

Relativistic and nonrelativistic finite-basis-set calculations of low-lying levels of hydrogenic atoms in intense magnetic fields

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A finite-basis-set method is used to calculate relativistic and nonrelativistic binding energies of an electron in a static Coulomb field and in magnetic fields of arbitrary strength ($0 < B \leq 10^{13}$ G). The basis set is composed of products of Slater- and Landau-type functions, and it contains the exact solutions at both the Coulomb limit ($B = 0$) and the Landau limit ($Z = 0$). Relativistic variational collapse is avoided and highly accurate results are obtained with the basis set. The relativistic corrections obtained for intense magnetic fields ($B \gtrsim 10^9$ G) differ from the previous relativistic calculations based on the adiabatic approximations. It is found that *the sign of the relativistic correction changes* from negative to positive near $B \approx 10^{11}$ G for the ground state and near $B \approx 10^{10}$ G for the $2p_{3/2}(\mu = -3/2)$ excited state of hydrogen. The method is checked to be very accurate by means of the virial theorem, sum rules, and the relativistic low- B limit where comparison can be made with perturbation results. In the nonrelativistic limit of the Dirac equation, our results agree with other accurate nonrelativistic calculations available and with our own calculations based on the Schrödinger equation, which converge to more significant digits than previous calculations for the whole range of magnetic fields.

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I. INTRODUCTION

There is considerable interest in astrophysics and solid-state physics to study hydrogenic atoms in intense magnetic fields [1–3]. Many nonrelativistic methods have been used [4–10], including the variational method [4, 6], Hartree-Fock approach [7], finite-element method [8], and bounds by eigenvalue-moment method [9] and by Kato's method [10]. With the increasing accuracy of the nonrelativistic calculations of hydrogenic atoms in intense magnetic fields [6–10], relativistic corrections become necessary. The relativistic correction, expected to be of order $(\alpha Z)^2$, was estimated in the adiabatic approximation [11]. However, the adiabatic approximation cannot provide accurate relativistic corrections since the error it introduces can be of the same order or larger than the relativistic correction itself. A comparison of the nonrelativistic results obtained using the adiabatic approximation with the most accurate nonrelativistic calculations indicates that this is the case. Recently, we reported briefly [12] a relativistic variational calculation that yields different results than previous adiabatic calculations. In this paper, we present the details of a variational method that yields very accurate results for both the Schrödinger and Dirac equations.

A finite-basis-set method is used to calculate both the relativistic and nonrelativistic binding energies of an electron in a Coulomb field and an arbitrary magnetic field. The advantages of this method over single-trial-function methods are that the size of the basis set can be systematically increased as a higher accuracy is required and that excited states can be also obtained simultaneously by the diagonalization procedure. The basis set that we intro-

duce in this work has, as its main advantage, the property that it contains the exact solutions at both the Coulomb limit ($B = 0$) and the Landau limit ($Z = 0$), and that it transforms from one limit to the other smoothly as one varies two nonlinear parameters λ and β which characterize the Coulomb and Landau orbitals, respectively. (The set can be generalized to contain two sets of nonlinear parameters $\{\lambda_i\}$ and $\{\beta_i\}$ to avoid near linear dependency for very large basis dimensions.) In the nonrelativistic case, the basis set gives an accurate upper bound on the energies. In the relativistic case, the basis set avoids variational collapse and converges to the exact energies both with the nonlinear parameters and with the size of the basis set.

Using this basis set we have obtained the most accurate relativistic and nonrelativistic binding energies of an electron in a Coulomb field and in intense magnetic fields to date, with an accuracy better than 1 part in 10^7 for $B \sim 10^{13}$ G and better than 1 part in 10^{16} for $B \lesssim 10^8$ G for hydrogen and higher accuracies for larger Z . This level of accuracy is obtained with less than 200 basis vectors in the relativistic case and less than 50 basis vectors in the nonrelativistic case (the size of the basis vectors for the Dirac equation is about four times the size for the Schrödinger equation because of the coupling of spin-up and spin-down states in the small and large components of the Dirac wave function). The binding energies obtained by the nonrelativistic limit of the Dirac Hamiltonian agree, to all converging digits, with the results given by the Schrödinger Hamiltonian and with other previous accurate nonrelativistic calculations. It is found that the sign of the relativistic correction changes from negative to positive near $B \approx 10^{11}$ G for the ground state and

near $B \approx 10^{10}$ G for the $2p_{3/2}(\mu = -3/2)$ excited state of hydrogen.

II. NONRELATIVISTIC APPROACH

The nonrelativistic Hamiltonian for an electron in a uniform magnetic field $\mathbf{B} = B\hat{z}$ with vector potential $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$ is given by (atomic units will be used throughout this paper except in certain physical discussions)

$$H_S = \pi^2/2 - Z/r + \sigma_z B/2 \\ = -\nabla^2/2 + B^2 \rho^2/8 - Z/r + (B/2)(l_z + \sigma_z), \quad (1)$$

where $\pi = \mathbf{p} + \mathbf{A}/c$, $\rho^2 = x^2 + y^2$, and l_z and σ_z are the z components of the orbital angular momentum and the Pauli matrix, respectively. The magnetic field is given in units of $(e/\hbar)^3 m_e^2 c \approx 2.35 \times 10^9$ G, where m_e is the mass of the electron and c is the speed of light; thus $B = 1$ corresponds to $(\hbar\omega_B)/(e^2/a_0) = 1$, where a_0 is the Bohr radius and $\omega_B = eB/(m_e c)$ is the cyclotron frequency of the electron. When $B \gtrsim 1$, the Landau radius $\rho_0 = \sqrt{2\hbar c/eB}$ is of the same order as or smaller than the Bohr radius, and the magnetic field will be called intense in this case [4]. The Hamiltonian commutes with the z component of the orbital angular momentum l_z and the parity operator, so that the corresponding quantum numbers m and π are good quantum numbers. (The Hamiltonian is unchanged under the transformations $z \rightarrow -z$ as well as $\mathbf{r} \rightarrow -\mathbf{r}$, therefore some authors use z parity to label the eigenstates. We employ the full parity notation in this paper in order to use the conventional labeling of eigenstates in the limit $B = 0$.)

