

# Magnetically bound states of electronic and positronic hydrogen ions: The case of zero orbital angular momentum

Daniel H. E. Dubin

*Department of Physics, University of California at San Diego, La Jolla, California 92093, USA*

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This paper considers the binding of an electron or a positron to a ground-state hydrogen atom in a uniform magnetic field  $B$ , concentrating on states with zero orbital angular momentum  $J$ . It is shown that the affinity of a positron to a hydrogen atom is  $2.23b^2e^2/a$ , where  $a$  is the Bohr radius,  $b \equiv B/B_0$ ,  $B_0 = 2.3505 \times 10^5$  T,  $b \ll 1$  is assumed, and the proton is assumed to have infinite mass. With these assumptions it is also shown that no  $J=0$  singlet or triplet excited state of  $H^-$  exists. These results are compared to a previous estimate of the electron affinity of  $J=0$  magnetically bound ions [V. G. Bezchastnov, P. Schmelcher, and L. S. Cederbaum, Phys. Rev. A **61**, 052152 (2000)].

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## I. INTRODUCTION

This paper discusses the effect of weak magnetic fields on the binding of a positron or electron to a neutral ground-state hydrogen atom. Here, weak fields refer to fields such that  $b \equiv a^2/r_q^2 \ll 1$ , where  $r_q = \sqrt{\hbar^2/eB}$  is the electron quantum Larmor radius and  $a = \hbar^2/me^2$  is the Bohr radius. Since  $b$  can also be written as  $b = B/B_0$  where  $B_0 = 2.3505 \times 10^5$  T, the weak-field regime corresponds to magnetic fields much less than  $10^5$  T.

It is well known that in the field-free limit, only a single bound state of  $H^-$  exists. Neglecting relativistic effects and assuming infinite nuclear mass, the affinity of this state has been calculated to be [2]

$$E_g = 0.027\,751\,0\dots e^2/a. \quad (1)$$

This state has zero orbital angular momentum  $J$ , and zero net spin (i.e., it is a singlet state) [2]. Furthermore a positron is not bound to hydrogen at all [3]. However, it has recently been shown that magnetic fields enable additional, much more weakly bound states of  $H^-$  [1,4], and that positrons can also be magnetically bound to form positronic  $H^+$  [5].

These states are bound by the weak short-range attraction of the outer charge to the atom, caused by the induced dipole moment of the atom in the field of the outer charge. The magnetic field provides extra confinement in the plane perpendicular to the field, resulting in bound states that would not otherwise exist. It was argued in Ref. [1] that the most deeply bound excited state of  $H^-$  is one with  $J=0$ . The electron affinity for this  $J=0$  excited state was estimated as  $E_b = 6.31b^2e^2/a$  [Eq. (43) of Ref. [1]]. We will show that this result does not apply to  $H^-$ , but does qualitatively describe positronic  $H^+$ . The calculation of Ref. [1] used an adiabatic assumption for the dynamics of the two electrons, neglected exchange effects, and neglected the overlap of the excited-state wave function with the  $H^-$  ground state. However, as pointed out in Ref. [1], these are not good approximations for the  $J=0$  state of  $H^-$ . In Ref. [1] it was stated that these effects would simply lead to a different numerical coefficient in the affinity of  $H^-$  but the same overall magnetic field

scaling. However, in later work it was conjectured that the estimate might not apply to  $H^-$  at all [6]; and we will see that this is in fact the case.

In this paper we use an approach that combines a variational method with perturbation theory to calculate the electron and positron affinities to hydrogen in the infinite nuclear mass approximation as a perturbation expansion in  $b$ , including exchange effects, ensuring that the wave function has no overlap with the ground state, and making no adiabatic approximations. We show that there are no  $J=0$  excited states of  $H^-$  in the weak-field regime  $b \ll 1$ , assuming infinite proton mass. We also show that a positronic  $H^+$  ion with  $J=0$  is bound in a weak magnetic field, with affinity

$$E_b = 2.23b^2e^2/a, \quad (2)$$

again assuming infinite proton mass. The error in the numerical coefficient is roughly 4%, and the affinity neglects terms of  $O(b^3)$ . Effects associated with a moving proton (i.e., finite proton mass) are discussed in Sec. III. The existence of a positronic bound state that has substantial overlap with the electron wave function has implications for the annihilation of positrons on hydrogen, which we discuss in Sec. III. The scaling of  $E_b$  with  $b^2$  agrees with the estimate of Ref. [1], because the induced-dipole binding considered in Ref. [1] is essentially the same for positrons and electrons, and for positrons the complicating effects of exchange interactions and overlap with a lower-energy state do not occur.

## II. VARIATIONAL CALCULATION OF MAGNETICALLY BOUND STATES

Schrödinger's equation for a hydrogen atom and an extra electron or positron in a uniform magnetic field  $B\hat{z}$  is

$$E\psi_e = \hat{H}\psi_e = \left[ -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} \mp \frac{1}{r_2} \pm \frac{1}{r_{12}} + \frac{1}{8}b^2(\rho_1^2 + \rho_2^2) - \frac{ib}{2} \left( \frac{\partial}{\partial\phi_1} \pm \frac{\partial}{\partial\phi_2} \right) \right] \psi_e, \quad (3)$$

where  $\psi_e(\mathbf{r}_1, \mathbf{r}_2)$  is the wave function, the subscript 1 denotes

the hydrogenic electron, and the subscript 2 denotes the weakly bound outer charge, the upper and lower signs correspond to either an electron or positron at position  $\mathbf{r}_2$ ,  $(\rho, \phi)$  are polar coordinates,  $r$  is the spherical radius,  $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ , distances are measured in units of the Bohr radius  $a$ , and energies are measured in units of  $e^2/a=27.2$  eV. The central proton is assumed to be fixed at the origin and relativistic and spin effects are neglected.

