Upper and lower bounds on the energy eigenvalues of the one-electron Dirac Hamiltonian

Z. Chen, G. Fonte,* and S. P. Goldman
Department of Physics, The University of Western Ontario, London, Ontario, Canada N6A 3K7
(Received 5 July 1994)

A variational method based on results for self-adjoint operators due to T. Kato [Proc. Phys. Soc. Jpn. **4**, 334 (1949)] is developed to calculate upper and lower bounds on the energy eigenvalues for the one-electron Dirac Hamiltonian. The method avoids relativistic variational collapse for any one-electron potential. This result is confirmed analytically in the case of the Coulomb potential and numerically in the case of hydrogenic atoms in very strong magnetic fields for which standard variational techniques cannot preserve bounds. The upper bound thus obtained converges rapidly to the best available numerical results, and provides a very efficient technique for the search of the optimal variational energy by means of a *minimization* procedure.

PACS number(s): 31.30.Jv, 32.60.+i, 31.10.+z

I. INTRODUCTION

Many accurate nonrelativistic atomic-structure calculations are based on finite-basis-set variational methods, especially for atoms with a few electrons, such as heliumlike atoms [1,2]. These methods can provide rigorous variational upper bounds on the energy eigenvalues due to the fact that the nonrelativistic Hamiltonian is bounded from below. However, the extension to the relativistic case is not simple, because the Dirac Hamiltonian is not bounded from below: its energy spectrum contains an infinite continuum of negative-energy states. As a consequence, the variational energy (Rayleigh-Ritz eigenvalue) is not necessarily an upper bound to the exact eigenvalue, and even worse, one may run into the problem of variational collapse in which, upon minimization, the variational eigenvalue may collapse to any value below the exact energy eigenvalue. Several methods have been developed to overcome this difficulty [3–8]. Recently, a method based on the operator $1/H_D$, where H_D is the one-electron Dirac Hamiltonian, was introduced [9] in which the upper bound on the ground-state energy can be obtained by maximizing the variational spectrum of $1/H_D$. Also recently, a minimum principle for Dirac scattering lengths was developed [10], which can also be used to provide a sufficient condition for the existence of a given number of bound states and lower bounds on the energy eigenvalues. For the single-electron Hamiltonian, a practical and effective way is to select a basis set based on boundary conditions and the nonrelativistic limit [6,11], but this method generally does not guarantee bounds on the energy. (Only for the Coulomb potential it has been proven that if a proper basis set is chosen, the variational energy is an upper bound on the true energy [6].) In this work, we propose a method for determining rigorous upper bounds to the eigenvalues of the Dirac Hamiltonian based on results found in a 1949 paper by Kato [12]. In that paper, Kato derives upper as well as lower bounds to the eigenvalues of an operator, by making use only of the self-adjointness of the operator, i.e., without requiring its half-boundedness. The efficiency of Kato's bounds [12] has recently been demonstrated in calculations of the nonrelativistic energies of hydrogenic atoms in strong magnetic fields. Very accurate upper and lower bounds have been obtained for the low-lying levels in strong magnetic fields [13] and for the Rydberg states in magnetic fields $B \approx 4.7 \times 10^4$ G [14]. Relativistic variational calculations have also been performed to obtain accurate relativistic corrections [11], although eigenvalues are obtained to high precision by *optimization* techniques, as no bounds are preserved in the calculation.

In this paper we apply Kato's bounds to the one-electron Dirac Hamiltonian; these bounds are described in Sec. II. Their efficiency is then confirmed analytically in the case of a Coulomb potential and numerically in the case of hydrogenic atoms in very strong magnetic fields in Sec. III. We finally discuss the results in Sec. IV.