In order to choose a proper basis set for variational calculations, we first consider two limit cases. When $B = 0$, the exact solutions can be constructed by the Slater-type basis functions

$$\exp(-\lambda r) r^n Y_{lm}(\theta, \phi), \quad (2)$$

where $n = 0, 1, 2, \dots, N$, λ is a nonlinear variational parameter, and $Y_{lm}(\theta, \phi)$ is the spherical harmonic. In the other limit, when $Z = 0$, the exact solutions are the Landau orbitals which can be written in cylindrical coordinates as [13]

$$\psi_{n\rho m\sigma}^{(S)} = \xi^{|m|/2} L_{n\rho}^{|m|}(\xi) \exp(-\xi/2) \exp(im\phi + ip_z z) \chi_\sigma, \quad (3)$$

where

$$\xi = (\rho/\rho_0)^2,$$

$L_{n\rho}^{|m|}$ are the associated Laguerre polynomials, and χ_σ is a two-component spin function with $\sigma = \pm 1$ corresponding to spin-up and spin-down states. The energy eigenvalues are given as

$$E = \frac{p_z^2}{2} + B \left(n_\rho + \frac{|m| + m + \sigma + 1}{2} \right), \quad (4)$$

where

$$n_\rho = 0, 1, \dots, \quad m = 0, \pm 1, \dots$$

The ground state is infinitely degenerate with $p_z = 0$, $\sigma = -1$, $n_\rho = 0$, and $m = 0, -1, -2, \dots$. The exact solutions in this case can therefore be constructed as a linear combination of the functions

$$\rho^{2n} \rho^{|m|} \exp(-\beta \rho^2) \exp(im\phi + ip_z z) \chi_\sigma, \quad (5)$$

with

$$n = 0, 1, 2, \dots, N,$$

and β a nonlinear variational parameter.

Combining the above two limit cases, we thus choose a set of basis functions of the form

$$\Phi_{nl} = r^n (\cos \theta)^{l-|m|} (\sin \theta)^{|m|} \exp(-\lambda r - \beta \rho^2) \\ \times \exp(im\phi) \chi_\sigma, \quad n = 0, 1, 2, \dots, N_r, \quad (6)$$

where for even- (odd-) parity states, l takes even (odd) integer values greater than or equal to $|m|$ up to $2N_\theta$ (for even parity) or $2N_\theta + 1$ (for odd parity). The variational procedure [14] consists of orthonormalizing the above basis set by the diagonalization of the overlap matrix $\langle \Phi_{nl} | \Phi_{n'l'} \rangle$, and then diagonalizing the Hamiltonian in the orthonormal basis set so that the optimal linear parameters in the trial function are determined (Hylleraas-Undheim procedure). The nonlinear parameters λ and β will then be determined by minimizing the variational eigenvalues.

The nonrelativistic Hamiltonian is bounded from below, therefore the variational eigenvalues calculated by the Hylleraas-Undheim procedure are upper bounds of the true eigenvalues of the Hamiltonian. The nonrelativistic results obtained by the basis set given by Eq. (6) are shown in Table I for the ground state and in Table II for the $2p_{3/2}(\mu = -3/2)$ excited state, where comparison is made with previous accurate nonrelativistic calculations and with the results obtained by taking the nonrelativistic limit of the Dirac equation (discussed in Sec. III). In all cases, our results, calculated with less than 50 basis vectors, have better convergence than any previous results.

The optimized nonlinear parameters λ and β are closely related to the two limits. As B increases, the value of the optimized β gets closer to the exact value $B/4$ for the $Z = 0$ limit. In the Coulomb limit, where B is very small, the optimized β is close to 0 and λ is close to Z for the ground state and Z/n for the excited states.

If we change \mathbf{r} to \mathbf{r}/Z in the Hamiltonian of Eq. (1), we obtain a simple scaling relation for the energy [15]

$$E(Z, B) = Z^2 E(1, B/Z^2). \quad (7)$$

Thus it will suffice to consider only the case $Z = 1$ in the nonrelativistic calculations.

III. RELATIVISTIC APPROACH

A. Variational method

The Dirac Hamiltonian for the problem is given by

$$H_D = c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta c^2 - \frac{Z}{r}, \quad (8)$$

where α and β are the standard 4×4 Dirac matrices. The Hamiltonian commutes with the z component of the total angular momentum and with the parity operator, so that the corresponding quantum numbers μ and π are conserved. Unlike the nonrelativistic Hamiltonian, the Dirac Hamiltonian is not bounded from below. The variational method may have difficulties of variational collapse, spurious roots, and continuum dissolution in the case of systems with more than one electron. Some theorems and techniques have been developed in recent years to overcome these difficulties [16–19]. It has been shown [19, 20] that the problems of variational collapse and spurious roots can be avoided by an appropriate choice of basis sets, and a rigorous proof of bounds can be obtained for the Coulomb case [20]. As a result, finite-basis-set techniques have been very successful for calculations involving the one-electron Dirac-Coulomb Hamiltonian or the many-electron Dirac-Hartree-Fock Hamil-

tonian (based on screened central potential approximations) [21]. In this paper, we extend the method to the case of a potential that has cylindrical symmetry only and apply it to hydrogenic atoms in intense magnetic fields.