Rather than solving Eq. (3) directly to find magnetically induced bound states with  $J=0$ , we apply the Rayleigh-Ritz variational method,

$$E \leq \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}, \quad (4)$$

where  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  is a variational wave function, with equality in Eq. (4) when  $\psi = \psi_e$ . By employing the assumption that the outer charge in the ion is weakly bound, with a wave function that varies slowly on the atomic scale, we are able to Taylor expand the inner products in Eq. (4) in powers of  $b$ , and so obtain variational equations for the wave function good to order  $b^2$ . Details of the calculation differ depending on whether the outer charge is a positron or an electron. We employ the following variational functions for  $\psi$ :

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1, \mathbf{r}_2) + \frac{\chi_0}{\sqrt{2\pi}} \Delta\psi(\mathbf{r}_1, \mathbf{r}_2) \quad (\text{electron}), \quad (5)$$

where

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2\pi}} [e^{-r_1} \chi(\rho_2, z_2) \pm e^{-r_2} \chi(\rho_1, z_1)], \quad (6)$$

and

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{\pi}} e^{-r_1} \chi(\rho_2, z_2) + \frac{\chi_0}{\sqrt{\pi}} \Delta\psi(\mathbf{r}_1, \mathbf{r}_2) \quad (\text{positron}), \quad (7)$$

where  $\Delta\psi$  is a function whose form will be determined presently by the variational method,  $\chi$  is the ground-state eigenfunction for an electron or positron in a magnetic field,

$$\chi(\rho, z) = \sqrt{\frac{b}{2\pi}} e^{-b\rho^2/4} f(z), \quad (8)$$

$\chi_0 = \chi(0, 0)$ , and  $f(z)$  is a function to be determined by the variational calculation, chosen so that  $\int_{-\infty}^{\infty} f^2 dz = 1$ .

We will find that

$$f(z) = \sqrt{k} e^{-k|z|} \quad (9)$$

where  $k > 0$  is of order  $b$ . This wave function is highly elongated in the  $z$  direction due to quantum uncertainty and the very weak binding of the outer charge. An identical form was also found for eigenfunctions with  $|J| \gg 1$  [5]. For future reference, note that the fact that Eq. (8) along with  $k = O(b)$  implies that

$$\chi_0 = O(b). \quad (10)$$

The function  $e^{-r_1}/\sqrt{\pi}$  is the ground-state wave function for an isolated hydrogen atom. The (appropriately symme-

trized) product of this function and  $\chi(\rho_2, z_2)$  provides an approximate two-particle wave function representing a hydrogen atom and a magnetically bound electron or positron.

The term  $\Delta\psi$  is a correction to this approximate wave function. By solving the variational problem for  $\Delta\psi$ , we will see that  $\Delta\psi$  is short ranged compared to  $\chi$ , and is, to lowest order in  $b$ , independent of the magnetic field. For the case of the singlet state [upper sign in Eq. (6)], the variation must be performed under the constraint that  $\psi$  has no overlap with the ground state of  $H^-$ .

### A. Positronic $H^+$ ion

We first consider the case of a positron. Substituting Eq. (7) for  $\psi$  in Eq. (4), we first evaluate  $\langle \psi | \psi \rangle$ :

$$\langle \psi | \psi \rangle = 1 + \frac{2\chi_0}{\pi} \langle e^{-r_1} \chi(\rho_2, z_2) | \Delta\psi(\mathbf{r}_1, \mathbf{r}_2) \rangle + \frac{\chi_0^2}{\pi} \langle \Delta\psi | \Delta\psi \rangle. \quad (11)$$

We now apply the following approximation: since  $\Delta\psi$  approaches zero on the atomic scale, and  $\chi$  is slowly varying on this scale,  $\chi(\rho_2, z_2)$  may be taken to be  $\chi(0, 0)$  in the inner product, yielding

$$\langle \psi | \psi \rangle = 1 + \frac{2\chi_0^2}{\pi} \langle e^{-r_1} | \Delta\psi \rangle + \frac{\chi_0^2}{\pi} \langle \Delta\psi | \Delta\psi \rangle + O(b^3). \quad (12)$$

The error in this approximation is of  $O(b^3)$ , since on the atomic scale  $\chi(\rho, z)$  varies from  $\chi(0, 0)$  by a fractional amount of order  $b$ , and  $\chi(0, 0)$  is already of  $O(b)$ . Next, we evaluate  $\langle \psi | \hat{H} | \psi \rangle$ . Again using the fact that  $\chi$  varies slowly on the atomic scale, the result is

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle = & -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f''(z_2) | f(z_2) \rangle - \frac{\chi_0^2}{\pi} \\ & \times \left\langle e^{-2r_1} \left| \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) \right\rangle + \frac{2\chi_0^2}{\pi} \\ & \times \left\langle e^{-r_1} \left| \left( -\frac{1}{2} + \frac{b}{2} + \frac{b^2 \rho_1^2}{8} - \frac{1}{2} \frac{f''(z_2)}{f(0)} - \frac{1}{r_{12}} \right. \right. \right. \\ & \left. \left. \left. + \frac{1}{r_2} \right) \right| \Delta\psi \right\rangle + \frac{\chi_0^2}{\pi} \langle \Delta\psi | \hat{H} | \Delta\psi \rangle + O(b^3), \quad (13) \end{aligned}$$

where the  $O(b^3)$  magnitude of the error follows from the same argument as for Eq. (12). The first term in Eq. (13) is the ground-state energy of hydrogen, and the second term is the ground-state energy of a free positron in a magnetic field. The third term is the well-known magnetic correction to the ground-state energy of hydrogen. The other terms arise from the interaction of the positron and the atom. The second inner product can be directly evaluated as

$$\left\langle e^{-2r_1} \left| \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) \right\rangle = -2\pi^2. \quad (14)$$

This term is the electrostatic energy of the hydrogen atom in a background charge of uniform density, which approximates the outer charge density on the atomic scale.

We now further approximate Eq. (13), keeping terms in the third inner product only to  $O(b^2)$ . Here we apply Eqs. (9) and (10). The result is

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle = & -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f''(z_2) | f(z_2) \rangle + 2\pi\chi_0^2 \\ & + \frac{2\chi_0^2}{\pi} \left\langle e^{-r_1} \left| \left( -\frac{1}{2} - \frac{1}{r_{12}} + \frac{1}{r_2} \right) \right| \Delta\psi \right\rangle \\ & + \frac{\chi_0^2}{\pi} \langle \Delta\psi | \hat{H}_0 | \Delta\psi \rangle + O(b^3) \end{aligned} \quad (15)$$

where  $\hat{H}_0$  is the Hamiltonian evaluated at  $B=0$ , given by

$$\hat{H}_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}}. \quad (16)$$

Substituting Eqs. (12) and (15) into Eq. (4) and Taylor expanding in  $b$ , we obtain, to order  $b^2$ ,

$$\begin{aligned} E \leq & -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f'' | f \rangle + \frac{2\chi_0^2}{\pi} \left\langle e^{-r_1} \left| \left( -\frac{1}{r_{12}} + \frac{1}{r_2} \right) \right| \Delta\psi \right\rangle \\ & + \frac{\chi_0^2}{\pi} \langle \Delta\psi | \left( \hat{H}_0 + \frac{1}{2} \right) | \Delta\psi \rangle + 2\pi\chi_0^2 + O(b^3). \end{aligned} \quad (17)$$

