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Variational studies of bound states of the H^- ion in a magnetic field

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Variational calculations of bound states of H^- ions in magnetic fields have been undertaken in an attempt to understand the role of magnetic field, exchange, and correlation in the binding, particularly for those states which are unbound in the absence of a field. Field-induced binding at weak fields is pictured as a trapping of the outer electron in two dimensions by the magnetic field and in the third dimension by the induced polarization of the inner H atom. Singlet and triplet states of various angular momenta are studied. Results are presented also for a number of He-atom levels. It is shown that positrons bind to H atoms in a magnetic field.

I. INTRODUCTION

The H^- ion, a proton with two electrons attached, has been studied theoretically for 50 years, and its electronic structure is by now very accurately understood.[1] At zero magnetic field H^- is known to have exactly one bound state,[2] a ^1S level, with total energy close to $-1.0555\ \mathcal{R}_H$, where $\mathcal{R}_H$ is the H-atom Rydberg.[3]

In contrast, the behavior of H^- ions in intense magnetic fields, fields strong enough to affect the H^- orbital wave function significantly, has been much less well explored. This problem has attracted attention in astrophysics with the discovery of very large magnetic fields in neutron stars and in some white dwarfs.[4-6] However, it would seem that the main experimental interest in H^- arises in the study of H^- analogs in semiconductors at low temperatures.

Since 1970, strong experimental evidence has accumulated for the existence of long-lived D^- ions, singly charged donor ions with two electrons attached, in the multivalley semiconductors Si and Ge.[7-11] Under properly applied stress, D^- levels in these materials are expected to be basically similar in structure to those of the H^- ion.[10] Recently, evidence has been put forward for the existence of D^- centers in CdS, a single-valley semiconductor; in this material the D^- ion should be very closely analogous to H^-.[12] Since, in the conduction band of semiconductors, the effective strength of an applied magnetic field on a D^- ion may be magnified by a factor of 10^4 or more relative to the same field applied to an H^- ion in vacuum, the study of H^--ion analogs at high effective fields is possible in the laboratory. Thus, there is motivation from semiconductor physics to re-examine the problem of the H^- ion in magnetic fields strong enough to sensibly alter the two-electron wave function.[13]

In this paper we will be concerned with calculating binding energies of various states of the H^- ion. These states can have orbital wave functions which are either symmetric upon interchange of electron coordinates (singlet states) or antisymmetric (triplet states). The magnetic field, $\vec{B}$ will be taken along the z direction, and the H^- states will be labeled by M_L, the component of total orbital angular momentum along $\hat{z}$. M_L can take on any integer value. Just like the Hamiltonian for the H atom in a magnetic field, the H^- Hamiltonian is invariant under reflection through a plane perpendicular to $\vec{B}$ and passing through the proton. This means that we should attach a z-parity quantum number ± 1 to the wave functions according to whether they are even or odd upon the above-mentioned reflection. Since no bound states of odd z-parity have been found, we suppress this quantum number and, unless otherwise specified, assume it to be $+1$ for all states considered.

By the "binding energy" of a state of the H^- ion, we mean the least amount of energy required to remove *one* of the electrons from the H^- ion to infinity without changing the spin configuration. The remaining hydrogen atom is left in its ground state in the magnetic field, and the distant electron in its lowest Landau level. (Thus a singlet H^- state can lie above the lowest triplet continuum edge when the Zeeman spin energy is included and still have a positive binding energy by our definition.)

For the hydrogen atom in a magnetic field, we use the Hamiltonian

$$H(1) = -\nabla_1^2 - 2/r_1 + \tfrac{1}{4}\gamma^2\rho_1^2 , \tag{1}$$

and for the H^- ion, the Hamiltonian

$$H = H(1) + H(2) + 2/|\vec{r}_1 - \vec{r}_2| + \gamma M_L , \tag{2}$$

where $\vec{r}_i$ is the displacement of electron i from the proton, $r_i^2 = \rho_i^2 + z_i^2$, and

$$\gamma = \hbar\omega_c/2\mathcal{R}, \quad \omega_c = eB/m^*c, \quad \mathcal{R} = m^*e^4/2\epsilon_0^2\hbar \ . \tag{3}$$

We have assumed an infinitely massive proton, ignored the Zeeman spin energy (which does not affect our binding energies), and have taken all lengths in units of the hydrogenic Bohr radius a_0 ($a_0 = \hbar^2\epsilon_0/m^*e^2$). Hamiltonians (1) and (2) have been divided through by the hydrogenic Rydberg $\mathcal{R}$ and are universal in the sense that they are valid for the simplest kind of donors and D^- centers in semiconductors, as well as for H atoms and H^- ions. For the latter, we take $m^* = m$ where m is the mass of the electron in vacuum and set the static dielectric constant, ϵ_0, equal to 1.

The magnetic field appears in (1) and (2) only through the dimensionless parameter γ, which therefore plays the role of an effective field strength. For H atoms or H^- ions, $\gamma = 1$ requires $B = 2.35 \times 10^5\,T$. For the semiconductor GaAs ($m^* = 0.0663m$, $\epsilon_0 = 12.6$), $\gamma = 1$ for $B \cong 6.5T$.

If we denote the ground-state eigenvalue of (1) by $E_{\mathrm{Hy}}(\gamma)$ then, since γ is the lowest energy possible for the free electron in the dimensionless magnetic field γ, the binding energy $E_B(S, \gamma)$ of the state S of the H^- ion is given by

$$E_B(S, \gamma) = E_{\mathrm{Hy}}(\gamma) + \gamma - E_{\mathrm{H}^-}(S, \gamma) , \tag{4}$$

where $E_{\mathrm{H}^-}(S, \gamma)$ is the eigenvalue of (2) corresponding to state S. State S is bound if $E_B(S, \gamma)$ is positive. We shall use (4) to calculate binding energies for various states S, but since neither E_{Hy} nor E_{H^-} is known exactly, we shall insert approximate values for these quantities. For E_{Hy} we use the most accurate values known to us (see Table I), for E_{H^-}, our calculated variational values. Since E_{Hy} will be known in general to much higher accuracy than E_{H^-}, and since the variational estimates of E_{H^-} are always higher than the true value, our calculated binding energies using (4) will be lower bounds to the true binding energy. [Thus, in comparing two binding energies obtained via (4) from two variational calculations of $E_{\mathrm{H}^-}(S, \gamma)$, the better calculation will be the one giving the higher binding energy.] Negative binding energies correspond to unbound states.