II. KATO'S BOUNDS

As mentioned in the Introduction, a remarkable feature of Kato's upper bounds is that, unlike the Rayleigh-Ritz bounds, they do not require the boundedness from below of the operator but only its self-adjointness. Thus, in principle, Kato's upper bounds can be applied to the Dirac Hamiltonian H_D for an electron in the presence of an arbitrary potential, as long as H_D is self-adjoint. A rigorous functional-analysis definition of self-adjointness is presented, for instance, in Ref. [15]. Notice that this definition is not analogous to the one usually reported in quantum-mechanics textbooks. In this context, the self-adjointness of the Dirac Hamiltonian is not an obvi-

*Permanent address: Dipartimento di Fisica, Università di Catania, Corso Italia 57, I-95129 Catania, Italy.

ous property (for an exhaustive review of the problem, see Ref. [16]). In the present paper we deal with the self-adjoint Hamiltonian (in a.u.):

$$H_D = c\boldsymbol{\alpha}\cdot\left(\mathbf{p}+\frac{1}{c}\mathbf{A}\right)+\beta c^2-\frac{Z}{r}\ , \tag{1}$$

where $\boldsymbol{\alpha}$ and β are the standard 4×4 Dirac matrices, Z is the nuclear charge, and $\mathbf{A}=\frac{1}{2}\mathbf{B}\times\mathbf{r}$, where $\mathbf{B}=B\hat{\mathbf{z}}$ is the magnetic field measured in units of $(e/\hbar)^3m^2c\approx 2.35\times 10^9$ G. A proof of the self-adjointness of H_D in (1) can be found in Ref. [17]. Reference [12] presents formulas related to the upper and lower bounds of eigenvalues (Weinstein's formula; formulas for nondegenerate and for degenerate or densely crowded eigenvalues) as well as formulas to estimate the error of an approximate wave function, which apply in a straightforward way to the Hamiltonian (1). In this section we shall present only the formulas used in the present paper.

We first evaluate, for an arbitrary normalized function $\psi\in\mathcal{D}(H_D)$ (domain of H_D), the quantities

$$\langle H_D\rangle=\langle\psi\,|H_D|\,\psi\rangle\ , \tag{2}$$

and the root-mean-square deviation

$$\sigma=\left(\langle H_D^2\rangle-\langle H_D\rangle^2\right)^{1/2}\ . \tag{3}$$

We can now state the following

Theorem (the Kato theorem). Consider the interval (a,b), where

$$a<\langle H_D\rangle<b. \tag{4}$$

Suppose that this interval contains as a unique point of the spectrum of H_D only a nondegenerate eigenvalue (say E_i) and that the quantities $\langle H_D\rangle$ and σ satisfy the inequalities

$$\begin{aligned} E_{\rm low} &= \langle H_D\rangle-\frac{\sigma^2}{b-\langle H_D\rangle} > a\ , \\ E_{\rm up} &= \langle H_D\rangle+\frac{\sigma^2}{\langle H_D\rangle-a} < b\ , \end{aligned} \tag{5}$$

then

$$E_{\rm low}\le E_i\le E_{\rm up}\ . \tag{6}$$

Formula (6) is called the generalized Ritz-Temple formula, because Kato's lower bound $E_{\rm low}$ extends the old Temple formula to excited states and to operators that are not necessarily half-bounded, while Kato's upper bound $E_{\rm up}$ generalizes the usual Rayleigh-Ritz upper bound. Notice that $E_{\rm up}$ is an upper bound for *any* choice of ψ, with the accuracy of the upper bound depending on the specific choice of ψ. A convenient choice of variational wave functions, both in nonrelativistic as well as in relativistic calculations, is given by the N-dimensional Rayleigh-Ritz method in which we obtain a set of N approximate normalized variational eigenfunctions ψ_{iN} corresponding respectively to the exact eigenvalues E_i, $i=0,1,2,\ldots,N-1$. There is, however, a fundamental difference between the relativistic and nonrelativistic Hamiltonians. In the nonrelativistic case, the quantity $\langle H\rangle_{iN}=\langle\psi_{iN}\,|H|\,\psi_{iN}\rangle$ is itself an upper bound to E_i: the Rayleigh-Ritz upper bound (Poincaré's theorem [18]). Moreover, the upper bound $\langle H\rangle_{iN}$ is indeed more accurate than $E_{\rm up}$. In the relativistic case, on the other hand, $\langle H\rangle_{iN}$ is not in general an upper bound of the eigenvalue E_i of the Dirac Hamiltonian, while Kato's upper bound $E_{\rm up}$ given by Eq. (5) is.