The choice of basis set is based on the following considerations.

(i) Exact solutions at both $Z = 0$ and $B = 0$ can be constructed from the basis set.

(ii) The basis set satisfies the boundary conditions at $r \rightarrow 0$ and ∞ . In fact, these conditions have been included with the conditions at the $B = 0$ and $Z = 0$ limits.

(iii) Properly balanced small- and large-component basis functions are used in the basis set, as can be achieved by considering the coupling of the Hamiltonian between large and small components. (We do not use kinetic balance [19] here, but plan to apply it to the case of finite

TABLE I. Nonrelativistic ground-state binding energies ($-E_{NR}$) (divided by Z^2 , in atomic units) of hydrogenic atoms in an intense magnetic field B (in units of 2.35×10^9 G). For $Z \neq 1$, E_{NR} in columns 3 and 4 is obtained by the scaling relation of Eq. (7), while E_{NR}^s is obtained in each case by taking the nonrelativistic limit of the Dirac equation. The numbers in column 3 give the previous most accurate nonrelativistic results.

Z	B	$-E_{NR}$	$-E_{NR}^f$	$-E_{NR}^s$
1	0.1	$\left\{ \begin{array}{l} 0.54752648040109 \\ 0.54752648040110 \end{array} \right\}^a$	0.5475264804010945	0.5475264804011
1	1	$\left\{ \begin{array}{l} 0.8311688966 \\ 0.8311688973 \end{array} \right\}^a$	0.83116889673	0.831168897
1	2	$\left\{ \begin{array}{l} 1.022213908 \\ 1.022213910 \end{array} \right\}^a$	1.02221390766	1.022213908
1	3	$\left\{ \begin{array}{l} 1.16453299 \\ 1.16453307 \end{array} \right\}^a$	1.1645329893	1.164532989
1	20	$\left\{ \begin{array}{l} 2.215396 \\ 2.215913 \end{array} \right\}^a$	2.215398515	2.2153985
		2.215398 ^b		
		2.215393 ^d		
1	200	4.7266 ^b	4.727145108	4.7271451
		4.727134 ^c		
		4.72708 ^d		
1	500		6.25708765	6.2570877
1	2000	$\left\{ \begin{array}{l} 9.2754 \\ 9.3102 \end{array} \right\}^e$	9.3047650	9.304765
		9.30448 ^b		
		9.30464 ^d		
1	5000		11.873408	11.87341
5	25	$\left\{ \begin{array}{l} 0.8311688966 \\ 0.8311688973 \end{array} \right\}^a$	0.83116889673	0.831168897
5	50	$\left\{ \begin{array}{l} 1.022213908 \\ 1.022213910 \end{array} \right\}^a$	1.02221390766	1.022213908
20	800	$\left\{ \begin{array}{l} 1.022213908 \\ 1.022213910 \end{array} \right\}^a$	1.02221390766	1.022213908

^aLower and upper bounds in Ref. [10].

^bReference [7].

^cReference [6].

^dReference [8].

^eLower and upper bounds in Ref. [5].

^fPresent results by the Schrödinger equation.

^gPresent results by nonrelativistic limit of the Dirac equation.

nuclear size.)

(iv) The basis functions have the correct nonrelativistic limit.

Similarly to the Schrödinger equation, the Dirac equation is exactly solvable at the $B = 0$ limit and the $Z = 0$ limit. The exact solutions for the Coulomb potential can be obtained from the superposition of functions of the form [16]

$$\psi_j = \begin{pmatrix} \phi_j(r)\chi_{\kappa\mu}/r \\ 0 \end{pmatrix},$$

$$\psi_{N+j} = \begin{pmatrix} 0 \\ i\phi_j(r)\chi_{-\kappa\mu}/r \end{pmatrix}, \quad j = 1, 2, \dots, N \quad (9)$$

where

$$\phi_j(r) = r^{\gamma-1+j}e^{-\lambda r}, \quad \gamma = \sqrt{\kappa^2 - (\alpha Z)^2}, \quad (10)$$

λ is a nonlinear parameter, κ is the Dirac quantum number, and $\chi_{\kappa\mu}$ is a two-component spherical spinor:

$$\chi_{\kappa\mu} = \sum_{m\sigma} \langle j\mu | m\sigma \rangle Y_{lm} \chi_{\sigma}. \quad (11)$$

When $Z = 0$, the solution of the Dirac equation can be obtained by considering [22] the square of the Hamiltonian in Eq. (8), which can be written as

$$H_D^2 = c^2\pi^2 + c^4 + c^2\sigma_z B$$

$$= 2c^2(H_S + c^2/2). \quad (12)$$

Thus H_D^2 has a spectrum similar to that of H_S with an eigenfunction given by

$$X_{n\rho m\sigma} = \begin{pmatrix} \psi_{n\rho m\sigma}^{(S)} \\ 0 \end{pmatrix}, \quad (13)$$

and eigenvalues

$$E_D^2 = c^4 + c^2p_z^2 + c^2B(2n_\rho + 1 + |m| + m + \sigma), \quad (14)$$

where m and $\sigma/2$ are the z components of the orbital angular momentum and the spin for the large component. Using the method given by Johnson and Lippman [22], the eigenfunctions for H_D can be expressed in terms of $X_{n\rho m\sigma}$ by the second-order equation

$$(H_D^2 - E_D^2)X_{n\rho m\sigma} = (H_D - E_D)(H_D + E_D)X_{n\rho m\sigma} = 0. \quad (15)$$

