Ground and excited states of the hydrogen negative ion in strong magnetic fields

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(Received 17 September 1999; published 16 May 2000)

The lowest bound states of the hydrogen negative ion and negative donor systems in a homogeneous magnetic field are investigated theoretically via a full configuration-interaction approach with an anisotropic Gaussian basis set. The broad magnetic field regime $\gamma=8\times10^{-4}-4\times10^{3}$ is covered. Nonrelativistic total energies, electron detachment energies, and transition wavelengths are presented assuming an infinite nuclear mass. The binding mechanisms are discussed in detail. The accuracy for the energies is enhanced significantly compared to previously published data.

PACS number(s): 32.60.+i, 32.30.−r, 32.10.−f, 71.55.−i

I. INTRODUCTION

The term ''strong field'' characterizes a situation for which the Lorentz force is of the order of magnitude or greater than the Coulomb binding force. For a hydrogen atom in the ground state the corresponding field strength cannot be reached in the laboratory, but only in astrophysical objects like white dwarfs ($B\approx10^{2}-10^{5}$ T) or neutron stars ($B\approx10^{7}-10^{9}$ T). Astrophysicists possess, therefore, a vivid interest in the behavior and properties of matter in strong magnetic fields: theoretically calculated data of magnetized atoms can be used for the determination of the decomposition and magnetic field configuration of astrophysical objects [1–4]. On the other hand, the strong magnetic field regime is accessible in the laboratory if one considers highly excited Rydberg states of, e.g., atoms [5,6].

In solid state physics donor states in semiconductors with parabolic conduction bands are systems which possess a Hamiltonian equivalent to the one of hydrogen within an effective-mass approximation. Due to screening effects the Coulomb force is much weaker than in the case of hydrogen. The regime where the ground state of the system is dominated by magnetic forces can therefore be reached for certain semiconductors in the laboratory. As an example we mention GaAs for which the effective mass is $m^{*}=0.067m_{e}$ and the static dielectric constant $\epsilon_{s}=12.53\epsilon_{0}$. Since the Hamiltonian of the atomic ion and the negative donor are connected through a scaling transformation the values for the energies given in the present work hold for both systems equally. The reader should, however, keep in mind that they are given in differently scaled units.

Apart from the above, atoms and molecules in strong magnetic fields are also of interest from a purely theoretical point of view. Due to the competition of the spherically symmetric Coulomb potential and the cylindrically symmetric magnetic field interaction we encounter a nonseparable, nonintegrable problem. Perturbation theory, which is possible in the weak and in the ultrastrong field regime, breaks down in the intermediate field regime. It is therefore necessary to develop new techniques to solve such problems. The neutral hydrogen atom in a strong magnetic field is now understood to a high degree (see [5,7] and references therein). Recently Kravchencko has published an ''exact'' solution which provides an infinite double sum for the eigenvalues [8]. With the presented method all energy values of bound states could, in principle, be calculated to arbitrary precision.

For two-electron atoms the situation is significantly different. The problems posed by the electron-electron interaction and the nonseparability on the one-particle level have to be solved simultaneously, which is much harder. The H^{-} ion provides an additional challenge since correlation plays an important role for its binding properties. Without a field it possesses only one bound state [9]. In the presence of a magnetic field and for the assumption of an infinitely heavy nucleus it could be shown [10] that there exists an infinite number of bound states. For laboratory field strengths these states are, due to the binding mechanism via a one-dimensional projected polarization potential, very weakly bound [11]. Some finite nuclear mass effects can be included via scaling relations [7,12–14]. However, the influence of the center-of-mass motion has not been investigated in detail so far. In the present work we assume an infinitely heavy nucleus which represents a good approximation for the slow H^{-} atomic ion in strong magnetic fields and describes simultaneously the situation of negatively charged donors D^{-} in the field. Relativistic corrections were neglected since they are assumed to be small compared to the electron detachment energy of the system. We will use in the following the spectroscopic notation ^{2S+1}M for the electronic states of the ion where M and S are the total magnetic and spin quantum numbers. Since states with negative z parity are not considered here we omit the corresponding label in our notation (see also Sec. II A).

Many authors have tackled the quantum-mechanical problem of H^{-} in a strong magnetic field. One of the first, who pursued a variational approach to this problem, was Henry *et al.* [15]. They give qualitative insights into the weak and intermediate field regime. Mueller *et al.* [16] qualitatively described the strong field ground state $^{3}(-1)$ and the $^{1}0$ state for high fields ($\gamma\approx4$ to $\gamma\approx20\,000$, where $\gamma=1$ a.u. corresponds to 2.3554×10^{5} T).

Larsen has published a number of papers on this problem [17–19]. On the one hand, he created very simple and physically motivated trial functions with only a small number of variational parameters. On the other hand, his energies were ''state of the art'' in variational calculations for a long time. In [17] he provides binding energies of the lowest $^{1}0$ state in the field regime $\gamma=0-5$ and of the $^{3}(-1)$ state in the re-

gime $\gamma=0-3$. He also presents figures showing the binding energies of the singlet and triplet state for $M=-2$ and $M=-3$. Later [19] he presents total and electron detachment energies for the lowest $^1 0$, $^3(-1)$, and $^3(-2)$ state in the high field regime. More specifically, the regime $\gamma=20-1000$ for the $^3(-1)$ state and $\gamma=20-200$ for the other states were investigated. Furthermore, Park and Starace [20] provided upper and lower bounds for energies and binding energies of the ground state $^1 0$ for weak fields.