III. APPLICATIONS

A. Coulomb potential

In this section we obtain analytical upper and lower bounds (5), in a most pathological one-electron example that exemplifies the problem of variational collapse in the case of the Dirac Hamiltonian. For an electron in a Coulomb potential, the radial Dirac Hamiltonian has the form

$$H_D=\begin{pmatrix} 1/\alpha^2-Z/r & (1/\alpha)(\kappa/r-d/dr) \\ (1/\alpha)\,(\kappa/r+d/dr) & -1/\alpha^2-Z/r \end{pmatrix}, \tag{7}$$

where $\alpha=1/c$ is the fine structure constant and κ is the Dirac quantum number. For the ground state ($\kappa=-1$), using the (wrong) radial trial function (without lower component)

$$\psi=2\lambda^{3/2}r\exp(-\lambda r)\begin{pmatrix}1\\0\end{pmatrix}, \tag{8}$$

where λ is a positive variational parameter, we obtain the variational energy (including the rest-mass energy) for the electron:

$$\langle H_D\rangle=1/\alpha^2-\lambda Z, \tag{9}$$

which collapses to $-\infty$ as $\lambda\to\infty$.

We can use the same "bad" trial function to calculate the Kato bound $E_{\rm up}$. The expectation value of H_D^2 for $\kappa=-1$ is readily obtained

$$\langle H_D^2\rangle=1/\alpha^4+2(\lambda Z)^2+(1/\alpha^2)[\lambda^2-2\lambda Z]. \tag{10}$$

We thus have

$$\sigma=\sqrt{\langle H_D^2\rangle-\langle H_D\rangle^2}=(\lambda/\alpha)\sqrt{(\alpha Z)^2+1}. \tag{11}$$

The parameter a in Kato's theorem can be chosen as $-1/\alpha^2$, since there are no energy levels between the ground-state and the negative continuum below $-1/\alpha^2$; the condition (4) is satisfied if

$$0<\lambda<2/(\alpha^2Z). \tag{12}$$

We thus obtain the following Kato's upper bound on the

ground-state energy (subtracting the rest-mass energy):

$$E_{\rm up} = -\lambda Z + \frac{\lambda^2[1+(\alpha Z)^2]}{2-\lambda Z\alpha^2}. \quad (13)$$

For λ satisfying inequality (12), the minimum of $E_{\rm up}$ is found to be

$$\min(E_{\rm up}) = -\frac{2Z^2}{(\sqrt{1+2\delta}+\sqrt{1+\delta})^2} \quad (14)$$

with

$$\lambda_{\rm min} = 2\frac{1-\sqrt{1+\delta}/\sqrt{1+2\delta}}{\alpha^2 Z},$$

where $\delta = (\alpha Z)^2$. For $0 \le \delta = (\alpha Z)^2 \le 1$, we obtain then

$$\min(E_{\rm up}) \ge -Z^2/2 > E_0 = -Z^2/(1+\sqrt{1-\delta}), \quad (15)$$

where E_0 is the relativistic ground-state energy. In other words, $E_{\rm up}$ is an upper bound on the relativistic energy. Moreover, $\min(E_{\rm up})$ yields the exact nonrelativistic value $-Z^2/2$ for $\delta = 0$; this result is expected, since our trial vector is exact in the nonrelativistic limit ($\alpha \to 0$).

It should be noted that a minimum value of σ with respect to a variation of the nonlinear parameter λ does not always correspond to the optimized value for the variational bounds on the energy. For example, σ in Eq. (11) approaches 0 as $\lambda \to 0$, given that when λ is very small, the normalized wave function $2\lambda^{3/2}e^{-\lambda r}r$ is close to zero everywhere in space giving an unphysical solution in which only the rest-mass term in the Dirac Hamiltonian has a nonzero expectation value.

