.86\times10^{-4}$ (2 Ry) for $H=20$ up to $\varepsilon_t = 4.4\times10^{-2}$ (2 Ry) for $H=500$, and the depth of the potential well for the singlet level varies from $\Delta\varepsilon_s = 7$ (2 Ry) for $H=20$ up to $\Delta\varepsilon_s = 40$ (2 Ry) for $H=500$. With increasing values of the magnetic field the molecular size decreases; for example, the energy minimum $U_a(R)$ localized at $R=0.46$ for $H=300$. As long as the molecular size remains comparable to or larger than the atomic size in an ultrahigh magnetic field, the solutions obtained above are asymptotically exact. This result will be true up to a value for magnetic field of about 1000, where the atomic size will be approximately equal to the molecular size.

IV. CONCLUSION

Thus our investigation, carried out above, indicates that a substantial change in the physical properties of matter occurs in the presence of an ultrahigh magnetic field. In particular, the hydrogen atoms can form a molecule with a ground state that is a triplet state but not a singlet state, as it is for a H_2 molecule in the absence of a magnetic field. The binding energy of the molecule in the triplet ground state is not too large; it is just about 1 eV, where as the depth of the potential well for the metastable singlet term may be of order of a few hundred eV. This value is about two orders of magnitude larger than the binding energy of the hydrogen molecule without magnetic field.

The behavior of such atoms in a magnetic field and the creation of spin-oriented molecules, which can strongly interact, creating a long polymeric chain or structures of the liquid crystal type, are of significant interest for astrophysics. Magnetic fields of the scale, which are interesting for our problem, of $10^{10}-10^{12}$ Oe, could exist on the surface of the neutron stars and pulsars.

Another subject of interest might be the behavior of a hydrogenlike system of excitons in semiconductor or dielectrics. The characteristic value of the "atomic" magnetic field for such a system is defined by the condition $H_c \gg \mu^2 e^3 c/\hbar^3\kappa^2$ (here μ is a reduced mass, κ is the dielectric constant) and it is available in laboratories. For example, the value of a few kOe is an "ultrahigh" field for InSb. This means that for low temperature and for definite conditions, the spin-oriented structure can be created due to the strong interaction of excitonic molecules in a strong magnetic field. The study of this problem is planned to be the subject of a separate paper.

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