We next minimize  $E$  by varying separately with respect to  $f$  and  $\Delta\psi$ . Noting that  $\chi_0 \propto f(0)$  according to Eq. (8), a variation with respect to  $f$  yields

$$-\frac{1}{2}f'' - k\delta(z_2)f(0) = \lambda f(z_2), \quad (18)$$

where  $\lambda$  is the Lagrange multiplier associated with the constraint that  $\int_{-\infty}^{\infty} f^2 dz_2 = 1$ , and where

$$\begin{aligned} k = & -\frac{b}{2\pi^2} \left[ 2 \left\langle e^{-r_1} \left| \left( -\frac{1}{r_{12}} + \frac{1}{r_2} \right) \right| \Delta\psi \right\rangle \right. \\ & \left. + \left\langle \Delta\psi \left| \left( \hat{H}_0 + \frac{1}{2} \right) \right| \Delta\psi \right\rangle \right] - b. \end{aligned} \quad (19)$$

Equation (18) is an eigenvalue problem with a single bound state for  $f$ , provided that  $k > 0$ . The solution for  $f$  is given by Eq. (9), and the eigenvalue is  $\lambda = -k^2/2$ . In other words, the  $z$  dependence of the wave function for the outer charge is approximately that of a particle bound to a  $\delta$ -function potential, because the induced dipole attraction that provides the binding is short ranged and  $f$  varies slowly on this scale.

Note that Eq. (19) implies  $k = -b$  if we take  $\Delta\psi = 0$ . This negative value of  $k$  arises from the electrostatic repulsion of the positron from the unperturbed hydrogen atom charge cloud, as described by Eq. (14). Thus, binding is possible only for  $\Delta\psi \neq 0$ , describing correlations between the electron and positron (i.e., polarization of the atom in the electric field of the positron).

Substituting the solution for  $f$  into Eq. (17) yields

$$E = -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{k^2}{2}. \quad (20)$$

The first three terms are the energy of a ground-state hydrogen atom and a free positron in a magnetic field, up to order  $b^2$  (neglecting spin energy). Thus, the last term in Eq. (20) provides the affinity  $E_b$  of the positron to the hydrogen atom:

$$E_b = \frac{k^2}{2}. \quad (21)$$

Note that Eq. (19) predicts that  $k$  is of  $O(b)$ , so Eq. (21) implies that the binding energy is of order  $b^2$ , and we are therefore justified in dropping  $O(b^3)$  terms in Eq. (17).

Next, we vary Eq. (17) with respect to  $\Delta\psi$ , holding  $f$  fixed. The result is

$$\left( \hat{H}_0 + \frac{1}{2} \right) \Delta\psi = e^{-r_1} \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right). \quad (22)$$

Thus,  $\Delta\psi$  is independent of magnetic field, as stated previously. However, Eq. (22) neglects the  $O(b^3)$  corrections to Eq. (17). Such corrections would add small  $O(b)$  corrections to Eq. (22), and hence to  $\Delta\psi$ . These corrections add  $O(b^3)$  terms to the affinity, and so are neglected.

We solve Eq. (22) for  $\Delta\psi(\mathbf{r}_1, \mathbf{r}_2)$  numerically using the Galerkin method. First, we note that symmetry implies that Eq. (22) has solutions of the form  $\Delta\psi = \Delta\psi(r_1, r_2, r_{12})$ . Second, we transform to perimetric coordinates [2] ( $u, v, w$ ) defined by

$$\begin{aligned} u &= (r_2 + r_{12} - r_1)\varepsilon, \\ v &= (r_1 + r_{12} - r_2)\varepsilon, \\ w &= 2(r_1 + r_2 - r_{12})\varepsilon, \end{aligned} \quad (23)$$

where  $\varepsilon$  is a free parameter of the coordinate system. In Ref. [2]  $\varepsilon$  was chosen as  $\varepsilon = \sqrt{1/2 + E_g} \approx 0.726$ , but here we will find that  $\varepsilon \sim 0.2-0.3$  provides the most rapidly convergent results for  $\Delta\psi$ .

These perimetric coordinates are independent, each running from 0 to  $\infty$ . Furthermore, it can be shown that [2]

$$d^3r_1 d^3r_2 = \frac{\pi^2}{32\varepsilon^6} (u+v)(2u+w)(2v+w) du dv dw. \quad (24)$$

We write  $\Delta\psi(u, v, w)$  as a sum over basis functions with  $(M+1)^3$  terms:

$$\Delta\psi = \sum_{\ell=0}^M \sum_{m=0}^M \sum_{n=0}^M a_{\ell mn} |\ell mn\rangle \quad (25)$$

where

$$|\ell mn\rangle = e^{-(u+v+w)/2} L_{\ell}(u) L_m(v) L_n(w) \quad (26)$$

and where  $L_{\ell}(u)$  is a Laguerre polynomial, defined by

$$L_{\ell}(u) = \sum_{k=0}^{\ell} \binom{\ell}{k} \frac{(-u)^k}{k!}. \quad (27)$$

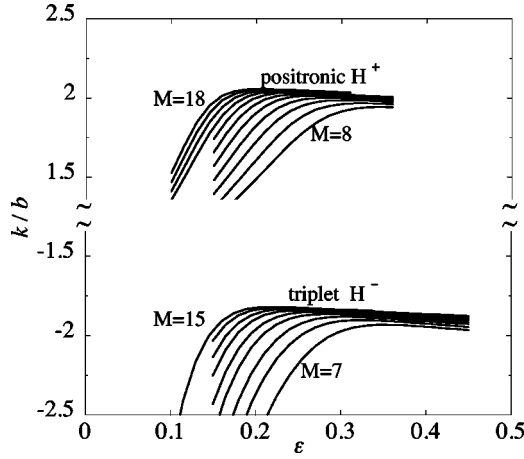


FIG. 1.  $k/b$  for different values of  $M$  and  $\varepsilon$ , evaluated for a  $J=0$  positronic  $H^+$  ion via Eq. (29), and for the triplet state of  $H^-$  via Eq. (51).