To check the lower bound $E_{\rm low}$ [Eq. (5)] for the ground-state energy, we can use the exact first excited-state energy

$$E_1 = -\frac{Z^2}{[2(1+\gamma)+\sqrt{2}(1+\gamma)^{3/2}]}, \quad (16)$$

with $\gamma = \sqrt{1-(\alpha Z)^2}$, as parameter b in the Kato theorem. The lower bound can then be written as

$$E_{\rm low} = -\lambda Z - \frac{\lambda^2[1+(\alpha Z)^2]}{\alpha^2(\lambda Z + E_1)}. \quad (17)$$

The maximum of $E_{\rm low}$ for λ satisfying the condition $-2/\alpha^2 \le -\lambda Z \le E_1 - 1/\alpha^2$ [see (4)] is

$$\max(E_{\rm low}) = -\frac{\left(\sqrt{1+\delta}+\sqrt{1+2\delta}\right)^2}{\alpha^2\left[2(1+\gamma)+\sqrt{2}(1+\gamma)^{3/2}\right]} < -\frac{1}{2\alpha^2}$$

with

$$\lambda_{\rm max} = -\frac{\left(1+\sqrt{1+\delta}/\sqrt{1+2\delta}\right)\left(1+\sqrt{(1+\gamma)/2}\right)}{\alpha^2 Z}.$$

This result confirms that $E_{\rm low}$ is below the true energy $-Z^2/(1+\sqrt{1-\delta})$ [Eq. (15)] as long as $\alpha Z \le 1$, which is required by the Dirac equation for the Coulomb potential of a point nucleus. The difference between this lower bound and the true energy, however, is very large due to the absence of the lower component in the basis vector.

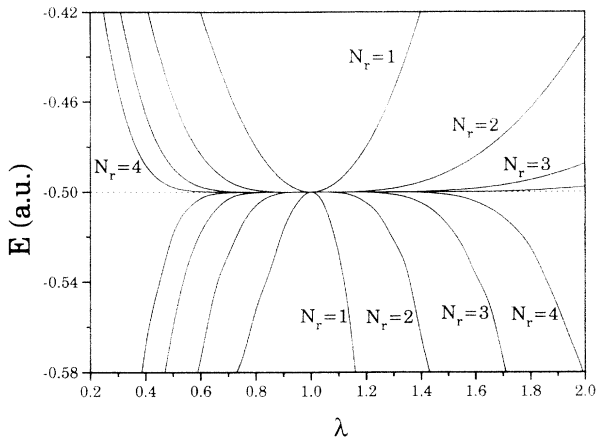

FIG. 1. Kato's upper and lower bounds on the relativistic ground-state energy of hydrogen (in a.u.) for B=0. λ is the nonlinear parameter and N_r is the number of radial basis functions in the basis set. The dotted line denotes the exact energy.

A much better lower bound can be obtained with both lower and upper components in the basis vectors. For example, if we use standard Slater-type basis vectors

$$\begin{pmatrix} \phi_i \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ \phi_i \end{pmatrix}, \quad (18)$$

with

$$\phi_i = 2\lambda^{3/2}e^{-\lambda r}r^{\gamma+(i-1)},$$

and $i = 1, 2, \ldots, N_r$, we obtain the upper and lower bounds coinciding with the exact energy for the optimized value of λ (the wave function is exact in this case consisting of the single basis vector $i = 1$). The dependence of the bounds on λ is plotted in Fig. 1. It shows that the best upper and lower bounds can be obtained by minimizing $E_{\rm up}$ and maximizing $E_{\rm low}$ with respect to the nonlinear parameters.

B. Strong magnetic fields

A relativistic variational method based on basis sets suitably chosen to represent the spatial symmetries was successfully applied to hydrogenic atoms in strong magnetic fields [11], giving very accurate relativistic energies for low-lying states. The method, however, fails to give upper bounds on the energies. The search for the optimized parameters in the basis set is based on the stationary properties of the eigenstates rather than the simple minimization procedure used in the nonrelativistic case. In the following, we will apply the method presented in Sec. II to this problem to obtain both upper and lower bounds on the ground-state energy.