Previous quantitative calculations have focused upon two states, the $M_L = 0$ singlet level which evolves from the ^1S zero-field H^- state when the magnetic field is adiabatically turned on, and the $M_L = -1$ triplet state, which does not bind at zero field but somehow becomes bound in the presence of a magnetic field. Basically two types of variational trial functions have been proposed. The earliest calculations employed linear combinations of large numbers of hydrogenlike Slater orbitals.[4] These calculations appear to be excellent for the $M_L = 0$ singlet state in "weak" fields ($\gamma \ll 1$) but are considerably less good for the $M_L = -1$ triplet level. Trial functions of this type have the disadvantage that it is not immediately obvious from the calculated results what is happening to the H^- wave function in the magnetic field. All other quantitative calculations[5, 6, 13] (with the exception of Ref. 12) have used variants of the trial function

$$\exp(iM_L\phi_1)\rho_1^{|M_L|} \exp[-\tfrac{1}{4}(\gamma_1\rho_1^2 + \gamma_2\rho_2^2)] f(z_1) g(z_2) \pm (1 \leftrightarrow 2). \tag{5}$$

These wave functions are simple and physically transparent; however, they are not at all well suited to the low- and intermediate-field region ($\gamma \gtrsim 5$), and, even at very high fields, they do not appear to give very accurate binding energies. In Refs. 5 and 6, γ_1 and γ_2 are set equal to their free-electron value γ, whereas in Ref. 13 they are treated as variational parameters. In Refs. 5 and 13, $f(z_1)\,g(z_2)$ is taken in the form

$$\exp-[-(\alpha z_1^2 + \beta z_2^2)]$$

with α and β varied, whereas in Ref. 6, f and g are determined in a Hartree-Fock calculation.

One question unanswered by the above-mentioned calculations is: At what magnetic field does the $M_L = -1$ triplet state first bind? The answer has been given in Ref. 14, where it is shown variationally that, in the limit $\gamma \to 0$, for each $M_L < 0$ there exists at least one bound state of H^-; therefore, the lowest $M_L = -1$ level begins to bind at an infinitesimal field. The trial function employed is

$$e^{iM_L\phi_1}\rho_1^{|M_L|} e^{-\gamma\rho_1^2/4} e^{-r_2} .$$

This simple trial function has no variational parameters; it is not suitable for *quantitative* calculations of binding even for the weakest fields.

In this paper, which is an extension of Ref. 12, variational calculations are presented using relatively simple and physically transparent trial functions which produce binding energies rivaling or exceeding those of the best previous calculations in the field range of greatest experimental interest in semiconductors, $0 \gtrsim \gamma \gtrsim 2$. Modifications for extending the calculations to still higher fields will be pointed out, but such calculations have not been pursued in general since it appears possible to extrapolate the results with sufficient accuracy to higher fields.

The purpose of this paper is not primarily to obtain extremely accurate binding energies for H^- ions in a magnetic field, but rather to gain an understanding of the physical mechanisms causing the binding. However, the justification of the physical hypotheses underlying our choice of trial functions ultimately resides in achieving accurate binding energies.

Calculations of binding energies of the lowest-lying states with $M_L = -2$ and -3 have not been reported previously. These states are of theoretical interest because they cast light on the role of exchange in the H^- problem. Results are presented here for $0 \leq \gamma \leq 3$.

The trial functions employed in the H^- problem turn out to be well suited for studying certain bound states of the He atom in a magnetic field. Some energies are tabulated.

Finally, it is shown that positrons bind to H^- atoms in magnetic fields although, as is already known, they do not at zero field.

II. GROUND STATE OF THE H ATOM IN A MAGNETIC FIELD

If there were no repulsion between the electrons in the H^- ion, the electronic orbitals in an applied magnetic field would be just those of a hydrogen atom in the field; that is, each orbital would be an eigenfunction of H(1) given by Eq. (1). Thus it is of interest for the H^- problem to examine the ground state of the H atom in a magnetic field. Although this problem has not been solved exactly, calculations show that when a magnetic field is slowly turned on, the ^1S wave function shrinks and changes in shape to something resembling an ellipsoid of revolution with major axis along the field. These two effects can be incorporated in a variety of ways in constructing trial functions; the energies obtained from some relatively simple forms are compared below.

Consider, for example, the class of functions given by

$$\phi^{(k)} = \left(\sum_{n=0}^{k} c_n z^{2n} \right) e^{-\delta r^2} e^{-\kappa r} . \tag{6}$$

These are quite convenient wave functions, even though all parameters (δ, κ, and $c_0 \cdots c_k$) are to be varied. The reason is that all integrals can be done analytically, and for given δ and κ the optimum c's can be obtained by solving linear equations. Optimum H-atom ground-state energies obtained from Eq. (6) are denoted $E_{\rm H}^{(k)}$. The variational energies $E_{\rm H}^{(k)}$ are most accurate at low fields, becoming exact at zero field, for which, of course, $\kappa = 1$, $c_0 = 1$, and all other parameters vanish in (6).

A two-parameter function which is much less satisfactory at low fields but which is still easier to handle is given with reference to Yafet, Keyes, and Adams (YKA) by[15]

$$\phi_{\rm YKA} = \exp[-\tfrac{1}{4}\gamma' \rho^2 - z^2/b^2] , \tag{7}$$

with corresponding optimized binding energies denoted by $E_{\rm H}^{(\rm YKA)}$. Even at strong fields, for which it is best suited, this function is not very accurate, $E_{\rm H}^{(\rm YKA)}$ being, for example, too low by ~ 0.36 $\mathcal{R}$ for $\gamma = 100$.

A related four-parameter function with which it is much less easy to work than (7) but which gives energies $E_{\rm H}^{(P)}$ of high accuracy over a wide range of fields is

$$\phi_P = \exp[-\tfrac{1}{4}\gamma' \rho^2 - z^2/b - \kappa(\rho^2 + \alpha z^2)^{1/2}] . \tag{8}$$

Hydrogen-atom binding energies obtained from these functions are compared to the extremely accurate variational values of Praddaude[16] and of Cabib[17] in Table I.

III. $M_L = 0$ SINGLET GROUND STATE

A. Low to moderate magnetic fields

States which are bound only in the presence of a magnetic field are qualitatively different from the $M_L = 0$ singlet ground state, which binds at

TABLE I. Comparison of ground-state binding energies of the H atom as calculated from various trial functions to the highly accurate results of Praddaude (Ref. 16), listed in the column labeled "Exact." The relevant trial functions are defined in Eqs. (6)–(8). All energies are in units of $\mathcal{R}$.