Taking moments of Eq. (22) with respect to these  $(M+1)^3$  basis functions yields a set of linear equations for the  $a_{\ell mn}$ 's:

$$\sum_{\bar{\ell}\bar{m}\bar{n}}^M \langle \ell mn | \hat{H}_0 + \frac{1}{2} | \bar{\ell}, \bar{m}, \bar{n} \rangle a_{\bar{\ell}\bar{m}\bar{n}} = \left\langle \ell mn \left| 2\varepsilon \frac{e^{-(2v+w)/4\varepsilon} (w-2v)}{(u+v)(2u+w)} \right. \right\rangle. \quad (28)$$

The matrix elements appearing in Eq. (28) can be evaluated analytically using Eqs. (24), (26), and (27), and the properties of Laguerre polynomials [2]. The form of the elements is too complex to merit display here, but a MATHEMATICA module that evaluates the elements is available upon request.

Once we obtain  $\Delta\psi$  by solving Eqs. (28) for a given value of  $\varepsilon$ , we then evaluate  $k$  using Eq. (19). Noting that  $k$  is in fact positive as required by Eq. (9), we obtain the positron affinity via Eq. (21). In so doing, we note that the expression for  $k$  can be simplified by using Eq. (22) in Eq. (19):

$$k = \frac{b}{2\pi^2} \left\langle e^{-r_1} \left| \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) \Delta\psi \right. \right\rangle - b = \frac{b}{2\pi^2} \sum_{\ell mn}^M a_{\ell mn} \left\langle \ell mn \left| 2\varepsilon \frac{e^{-(2v+w)/4\varepsilon} (w-2v)}{(u+v)(2u+w)} \right. \right\rangle - b, \quad (29)$$

where in the second equality we have used Eqs. (23) and (25).

Values of  $k/b$  as a function of  $\varepsilon$  are plotted in Fig. 1 for different values of  $M$ . For each  $M$  value, a maximum  $k$  value,  $k_{\max}$ , occurs at a particular value of  $\varepsilon$ , providing the best estimate for  $E_b$  at that  $M$  value. The values of  $k_{\max}$  are provided in Table I versus  $M$ , along with the values of  $\varepsilon$  at which they occur, and the positron affinity that results from Eq. (21).

A fit to the data of the form

TABLE I. Solution for positronic  $H^+$  affinity  $E_b$  versus  $M$ .

$M$	$k_{\max}/b$	$\varepsilon$ for $k=k_{\max}$	$E_b/b^2$
7	1.91012	0.37615	1.8243
8	1.94245	0.34697	1.8866
9	1.96611	0.32303	1.9328
10	1.98574	0.30216	1.9716
11	2.00059	0.28332	2.0012
12	2.01342	0.26719	2.0269
13	2.02337	0.25303	2.0470
14	2.03219	0.24157	2.0649
15	2.03924	0.22949	2.0792
16	2.04553	0.22035	2.0921
17	2.05070	0.21071	2.1027
18	2.05544	0.20099	2.1124
$\infty$	$2.11 \pm 0.04$		$2.23 \pm 0.08$

$$k_{\max}(M) = k_{\max}(\infty) - \alpha/M^\beta$$

(see Fig. 2) yields  $k_{\max}(\infty)/b = 2.11 \pm 0.04$ ,  $\alpha = (3.41 \pm 0.6)b$ , and  $\beta = 1.44 \pm 0.1$ .

The positron affinity to ground-state hydrogen is therefore found to be  $E_b = (2.23 \pm 0.08)b^2$ , which is the result quoted in Eq. (2).

## B. Electron affinity

We now repeat the previous calculation, applying it to the case where the outer charge is an electron. The calculation depends on whether the two-electron system has spin zero (a singlet) or spin 1 (a triplet). We will find that for  $b \ll 1$ , no  $J=0$  excited state exists in either case.

For the triplet state, we employ Eq. (5) for  $\psi$ , taking the lower sign in Eq. (6). For the singlet state, we take the upper sign, but we must also ensure that  $\psi$  is orthogonal to the ground state of  $H^-$ ,  $\psi_g$ . This is most easily assured by choosing  $\Delta\psi$  in Eq. (5) as

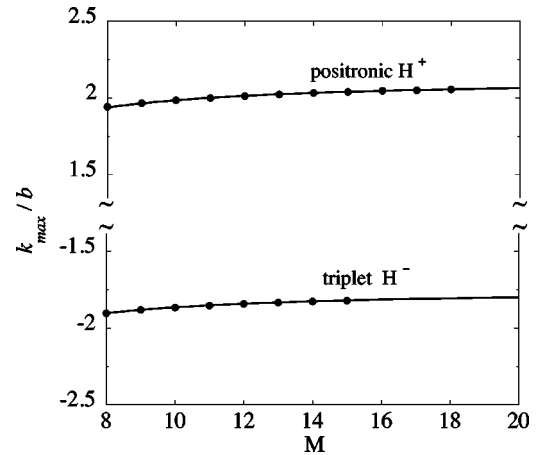


FIG. 2.  $k_{\max}/b$  versus  $M$ , taken from Tables I and II. Lines are the fits described in the text.

$$\Delta\psi = -\frac{\sqrt{2\pi}}{\chi_0} \langle \psi_g | \psi_0 \rangle \psi_g + \Delta\psi_s \quad (30)$$

where  $\Delta\psi_s(\mathbf{r}_1, \mathbf{r}_2)$  is a symmetric function under interchange of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , chosen so that

$$\langle \Delta\psi_s | \psi_g \rangle = 0. \quad (31)$$

Then Eq. (5) can be written, for the singlet state, as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1, \mathbf{r}_2) - \langle \psi_0 | \psi_g \rangle \psi_g(\mathbf{r}_1, \mathbf{r}_2) + \frac{\chi_0}{\sqrt{2\pi}} \Delta\psi_s(\mathbf{r}_1, \mathbf{r}_2). \quad (32)$$

Proceeding with the evaluation of the inner products required in the Rayleigh-Ritz method, Eq. (4), we use Eqs. (5) and (6) to obtain

$$\begin{aligned} \langle \psi | \psi \rangle &= 1 \pm 2 \left\langle \frac{\chi(\mathbf{r}_1)\chi(\mathbf{r}_2)}{2\pi} \left| e^{-r_1-r_2} \right. \right\rangle \\ &+ 2 \frac{\chi_0}{2\pi} \langle \Delta\psi | [\chi(\mathbf{r}_2)e^{-r_1} \pm \chi(\mathbf{r}_1)e^{-r_2}] \rangle + \frac{\chi_0^2}{2\pi} \langle \Delta\psi | \Delta\psi \rangle. \end{aligned} \quad (33)$$