The same basis set as the one in Ref. [11] is used, which, in spherical coordinates, can be written as

$$\Phi_{nl}^{(k)} = F_{nl}^{(k)}e^{im_k\phi}w_k,$$

with

$$F_{nl}^{(k)} = N_{nl}^{(k)} f_0(r,\rho) r^n \cos\theta^{l-|m_k|} (\sin\theta)^{|m_k|},$$

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

$$n = 0, 1, \ldots, N_r, \quad k = 1, 2, 3, 4,$$

where $\rho = r\sin\theta$, $m_k = \mu - \nu_k/2$, $\nu_1 = \nu_3 = 1$, $\nu_2 = \nu_4 = -1$, λ and β are nonlinear variational parameters, and the parameter γ is determined by the boundary condition as $r \to 0$ to be $\sqrt{\kappa^2 - (\alpha Z)^2}$ with κ taking the values corresponding to the $B = 0$ limit. The normalization constant $N_{nl_k}^{(k)}$ is determined by

$$\int |F_{nl_k}^{(k)}|^2 r^2 dr d\chi = 1,$$

where $\chi = \cos\theta$. The four component spin functions w_k have the form

$$w_1 = \begin{pmatrix} \chi_1 \\ 0 \end{pmatrix}, \quad w_2 = \begin{pmatrix} \chi_{-1} \\ 0 \end{pmatrix},$$

$$w_3 = \begin{pmatrix} 0 \\ i\chi_1 \end{pmatrix}, \quad w_4 = \begin{pmatrix} 0 \\ i\chi_{-1} \end{pmatrix}.$$

For even (odd) parity states, the value of l for the large components ($k = 1, 2$) takes an even (odd) number greater 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 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, where N_θ is an integer used to determine the maximum value of l in the basis set.

The Hamiltonian H_D for the problem is given by expression (1). This 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.

The matrix elements of H_D with respect to the basis vectors are calculated in Ref. [11] and are given as

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

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

$$\langle \Phi_{nl_1}^{(1)} | H_D | \Phi_{n'l_4}^{(4)} \rangle = c \int r^2 dr d\chi F_{nl_1}^{(1)} F_{n'l_4}^{(4)} \left[(\gamma - 1 + n' - l_4)\frac{\sin\theta}{r} - \lambda\sin\theta - \left(2\beta + \frac{B}{2}\right)\rho + \frac{|m_4| - m_4}{\rho} \right], \tag{19a}$$

$$\langle \Phi_{nl_2}^{(2)} | H_D | \Phi_{n'l_3}^{(3)} \rangle = c \int r^2 dr d\chi F_{nl_2}^{(2)} F_{n'l_3}^{(3)} \left[(\gamma - 1 + n' - l_3)\frac{\sin\theta}{r} - \lambda\sin\theta - \left(2\beta - \frac{B}{2}\right)\rho + \frac{|m_3| + m_3}{\rho} \right]. \tag{19b}$$

In order to calculate the bounds we also need to calculate the matrix elements of H_D^2. Using the relation

$$\left[\boldsymbol{\sigma} \cdot \left(\mathbf{p} + \frac{1}{c}\mathbf{A}\right)\right]^2 = p^2 + Bl_z + \frac{1}{4}B^2\rho^2 + B\sigma_z$$

where the σ_i are the Pauli spin matrices, the nonvanishing matrix elements of H_D^2 can be written as

$$\langle \Phi_{nl}^{(k)} | H_D^2 | \Phi_{nl}^{(k')} \rangle = \delta_{kk'} \left\langle F_{nl}^{(k)} \left| \left(\frac{1}{\alpha^2} - \frac{Z}{r}\right)^2 + \frac{1}{\alpha^2}\left(p^2 + \frac{1}{4}B^2\rho^2 + B(m_k + \sigma_k)\right) \right| F_{nl}^{(k)} \right\rangle$$

for $k, k' = 1, 2$,

$$\langle \Phi_{nl}^{(k)} | H_D^2 | \Phi_{nl}^{(k')} \rangle = \delta_{kk'} \left\langle F_{nl}^{(k)} \left| \left(\frac{1}{\alpha^2} + \frac{Z}{r}\right)^2 + \frac{1}{\alpha^2}\left(p^2 + \frac{1}{4}B^2\rho^2 + B(m_k + \sigma_k)\right) \right| F_{nl}^{(k)} \right\rangle$$