The solution for H_D can therefore be written as

$$\Psi_{n\rho\mu\sigma}^{(D)} = (H_D + E_D)X_{n\rho m\sigma}^{(S)}. \quad (16)$$

Based on the above considerations, we choose the following basis set:

$$\Phi_{nlk}^{(k)} = r^{\gamma-1+n}e^{-\lambda r-\beta(r\sin\theta)^2}(\cos\theta)^{l_k-|m_k|}$$

$$\times (\sin\theta)^{|m_k|}e^{im_k\phi}w_k,$$

$$n = 0, 1, \dots, N_r, \quad k = 1, 2, 3, 4 \quad (17)$$

TABLE II. Relativistic ($-E$) and nonrelativistic ($-E_{NR}$) binding energy (in atomic units) for the $2p_{3/2}(\mu = -3/2)$ excited state of hydrogen in an intense magnetic field B (in units of 2.35×10^9 G). The relativistic correction is given by $\delta E = (E - E_{NR})/|E_{NR}|$.

B	$-E_{NR}$	$-E_{NR}$	$-E^f$	δE^f
0.1	$\left\{ \begin{array}{l} 0.2008456723729 \\ 0.2008456723746 \end{array} \right\}^a$ 0.2008457 ^b 0.2008456 ^c	0.200845672 ^d 0.20084567237333 ^e	0.200845897	-1.12×10^{-6}
1	$\left\{ \begin{array}{l} 0.45659706 \\ 0.45659710 \end{array} \right\}^a$ 0.4565971 ^b 0.4565969 ^c	0.45659706 ^d 0.4565970584 ^e	0.45659724	-3.94×10^{-7}
10	$\left\{ \begin{array}{l} 1.12542 \\ 1.12627 \end{array} \right\}^a$ 1.125422 ^b 1.125422 ^c	1.12542234 ^d 1.1254223418 ^e	1.12542204	2.67×10^{-7}
100	$\left\{ \begin{array}{l} 2.63474 \\ 2.63480 \end{array} \right\}^b$ 2.634758 ^c	2.63476066 ^d 2.634760665 ^e	2.63475395	2.55×10^{-6}
1000	$\left\{ \begin{array}{l} 5.63841 \\ 5.63844 \end{array} \right\}^b$ 5.638416 ^c	5.6384211 ^d 5.63842105 ^e	5.6383673	9.54×10^{-6}

^aLower and upper bounds in Ref. [10].

^bReference [7].

^cReference [8].

^dPresent results by the nonrelativistic limit of the Dirac equation.

^ePresent nonrelativistic results by the Schrödinger equation.

^fPresent relativistic results.

where $m_k = \mu - \sigma_k/2$, $\sigma_1 = \sigma_3 = 1$, $\sigma_2 = \sigma_4 = -1$, λ and β are nonlinear variational parameters, and the parameter γ is determined by the boundary condition as $r \rightarrow 0$ to be $\sqrt{\kappa^2 - (\alpha Z)^2}$ with κ taking the values corresponding to the $B = 0$ limit. The four-component spin functions w_k have the form

$$\begin{aligned} w_1 &= \begin{pmatrix} \chi_1 \\ 0 \end{pmatrix}, \quad w_2 = \begin{pmatrix} \chi_{-1} \\ 0 \end{pmatrix}, \\ w_3 &= \begin{pmatrix} 0 \\ \chi_1 \end{pmatrix}, \quad w_4 = \begin{pmatrix} 0 \\ \chi_{-1} \end{pmatrix}. \end{aligned} \quad (18)$$

For even- (odd-) parity states, the value of l_k for the large components ($k = 1, 2$) takes an even (odd) number greater than or equal to $|m_k|$ up to $2N_\theta$ (for even parity) or $2N_\theta + 1$ (for odd parity), while for the small components ($k = 3, 4$) it takes an odd (even) number greater than or equal to $|m_k|$ up to $2N_\theta + 1$ (for even parity) or $2N_\theta$ (for odd parity), since the small component has a different nonrelativistic parity than the large component. For example, for the ground state (with $\pi = 1$, $\mu = -1/2$), the powers l_k are given by

$$l_1 = 2, 4, \dots, 2N_\theta, \quad l_2 = 0, 2, \dots, 2N_\theta,$$

$$l_3 = 1, 3, \dots, 2N_\theta + 1, \quad l_4 = 1, 3, \dots, 2N_\theta + 1.$$

Note that for the ground state when $N_\theta = 0$, there will be no vectors corresponding to $k = 1$; the total number of vectors will be $M = (4N_\theta + 3)(N_r + 1)$.

The basis set has a form similar to that for the spherical case: $f_n(r)Y_{lm}(\theta, \phi)$. The radial function $f_n(r)$ is replaced by $f_n(r, \theta) = r^{\gamma-1+n}e^{-\lambda r - \beta \rho^2}$, which includes the radial dependence for the Coulomb potential and the exponential cylindrical dependence for the magnetic field. For the angular part, $Y_{lm}(\theta, \phi)$ is replaced by $(\cos \theta)^{l-|m|}(\sin \theta)^{|m|}e^{im\phi}$, so that through the diagonalization of the Hamiltonian, it can reproduce the $(\cos \theta)^{2n}(\sin \theta)^{|m|}e^{im\phi}$ term for the $Z = 0$ case and $Y_{lm}(\theta, \phi)$ for the $B = 0$ case, yielding a proper mixing in the intermediate case. This approach is very efficient for intense magnetic fields. In this case, the excitation energies of the Landau levels are larger than those of the Coulomb potential, so that the major contributions to the ground-state energy are the ground state of the Landau levels and many low-lying Coulomb states.