We again apply the approximation that  $\chi$  varies slowly on the atomic scale, replacing it by  $\chi_0$  in the inner products. For the singlet case we require  $\langle \psi_0 | \psi_g \rangle$ , which can be approximated as

$$\langle \psi_0 | \psi_g \rangle = \frac{\chi_0}{\sqrt{2\pi}} \langle (e^{-r_1} + e^{-r_2}) | \psi_g \rangle + O(b^2). \quad (34)$$

Then using the fact that  $\langle e^{-r_1} | e^{-r_2} \rangle = 64\pi^2$ , we obtain for the triplet state

$$\begin{aligned} \langle \psi | \psi \rangle &= 1 + \frac{\chi_0^2}{2\pi} [-128\pi^2 + 2\langle \Delta\psi | (e^{-r_1} - e^{-r_2}) \rangle + \langle \Delta\psi | \Delta\psi \rangle] \\ &+ O(b^3), \end{aligned} \quad (35)$$

and for the singlet state

$$\begin{aligned} \langle \psi | \psi \rangle &= 1 + \frac{\chi_0^2}{2\pi} [128\pi^2 + 2\langle \Delta\psi_s | (e^{-r_1} + e^{-r_2}) \rangle \\ &- \langle \psi_g | (e^{-r_1} + e^{-r_2}) \rangle^2 + \langle \Delta\psi_s | \Delta\psi_s \rangle] + O(b^3). \end{aligned} \quad (36)$$

The extra term in the square brackets arises from the overlap of the  $H^-$  ground state with  $\psi_0$ .

Next we evaluate  $\langle \psi | \hat{H} | \psi \rangle$ . For the singlet state, Eqs. (5) and (30) imply

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \langle \psi_0 | \hat{H} | \psi_0 \rangle + \langle \psi_g | \hat{H} | \psi_g \rangle \langle \psi_g | \psi_0 \rangle^2 + \frac{\chi_0^2}{2\pi} \langle \Delta\psi_s | \hat{H} | \Delta\psi_s \rangle \\ &- 2\langle \psi_g | \psi_0 \rangle \langle \psi_0 | \hat{H} | \psi_g \rangle + \frac{2\chi_0}{\sqrt{2\pi}} \langle \Delta\psi_s | \hat{H} | \psi_0 \rangle \\ &- \frac{2\chi_0}{\sqrt{2\pi}} \langle \Delta\psi_s | \hat{H} | \psi_g \rangle \langle \psi_g | \psi_0 \rangle. \end{aligned} \quad (37)$$

Using Eq. (34), and dropping terms of order  $b^3$  or higher, we may neglect magnetic corrections to the ground state  $\psi_g$ ,

and replace  $\hat{H}$  by  $\hat{H}_0$  in all but the first term, where

$$\hat{H}_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} \quad (38)$$

is the Hamiltonian evaluated at  $B=0$ . Then applying  $\hat{H}_0\psi_g = -(\frac{1}{2} + E_g)\psi_g$ , along with Eq. (31), yields

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \langle \psi_0 | \hat{H} | \psi_0 \rangle + \frac{\chi_0^2}{2\pi} \left[ \left( E_g + \frac{1}{2} \right) \langle \psi_g | (e^{-r_1} + e^{-r_2}) \rangle^2 \right. \\ &\left. + 2\langle \Delta\psi_s | \hat{H}_0 | (e^{-r_1} + e^{-r_2}) \rangle + \langle \Delta\psi_s | \hat{H}_0 | \Delta\psi_s \rangle \right] + O(b^3). \end{aligned} \quad (39)$$

The second term in the square brackets can be reduced to

$$\begin{aligned} \langle \Delta\psi_s | \hat{H}_0 | (e^{-r_1} + e^{-r_2}) \rangle &= -\frac{1}{2} \langle \Delta\psi_s | (e^{-r_1} + e^{-r_2}) \rangle \\ &+ \left\langle \Delta\psi_s \left| \left[ e^{-r_1} \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) + e^{-r_2} \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) \right] \right. \right\rangle. \end{aligned} \quad (40)$$

The first term in Eq. (39) can also be evaluated to  $O(b^2)$ , yielding

$$\begin{aligned} \langle \psi_0 | \hat{H} | \psi_0 \rangle &= -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f | f'' \rangle \\ &+ \frac{\chi_0^2}{\pi} \left\langle \left[ e^{-2r_1} \left| \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) \right. \right] \right\rangle \\ &- \frac{1}{2} \langle e^{-r_1} | e^{-r_2} \rangle + \left\langle e^{-r_1-r_2} \left| \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) \right. \right\rangle + O(b^3). \end{aligned} \quad (41)$$

Each inner product in the square brackets can be evaluated analytically, resulting in

$$\langle \psi_0 | \hat{H} | \psi_0 \rangle = -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f | f'' \rangle - 46\pi\chi_0^2 + O(b^3). \quad (42)$$

Finally, we substitute Eqs. (36), (39), (40), and (42) into Eq. (4), and expand to  $O(b^2)$  noting that  $\langle f | f'' \rangle = O(b^2)$ . The result for the singlet state is

$$\begin{aligned} E &\leq -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f | f'' \rangle - 14\pi\chi_0^2 + \frac{\chi_0^2}{2\pi} \\ &\times \left\{ E_g \langle \psi_g | (e^{-r_1} + e^{-r_2}) \rangle^2 + \langle \Delta\psi_s | \left( \hat{H}_0 + \frac{1}{2} \right) | \Delta\psi_s \rangle \right. \\ &+ 2 \left\langle \Delta\psi_s \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} \right. \right. \right. \\ &\left. \left. \left. + \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right. \right\rangle \right\} + O(b^3). \end{aligned} \quad (43)$$

For the triplet state, the same analysis yields



$$\begin{aligned}
E \leq & -\frac{1}{2} + \frac{b}{2} + \frac{b^2}{4} - \frac{1}{2} \langle f|f'' \rangle + 10\pi\chi_0^2 \\
& + \frac{\chi_0^2}{2\pi} \left\langle \left\langle \Delta\psi \left| \left( \hat{H}_0 + \frac{1}{2} \right) \right| \Delta\psi \right\rangle \right. \\
& \left. + 2 \left\langle \Delta\psi \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} - \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle \right\rangle \\
& + O(b^3). \tag{44}
\end{aligned}$$

Here there are no terms involving the ground state, and the coefficient of  $\pi\chi_0^2$  differs due to the antisymmetry of  $\psi_0$ .