In the 1990s several authors [21–24] improved the accuracy of the binding energies and total energies by new techniques. Vincke and Baye [21] report total ionization energies for the lowest singlet and triplet states with $M=0$, -1, and -2 for a few field strengths in the regime $\gamma=4-400$. They are to our knowledge the first who reported that the $^1(-1)$ state becomes bound for sufficiently high field strengths and realized that the $^1(-2)$ state is slightly stronger bound than the corresponding triplet state in the high field regime. Larsen and McCann present in [22] one-particle binding energies for the $^1 0$ state in the broad magnetic field regime $\gamma=0-200$. In [23] the same authors consider, furthermore, the singlet and triplet states of $M=-1,-2$. The triplet states are calculated for $\gamma=0.5-200$, the $^1(-1)$ state in the field regime $\gamma=55-2000$, and the $^1(-2)$ state is calculated for a few field strength in the range $\gamma=1-100$. Blinowski and Szwacka [24] have subsequently used a Gaussian basis set, similar to the one used in our calculation. They present results for the $^1 0$ state, which are less accurate than those of Ref. [22].

We also mention some Hartree-Fock calculations: very early Virtamo [25] has investigated the ground-state energies for $\gamma\approx 20-20\,000$. Thurner *et al.* [26] (results published in [7]) have calculated triplet states for $M=-1$, -2, and -3 for many field strengths in the broad range $\gamma=2\times10^{-4}-2\times10^3$. However, since they use spherical wave functions for weak fields and cylindrical ones for high fields, there remains a gap of inaccurate results in the intermediate field regime.

In the present investigation we provide lower variational energies and higher one-particle binding energies for the atomic H^- problem and, respectively, the negatively charged donor center D^- problem in a strong magnetic field compared to all other published data so far. An exception is the field free situation: the calculation by Pekeris [27] gives $-0.527\,75$ a.u. for the ground-state binding energy whereas we obtain $-0.527\,548\,8$ a.u. Clearly the field-free situation is much better understood than the case of a strong field.

The paper is organized as follows: in Sec. II we consider the symmetries of the Hamiltonian and the basis set we use in our calculations. In Sec. III we will report on the strategy we employed for the selection of basis functions in order to obtain accurate results. Section IV contains the discussion of our results and a comparison with the literature.

II. HAMILTONIAN, SYMMETRIES, AND BASIS SET

A. Hamiltonian and symmetries

In the following we assume an infinite nuclear mass (fixed donor). The magnetic field is chosen to point along the z direction. The nonrelativistic Hamiltonian takes in atomic units the form

$$H=H_1+H_2+\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \tag{2.1}$$

with

$$H_i=\frac{1}{2}\boldsymbol{p}_i^2+\frac{1}{2}\gamma l_{z_i}+\frac{\gamma^2}{8}(x_i^2+y_i^2)-\frac{1}{|\boldsymbol{r}_i|}+\gamma s_{zi}. \tag{2.2}$$

The Hamiltonian is splitted in its one-particle operators, where $1/2\gamma l_{z_i}$ is the Zeeman term, $\gamma^2/8(x_i^2+y_i^2)$ is the diamagnetic term, $-1/|\boldsymbol{r}_i|$ is the attractive Coulomb interaction with the nucleus (donor) and γs_{zi} the spin Zeeman term (we take the g factor equal 2). The two-particle operator $1/|\boldsymbol{r}_1-\boldsymbol{r}_2|$ represents the repulsive electron-electron interaction.

The Hamiltonian (2.1) possesses four independent symmetries and associated quantum numbers: the total spin S^2, the total z projection of the spin S_z, the z component of the total angular momentum M, and the total z parity Π_z (parity is also conserved but not a further independent symmetry).

B. One-particle basis set

For our calculation we use an anisotropic Gaussian basis set, which has been put forward by Schmelcher and Cederbaum in Ref. [28], for the purpose of investigating atoms and molecules in strong magnetic fields. It has already successfully been applied to helium [12,13], H_2^+, [29] and H_2 [30].

Adapted to the problem discussed here this one-particle basis set for the spatial part reads in the cylindrical coordinates as follows:

$$\Phi_i(\rho,\phi,z)=\rho^{n_{\rho_i}}z^{n_{z_i}}\ e^{-\alpha_i\rho^2-\beta_i z^2}\exp(im_i\phi). \tag{2.3}$$

These functions are eigenfunctions of the symmetry operations of the one-particle Hamiltonian H_i, i.e., eigenfunctions of l_z and π_z. The additional parameters n_{ρ_i} and n_{z_i} obey the following restrictions:

$$n_{\rho_i}=|m_i|+2k_i, \quad k_i=0,1,2,\ldots \quad \text{and}$$
$$m_i=\ldots,-2,-1,0,1,2,\ldots \tag{2.4}$$

$$n_{z_i}=\pi_{z_i}+2l_i, \quad l_i=0,1,2,\ldots \quad \text{and} \quad \pi_{z_i}=0,1. \tag{2.5}$$

The exponents α_i and β_i serve as positive, nonlinear variational parameters. Due to these parameters, the one-particle functions are flexible enough to be adapted to the situation of an arbitrary field strength: in the weak magnetic field regime a basis set with an almost isotropic choice of parameters $\alpha_i\approx\beta_i$ describes the slightly perturbed spherical symmetry. For very high magnetic fields it is appropriate to choose $\alpha=\gamma/4$ since $\rho^{|m_i|}\exp(-\gamma/4\,\rho^2)$ yields the ρ dependence of the lowest Landau level for a given magnetic quantum number. The β_i will be well tempered in a wide region. In the intermediate field regime the basis is composed of functions with certain magnetic-field-dependent sets of $\{\alpha_i,\beta_i\}$ which mediate the extreme cases. The optimal choice is found by searching the set of $\{\alpha_i,\beta_i\}$ which yields the lowest eigen-

values of the one-particle Hamiltonian. The parameters $\{\alpha_i,\beta_i\}$ are successively optimized using the pattern search algorithm. In this manner we have optimized up to five excited states in every symmetry subspace. The starting values for the parameters $\{\alpha_i,\beta_i\}$ have to be chosen very carefully to find a deep local or even the global minimum. Since the search in this high-dimensional space is very time consuming, an optimal choice of the k_i and l_i is crucial: for every new k_i,l_i configuration a new optimization procedure has to be started. The resulting binding energies for the neutral hydrogen atom were identical to 7–9 digits with the one given in [8] for almost all field strengths for the ground state and 5–7 digits were recovered for states with higher magnetic quantum number $|m_i|$.