for $k, k' = 3, 4$, and

$$\langle\Phi^{(1)}_{nl}|H_D^2|\Phi^{(3)}_{n'l'}\rangle = \frac{Z}{\alpha}\left\langle F^{(1)}_{nl}\left|[3-2(\tau+n'-l')]\,\frac{\chi}{r^2}+2\lambda\frac{\chi}{r}-2(l'-|m_3|)\frac{1}{r^2\chi}\right|F^{(3)}_{n'l'}\right\rangle,$$

$$\langle\Phi^{(2)}_{nl}|H_D^2|\Phi^{(4)}_{n'l'}\rangle = \frac{Z}{\alpha}\left\langle F^{(2)}_{nl}\left|[3-2(\tau+n'-l')]\,\frac{\chi}{r^2}+2\lambda\frac{\chi}{r}-2(l'-|m_4|)\frac{1}{r^2\chi}\right|F^{(4)}_{n'l'}\right\rangle,$$

$$\langle\Phi^{(1)}_{nl}|H_D^2|\Phi^{(4)}_{n'l'}\rangle = \frac{Z}{\alpha}\langle F^{(1)}_{nl}|\,[3-2(\tau+n'-l')]\,\frac{\sin\theta}{r^2}+2\lambda\frac{\sin\theta}{r}+(4\beta-B)\sin\theta-2(|m_4|+m_4)\frac{1}{r^2\sin\theta}|F^{(4)}_{n'l'}\rangle, \quad (20a)$$

with

$$\begin{aligned}\langle F^{(k)}_{nl}|p^2|F^{(k)}_{nl}\rangle = \langle F^{(k)}_{nl}|\,&[4\beta(\gamma+|m_k|+n-l)-\lambda^2]+2\lambda(\gamma+n)/r\\ &-(\gamma-1+n-l)(\gamma+n+l)/r^2-(l-|m_k|)(l-|m_k|-1)/z^2\\ &-4\beta(\gamma-1+n-l)\chi^2-4\lambda\beta r\sin^2\theta-4\beta^2r^2\sin^2\theta|F^{(k)}_{nl}\rangle. \end{aligned}\quad (20b)$$

Since the Hamiltonian H_D is self-adjoint and all the matrix elements are real, we can obtain the other matrix elements using the symmetry property

$$\langle\Phi^{(k)}_{nl}|H_D|\Phi^{(k')}_{n'l'}\rangle = \langle\Phi^{(k')}_{n'l'}|H_D|\Phi^{(k)}_{nl}\rangle,\quad \langle\Phi^{(k)}_{nl}|H_D^2|\Phi^{(k')}_{n'l'}\rangle = \langle\Phi^{(k')}_{n'l'}|H_D^2|\Phi^{(k)}_{nl}\rangle.$$

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

$$\begin{aligned}T(j,l,m) &= \int_0^\infty dr\int_{-1}^1 d\chi r^j\chi^l(1-\chi^2)^m\exp[-2\lambda r-2\beta r^2(1-\chi^2)], \quad (21)\\ &= (8\beta)^{-\frac{j+1}{2}}\Gamma(j+1)\int_{-1}^1 d\chi\chi^l(1-\chi^2)^{m-\frac{j+1}{2}}U\left[\frac{j+1}{2},\frac{1}{2},\frac{\lambda^2}{2\beta(1-\chi^2)}\right],\end{aligned}$$

where Γ is the gamma function and $U(c,d,e)$ is the confluent hypergeometric function which can be evaluated by Kummer's formula or by an asymptotic expansion [19].

Usual variational procedures [20] are applied here: the overlap matrix $\langle\Phi^{(k)}_{nl}|\Phi^{(k')}_{n'l'}\rangle$ is first diagonalized to obtain the orthogonal basis vectors; the matrix elements of H and H^2 in the orthogonal basis set are then obtained by the corresponding unitary transformation; the Hamiltonian is then diagonalized and the expectation value of H^2 is calculated for the selected energy level.