Field	H-atom ground-state binding energies from various wave functions					
γ	$E_{\rm H}^{(0)}$	$E_{\rm H}^{(1)}$	$E_{\rm H}^{(2)}$	$E_{\rm H}^{(\rm YKA)}$	$E_{\rm H}^{(P)}$	Exact
0.2	1.180 63	1.180 75	1.180 75	1.032	1.180 75	1.180 76
0.5	1.391 9	1.394 1	1.394 3	1.251	1.394 3	1.394 5[a]
1.0	1.647	1.660 3	1.661 7	1.524	1.662 0	1.662 33
2.0	1.982	2.033 3	2.042 0	1.908	2.043 8	2.044 42
3.0	2.199	2.301 8	2.321 9	2.191	2.328 2	2.329 05
5.0	2.460	2.685 3	2.735 8	2.616	2.759 4	2.760 81
10.0	2.657	3.240	3.387 7	3.331	3.492 8	3.495 61

[a] From Ref. 17.

zero magnetic field; we defer consideration of them to Sec. IV and focus here on the effects of the magnetic field on the zero-field ground state of H$^-$. Perhaps the simplest of the accurate trial functions proposed for this state in the absence of field is the Chandrasekhar wave function[1] ψ_{CH} given by

$$\psi_{\text{CH}} = (1 + C\,|\vec{r}_1 - \vec{r}_2|)[\exp(-r_1/a_1 - r_2/a_2) + (1 \longleftrightarrow 2)]. \tag{9}$$

Here the electrons are in ground-state hydrogenic orbitals; they are encouraged to stay apart, keeping down their repulsive interaction energy, by the correlation factor $(1 + C|\vec{r}_1 - \vec{r}_2|)$, which becomes relatively small as $|\vec{r}_1 - \vec{r}_2| \to 0$. The best values of a_1, a_2, and C are 0.930, 2.092, and 0.312, respectively. With these values the binding energy obtained is 0.0518 $\mathcal{R}$ as opposed to the "exact" value of 0.0555$\mathcal{R}$.[1,3]

To generalize Eq. (9) for the magnetic field case, one might well replace the hydrogenic ^1S orbitals there by some convenient orbitals appropriate to the H atom in a magnetic field. However, a simpler approach, and the one adopted here, is to take trial functions of the form

$$\psi^{(k)} = \sum_n c_n (z_1^{2n} + z_2^{2n}) \exp[-\delta(r_1^2 + r_2^2)]\,\psi_{\text{CH}}. \tag{10}$$

These functions are analogous to those in Eq. (6) in that the zero-field wave function is multiplied by a factor producing shrinkage $\{\exp[-\delta(r_1^2 + r_2^2)]\}$, as well as a shape-changing factor similar in effect to the one used in Eq. (6). Thus $\psi^{(k)}$ is an example of an H$^-$ wave function which becomes qualitatively just like the H-atom ground state in the magnetic field.

The variational energies

$$E_S^{(k)} \equiv \langle \psi^{(k)} | \text{H} | \psi^{(k)} \rangle / \langle \psi^{(k)} | \psi^{(k)} \rangle \tag{11}$$

are evaluated by introducing Hylleraas coordinates,[18] performing all angular integrations and the integration over the coordinate $u\,(u = |\vec{r}_1 - \vec{r}_2|)$ analytically and then evaluating the remaining two-dimensional integrals by computer. All parameters ($c_0 \cdots c_k$, δ, C, a_1, and a_2) are varied to obtain the binding energies $E_S^{(0)}$, $E_S^{(1)}$, $E_S^{(2)}$ listed in Table II and plotted in Fig. 1.

At a fixed value of k, both $\phi^{(k)}$ and $\psi^{(k)}$ give energies (for the H atom and H$^-$ ion, respectively) which become less accurate with increasing magnetic field. From knowledge of the accuracy of energies obtained from $\phi^{(k)}$ (see Table I), it is possible to develop schemes for estimating the error in energies obtained from $\psi^{(k)}$. A simple and reasonably accurate method of extrapolating $E_S^{(k)}$ to infinite k would be most welcome since actually increasing the k value in evaluating $E_S^{(k)}$ from Eq. (11), although certain to improve the energy at the higher fields, becomes very laborious. One method of extrapolation is described below.

TABLE II. Comparison of H$^-$ $M_L = 0$ singlet ground-state binding energies calculated using $\psi^{(k)}$ of Eq. (10) with the energies, $E_S^{(\text{SO})}$ of Ref. 4, using the Slater-orbital expansion. $E_S^{(\text{Ex})}$ is extrapolated from $E_S^{(1)}$ and $E_S^{(2)}$ as described in the text. All energies are in units of $\mathcal{R}$. The numerical accuracy of $E_S^{(k)}$ ($k = 0, 1, 2$) is estimated to be ±1 in the last-quoted digit.

Field	H$^-$ singlet ground-state binding energies from various wave functions				
γ	$E_S^{(0)}$	$E_S^{(1)}$	$E_S^{(2)}$	$E_S^{(\text{SO})}$	$E_S^{(\text{Ex})}$
0.0	0.0518	0.0519	0.0519	0.0537	0.0555
0.1	0.126	0.1267	0.1268	0.1276	0.130
0.2	0.168	0.1735	0.1737	0.1736	0.177
0.5	0.233	0.2543	0.2576		0.262
1.0	0.2503	0.3169	0.3309		0.341
2.0		0.3508	0.3937		0.427
3.0		0.3322	0.4082		0.475
5.0		0.2180	0.3658		0.519

In ψ_{CH}, given by Eq. (9), two orbitals appear, an inner electron orbital, $\exp(-r/0.93)$, and an outer orbital, $\exp(-r/2.092)$. The outer orbital will be the more strongly affected by magnetic fields in the range $0 < \gamma \leq 5$, and it is reasonable to attribute the error in $E_S^{(k)}$ for $\gamma \gtrsim 0.5$ largely to the failure of $\psi^{(k)}$ to describe properly the effect of the field on the outer orbital. At zero field this outer orbital is that of a ^1S electron with a Rydberg constant of $\hbar^2/[2m(2.092\,a_0)^2] = 0.2285\mathcal{R}$. Thus in a magnetic field it is not unreasonable to attribute to this orbital an effective γ value of $(\frac{1}{2}\hbar\omega_c)/(0.2285\mathcal{R}) = 4.38\,\gamma$. Denoting by

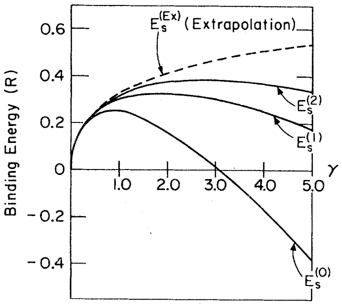

FIG. 1. Comparison of binding energies for the $M_L = 0$ singlet ground state of the H$^-$ ion from various trial functions given by Eq. (10). $E_S^{(\text{Ex})}$ is the extrapolated binding energy from Eq. (13) and is expected to be closest to the true binding energy. Some points used to plot the various curves can be found in Table II.