We point out that Blinowski and Szwacka [24] have used a similar basis set, but without the monomers ρ^{2k_i} and z^{2l_i}. The additional monomers, however, decisively enhance the flexibility and accuracy of the calculations.

C. Two-particle configurations

As a next step we build two-particle configurations from our optimized one-particle basis set and represent the Hamiltonian (2.1) in this configuration space. This is done for each total symmetry (S^2,Π_z,L_z) separately. The corresponding spectrum of H^- is then obtained by diagonalizing the Hamiltonian matrix. We hereby use all possible excited two-particle configurations constructed from our optimized one-particle basis set, i.e., our approach is a full configuration-interaction method (full CI). The two-particle functions are constructed from the one-particle functions by selecting combinations for $m_i+m_j=M$ and $\pi_{zi}+\pi_{zj}=\Pi_z$. The spin part can be trivially separated. Due to the antisymmetrization of the spatial wave function the configuration space of the triplet states is slightly smaller than that of the singlet states since for triplet configurations there are no combinations with $i=j$.

As our basis set is not orthogonal we have to solve a finite-dimensional generalized real symmetric eigenvalue problem

$$(\underline{\underline{H}}-E\underline{\underline{S}})\cdot\underline{c}=0 \tag{2.6}$$

where $\underline{\underline{H}}$ is the matrix representation of the Hamiltonian and $\underline{\underline{S}}$ the overlap matrix. The resulting energies E are strict upper bounds to the exact eigenvalues in the given subspace of symmetries.

Some technical remarks concerning the calculation of the matrix elements are in order. All matrix elements can be evaluated analytically. With the exception of the electron-electron integrals all expressions can be calculated very rapidly. The electron-electron integrals, however, deserve a special treatment: through a combination of transformation techniques as well as analytical continuation formulas for the series of involved transcendental functions their representation has been simplified enormously (for details see Ref. [12] and in particular [13]). It is due to this extremely efficient implementation of the electron-electron integral that large basis sets of the order of $2500-4000$ could be used in the present work to perform configuration-interaction (CI) calculations for many field strengths.

III. SELECTION OF THE BASIS FUNCTIONS

Since the single bound state in the absence of the external field is bound only due to correlation, and all the other states in the presence of the magnetic field are only weakly bound, it is very important to include correlation by a proper choice of the one-particle basis functions building up the two-particle configurations. For the $M=0$ singlet state this was achieved by selecting one-particle basis functions not only with $m_1=m_2=0$ but also with $m_1=-m_2\neq 0$. This allows one to describe the angular correlation which is particular important for the ^{10} state. In general the enhanced binding properties of negative ions in the presence of a magnetic field are due to a balanced competition of the different interactions. On the one hand, the confinement due to the magnetic field raises the kinetic energy and the electrostatic repulsion due to the electron-electron interaction. These effects tend to lower the binding energy. On the other hand, the confinement raises the nuclear attraction energy, the exchange energy, and to some extent also the correlation energy which tend to enhance the binding energy. Of course one has to distinguish between, for example, the ^{10} state whose binding properties are dominated by correlation effects and the excited bound states with nonzero magnetic quantum numbers which possess a significant contribution to their binding energy through exchange effects and due to the occupation of the series of tightly bound hydrogenic orbitals $1s,2p_{-1},3d_{-2},\ldots$, etc.

For a description of the lowest states with $|M|>0$ an effective one-particle picture can be employed [17]: the hydrogen negative ion consists of a tightly bound core electron with magnetic quantum number zero and a significantly less bound electron which carries the magnetic quantum number of the ion. The core electron is then described by one-particle basis functions with $m_1=0$. The outer electron is described by one-particle functions with $m_2=M$ in order to take into account the fact that it is weakly bound and thus spatially extended. In order to go beyond this effective one-particle picture we used, similar to the case $M=0$, one-particle functions with other magnetic quantum numbers to obtain in particular the correlation behavior.

The above picture is not valid for the tightly bound states in the high field regime: the number of functions with different magnetic quantum numbers can be reduced as we increase the field strength. This reduction in the number of basis functions is also suggested by the occurrence of linear dependencies for strong fields. The extent of this reduction can be seen from the fact that the number of two-particle basis functions drops from 4000 for $\gamma=0$ to less than 3000 for $\gamma=4000$ for the ^{10} state.