The variational procedure is similar to that for the Schrödinger equation. The basis set is first orthonormalized by the diagonalization of the overlap matrix $\langle \Phi_{nl_k}^{(k)} | \Phi_{n'l_k'}^{(k)} \rangle$, which yields M orthonormal basis vectors of the form

$$\psi_i^{(k)} = \sum_{nl_k} b_{inl_k}^{(k)} \Phi_{nl_k}^{(k)}. \quad (19)$$

The matrix elements of the Hamiltonian in the basis set of Eq. (17) can be expressed in terms of a double integral which can be reduced to a single integral of a confluent hypergeometric function. The details of the calculations

are given in the Appendix.

The variational solutions to the Hamiltonian in Eq. (8) are then obtained with trial functions of the form

$$\Psi_{ir}^i = \sum_{jk} a_{ij}^{(k)} \psi_j^{(k)}. \quad (20)$$

Since we are looking for stationary states, we diagonalize the Hamiltonian in the orthonormal basis vectors to determine the linear variational parameters $a_{ij}^{(k)}$ for certain values of N_r , N_θ , λ , and β . This procedure yields $N_+ + N_- = M$ variational eigenvalues and eigenstates, where N_+ and N_- are the number of basis vectors for positive-energy and negative-energy states, respectively.

The procedure to optimize the nonlinear parameters needs to be generalized since the Dirac Hamiltonian is no longer bounded from below. Instead of simply minimizing the variational energy with respect to the nonlinear parameters, we use the stationary property of the variational eigenvalues to determine the nonlinear parameters. If the basis set is complete when $N \rightarrow \infty$, then in the vicinity of the true energy, the change of the variational eigenvalue $E(\lambda, \beta)$ with the nonlinear parameters λ and β should be at its minimum and should decrease as the size of the basis set increases. Thus a smoother range of $E(\lambda, \beta)$ against λ and β should be achieved as the powers N_r and N_θ are increased as shown in Fig. 1. We therefore determine the optimal value of the energy by searching for the most stable range of the variational eigenvalue $E(\lambda, \beta)$ against λ and β for certain values of N_r and N_θ . This procedure yields variational eigenvalues which converge to the exact energies but are not necessarily upper bounds of the energies. As expected from the results for the two limit cases, the optimized value of λ is close to Z for the ground state when B is small, while the optimized value of β is close to $B/4$ when B is large.

The results obtained by the above procedure have converged to more than 16 digits for $B \lesssim 0.1$ (10^8 G), and to more than 7 significant digits accuracy for $0.1 < B \leq 5000$ ($10^8 < B \lesssim 10^{13}$ G) with less than 200 basis vectors. Note, however, that there is no upper

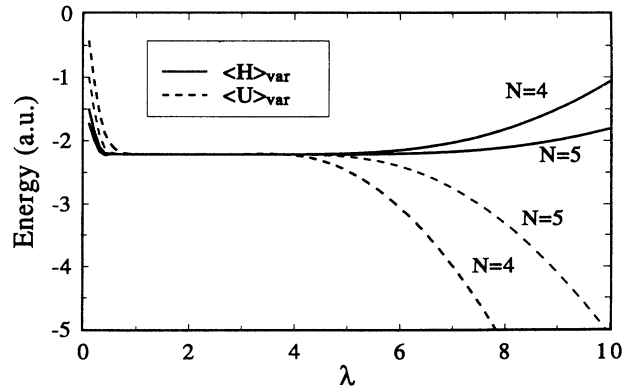


FIG. 1. The variational energies $\langle H \rangle_{\text{var}}$ and $\langle U \rangle_{\text{var}}$ defined in Eq. (24) plotted against the nonlinear variational parameter λ for the ground state of hydrogen with $B = 2$ (4.7×10^9 G). The size of the basis set is given by $N_r = N$ and $N_\theta = 2$.

bound on the energy globally: the convergence can be achieved from both sides of the true energy. A comparison with previous results for hydrogenic atoms is made in Table III for the ground state and in Table II for an excited state. Our relativistic results differ substantially from the previous relativistic calculations performed using adiabatic approximations [11].

The dependence of the relative relativistic corrections on B for the ground state and the $2p_{3/2}(\mu = -3/2)$ excited state of hydrogen is plotted in Fig. 2. It shows that the relativistic correction changes sign near $B = 40$ ($\approx 10^{11}$ G) for the ground state and near $B = 4.5$ ($\approx 10^{10}$ G) for the $2p_{3/2}(\mu = -3/2)$ excited state of hydrogen. The relativistic correction for the ground state is generally larger than that for the excited states, which is expected from the fact that the inner-shell electron moves faster than the outer-shell electron.

B. Methods used to check the relativistic results

1. Sum rule

Starting from the Dirac Hamiltonian and related commutation relations, we can derive various sum rules [23]. For example, starting from the commutation relation

$$\langle 0 | [[H, r], r] | 0 \rangle = 0, \quad (21)$$

we have

$$\sum_n |\langle n | r | 0 \rangle|^2 (E_n - E_0) = 0, \quad (22)$$

where \sum_n denotes summation over discrete states and integration over the continuum states. This sum rule can be used also to check the completeness of the basis set

when the infinite sum is replaced by the sum over finite basis vectors. The results of the sum rule of Eq. (22) is given in Table IV. They indicate that the basis set is approaching completeness as the size of the basis set is increased. Note that the variational calculation of the sum rule is not optimized, but rather performed using the basis set that optimizes the ground state.