$\mathcal{E}^{(k)}(\gamma)$ the error in the computed energy of a hydrogen atom with a Rydberg constant of $0.2285\mathcal{R}$ in a field of $4.38\,\gamma$ when this energy is calculated variationally using $\phi^{(k)}$, we shall assume that the errors in the H$^-$ energies $E_S^{(k)}$, in Table I, are given by

$$A_0(\gamma)\mathcal{E}^{(k)}(\gamma)+A\ , \tag{12}$$

where $A_0(\gamma)$ is independent of k, and A independent of γ. We define an extrapolated binding energy and obtain an equation for A_0 by requiring

$$\begin{aligned} E_S^{(\mathrm{Ex})} &= E_S^{(1)}+A_0(\gamma)\mathcal{E}^{(1)}(\gamma)+A \\ &= E_S^{(2)}+A_0(\gamma)\mathcal{E}^{(2)}(\gamma)+A\ . \end{aligned} \tag{13}$$

A is determined at $\gamma=0$, where $\mathcal{E}^{(1)}=\mathcal{E}^{(2)}=0$, to be $0.0036\mathcal{R}$ from the known zero-field binding energy of the H$^-$ ion.[3] For $1\leq\gamma\leq 5$, $A_0(\gamma)$ is found to be nearly constant, deviating from the value 1.52 by not more than 1.5%.

Equation (13) simply requires that the energy extrapolated via (12) from a variational calculation using $\psi^{(1)}$ should equal that from $\psi^{(2)}$. If there is merit in this scheme, then it should also be true that

$$E_S^{(\mathrm{Ex})} \cong E_S^{(0)}+A_0(\gamma)\mathcal{E}^{(0)}(\gamma)+A \equiv E_S^{\prime(\mathrm{Ex})}\quad .$$

Checking at $\gamma=1$, we find $E_S^{\prime(\mathrm{Ex})}=E_S^{(\mathrm{Ex})}-0.0023\mathcal{R}$. Comparing the apparent error in $E_S^{\prime(\mathrm{Ex})}$ (which is $0.0023\mathcal{R}$) with that of $E_S^{(0)}$ from Table II (0.091) shows, gratifyingly, that a nearly 40-fold reduction of apparent error has been accomplished in $E_S^{(0)}$ at $\gamma=1$. This result also suggests that $E_S^{(\mathrm{Ex})}$, although not a rigorous lower bound, may nevertheless underestimate the true binding energy at the higher fields.

B. High-field limit

At extremely high fields where the inner electron orbital becomes dominated by magnetic forces ($\gamma\gg 1$), the trial functions $\psi^{(k)}$ are not useful. The motion of both electrons in directions perpendicular to z is determined by the magnetic field, and H in Eq. (2) becomes approximately separable.

In this limit a trial function of the form

$$\{1+C\ \tanh^2[\epsilon(z_1-z_2)]\}\{\exp[-\kappa(z_1^2+\alpha^2)^{1/2}-\beta(z_2^2+\alpha^2)^{1/2}]+(1\longleftrightarrow 2)\}\exp[-\tfrac{1}{4}\gamma'(\rho_1^2+\rho_2^2)] \tag{14}$$

which is similar in concept to the Chandrasekhar wave function of Eq. (9), is thought to be appropriate. The correlation is provided by the first factor, which goes to 1 when the electron separation in the z direction is small, and to $1+C$ when large. Although it is undoubtedly possible to improve upon the correlation factor of Eq. (14), a spherically symmetric correlation, that is, correlation depending upon $|\vec{r}_1-\vec{r}_2|$, which is appropriate at zero field, does not seem suitable in the high-field limit because such correlation admixes high-energy components (energies of order γ) into the x-y motion of the electrons. Put another way, the wave function is expected to be stiff to perturbations in the x-y motion but relatively loose in its z motion at very large γ.

The distinction between inner and outer orbitals disappears in the high-field limit, at least for the trial function (14). Both κ and β when optimized assume a common value 2.29 at $\gamma=100$, representing a nearly 30% expansion of the wave function in the z direction relative to its size when electron-electron repulsion is turned off. On the other hand, for $\gamma=100$, γ' in (14) is only 1% smaller with electron-electron repulsion acting than without, demonstrating strikingly the relative stiffness of the wave function to changes in the x-y motion at high fields.

Correlation is very important for obtaining good energies for $\gamma\gg 1$, just as it is at $\gamma=0$. For $\gamma=100$ the binding energy found employing (14) and optimizing all six parameters is $1.44\mathcal{R}$ (assuming $7.56\mathcal{R}$ for the H-atom binding in this field), but if C is set equal to zero (no correlation) and κ, α, β, and α' are then optimized, the best binding energy obtained is only $1.14\mathcal{R}$.

It is to be expected that the trial function (14) would be much better at very high fields than the function used in Ref. 13 (which is obtained from (5) by setting $M_L=0$ and replacing f and g by Gaussians) primarily because of correlation, but also because the orbitals $\exp[-\kappa(z^2+\alpha^2)^{1/2}]$ are better than Gaussian z orbitals. However, for $\gamma<5$ the ansatz of Ref. 13 gives the stronger binding because that ansatz allows distinct inner and outer orbitals, through the two-parameter factor $\exp[-\frac{1}{4}(\gamma_1\rho_1^2+\gamma_2\rho_2^2)]$.

IV. BOUND STATES INDUCED BY A MAGNETIC FIELD

For $M_L\neq 0$ the hydrogen atom does not bind an extra electron at zero field. In weak fields, binding in $M_L<0$ levels can occur by means of the mechanism discussed in Ref. 12 and recapitulated here.

An extra electron bound to the H atom in weak fields is, presumably, only weakly bound and therefore travels in an extended orbit around the central atom. The Coulomb field of this outer electron polarizes the H atom, inducing a dipole moment $\vec{p}$, which, in turn, produces at the electron an attractive potential of strength proportional to p/r^2. But, since p itself is proportional to the electric field of the distant electron evaluated at the center of the atom ($p \propto r^{-2}$) the attractive potential at large distances varies as r^{-4}. The combination of this attractive field and the two-dimensional confinement of the outer electron in the magnetic field produces binding.