IV. RESULTS AND DISCUSSION

As already mentioned the H^- ion possesses only one bound state in the absence of the magnetic field [9]. Turning on the field it has been shown [10] that there exists (for

infinite nuclear mass) for any nonzero field an infinite number of bound states. The corresponding proof [10] relies on the physical picture [11] that the external electron is for weak fields far from the neutral atomic core and experiences, therefore, to lowest order a polarization potential due to the induced dipole moment of the core. Perpendicular to the field the motion of the external electron is dominated by the field and it occupies approximately Landau orbitals whereas parallel to the field it is weakly bound due to the projection of the mentioned polarization potential on the Landau orbitals which yields a one-dimensional binding along the field. For typical strong laboratory fields the corresponding binding energies are of the order of 10^{-6} eV for the hydrogen atom negative ion and are significantly larger for more electron atoms with a larger polarizability. To investigate these states in the weak field regime goes clearly beyond the feasibility of the present method. Instead we will investigate a number of states, starting from the value of the field strength for which they become significantly bound, which means that the outer electron is already relatively close to the core and possesses a binding energy of at least a few meV. Clearly in that case the picture of the polarization potential is no longer valid since exchange and correlation effects rule the binding properties of the ion. Within our approach we could find one bound state for each negative magnetic quantum number of the ion considered ($-3 \leqslant M \leqslant 0$) for both singlet and triplet states, except the $^3 0$ state, which is unbound. Their behavior has been studied for the complete range of field strengths $0.01 \leqslant \gamma \leqslant 4000$. The one bound state of the H^- ion in the absence of the field represents, in the above sense, an exception since it is already significantly bound without the field. All these states possess positive *z* parity and *no bound states could be found for negative z* parity.

A. Threshold energies

The electron detachment energy is defined to be the energy we need to remove one electron from the atom without changing the quantum numbers of the total system. The corresponding lowest threshold energy E_T for the H^- ion can be expressed as

$$E_T = \frac{\gamma}{2}(|M| + M + 2 + g_e M_s) - I(\mathrm{H}), \tag{4.1}$$

where $I(\mathrm{H})$ is the binding energy of the ground state of the neutral hydrogen atom in a magnetic field. The term $\gamma/2(|M|+M+2)$ is the energy of an electron in the lowest Landau level with magnetic quantum number $m=M$ where the spin part is omitted. This means that the free electron carries the whole angular momentum of the state. For magnetic quantum numbers $M \leqslant 0$ the threshold energy E_T is independent of the angular momentum *M*, i.e., there is only a singlet and a triplet threshold. The threshold energy is then $E_T = \gamma - I(\mathrm{H})$ for singlet states and $E_T = -I(\mathrm{H})$ for triplet states. We denote the electron detachment energy by $I(H^-)$ which is given by $I(H^-) = E_T - E_{tot}$ where E_{tot} is the total energy of the considered state of H^-.

B. Total, electron detachment, and transition energies

Before we discuss the individual states and their properties let us describe some general features of the states considered here. The total energy of the singlet states is monotonically increasing with increasing field strength. This fact is caused by the increase of the field-dependent kinetic energy. In contrast to this the total energy of the triplet states is monotonically decreasing with increasing field strengths. This is a consequence of the additional spin Zeeman term (we consider here only the $S_z = -1$ component of the spin triplet states). *The electron detachment energies are monotonically increasing with increasing field strength for all states considered here, i.e., both singlet and triplet states.* This has to be seen in view of the above-mentioned fact that the zero-point kinetic (Landau) energy of the electrons is raised in the presence of the magnetic field and therefore the threshold energy for loosing one electron is raised in the same way.

For the $^1 0$ state the total energy raises from $-0.527\,548\,75$ at $\gamma = 0$ to 3986.498 70 at $\gamma = 4000$. This state is the most tightly bound state for all field strengths. The detachment energy increases from 0.027 549 a.u. at $\gamma = 0$ to 2.298 05 a.u. at $\gamma = 4000$. There are two reasons which give rise to the fact that this state is the most tightly bound one. On the one hand, the electrons are in this state much closer to the nucleus than in other states. This increases the binding due to the attractive nuclear potential energy. On the other hand, correlation has an important impact on the binding energy. Both effects are reinforced with increasing field strength as the electrons become more and more confined in the *x*-*y* plane perpendicular to the magnetic field. These effects overcome the influence of the static electron-electron repulsion. The total energies and the detachment energies of the $^1 0$ state are presented in Table I. It can be seen that the detachment energies for this most tightly bound state could be improved by 1–2 % for all field strengths compared to the existing literature. This is not correct for a vanishing field, where much more efficient basis sets like the Hylleraas basis set are available. For numerical reasons the relative accuracy for the detachment energies is largest in the intermediate field regime.

The $^3 0$ state is not bound for all considered field strengths. This can be understood in an effective particle picture as follows: for triplet states the spatial two-particle wave function is antisymmetric with respect to particle exchange and therefore the two particles have to occupy different spatial orbitals, i.e., we are exclusively dealing with excited configurations. For $M \neq 0$ it is (see later) possible to obtained tightly bound triplet states in a strong magnetic field by occupying different orbitals of the hydrogenic series $(1s, 2p_{-1}, 3d_{-2}, \ldots)$ which yields the one-particle excited configurations of the type $1s2p_{-1}, 1s3d_{-2}, \ldots$. For the case of the $^3 0$ state, however, we have $M = 0$ and only configurations constructed from pairs of two orbitals with $(m, -m)$ are allowed which are either of doubly excited character $(m \neq 0)$ or a singly excited configuration with $m = 0$. Therefore no magnetically tightly bound configurations are allowed for the $^3 0$ state which illuminates its unbound char-

TABLE I. Nonrelativistic fixed nucleus total and electron detachment energies of the field-free ground state $^1 0$ ($^1S_0$) of H^-. We also provide the results for the electron detachment energies given in the literature so far.