2. Virial theorem

The virial theorem can also be used to check the completeness of the basis set [24]. It follows from the Dirac Hamiltonian Eq. (8) that

$$\langle H \rangle_{\text{exact}} = \langle \beta \rangle_{\text{exact}} m_e c^2 + 2e \langle \alpha \cdot \mathbf{A} \rangle_{\text{exact}}, \quad (23)$$

where $\langle \rangle_{\text{exact}}$ denotes the expectation value for an exact energy eigenstate. [Note that Eq. (23) will not be valid in general for an arbitrary variational state.] For a variational state to be a good approximation of the energy eigenstate, it is necessary, but not sufficient, that the difference

$$\langle H \rangle_{\text{var}} - \langle U \rangle_{\text{var}},$$

where

$$\langle U \rangle_{\text{var}} = \langle \beta \rangle_{\text{var}} m_e c^2 + 2e \langle \alpha \cdot \mathbf{A} \rangle_{\text{var}} \quad (24)$$

should be small. In Eq. (24) the symbol $\langle \rangle_{\text{var}}$ denotes the expectation value for a variational state. We found that the difference between $\langle H \rangle_{\text{var}}$ and $\langle U \rangle_{\text{var}}$ indeed decreases as N_r and N_θ increase as shown in Fig. 1 and Table IV. Moreover, the minimum of the difference is consistently in the most stable range of $E(\lambda, \beta)$. This

TABLE III. Relativistic ($-E$) ground-state binding energies (divided by Z^2 , in atomic units) of hydrogenic atoms in an intense magnetic field B (in units of 2.35×10^9 G). The relativistic correction is given by $\delta E = (E - E_{\text{NR}})/|E_{\text{NR}}|$.

Z	B	$-E^a$	δE^a	$-E^b$	δE^b
1	0.1			0.5475324083429	-1.08×10^{-5}
1	1			0.831173226	-5.21×10^{-6}
1	2	0.89977712	0.57×10^{-6}	1.022218029	-4.03×10^{-6}
1	3			1.164537038	-3.48×10^{-6}
1	20	2.1493075	0.23×10^{-5}	2.21540091	-1.09×10^{-6}
1	200	4.6916844	0.77×10^{-5}	4.7271233	4.61×10^{-6}
1	500			6.2570326	8.81×10^{-6}
1	2000	9.2867088	0.215×10^{-4}	9.304593	1.85×10^{-5}
1	5000			11.87308	2.78×10^{-5}
5	25			0.831277196	-1.303×10^{-4}
5	50			1.022317006	-1.009×10^{-4}
20	800			1.023879534	-1.629×10^{-3}

^aAdiabatic approximations, Ref. [11].

^bPresent results.

TABLE IV. For fixed λ and β , the relativistic variational energy $\langle H \rangle_{\text{var}}$, virial energy $\langle U \rangle_{\text{var}}$ defined in Eq. (24), and the sum of Eq. (22) for the ground state of hydrogen in a magnetic field $B = 20$ (in units of 2.35×10^9 G) for different sizes of the basis set.

N_r	$2N_\theta$	$-\langle H \rangle_{\text{var}}$	$-\langle U \rangle_{\text{var}}$	Sum
3	2	2.210739078	2.296827516	1.1×10^{-2}
4	4	2.215126434	2.214880767	1.8×10^{-3}
5	4	2.215253245	2.216075286	8.7×10^{-4}
6	6	2.215375385	2.215136890	1.4×10^{-4}
7	6	2.215393789	2.215332504	6.5×10^{-5}
8	8	2.215399761	2.215378719	1.2×10^{-5}
9	8	2.215400728	2.215396096	7.2×10^{-6}
10	10	2.215400912	2.215400317	3.2×10^{-6}
11	10	2.215400913	2.215401060	1.4×10^{-6}

property can also be used to optimize the variational energies with respect to nonlinear parameters λ and β [25].

3. Perturbation and low- B limit

The variational results are also checked by comparing with the relativistic perturbation results (relativistic general Paschen-Back effect) of hydrogen for low and intermediate magnetic field B . Using the perturbation method, by diagonalizing $\alpha \mathbf{A}$ in the subspace of hydrogenic states with fixed n , the relativistic energy eigenvalues are given by [26]

$$E_1^P = (\gamma_1 - 1)/\alpha^2 - B(2\gamma_1 + 1)/6 \quad (25)$$

for the ground state and

$$E_2^P = (\gamma_2/2 - 1)/\alpha^2 - B(2\gamma_2 + 1)/5 \quad (26)$$

for the $2p_{3/2}(\mu = -3/2)$ excited state, where $\gamma_k = \sqrt{k^2 - (\alpha Z)^2}$. The relative relativistic corrections on the energies can then be written as

$$\delta E_1^P = \frac{E_1^P - E_{1\text{NR}}^P}{|E_{1\text{NR}}^P|} = -\frac{1}{2}(\alpha Z)^2 \frac{Z^2/4 - B/3}{Z^2/2 + B/2} \quad (27)$$

and

$$\delta E_2^P = \frac{E_2^P - E_{2\text{NR}}^P}{|E_{2\text{NR}}^P|} = -\frac{1}{2}(\alpha Z)^2 \frac{Z^2/64 - B}{Z^2/8 + B} \quad (28)$$

for the ground state and the excited state, respectively, where $E_{1\text{NR}}^P$ and $E_{2\text{NR}}^P$ are the corresponding nonrelativistic energies. The quadratic term in the nonrelativistic case is implicitly included in the approximation, while it will vanish when taking the nonrelativistic limit $\alpha \rightarrow 0$. Figure 2 and Table V show that our variational results agree very well with the perturbation results for the range of B where the perturbation method is valid. Note that although the perturbation results for E_1^P and $E_{1\text{NR}}^P$ are accurate to 10^{-5} a.u. only for $B \lesssim 10^{-2}$, their difference yields correct results up to $B \lesssim 10^{-1}$ for the ground state.