The physical picture just presented should apply to all bound states with $M_L \neq 0$ in weak magnetic fields. To give this picture quantitative embodiment in a variational calculation, we introduce a trial function of the form

$$\Phi_{M_L}(\vec{r}_1)\chi(\vec{r}_1, \vec{r}_2) \pm (1 \longleftrightarrow 2) ,$$

where $\Phi_{M_L}(\vec{r}_1)$ is the orbital for the outer electron and $\chi(\vec{r}_1, \vec{r}_2)$, for large r_1, approximates the ground-state wave function in a magnetic field of a hydrogen atom which is polarized by an electron at $\vec{r}_1$.

To determine a form for χ, we calculate the zero-magnetic-field ground-state wave function $\psi(\vec{r}_1, \vec{r}_2)$ of a hydrogen atom located at the origin when perturbed weakly by a distant electron at $\vec{r}_1$. The Schrödinger equation can be written

$$(H_0 + H_1)\psi = E\psi,$$

$$H_0 = -\nabla_2^2 - 2/r_2$$

$$H_1 = (2/|\vec{r}_1 - \vec{r}_2| - 2/r_1) . \tag{15}$$

Since it is assumed $r_2/r_1 \ll 1$, H_1 can be expanded to lowest order as

$$H_1 \cong 2(\vec{r}_1 \cdot \vec{r}_2)/r_1^3 = 2r_2(\cos\theta_{12})/r_1^2 , \tag{16}$$

and this term considered a perturbation. Note that the right-hand side of (16) describes the potential of a uniform electric field of strength $2/r_1^2$ directed along $\vec{r}_1$.

The unperturbed ground-state wave function is $\exp(-r_2)$, and the exact solution to (15) can be written completely generally as

$$\psi = e^S e^{-r_2} , \tag{17}$$

where e^S is a unitary transformation carrying e^{-r_2} into the exact ground-state wave function. The perturbation solution is found by expanding e^S as $(1+S)$, inserting (17) into (15) and solving for S to lowest order in r_2/r_1. Equating terms of order r_2/r_1 gives

$$([H_0, S] + H_1)e^{-r_2} = 0 , \tag{18}$$

which takes the explicit form

$$-\nabla_2^2 S + 2\frac{\partial S}{\partial r_2} = -\frac{2r_2 \cos\theta}{r_1^2} , \tag{19}$$

where the z axis is now chosen along $\vec{r}_1$. It is easy to verify that

$$S = -(\tfrac{1}{2}r_2^2 + r_2)(\cos\theta)/r_1^2$$

is a solution of (19); so that the required perturbed zero-field ground-state wave function is, in lowest order,[19]

$$\psi(r_1, r_2) = \{1 - [(\tfrac{1}{2}r_2^2 + r_2)/r_1^2]\cos\theta_{12}\} e^{-r_2} . \tag{20}$$

As it stands, $\psi(\vec{r}_1, \vec{r}_2)$ is not a suitable form for $\chi(\vec{r}_1, \vec{r}_2)$ for at least two reasons. First, when $r_1 \to 0$ the polarization given by (20) goes to infinity. That divergence is unphysical and turns out to be unacceptable for $M_L = -1$. Second, no provision for the effect of the magnetic field on the hydrogen-atom wave function has been made.

These deficiencies can be cured in many ways. To solve the first problem, we have chosen to replace $(\tfrac{1}{2}r_2^2 + r_2)/r_1^2$ by $P(r_1, r_2)$ where

$$P(r_1, r_2) = C(\tfrac{1}{2}r_2^2 + r_2)/[(r_1^2 + b)(\beta r_2^2 + 1)] .$$

The variational parameters C and b provide an adjustable polarization strength and a leveling off of the electric field, respectively.

A number of choices are available for taking the magnetic field into account. If we were interested only in very small magnetic fields, we could have introduced the term $\gamma^2\rho_2^2/4$ into (15) and treated it as a weak perturbation, just as we treated H_1. In that case, we would have found

$$\psi(\vec{r}_1, \vec{r}_2)\{1 - \tfrac{1}{24}\gamma^2[r_2^2 + (\tfrac{3}{2} + r_2)\rho_2^2]$$

$$- [(\tfrac{1}{2}r_2^2 + r_2)/r_1^2]\cos\theta_{12}\} e^{-r_2} ,$$

which could be used as the starting point for a variation-perturbation procedure. A better approach for higher magnetic fields would be to replace $\exp(-r_2)$ in (20) by, for example, $\phi^{(k)}(r_2)$ with sufficiently large k. At the likely sacrifice of some accuracy, we have chosen instead two forms for χ,

$$\chi^{(0)}(\vec{r}_1, \vec{r}_2) = [1 + P(r_1, r_2)\cos\theta_{12}]$$

$$\times \exp(-\delta r_2^2 - \kappa r_2),$$

$$\chi^{(1)}(r_1, r_2) = [1 + c_1 z_2^2 + P(r_1, r_2)\cos\theta_{12}]$$

$$\times \exp(-\delta r_2^2 - \kappa r_2). \tag{21}$$

A drawback of these wave functions at the higher magnetic fields is that they do not take into account, except in an average way, the variation of the polarizability of the inner atom with the angle between $\vec{r}_1$ and the magnetic field.[20]

For the outer orbital we have tried to obtain considerable flexibility, choosing a wave function

TABLE III. Comparison of H⁻ $M_L=-1$ triplet binding energies $E_T^{(0)}$ and $E_T^{(1)}$ calculated using (21) and (22) with the energies $E_T^{(SO)}$ from Ref. 4, employing the Slater-orbital expansion. $E_T^{(Ex)}$ is extrapolated from $E_T^{(0)}$ and $E_T^{(1)}$ as described in the text. All energies are in units of ℛ. The numerical accuracy of $E_T^{(0)}$ and $E_T^{(1)}$ is estimated to be ± 1 in the last-quoted digit.

Field	H⁻ triplet $M_L=-1$ binding energies from various wave functions			
γ	$E_T^{(0)}$	$E_T^{(1)}$	$E_T^{(SO)}$	$E_T^{(Ex)}$
0.0	0.0	0.0	−0.0073	
0.05		0.0005	−0.0038	
0.10		0.0032	−0.0022	
0.20		0.0144	0.0079	
0.50	0.0504	0.0538	0.0319	0.0544
1.0	0.0825	0.0983		0.101
1.5	0.0874	0.1249		0.133
2.0	0.0806	0.1416		0.155
3.0	0.0412	0.1571		0.188

essentially similar to ϕ_P of Eq. (8). Recalling that the lowest-lying free particle Landau-level wave function of given M_L is

$$e^{iM_L\phi}\rho^{|M_L|}e^{-(\gamma/4)\rho^2},$$

we have taken

$$\Phi_{M_L}(\vec{r}_1) = \exp(iM_L\phi_1)\rho_1^{|M_L|}\exp[-\tfrac{1}{4}\gamma'\rho_1^2-\kappa(\rho_1^2+\alpha z_1^2)^{1/2}], \tag{22}$$

where γ', κ, and α are variational parameters, and ϕ_1 is the polar angle of $\vec{r}_1$ in circular cylindrical coordinates. Binding energies for triplet $M_L=-1$ levels are given in Table III for trial functions employing χ^0 and for those employing $\chi^{(1)}$. No bound singlet states were found.