γ	E_{tot}	$I(H^-)$	$I_{Lit}(H^-)$
0	−0.52754875	0.02754875	0.2775 [a]
8×10^{-4}	−0.52754430	0.02794446	
1×10^{-3}	−0.52754053	0.02804078	0.02735 [b]
2×10^{-3}	−0.52753777	0.02853877	0.02785 [b]
5×10^{-3}	−0.52749800	0.03000425	0.0293 [b]
8×10^{-3}	−0.52740873	0.03142473	
0.01	−0.52734972	0.03237472	0.0317 [b]
0.02	−0.52677018	0.03687014	0.0362 [b]
0.05	−0.52314046	0.04876375	
0.08	−0.51715770	0.05874669	
0.1	−0.51223522	0.06470874	0.0634 [c]
0.2	−0.47868356	0.08830200	0.08685 [c]
0.5	−0.32804874	0.13083820	0.130 [d]
0.8	−0.13939006	0.15710667	
1.0	−0.00178881	0.17061922	0.1695 [d]
2.0	0.75990486	0.21788123	0.2175 [d]
5.0	3.3234387	0.2961625	0.2955 [d]
8.0	6.0350437	0.3455713	
10.0	7.8806402	0.3715626	0.371 [d]
20.0	17.319887	0.464715	0.463 [d]
50.0	46.359385	0.622747	0.618 [d]
80.0	75.753770	0.721953	
100.0	95.436219	0.773977	0.7665 [d]
200.0	194.31374	0.95911	0.9385 [d]
500.0	492.47687	1.26604	
800.0	791.35985	1.45501	
1000.0	990.78459	1.55299	
2000.0	1988.8003	1.8949	
4000.0	3986.4978	2.2981	

[a]See Pekeris [27].
[b]See Park and Starace [20].
[c]See Larsen [17].
[d]See Larsen [22].

acter for any field strength. All singlet and triplet electron detachment energies of all the considered bound states are presented also graphically: Fig. 1 shows the singlet detachment energies and Fig. 2 the corresponding energies for the triplet states.

It is important to mention that the global ground state of the ion undergoes a crossover with respect to its symmetry with increasing field strength. For weak fields the $^1 0$ state is the ground state of the system, whereas in strong fields the $^3(-1)$ state becomes the ground state which was first shown in Ref. [15]. This is caused by the spin Zeeman term, which lowers the total energy of the triplet states. The crossover takes place at $\gamma_c \approx 0.05$ which corresponds to approximately 10^4 T for the H^- ion. The $^3(-1)$ state is very weakly bound when it becomes the ground state (at γ_c the detachment energy is $\approx 3\times10^{-4}$ a.u.). This prevents us from localizing more exactly the field strength at which the crossover takes place. The $^3(-1)$ state, being the ground state of the anion for $\gamma > \gamma_c$, never becomes the most tightly bound state. At $\gamma = 4000$ its electron detachment energy is 1.25 a.u. and therefore much less than the detachment energy of the $^1 0$ state. This is due to the fact that the tightly bound states are formed by occupying the hydrogenic series $1s, 2p_{-1}, 3d_{-2}, \ldots$ (as mentioned above) and the $^1 0$ states allows for the $1s^2$ configuration yielding the strongest binding although it represents an excited state for $\gamma > \gamma_c$ due to its spin character.

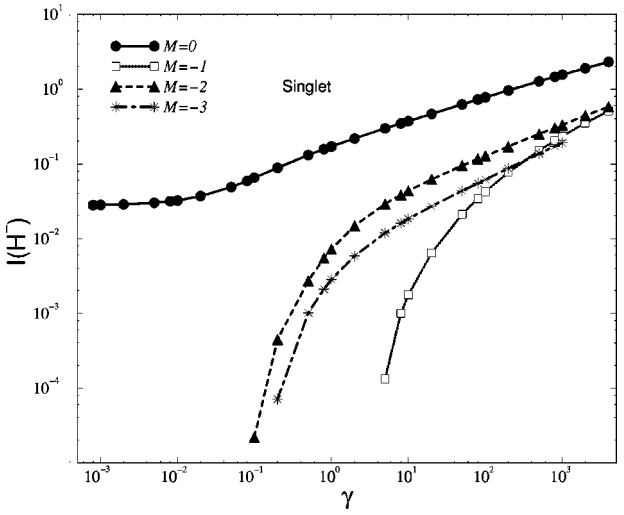

FIG. 1. Electron detachment energies of the singlet states in atomic units. Note that the $M=-1$ singlet state is not bound for weak fields and is for $5 \lesssim \gamma \lesssim 300$ weaker bound than all other states considered. For $\gamma \approx 300$ and $\gamma \gtrsim 4000$ we encounter crossings of the detachment energies of the $^1(-1)$ with those of the $^1(-3)$ and $^1(-2)$ states, respectively.

The singlet state $^1(-1)$ is not bound for weak fields. It becomes bound in the regime $\gamma \approx 1-5$ which is an unexpected behavior. The $^1(-1)$ state lies higher in the spectrum than the bound $^1(-2)$ and $^1(-3)$ states for the intermediate

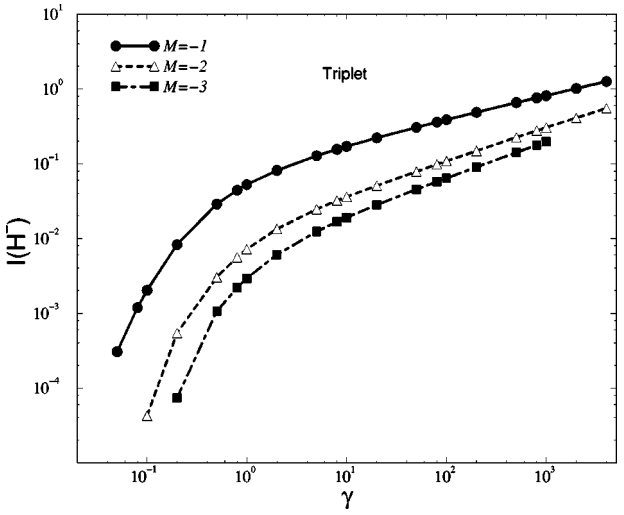

FIG. 2. Electron detachment energies of the triplet states in atomic units.