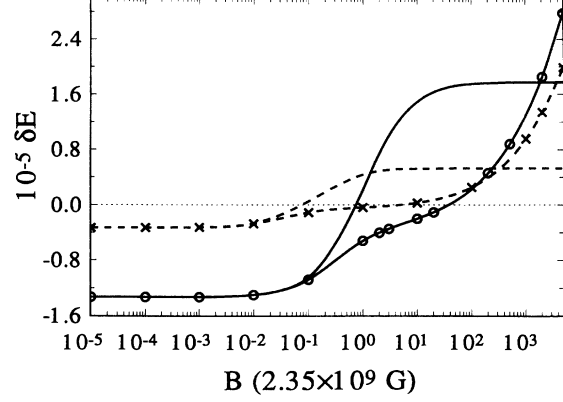


FIG. 2. Relative relativistic correction $\delta E = (E - E_{\text{NR}})/|E_{\text{NR}}|$ for the energy eigenvalues of hydrogen as a function of the magnetic field B (in units of 2.35×10^9 G). The results of the present paper are given by the solid line with open circles for the ground state and by the dashed line with crosses for the $2p_{3/2}(\mu = -3/2)$ excited state. The perturbation results given by Eqs. (27) and (28), valid for the relativistic correction only for $B \lesssim 10^{-2}$, are plotted as a solid line and a dashed line for the ground state and the excited state, respectively.

4. Nonrelativistic limit

The nonrelativistic limit for strong B is obtained by taking $\alpha \rightarrow 0$ in the Dirac Hamiltonian but keeping αB fixed. In the framework of the Schrödinger equation, the nonrelativistic binding energies with $Z \neq 1$ can be calculated by the scaling relation Eq. (7). In the case of the Dirac equation, however, there is no such scaling relation and it is then necessary to perform separate calculations for different values of Z .

In the nonrelativistic limit, however, unlike the adiabatic calculations, our results agree with the most accurate nonrelativistic calculations available as shown in Table I for the ground state and in Table II for an excited state. Moreover, for $B \geq 20$, our results taking the nonrelativistic limit converge to more significant digits than previous nonrelativistic calculations and agree with our

TABLE V. Comparison of the relativistic ground-state binding energy $|E|$ (in atomic units) of hydrogen, calculated in the present paper, with relativistic hydrogenic perturbation results E_1^P given by Eq. (25) for low and intermediate magnetic field B (in units of 2.35×10^9 G).

B	$ E_1^P $	$ E $
0	0.500006657	0.500006657
10^{-7}	0.500006707	0.500006707
10^{-5}	0.500011657	0.500011657
10^{-3}	0.500506648	0.500506398
10^{-1}	0.550005769	0.547532408
1	0.999997781	0.831173226
2	1.499988906	1.022218029
3	1.999980031	1.164537038

more accurate results based on the Schrödinger equation. Note that, as shown in Table I, the previous nonrelativistic calculations do not agree to their quoted precision for $B \geq 200$.

IV. CONCLUSION AND DISCUSSIONS

Given the absence of an upper bound to the relativistic energy spectrum, we have paid special attention to the convergence and stability of our results. The variational method we used has avoided variational collapse, otherwise the variational eigenvalues would not converge with the nonlinear parameters and the size of the basis set, and the virial theorem would not be satisfied. The variational eigenvalues could have still converged to wrong values due to the incompleteness of the basis set or the possible presence of spurious roots. This possibility has been eliminated by checking that the results have the correct nonrelativistic limit, relativistic low- B limit, and satisfy the sum rule and the virial theorem.

We have also confirmed our previous relativistic results [27] which were obtained using Slater-type basis functions for $B < 10$. The present method, however, yields a much higher precision with fewer basis vectors for the full range of values of B .

Our calculations indicate the necessity to include relativistic corrections given the current numerical accuracy of the nonrelativistic calculations. For a complete description of a hydrogenic atom to the level of accuracy presented, it is also necessary to include other small effects, such as the effects of finite nuclear mass and finite nuclear size, the interaction between the magnetic moments of the electron and nucleus, and other radiative corrections. The finite-nuclear-size correction can be calculated exactly in the context of the method presented here by replacing the Coulomb potential by an appropriate finite-nuclear-size potential, while the effect of finite nuclear mass can be obtained to lowest order by introducing the reduced mass in the nonrelativistic Hamiltonian. The other corrections can be calculated perturbatively using the optimized variational wave functions obtained in the present work.

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APPENDIX

We write our basis functions as

$$\Phi_{nlk}^{(k)} = F_{nlk}^{(k)} e^{im_k \phi}, \quad (A1)$$

with

$$F_{nlk}^{(k)} = N_{nlk}^{(k)} f_0(r, \rho) r^n \chi^{l_k - |m_k|} (\sin \theta)^{|m_k|}, \quad (A2)$$

$$f_0(r, \rho) = r^{\gamma-1} e^{-\lambda r - \beta \rho^2}, \quad (A3)$$

where $\chi = \cos \theta$, and $N_{nlk}^{(k)}$ is a normalization constant satisfying

$$\int |F_{nlk}^{(k)}|^2 r^2 dr d\chi = 1. \quad (A4)$$

The Dirac Hamiltonian of Eq. (8) has the matrix form

$$H_D = \begin{pmatrix} c^2 - Z/r & c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ c\boldsymbol{\sigma} \cdot \boldsymbol{\pi} & -c^2 - Z/r \end{pmatrix}. \quad (A5)$$