At all fields studied the optimum value of γ' in (22) remains only slightly below γ; for $\gamma \geq 0.5$, $\kappa\,\alpha^{1/2}$, the parameter determining the spread of the wave function in the z direction, is larger than, but within 10% of, the square root of the corresponding binding energy $E_T^{(1)}$ of Table III. At lower values of γ, $\kappa\,\alpha^{1/2}$ grows relative to $(E_T^{(1)})^{1/2}$ becoming 30% larger at $\gamma=0.1$.

The present results show one reason why previous variational calculations of the $M_L=-1$ triplet state are unsatisfactory in the low-to-intermediate-field regime. The orbital of the outer electron is found here to be quite similar to that of a hydrogen electron in a high magnetic field, even at the lowest fields. On the other hand, the inner orbital is at low fields, essentially a low-field hydrogen-atom orbital. Thus a satisfactory variational description must be flexible enough to encompass the two regimes, high and low field, in a single wave function.

The trial function of Ref. 13 uses essentially high-field orbitals for both inner and outer electrons, giving an especially unsuitable description of the *inner* orbital at weak fields, whereas the Slater-orbital expansion of Ref. 4 has difficulty representing high-field wave functions, thereby giving an inaccurate description of the *outer* orbital. Graphical comparison of the results of these calculations with $E_T^{(1)}$ is made in Fig. 2, using the values set down in Table III.

As in Sec. III, it is possible to extrapolate the energies at the higher fields in a systematic way, thereby, it is hoped, obtaining close approximations to the true binding energies. In this case inaccuracy in the *inner* orbital is assumed responsible for the major part of the error in $E_T^{(0)}$ and $E_T^{(1)}$. Denoting by $\mathcal{E}_{\text{in}}^{(k)}(\gamma)$ the error in the H-atom energies $E_{\text{H}}^{(k)}(\gamma)$ calculated from trial functions $\phi^{(k)}$ of Eq. (6), we assume that the error in $E_T^{(k)}$ is simply $A_1(\gamma)\mathcal{E}_{\text{in}}^{(k)}(\gamma)$ and solve for A_1 from

$$\begin{aligned} E^{(\text{Ex})} &= E_T^{(0)}+A_1(\gamma)\mathcal{E}_{\text{in}}^{(0)}(\gamma) \\ &= E_T^{(1)}+A_1(\gamma)\mathcal{E}_{\text{in}}^{(1)}(\gamma)\,. \end{aligned} \tag{23}$$

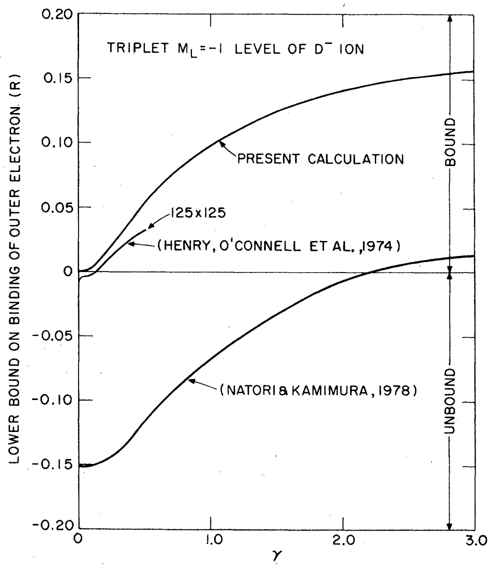

FIG. 2. Comparison of lower bounds to the binding energy of the $M_L=-1$ triplet level of the H⁻ ion as calculated by various authors. The curve marked "present calculation" is a plot of $E_T^{(1)}$ (see Table III); the curve marked "Henry, O'Connell *et al.*" comes from Ref. 4 and is tabulated in Table III as $E_T^{(SO)}$. The trial function for $E_T^{(1)}$ uses $\chi^{(1)}$ from Eq. (21) and Φ_{-1} from Eq. (22). The point marked "125 × 125" was calculated from a 125 × 125 determinant involving Slater orbitals. The ansatz for the "Natori and Kamimura" curve is described in Ref. 13.

For $1 \leq \gamma \leq 3$, $A_1(\gamma)$ is found to remain essentially constant, staying within ±6% of the value 1.18. Extrapolated energies $E_T^{(\text{Ex})}$ found from solving (23) are listed in Table III.

We have not investigated the extreme high-field limit for $|M_L| > 0$. As mentioned earlier, Virtamo has studied the $M_L = -1$ level at large values of γ using the wave function of Eq. (5) with $\gamma_1 = \gamma_2 = \gamma$ and determined the orbitals f and g numerically by the Hartree-Fock method.[6] For $\gamma = 100$, Virtamo found a two-electron binding energy of $-8.147\mathcal{R}$, which corresponds to a binding energy of about $0.59\mathcal{R}$. A major drawback of this calculation is that correlation is not taken into account. Correlation can be expected to be important in the high-field limit, although it is likely of less importance for the $M_L = -1$ state then for the $M_L = 0$ state calculated in Sec. III B.

Calculations of the binding energies for $M_L = -2$ and -3 have been made using trial functions defined by Eqs. (14), (21), and (22). Figure 3 displays extrapolated energies for these levels plotted as functions of γ. These extrapolated energies $E^{(\text{Ex})}(M_L)$ are calculated from the variational binding energies $E^{(1)}(M_L)$ found using $\chi^{(1)}$ in the wave function (14), by

$$E^{(\text{Ex})}(M_L) = E^{(1)}(M_L) + \mathcal{E}_{\text{in}}^{(1)}(\gamma) \quad M_L = -2, -3 \, .$$

[A few spot checks confirming this formula at various values of γ were made by comparing $E^{(\text{Ex})}(M_L)$ with $E^{(0)}(M_L) + \mathcal{E}_{\text{in}}^{(0)}(\gamma)$.]