TABLE II. Nonrelativistic total and electron detachment energies (atomic units) of singlet and triplet states with $M=-1$ as a function of the magnetic field strength γ. These states evolve from the $^1P_{-1}$ and $^3P_{-1}$ states for zero magnetic field.

	$^1(-1)$			$^3(-1)$		
γ	E_{tot}	$I(H^-)$	$I_{Lit}(H^-)$	E_{tot}	$I(H^-)$	$I_{Lit}(H^-)$
0.05				−0.52468218	0.00030547	0.00025 [a]
0.08				−0.53959063	0.00117963	
0.1				−0.54954554	0.00201906	0.0016 [a]
0.2				−0.59861960	0.00823804	0.0072 [a]
0.5				−0.72586763	0.02865709	0.027875 [b]
0.8				−0.82643425	0.04415086	
1.0				−0.88359474	0.05242585	0.0518 [b]
2.0				−1.1036308	0.0814168	0.0805 [b]
5.0	3.6194699	0.0001312		−1.5081497	0.1277508	0.1263 [b]
8.0	6.3792043	0.0009946		−1.7751617	0.1557768	
10.0	8.2504454	0.0017574		−1.9181202	0.1703230	0.168 [b]
20.0	17.778209	0.006392		−2.436716	0.221318	0.2175 [b]
50.0	46.961089	0.021050		−3.323515	0.305655	0.309 [b]
80.0	76.441490	0.034306		−3.882658	0.358381	
100.0	96.167783	0.042402	0.00281 [b]	−4.175890	0.386100	0.38015 [b]
200.0	195.19141	0.07671	0.0407 [b]	−5.21214	0.48500	0.4771 [b]
500.0	493.59274	0.15017		−6.90934	0.65226	
800.0	792.61061	0.20426		−7.94296	0.75783	
1000.0	992.10306	0.23452	0.1727 [b]	−8.47584	0.81343	
2000.0	1990.3441	0.3511	0.2732 [b]	−10.3165	1.0117	
4000.0	3988.2901	0.5057		−12.4576	1.2534	

[a]See Larsen [17].

[b]See Larsen and McCann [23].

field region. In the high field region, however, it crosses both states. The crossing with the $^1(-3)$ takes place at $\gamma\approx 300$; the crossing with the $^1(-2)$ state is at $\gamma\gtrsim 4000$. Unfortunately, the accuracy of our method is not sufficient to provide a closer look at this crossing. The fact that the $^1(-1)$ state is not bound for weak fields but bound for strong fields is a consequence of the complicated interplay of the different interactions. The Coulomb repulsion of the two electrons is much weaker for the spatially antisymmetric triplet states compared to the singlet states. The electron-electron repulsion is higher for the states with $M=-1$ compared to the states with $M<-1$. This pushes the $|M|=1$ singlet states for weak fields beyond the threshold energy, i.e., makes them unbound. The total ionization and the detachment energies of the singlet and triplet states with $M=-1$ are presented in Table II. The suppression of the binding for the singlet state can clearly be seen from this table: the detachment energy of the singlet is 100 times lower than for the triplet at $\gamma=10$, but at $\gamma=4000$ the ratio is of the order 2. The comparison with the literature (see Table II) shows that our detachment energies are variationally lower by several percent than the best available data. For the situation of weakly bound states the improvement is significantly larger.

Let us now consider the energies for the states with $M=-2$ which are presented in Table III. Focusing on the detachment energies we realize that for weak fields the triplet state possesses a larger detachment energy than the singlet state, but for intermediate and high fields the singlet state is stronger bound than the triplet one, i.e., we encounter a crossover which is presented in Fig. 3. Compared to the data of Ref. [23], our method yields 5–10 % higher variational detachment energies for the triplet state and several times higher detachment energies for the singlet one. If we consider the singlet-triplet splitting which is the difference of the total energies between the singlet and the triplet state, where the spin-Zeeman shift is omitted, it can be observed that for all states this splitting behaves monotonically increasing with increasing field strength in the weak field regime. The splitting for the states with $M=-2$ and $M=-3$ are shown in Fig. 4. The splitting for the $M=-2$ states increases in weak fields, but for high fields this splitting decreases and becomes negative above some critial field strength. It seems that the Coulomb repulsion, due to antisymmetrization of the wave function is dominated by correlation effects. That the above observation is in fact a consequence of correlation is supported by Vincke and Baye [21]: the reversed order concerning the detachment energies (see Fig. 3) occurs if they include so-called transverse mixing, which simulates correlations in their approach.

For states with $M=-3$ only a few published data are available. These states are only weakly bound, although they are stronger bound for $\gamma\gtrsim 300$ than the $^1(-1)$ state. The singlet state has for $\gamma=0.2$ a detachment energy of 7.1×10^{-5} a.u. and at $\gamma=1000$ its detachment energy is 0.19.

TABLE III. Nonrelativistic total eigenenergies and electron detachment energies (atomic units) of singlet and triplet states with $M=-2$ as a function of the magnetic field strength γ. These states evolve from the $^1D_{-2}$ and $^3D_{-2}$ states in the absence of a magnetic field.