Variation of either Eq. (43) or (44) with respect to  $f$ , using the fact that  $\chi_0 \propto f(0)$ , again yields Eq. (18) for  $f$ . The form of  $k$  differs depending on the symmetry of the state:

$$\begin{aligned}
k = 7b - \frac{b}{(2\pi)^2} & \left\{ E_g \langle \psi_g | (e^{-r_1} + e^{-r_2})^2 \right. \\
& + \langle \Delta\psi_s | \left( \hat{H}_0 + \frac{1}{2} \right) | \Delta\psi_s \rangle \\
& \left. + 2 \left\langle \Delta\psi_s \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} + \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle \right\} \\
\text{(singlet),} & \tag{45}
\end{aligned}$$

$$\begin{aligned}
k = -5b - \frac{b}{(2\pi)^2} & \left\{ \langle \Delta\psi | \left( \hat{H}_0 + \frac{1}{2} \right) | \Delta\psi \rangle \right. \\
& \left. + 2 \left\langle \Delta\psi \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} - \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle \right\} \\
\text{(triplet).} & \tag{46}
\end{aligned}$$

In order for a bound state to exist,  $k$  must be positive. We will show numerically that this is not the case.

Variation of Eqs. (45) and (46) with respect to  $\Delta\psi$  yields, for the triplet state,

$$\left( \hat{H}_0 + \frac{1}{2} \right) \Delta\psi = - \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} + \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2}, \tag{47}$$

and for the singlet state

$$\left( \hat{H}_0 + \frac{1}{2} \right) \Delta\psi_s = \lambda \psi_g - \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} - \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2}, \tag{48}$$

where  $\lambda$  is a Lagrange multiplier associated with the constraint that  $\langle \Delta\psi_s, \psi_g \rangle = 0$ . Taking an inner product of both sides of Eq. (48) with respect to  $\psi_g$  yields the value of  $\lambda$ :

$$\lambda = \left\langle \psi_g \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} + \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle. \tag{49}$$

Furthermore, substitution of Eqs. (47) and (48) into Eqs. (45) and (46), respectively, allows us to simplify the forms of  $k$  for singlet and triplet states:

TABLE II. Best values of  $k$  for the triplet state of  $H^-$ .

$M$	$k_{\max}/b$	$\varepsilon$ for which $k=k_{\max}$
7	-1.9329	0.3512
8	-1.9032	0.3231
9	-1.8831	0.3033
10	-1.8657	0.2822
11	-1.8533	0.2670
12	-1.8422	0.2514
13	-1.8340	0.2391
14	-1.8265	0.2281
15	-1.8207	0.2172
$\infty$	$-1.76 \pm 0.01$	

$$\begin{aligned}
k = 7b - \frac{b}{(2\pi)^2} & \left\{ E_g \langle \psi_g | (e^{-r_1} + e^{-r_2})^2 \right. \\
& \left. + \left\langle \Delta\psi_s \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} + \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle \right\} \\
\text{(singlet),} & \tag{50}
\end{aligned}$$

$$\begin{aligned}
k = -5b - \frac{b}{(2\pi)^2} & \left\{ \langle \Delta\psi | \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} - \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle \right\} \\
\text{(triplet).} & \tag{51}
\end{aligned}$$

Finally, we solve Eqs. (47) and (48) using the Galerkin method, using the same basis functions as before [Eq. (26)], written in perimetric coordinates. For the singlet case we also require  $\psi_g$ . Following Pekeris [2], we expand  $\psi_g$  in the same basis functions and the same perimetric coordinates, using the same value of  $\varepsilon$  as we use in determining  $\Delta\psi$ , and keeping the same number of terms  $M$ .

In Fig. 1 we display  $k(M, \varepsilon)$  for the triplet case as a function of  $\varepsilon$ , for increasing values of  $M$ . One can see the maximum possible  $k$  value remains negative. For each  $M$ , this maximum value is given in Table II, along with the value of  $\varepsilon$  at which the maximum occurs.

A fit to this data of the form  $k_{\max}(M) = k_{\max}(\infty) - \alpha/M^\beta$  yields  $k_{\max}(\infty) = (-1.759 \pm 0.02)b$ , with  $\alpha = 2.449b$  and  $\beta = 1.36$  (see Fig. 2).

Therefore, the triplet state is not bound for weak magnetic fields. This is consistent with previous numerical calculations of the triplet state [7], where it was observed that the triplet state remains unbound for all field strengths that were considered, over the range  $8 \times 10^{-4} < b < 4000$ .

Turning next to the singlet state, we plot values of

$$\bar{k}_1(M, \varepsilon) \equiv - \langle \psi_g | (e^{-r_1} + e^{-r_2})^2 E_g / (2\pi)^2$$

and

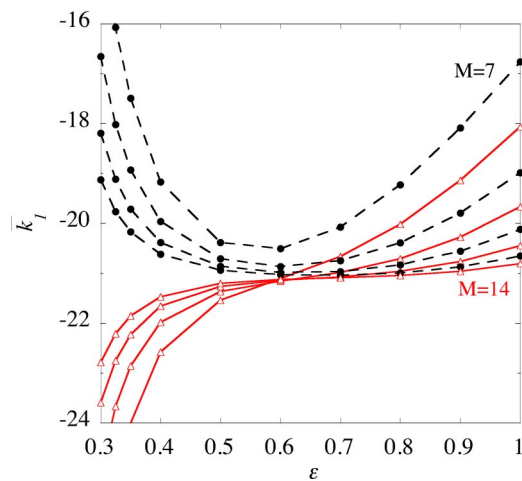


FIG. 3. (Color online)  $\bar{k}_1$  for different values of  $M$  and  $\varepsilon$ , evaluated for the excited  $J=0$  singlet state of  $H^-$ . Dashed lines correspond to odd  $M$ .

$$\bar{k}_2(M, \varepsilon)$$

$$\equiv - \left\langle \Delta \psi_s \left| \left[ \left( \frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{-r_1} + \left( \frac{1}{r_{12}} - \frac{1}{r_1} \right) e^{-r_2} \right] \right\rangle / (2\pi)^2$$

along with  $k/b = \bar{k}_1 + \bar{k}_2 + 7$  in Figs. 3–5. As a test of the code, we also plot values of  $E_g$  in Fig. 6. Convergence to the known result of 0.02775... can be seen for a range of  $\varepsilon$  as  $M$  increases. The maximum value of  $\bar{k}_2$  at a given value of  $M$  is listed in Table III, along with the limit at  $M \rightarrow \infty$ , found by fitting to the form  $k_{2 \max}(M) = k_{2 \max}(\infty) + \alpha/M^\beta$ .