Figure 3 portrays a number of interesting features of the $M_L < -1$ levels of H$^-$. First, both singlet and triplet states bind. Second, although both singlet and triplet binding energies increase monotonically with increasing magnetic field, for given M_L the triplet binding increases more rapidly than the singlet. Third, at a given field the singlet-triplet splitting is smaller in magnitude for the $M_L = -3$ state than for the $M_L = -2$. Fourth, for a given magnetic field and permutation symmetry (singlet or triplet), the binding decreases as $|M_L|$ increases.

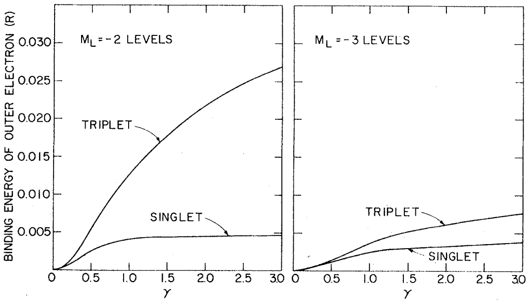

FIG. 3. Extrapolated H$^-$-ion binding energies of the deepest $M_L = -2$ and $M_L = -3$ levels of triplet or singlet symmetry.

These features have a simple physical interpretation. When the outer orbital keeps the electron far away from the inner atom, the binding is relatively weak (due to the rapid diminution of the strength of the attraction potential with distance from the atom), and singlet-triplet splittings, which depend upon overlap of inner and outer orbitals, are small. Since the outer orbital penetrates least at low γ and high $|M_L|$ we expect in that regime to find the weakest binding and the smallest singlet-triplet splitting. It is well known that electron-electron repulsion tends to be weaker in antisymmetric states, which vanish when the electrons come together, than in symmetric states. Thus triplet states have stronger binding than the corresponding singlets (but only for $|M_L| > 0$).

The $M_L = -1$ level is the most penetrating of all the $|M_L| > 0$ states at any field. There, these calculations indicate, the singlet-triplet splitting exceeds the triplet binding energy at all fields investigated, and the singlet fails to bind.

The above arguments do not apply to the $M_L = 0$ ground state, for which a dominant role is played by the exchange integral of the Coulomb attraction, $-2/r_1 - 2/r_2$. This exchange integral, which is negative in the $M_L = 0$ singlet state, is small in magnitude for H$^-$ states which are constructed from orbitals of differing symmetry or which involve a nonpenetrating orbital. Only the $M_L = 0$ state, among those considered, has orbitals which are of the same symmetry and penetrate strongly to the center of the atom. Physically, both electrons want to get close to the proton simultaneously and are willing to pay the price of increased electron-electron repulsion (entailed by placing them in a singlet state) to do so. Thus the singlet is the deeper state for $M_L = 0$. We have been unable to find a bound $M_L = 0$ triplet state.

All of the bound states discussed so far have even z parity; that is, when $z_1 \rightarrow -z_1$ and $z_2 \rightarrow -z_2$, the wave functions are unchanged. We have searched without success for bound excited states of odd z parity for $M_L = 0$ and $M_L = -1$, using an outer orbital of the form given by (22) multiplied by z_1.

It is easy to see why it might be difficult to produce binding with states of this symmetry. If we neglect exchange, we can visualize the field-induced binding of states as resulting from a combination of confinement in the x-y plane by the magnetic field and binding in the z direction by a one-dimensional attractive effective potential in z, which is the total potential seen by the outer electron averaged over its motion in the x and y directions.[14] One-dimensional attractive potentials readily produce bound states. For example, it is well known that the one-dimensional square well, regardless of its depth or range, always has at least one bound state and that this state has even parity.[19] To bind, in addition, a state of odd parity, however, is more difficult, requiring a certain minimum value of depth times the square of the range.

One is led to ask whether sufficient attraction exists to bind states of odd z parity in the high-field region, where large binding is found for the lowest $M_L = 0$ and $M_L = -1$ levels. We have attempted to find such bound states using the trial function

$$\exp[-\tfrac{1}{4}\gamma'(\rho_1^2+\rho_2^2)][1-P(z_1,z_2)]z_1 \times \exp[-\beta(z_1^2+\alpha^2)^{1/2} - \kappa(z_2^2+\alpha^2)^{1/2}]. \quad (24)$$

where

$$P(z_1,z_2) = C[\bar{\kappa}(z_2)z_2^2 + z_2](\tanh Az_1)/(z_1^2+D),$$

$\bar{\kappa}(z_2) = \kappa$ for $z_2 > 0$ and $= -\kappa$ for $z_2 < 0$, and γ', C, A, D, κ, β, and α are variational parameters. The wave function (24) represents a polarized H atom in a strong magnetic field multiplied by a strong-field orbital of odd z parity for the outer electron. Exchange is neglected, since, for weak binding, $\beta \ll \kappa$, and the overlap of inner and outer electron wave functions should be small. No bound state was found at $\gamma = 100$.

Failure to find binding of a state with a single node in its z orbital at high magnetic fields suggests that states with z orbitals of more than one node may also not bind. A possible exception, however, might be excited $M_L = 0$ singlet states of even z parity. It would be interesting to know whether magnetic field thresholds exist at which such states begin to bind.

V. He ATOMS IN A MAGNETIC FIELD

The wave functions introduced in this paper for treating the H^- ion are also useful for calculating the effect of magnetic fields on certain levels of the He atom. If, in the definition of $H(i)$ ($i = 1$ or 2) in Eq. (1), we replace $-2/r_1$ by $-4/r_1$, then Eq. (2) becomes the Hamiltonian of a He atom in a magnetic field. The trial function $\psi^{(2)}$ defined by Eq. (10) can be used in conjunction with the He Hamiltonian to calculate the magnetic field dependence of the energy of the He 1^1S state. At zero field $\psi^{(2)}$ gives a ground-state energy of $-5.8029\mathcal{R}$, which is to be compared to the exact value[3] of $-5.80745\mathcal{R}$. Two-electron binding energies at various values of γ are listed in Table IV.

TABLE IV. Variational estimates of energies required to remove both electrons from a He atom in the state listed at the top of each column. Each state in a magnetic field is designated by the zero-field He state, which it approaches when the magnetic field is adiabatically switched off. All energies are in units of $\mathcal{R}$.