	$^1(-2)$			$^3(-2)$		
γ	E_{tot}	$I(H^-)$	$I_{Lit}(H^-)$	E_{tot}	$I(H^-)$	$I_{Lit}(H^-)$
0.1	−0.44754846	$2.20\ 10^{-5}$		−0.54756898	$4.25\ 10^{-5}$	
0.2	−0.39082732	0.00044576		−0.59092467	0.00054311	
0.5	−0.19993316	0.00272262		−0.70022629	0.00301575	0.0023 [a]
0.8	0.01224680	0.00546981		−0.78790031	0.00561691	
1.0	0.16158323	0.00724788	0.0015 [a]	−0.83835741	0.00718852	0.0064 [a]
2.0	0.96305720	0.01472889		−1.03557327	0.01335936	0.0123 [a]
5.0	3.5905353	0.0290659		−1.4049975	0.0245987	0.02290 [a]
8.0	6.3421331	0.0384819		−1.6512176	0.0318326	
10.0	8.2087000	0.0435028	0.006 [a]	−1.7838114	0.0360142	0.0335 [a]
20.0	17.722831	0.061762		−2.2663464	0.0509479	0.047 [a]
50.0	46.888223	0.093916		−3.096448	0.078587	0.0719 [a]
80.0	76.360491	0.115232		−3.621917	0.097640	
100.0	96.083393	0.126803	0.03 [a]	−3.897965	0.108128	0.09895 [a]
200.0	195.10291	0.16995		−4.87531	0.14817	0.13535 [a]
500.0	493.49377	0.24914		−6.48097	0.22388	
800.0	792.51251	0.30235		−7.46090	0.27576	
1000.0	992.00594	0.33164		−7.96662	0.30420	
2000.0	1990.2556	0.4397		−9.7152	0.4105	
4000.0	3988.2159	0.5799		−11.7535	0.5493	

[a]See Larsen and McCann [23].

The electron detachment energies of the triplet state are of the same order of magnitude and the absolute value of the singlet triplet splitting is the lowest of the states considered here. As a consequence a careful convergence study of the results (detachment energy) is indispensable. Our data are given in Table IV.

The wavelengths of the transitions of the singlet states are presented in Fig. 5. The wavelengths are monotonically decreasing with increasing field strength except for the transition from the $^1(-1)$ state to the $^1(-2)$ state. As mentioned above these states cross at $\gamma \gtrsim 4\,000$. Therefore the corresponding wavelength for this transition diverges at the crossing field strength. The transition wavelengths for the triplet states shown in Fig. 6 are also monotonically decreasing with increasing field strength.

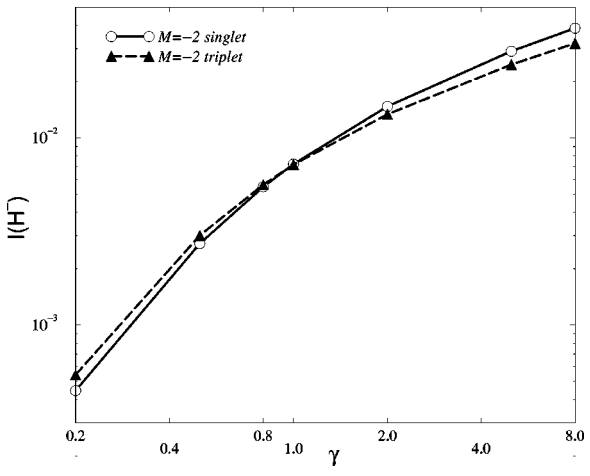

FIG. 3. Electron detachment energies of the singlet and triplet state of the $M=-2$ states in atomic units. Note that the singlet and triplet state reverse their order: For low field strengths the triplet state is more bound whereas for high fields ($\gamma \gtrsim 1$) the singlet state is more bound than the triplet state.

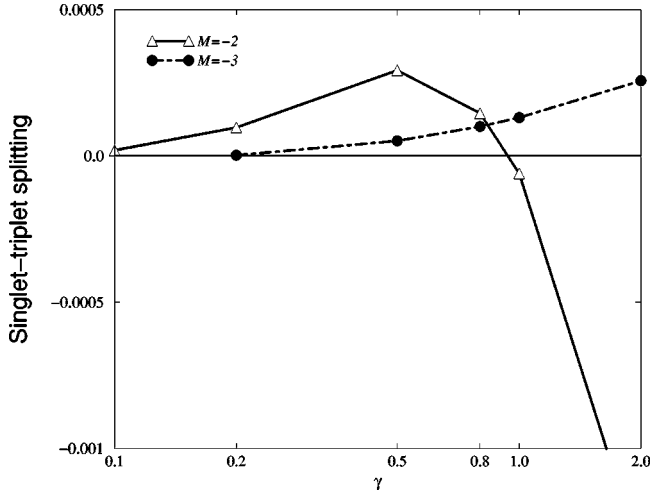

FIG. 4. Singlet triplet splitting for the $M=-2$ and the $M=-3$ states in atomic units. The splitting due to the spin Zeeman term is omitted. Note that the splitting of the $M=-2$ states increases for low fields but decreases for high fields, whereas the splitting for the $M=-3$ states increases monotonically with increasing field strength.

TABLE IV. Nonrelativistic total and electron detachment energies (atomic units) of singlet and triplet states with $M=-3$ as a function of the magnetic field strength γ. These states evolve from the $^1F_{-3}$ and $^3F_{-3}$ states in the absence of a magnetic field.

	$^1(-3)$		$^3(-3)$		
γ	E_{tot}	$I(H^-)$	E_{tot}	E_{tot} (Lit.)	$I(H^-)$
0.2	−0.39045232	7.075×10^{-5}	−0.59046132		7.975×10^{-5}
0.5	−0.19822524	0.00101470	−0.69827772		0.00106718
0.8	0.01561745	0.00209916	−0.38448370		0.00220031
1.0	0.16602786	0.00280324	−0.83410348	−0.7092618 [a]	0.00293459
2.0	0.97196637	0.00581972	−1.02829096		0.00607705
5.0	3.6077963	0.0118049	−1.3927524		0.0123535
8.0	6.3646091	0.0160059	−1.6361379		0.0167528
10.0	8.2339720	0.0182308	−1.7669036		0.0191064
20.0	17.757749	0.026853	−2.243571		0.028172
50.0	46.938916	0.043223	−3.063189		0.045328
80.0	76.420911	0.054812	−3.581678		0.057401
100.0	96.148914	0.061282	−3.853929		0.064125
200.0	195.18642	0.08643	−4.81732		0.09017
500.0	493.60717	0.13574	−6.39799		0.14091
800.0	792.64412	0.17074	−7.36188		0.17675
1000.0	992.14738	0.19020	−7.8591	−7.686295 [a]	0.19663

[a]See Thurner *et al.* [7].