The matrix elements of the Hamiltonian between basis vectors with the same spin function can then be simply written as

$$\langle \Phi_{nlk}^{(k)} | H | \Phi_{n'l'_k}^{(k)} \rangle = c^2 \langle \Phi_{nl}^{(k)} | \Phi_{n'l'_k}^{(k)} \rangle - Z \left\langle \Phi_{nl}^{(k)} \left| \frac{1}{r} \right| \Phi_{n'l'_k}^{(k)} \right\rangle \quad (A6)$$

for the large components ($k = 1, 2$) and

$$\langle \Phi_{nlk}^{(k)} | H | \Phi_{n'l'_k}^{(k)} \rangle = -c^2 \langle \Phi_{nl}^{(k)} | \Phi_{n'l'_k}^{(k)} \rangle - Z \left\langle \Phi_{nl}^{(k)} \left| \frac{1}{r} \right| \Phi_{n'l'_k}^{(k)} \right\rangle \quad (A7)$$

for the small components ($k = 3, 4$). In order to calculate the matrix elements between large and small components, it is convenient to write $\boldsymbol{\sigma} \cdot \boldsymbol{\pi}$ as

$$\boldsymbol{\sigma} \cdot \boldsymbol{\pi} = \sigma_z \pi_z + \sigma_+ \pi_- + \sigma_- \pi_+, \quad (A8)$$

where

$$\sigma_{\pm} = (\sigma_x \pm i\sigma_y)/2, \quad \pi_{\pm} = \pi_x \pm i\pi_y, \quad (A9)$$

thus

$$\begin{aligned} \sigma_z \chi_{\sigma} &= \sigma \chi_{\sigma}, \\ \sigma_+ \chi_{-1} &= \chi_1, \\ \sigma_- \chi_1 &= \chi_{-1}. \end{aligned} \quad (A10)$$

In cylindrical coordinates we have

$$\pi_{\pm} = -i \exp(\pm i\phi) \left(\frac{\partial}{\partial \rho} \pm \frac{i}{\rho} \frac{\partial}{\partial \phi} \mp \frac{B}{2\rho} \right), \quad (A11)$$

$$\pi_z = -i \frac{\partial}{\partial z}.$$

Using the above relations, we obtain the nonvanishing matrix elements of the Hamiltonian between basis vectors with different spin functions as

$$\langle \Phi_{nl_1}^{(1)} | H | \Phi_{n'l_3}^{(3)} \rangle = -c \int r^2 dr d\chi F_{nl_1}^{(1)} F_{n'l_3}^{(3)} \left((\gamma - 1 + n' - l_3) \frac{\chi}{r} - \lambda \chi + \frac{l_3 - |m_3|}{z} \right), \quad (\text{A12a})$$

$$\langle \Phi_{nl_2}^{(2)} | H | \Phi_{n'l_4}^{(4)} \rangle = c \int r^2 dr d\chi F_{nl_2}^{(2)} F_{n'l_4}^{(4)} \left((\gamma - 1 + n' - l_4) \frac{\chi}{r} - \lambda \chi + \frac{l_4 - |m_4|}{z} \right), \quad (\text{A12b})$$

$$\langle \Phi_{nl_1}^{(1)} | H | \Phi_{n'l_4}^{(4)} \rangle = c \int r^2 dr d\chi F_{nl_1}^{(1)} F_{n'l_4}^{(4)} \left[(\gamma - 1 + n' - l_4) \frac{\sin \theta}{r} - \lambda \sin \theta - \left(2\beta + \frac{B}{2} \right) \rho + \frac{|m_4| - m_4}{\rho} \right], \quad (\text{A12c})$$

$$\langle \Phi_{nl_2}^{(2)} | H | \Phi_{n'l_3}^{(3)} \rangle = c \int r^2 dr d\chi F_{nl_2}^{(2)} F_{n'l_3}^{(3)} \left[(\gamma - 1 + n' - l_3) \frac{\sin \theta}{r} - \lambda \sin \theta - \left(2\beta - \frac{B}{2} \right) \rho + \frac{|m_3| + m_3}{\rho} \right]. \quad (\text{A12d})$$

Since the Hamiltonian is Hermitian and all the matrix elements are real, we have the symmetry property

$$\langle \Phi_{nl_k}^{(k)} | H | \Phi_{n'l_{k'}}^{(k')} \rangle = \langle \Phi_{n'l_{k'}}^{(k')} | H | \Phi_{nl_k}^{(k)} \rangle \quad (\text{A13})$$

All the matrix elements can be expressed in terms of the integral

$$\begin{aligned} T(a, l, m) &= \int_0^\infty dr \int_{-1}^1 d\chi r^a \chi^l (1 - \chi^2)^m \exp[-2\lambda r - 2\beta r^2(1 - \chi^2)] \\ &= (8\beta)^{-[(a+1)/2]} \Gamma(a+1) \int_{-1}^1 d\chi \chi^l (1 - \chi^2)^{m-[(a+1)/2]} U\left(\frac{a+1}{2}, \frac{1}{2}, \frac{\lambda^2}{2\beta(1 - \chi^2)}\right), \end{aligned} \quad (\text{A14})$$

where Γ is the gamma function and $U(a, b, x)$ is the confluent hypergeometric function which can be evaluated by Kummer's formula or by an asymptotic expansion [28]. However, in some cases, the cancellations occurring in the evaluation of $U(a, b, x)$, due to oscillations in the summation, can reduce the accuracy. If this happens, we then perform the double integral numerically. The radial integral from 0 to ∞ is mapped to the integral from 0 to 1, which can then be evaluated accurately by Gaussian quadrature. Generally, quadruple precision is needed when more than 150 vectors are used in the basis set to avoid the problem of near linear dependence. The matrix elements in the orthonormal basis vectors are then obtained through the transformation given by Eq. (19).

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