The best estimates for  $\bar{k}_1$  come from fitting the data at fixed  $\varepsilon$  values to the form  $\bar{k}_1(M) = \bar{k}_1(\infty) + \alpha/M^\beta$ . The resulting data are displayed in Table IV. Since  $\bar{k}_1(\infty) \approx -21$  and  $\bar{k}_2(\infty) \approx 8$ , Eq. (50) implies  $k(\infty)/b = -21 + 8 + 7 \approx -6$ , with an estimated error of roughly  $\pm 0.5$ . Since  $k$  is negative there is no bound singlet state.

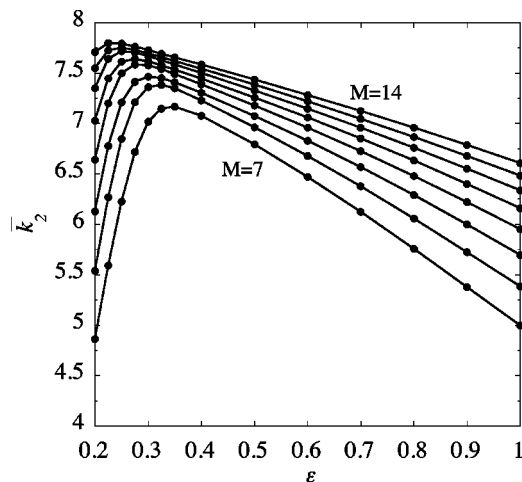


FIG. 4.  $\bar{k}_2$  for different values of  $M$  and  $\varepsilon$ .

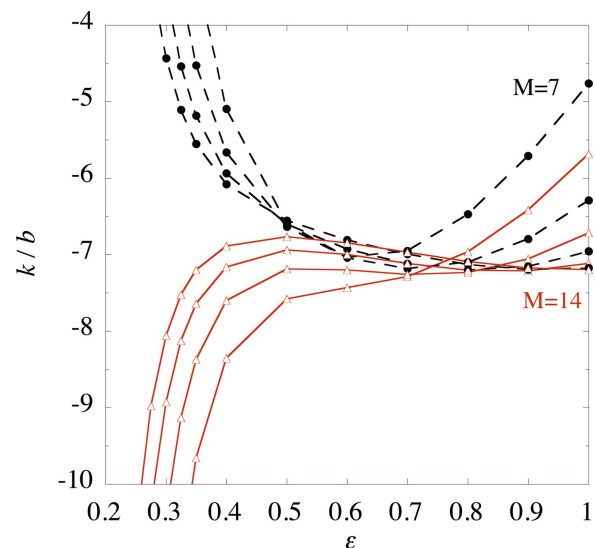


FIG. 5. (Color)  $k/b$  for different values of  $M$  and  $\varepsilon$  for the singlet state of  $H^-$ . Dashed lines correspond to odd  $M$ .

Therefore, for  $b \ll 1$  the only bound state of  $H^-$  with zero angular momentum is the ground-state singlet. There are no magnetically bound excited states of  $H^-$  with zero orbital angular momentum.

Although this contradicts the previous estimate of Ref. [1] for the binding energy of magnetically bound  $H^-$ , the authors of that work later [6] pointed out that the estimate might not apply to  $H^-$  because their approach neglected the symmetry of the wave function, and did not ensure that the wave function is orthogonal to the ground state. As we have seen, these effects are essential in accurately determining the energy, and for  $H^-$  are sufficient to destroy the  $J=0$  excited bound state, which substantiates the concerns put forward in Ref. [6]. However, we also saw that the bound-state scaling  $E_b \propto b^2 e^2/a$  does apply to positronic  $H^+$ , which does not have a field-free bound state. This is consistent with the intuition of Ref. [6] that this scaling applies to ions without field-free bound states, such as positronic  $H^+$  or  $He^-$ , but may not apply to ions with such states.

References [1,4,6] were also concerned with  $J \neq 0$  excited states, for which the effects of symmetry and ground-state

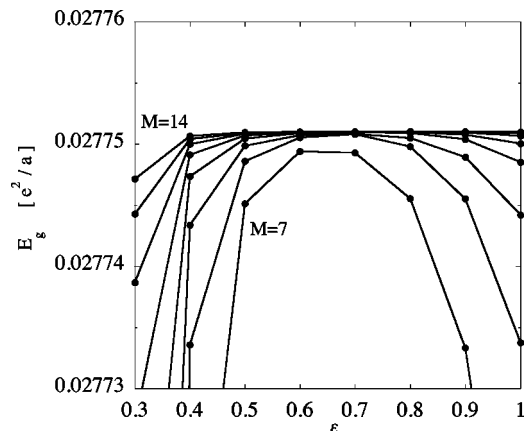


FIG. 6. Ground-state energy of  $H^-$ , in atomic units, versus  $\varepsilon$  for different values of  $M$ .

overlap are not important. In fact, it is worth noting that  $J \neq 0$  bound states can also be derived using a straightforward modification of the variational functions employed in Eqs. (5)–(8), and that the resulting bound-state energies closely follow those of Ref. [1], particularly for  $J \gg 1$ .

### III. DISCUSSION

The positron affinity to hydrogen given by Eq. (2) was calculated assuming that the proton was fixed at the origin. However, for such weak binding, motional effects of the central proton can be quite important. For example, it is well known that motion of the central proton couples to the positron motion through the magnetic field [4,5,8–12], and this can, in certain circumstances, excite the positron into the continuum [4,5,8,9].