Choosing in the Kato theorem the parameters $a = -1/\alpha^2$ and $b = E_{1\text{var}}$ for the ground state, where $E_{1\text{var}}$ is the optimized variational energy for the first excited state, we can then calculate the upper and lower bounds on the energies according to Eq. (5). The uncertainty introduced by using $E_{1\text{var}}$ as parameter b is given by

$$|\Delta E_{\text{low}}| = \frac{\sigma^2}{b-E_{1\text{var}}}|\Delta b|, \quad (22)$$

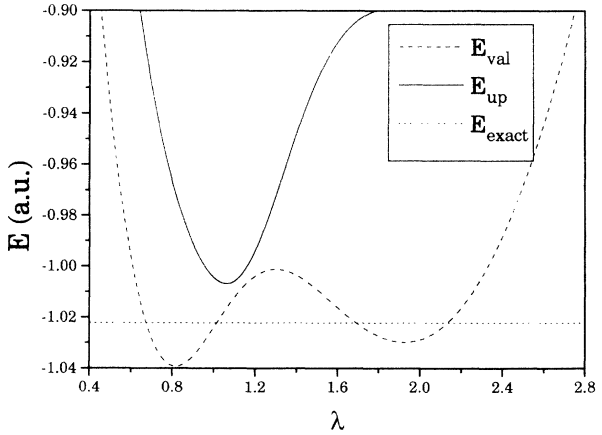

FIG. 2. Comparison of Kato's upper bound with the variational energy of the ground-state of hydrogen for $B = 4.7\times10^9$ G with N=2 basis vectors (one radial basis function).

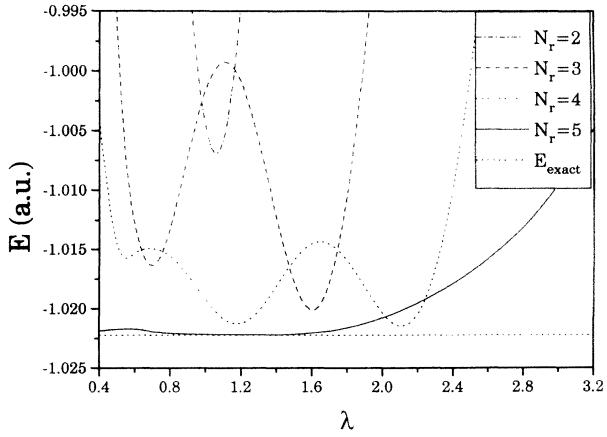

FIG. 3. Kato's upper bound on the relativistic ground-state energy of hydrogen for $B = 4.7 \times 10^9$ G. λ is the nonlinear parameter and N_r is the number of radial basis functions.

TABLE I. Relativistic variational calculations of the binding energies ($-E_{\rm var}$) and their upper ($-E_{\rm up}$) and lower bounds ($-E_{\rm low}$) (in atomic units) for the ground state of hydrogenic atoms in an intense magnetic field B (in units of 2.35×10^9 G). N_r and N_θ give the number of radial and angular basis functions used, respectively. The squared root of the variance for the Hamiltonian is given by σ.

B	$E_{\rm var}$	$E_{\rm up}$	$E_{\rm low}$	N_r	N_θ	σ
0.1	0.5475324083429	0.5475324083429	0.547532408344	10	5	6.83×10^{-7}
2	1.0222180290	1.0222180290	1.0222182	10	5	2.73×10^{-4}
20	2.21540091	2.21540088	2.2155	9	5	8.99×10^{-3}
200	4.7271233	4.7271233	4.72716	9	5	7.37×10^{-3}

which is of order of 10^{-10}. The dependence of the variational energy $E_{\rm var}$ on the nonlinear parameter λ for a basis set with $N = 2$ vectors is plotted in Fig. 2. We show Kato's upper bounds as a function of λ for different sizes of the basis set in Fig. 3. The figures show that $E_{\rm up}$ is always above the true energy (choosing for the "true energy" the best available numerical value [11]), while the variational energy can have values above or below the true energy. In Table I we list the upper and lower bounds calculated for various values of the magnetic field B and compare them with previous results [11]. The accuracy for the upper bounds is similar to that obtained by direct variational calculations (which lack bounds) with the advantage that since $E_{\rm up}$ is *always* an upper bound, we can search for the optimal variational parameters by a *minimization* of $E_{\rm up}$.