Field	Two-electron binding energies of He levels			
γ	^1S	2^1P_{-1}	2^1P_0	2^3P_{-1}
0.2	6.1871	4.6888	4.5607	4.7269
0.5	6.7077	5.1500	4.9091	5.2370
1.0	7.4544	5.7599	5.3837	5.9275
2.0	8.6532	6.7182	6.1381	7.0126

Wave functions of the form (14), with χ given by $\chi^{(1)}$ of (21), and with Φ_M given by (22) are appropriate for calculations of singlet or triplet He $2P_{\pm 1}$, $3D_{\pm 2}$, $4F_{\pm 3}$, ... levels, whereas, if Φ_{M_L} is multiplied by z_1, the resulting wave functions should be suitable for calculating energies of $2P_0$, $3D_{\pm 1}$, $4F_{\pm 2}$, ... levels. At zero magnetic field, $-4.2471\mathcal{R}$ and $-4.2645\mathcal{R}$ are obtained for the 2^1P and 2^3P energies, respectively; these are to be compared to the more accurate values of $-4.24768\mathcal{R}$ and $-4.26632\mathcal{R}$ for the corresponding states found by Accad and co-workers.[22] Two-electron binding energies obtained for the He 2^1P_{-1}, 2^1P_0, and 2^3P_{-1} levels are listed in Table IV.

The $3D_{-2}$, $4F_{-3}$, and higher angular momentum states of He have weakly penetrating outer orbitals and, at least for low magnetic fields, can be quite accurately described by assuming that the inner He^+ ion acts as if it were a point positive charge so far as the motion of the outer electron is concerned. For the 3^3D level at zero field we obtain, for example, an energy of $-4.11136\mathcal{R}$, where the last digit is uncertain due to numerical error. (If the inner core behaved exactly like a point charge, the energy would have been $-4.11111\mathcal{R}$.) Some of the even z-parity low-lying He levels in a magnetic field have been calculated previously using the Slater-orbital expansion approach,[4, 23] a method which should give accurate energies for He at low fields. Unfortunately, detailed comparison with the present calculation is difficult because the results of Ref. 23 are presented only graphically. To within the uncertainty in reading the graph, which can amount to several percent in the energy, the results in Table IV agree with those plotted in Ref. 23 for the corresponding states.

With extrapolation techniques similar to those described for the H^- ion, it is expected that the trial functions introduced here can give useful He energies for γ as high as 20.

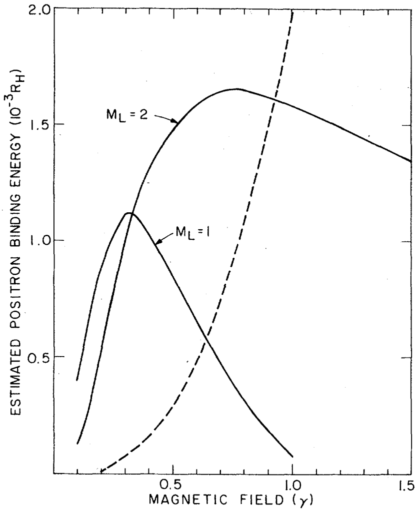

FIG. 4. Estimated binding energy of a positron to a hydrogen atom for $M_L=1$ and $M_L=2$. Lower bounds to binding energies can be obtained by subtracting the dashed curve from the solid curves.

VI. BINDING OF POSITRONS TO H ATOMS

Strong theoretical evidence supports that the assertion that a hydrogen atom does not bind a positron at zero magnetic field.[24] Zero-field binding commences when the positron mass exceeds the electron mass by a factor of ~2.2.

From the arguments presented here, however, it seems clear that a positron should bind to the H atom in states with sufficiently large $|M_L|$ when weak magnetic fields are present. In such states the positron remains far from the proton and experiences only the force of the magnetic field and the attractive polarization potential of the atom. In this respect the positron–H-atom system is very similar to the H^- ion, which, we have found, binds in both singlet and triplet states for $|M_L|>1$.

The positron–H-atom Hamiltonian is

$$-\nabla_1^2+\frac{2}{r_1}-\nabla_2^2-\frac{2}{r_2}-\frac{2}{|\vec{r}_1-\vec{r}_2|}$$

$$+\gamma\left(-\frac{1}{i}\frac{\partial}{\partial\phi_1}+\frac{1}{i}\frac{\partial}{\partial\phi_2}\right)+\frac{\gamma^2(\rho_1^2+\rho_2^2)}{4}, \qquad (25)$$

which, except for some signs, is the same as the H^- Hamiltonian of Eq. (2). In (25) $\vec{r}_1$ is the displacement of the positron from the proton. The trial function to be employed is

$$\Phi_{M_L}(\vec{r}_1)\chi^{(1)}(\vec{r}_1,\vec{r}_2), \qquad (26)$$

where $\chi^{(1)}$ is given by (21), and Φ_{M_L} by (22) with the proviso that M_L is here taken positive. Estimated binding energies, energies obtained by replacing $E_{\mathrm{Hy}}(\gamma)$ in (3) by $E_{\mathrm{H}}^{(1)}$(see Table I) and $E_{\mathrm{H}^-}(\gamma)$ by variational energies obtained from (25) using the trial function (26), are plotted for $M_L=1$ and $M_L=2$ levels in Fig. 4. A rigorous lower bound for the binding energies can be obtained from Fig. 4 by subtracting the ordinate of the dashed curve at the value of γ of interest. Thus rigorous binding is indicated for the portions of the solid curves to the left of the dashed curve. No binding was found for $M_L=0$.

These calculations suggest that, at low fields, the ground state is the $M_L=1$ level, but that, as the field increases, the M_L associated with the ground-state wave function shifts to successively higher values. Further, for each state the binding first increases until a maximum is attained and then decreases with increasing field.

This behavior is consistent with our physical picture of states which are bound only in the presence of a magnetic field. At low fields an increase in field brings the positron closer to the atom where the dipole attractive field is stronger; hence the binding increases at first. When the field becomes sufficiently large, the positron wave function begins to penetrate significantly inside the atom where the repulsion of the proton is dominant. At some point, further increase in the field, by forcing the positron closer to the proton, may actually produce a decrease in binding. Since they have smaller penetration, states of higher M_L may bind more strongly than those of lower M_L at high fields.

The foregoing results and discussion though plausible, are not altogether convincing. One can criticize the appropriateness of the trial function (26) at the higher fields. For example, it is not clear that $\Phi_{M_L}(r_1)$ dies off rapidly enough as the positron approaches the proton. Also, no configurations in which the electron and the positron form a positronium atom are admixed in the trial function employed, although such configurations are known to be very important when the positron is sufficiently massive.

Whether a trial function sufficiently flexible to encompass these possibilities would give behavior qualitatively different from that displayed in Fig. 4 is unclear. However, Fig. 4 does demonstrate that the polarization force is sufficient to bind a positron to a hydrogen atom in a weak magnetic field.

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