In addition, effects due to motion of the proton may be expected to shift the bound-state energy given by Eq. (2). Considerable effort has gone into calculating these shifts for ground-state  $H^-$  [10–13], where they are observed to reduce the affinity. For small  $b$  the largest shifts are due to mass polarization terms and zero-point ion cyclotron energy, and are of order  $m/M$  and  $bm/M$  [10]. If this is also the case for magnetically bound ions, then magnetically bound states may exist only for  $b$  larger than some value that depends on  $m/M$  [4]. On the other hand, one cannot rule out that the finite-nuclear-mass shifts might *increase* the binding energy of magnetically bound ions, although this seems unlikely, particularly in light of the stability limits discussed in Refs. [4,5,9]. A definite answer to this important question must await further calculations.

The outer charge in a magnetically bound ion could be lost through field ionization due to ambient or applied electric fields. Since binding in the axial direction is weak, electric fields in the axial direction are most important. A straightforward calculation [14] of the ionization rate due to an axial electric field  $F$  yields, for small fields, an ionization rate given in atomic units by

$$\nu_{\text{ion}} = k^2 e^{-2k^3/3|e|}, \tag{52}$$

where  $\varepsilon = Fa^2/e$ ; or in Gaussian units by

TABLE III.  $\bar{k}_2$  max versus  $M$ .

$M$	$\bar{k}_2$ max	$\varepsilon$ at which $\bar{k}_2 = \bar{k}_2$ max
7	7.17	0.343
8	7.39	0.318
9	7.47	0.304
10	7.59	0.284
11	7.64	0.269
12	7.72	0.257
13	7.75	0.243
14	7.80	0.233
$\infty$	$8.3 \pm 0.4$	

$$\nu_{\text{ion}} = 1.84 \times 10^{17} \text{ Hz} \times b^2 e^{-(1.07 \times 10^8 b^3)/F(\text{statvolt/cm})},$$

where we have used the value  $k = 2.11b$ , from Table I. This field ionization rate is very large unless the electric field is very small, or the magnetic field is very large. For  $B = 10$  T, a field  $F = 13$  mV/m gives  $\nu_{\text{ion}} = 1 \text{ s}^{-1}$ .

Another positron loss process is annihilation with the bound electron. However, since the positron is only weakly bound to the ion, this loss process is rather slow. One can estimate the positron lifetime using known results for the annihilation rate of a low-energy positron in a hydrogen gas [15],

$$\nu_H = \pi r_0^2 c Z_{\text{eff}} n_H,$$

where  $r_0$  is the classical electron radius,  $n_H$  is the density of the hydrogen gas, and  $Z_{\text{eff}} \approx 8$  for atomic hydrogen. Turning this around, we can obtain the annihilation rate of a hydrogen atom in a positron gas of density  $n_p$  as

$$\nu_p = \pi r_0^2 c Z_{\text{eff}} n_p.$$

Finally, to estimate the lifetime of the positronic ion, we treat the weakly bound positron as a low-density gas with density of roughly  $\chi_0^2$  (neglecting the correlation effects contained in  $\Delta\psi$ , since these are presumably approximated by  $Z_{\text{eff}}$ ). This gives us an annihilation rate of

TABLE IV.  $\bar{k}_1$  versus  $M$ .

$M$	$\bar{k}_1$ at $\varepsilon = 0.6$	$k_1$ at $\varepsilon = 0.7$	$\bar{k}_1$ at $\varepsilon = 0.8$	$\bar{k}_1$ at $\varepsilon = 0.9$
7	-20.508	-20.075	-19.230	-18.086
8	-21.110	-20.666	-20.020	-19.140
9	-20.869	-20.751	-20.391	-19.794
10	-21.158	-20.985	-20.712	-20.277
11	-20.984	-20.969	-20.834	-20.556
12	-21.146	-21.073	-20.962	-20.764
13	-21.028	-21.040	-20.995	-20.874
14	-21.129	-21.093	-21.048	-20.962
$\infty$	$-21.1 \pm 0.05$	$-21.1 \pm 0.05$	$-21.2 \pm 0.04$	$-21.4 \pm 0.06$



$$\nu_p \approx \frac{r_0^2 c Z_{\text{eff}} k b}{2a^3} = 8.5 \frac{r_0^2 c b^2}{a^3}, \quad (53)$$

where we have used the value for  $k$  from Table I, and  $Z_{\text{eff}} = 8$ .

For bound positronic states, the exact annihilation rate can be evaluated using the formula [16]

$$\nu_p = \frac{\pi r_0^2 c}{a^3} \frac{\langle \psi | \delta(\mathbf{r}_1 - \mathbf{r}_2) | \psi \rangle}{\langle \psi | \psi \rangle}.$$

The required inner products can be simplified using Eqs. (7) and (12):

$$\nu_p = \frac{r_0^2 c}{a^3} \chi_0^2 \int d^3 r_1 [e^{-r_1} + \Delta \psi(\mathbf{r}_1, \mathbf{r}_1)]^2,$$

where we have dropped terms of  $O(b^3)$  or higher, and have, as usual, approximated  $\chi(\rho_1, z_1)$  by  $\chi_0$  in the integral. The integral can be evaluated analytically using Eqs. (23), (25), and (26), and the properties of Laguerre polynomials. Keeping terms in the sums up to  $M=14$ , we find that the integral asymptotes to  $27 \pm 0.3$ . Thus,

$$\begin{aligned} \nu_p &= \frac{(27 \pm 0.3) r_0^2 c}{2\pi a^3} k b \approx 9.1 \frac{r_0^2 c}{a^3} b^2, \\ &= 1.5 \times 10^{11} b^2 \text{ s}^{-1}, \end{aligned} \quad (54)$$

in close agreement with the estimate of Eq. (53). In a magnetic field of 10 T,  $\nu_p = 0.03 \text{ s}^{-1}$ .

Finally, we note that the variational perturbation method used here can be generalized to magnetically bound ions with more electrons, such as  $\text{He}^-$ , or positronic  $\text{He}^+$ . Given the larger number of degrees of freedom in these ions, the wave function can no longer be described using basis functions expressed in perimetric coordinates; but other basis functions are available, such as correlated Gaussian basis functions. Although such basis sets have been used extensively to obtain accurate results for ionic energy levels [17], our calculation for positronic  $\text{H}^+$  indicates that high-accuracy wave functions are required in order to achieve even moderately accurate affinities:  $M=18$  corresponds to a basis set of 6859 functions, required to achieve 4% accuracy in the positron affinity. Evidently, the affinity is strongly affected by fine details in the wave function. It remains to be seen whether such fine detail is achievable in calculations with larger numbers of electrons.

#### ACKNOWLEDGMENT

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