Finally we comment on corrections due to the finite nuclear mass. There are two kinds of corrections that are relevant here. One correction is special for ions in strong magnetic fields and which describes the coupling between the center of mass motion and the electronic motion. This coupling is due to a motional electric field of intrinsic dynamical origin seen by the moving ion in a magnetic field [31]. The second kind of corrections are due to the replacement of the naked masses by reduced ones which can be easily included in our data by performing the corresponding shifts [12–14] . A full dynamical treatment of the atomic ion, including the collective motion, goes clearly beyond the scope of the present investigation. It is important to note that for the case of the fixed negative donors there naturally occur no such corrections.

V. BRIEF SUMMARY

We have investigated the H^- ion, negative donors D^-, respectively, in a strong magnetic field via a fully correlated approach. The key ingredient is an anisotropic Gaussian basis set, whose one-particle wave functions are nonlinearly optimized in order to obtain the spectrum of the one-particle Hamiltonian. In contrast to other basis sets, which are appro-

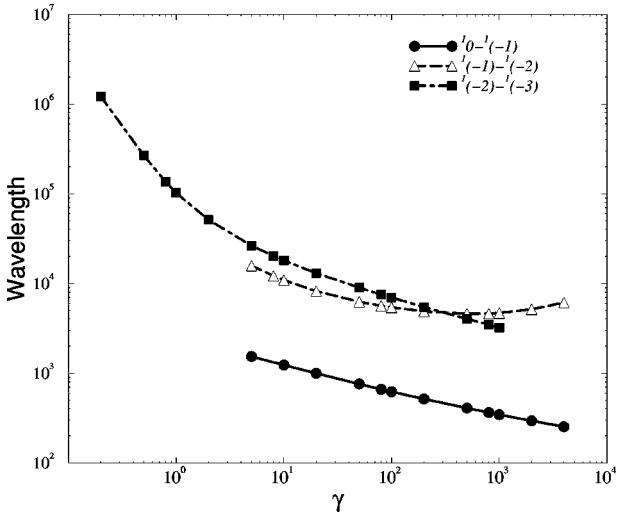

FIG. 5. Singlet transition wavelengths between the considered *bound* states in Ångstrøm as a function of the field strengths in atomic units on a logarithmic scale.

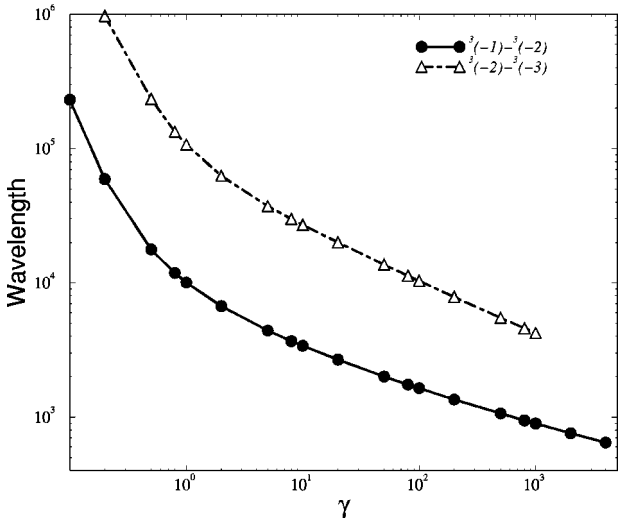

FIG. 6. Triplet transition wavelengths between the considered states in Ångstrøm as a function of the field strength in atomic units on a logarithmic scale.

priate either for the low field or for the high field regime, our basis set is flexible enough to be adapted to the situation of arbitrary field strength and especially suited for the intermediate field regime. All calculations were performed in the infinite mass frame neglecting relativistic corrections.

We have investigated the low field ground state $^1 0$, as well as singlet and triplet states for $M=-1,-2,-3$ for the broad field regime $\gamma=8\times10^{-4}-4\times10^{3}$. For all states and almost all field strengths we could reach at least 1–2 % higher binding energies, compared to all other published data. For some states our binding energies were larger by a factor up to 2. The global ground state undergoes a crossover with respect to its symmetry which is well known in the literature [15]: for weak fields $\gamma\lesssim5\times10^{-2}$ the global ground state is the $^1 0$ state, whereas for $\gamma\gtrsim5\times10^{-2}$ it is the $^3(-1)$ state, which is much weaker bound than the $^1 0$ state for all field strengths. The $^1(-1)$ state becomes bound for $\gamma\lesssim5$ and it crosses the $^1(-3)$ state at $\gamma\approx300$ and the $^1(-2)$ state at $\gamma\gtrsim4000$. We have also investigated the electronic states with $M=-2$ in detail. For $\gamma\lesssim1$ the triplet state is stronger bound than the singlet, whereas for $\gamma\gtrsim1$ the singlet is stronger bound than the triplet. Explanations for the binding mechanisms of the considered states have been provided. The transition wavelengths for all allowed transitions as a function of the field strength are thereby obtained. No stationary transitions which could be of relevance to the astrophysical observation in magnetized white dwarfs have been observed.

ACKNOWLEDGMENTS

The Deutsche Forschungsgemeinschaft (O.A.A.) is gratefully acknowledged for financial support. We thank W. Becken for many fruitful discussions and for his help concerning computational aspects of the present work.

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