IV. CONCLUSION

The present paper shows that the Kato theorem provides a simple and effective way to find upper and lower bounds to the eigenvalues of the Dirac Hamiltonian. From this point of view, if one considers the quantity $E_{\rm up}$ [Eq. (5)] instead of the usual variational energy, variational collapse is avoided and relativistic variational calculations share with the nonrelativistic counterparts the property of providing rigorous upper bounds. A crucial requirement for obtaining Kato's upper and lower bounds is the knowledge *a priori* of the two parameters a and b, satisfying the conditions in the Kato theorem. In the case of hydrogenic atoms in strong magnetic fields, we have found accurate upper and lower bounds on the ground-state energy, by choosing $a = -1/\alpha^2$ and $b = E_{1,\rm var}$ (optimized variational energy for the first excited state). Of these two choices, the former is rigorous, due to the fact that $-1/\alpha^2$ represents the beginning of the negative continuous spectrum, whereas the latter is not. Moreover, in the case of excited-states calculations, the problem of determining a and b is even more difficult, because the previous choice of a is no longer possible. A simple and rigorous method for finding a and b for any state can be found in Ref. [14]. This method can also be extended to the Dirac Hamiltonian. Work on this extension is currently in progress and will be reported in a next paper dealing with excited states. Finally, it should be observed that the Kato theorem provides an effective way to search for the optimal nonlinear parameters in relativistic variational calculations by the *minimization* of $E_{\rm up}$. The method can be readily extended to other one-electron potentials, in particular to the description of many-electron systems based on the (screened one-electron) Dirac-Hartree-Fock Hamiltonian.

ACKNOWLEDGMENTS

Research support from the Natural Sciences and Engineering Research Council of Canada, the Academic Development Fund of the University of Western Ontario, and the Istituto Nazionale di Fisica Nucleare, Sezione di Catania, is gratefully acknowledged.

[1] Y. Accad, C. L. Pekeris, and B. Schiff, Phys. Rev. A **4**, 516 (1971).
[2] G. W. F. Drake, Can. J. Phys. **66**, 586 (1981).
[3] L. Rosenberg and L. Spruch, Phys. Rev. A **34**, 1720 (1986).
[4] J. D. Talman, Phys. Rev. Lett. **57**, 1091 (1986).
[5] See, for example, G. W. F. Drake and S. P. Goldman, Phys. Rev. A **23**, 2093 (1981); Adv. At. Mol. Phys. **25**, 393 (1988) and references therein.
[6] S. P. Goldman, Phys. Rev. A **31**, 3541 (1985).
[7] I. P. Grant, J. Phys. B **19**, 3187 (1986).
[8] For a review, see W. Kutzelnigg, Int. J. Quantum Chem. **25**, 107 (1984) and references therein.
[9] R. N. Hill and C. Krauthauser, Phys. Rev. Lett. **72**, 2151

(1994).
[10] L. Rosenberg (unpublished).
[11] S. P. Goldman and Z. Chen, Phys. Rev. Lett. **67**, 1403 (1991); Z. Chen and S. P. Goldman, Phys. Rev. A **45**, 1722 (1992).
[12] T. Kato, Proc. Phys. Soc. Jpn. **4**, 334 (1949).
[13] G. Fonte, P. Falsaperla, G. Schiffrer, and D. Stanzial, Phys. Rev. A **41**, 5807 (1990).
[14] P. Falsaperla and G. Fonte, Phys. Rev. A **47**, 4143 (1993).
[15] T. Kato, *Perturbation Theory for Linear Operators* (Springer-Verlag, New York, 1966).
[16] B. Thaller, *The Dirac Equation* (Springer, New-York, 1992) and references therein.
[17] K. Jörgen, in *Proceedings of the Conference on the Theory of Ordinary and Partial Differential Equations, Dundee, Scotland*, Lecture Notes in Mathematics Vol. 280 (Springer, New York, 1972).
[18] A. Weinstein and W. Stenger, *Intermediate Problems for Eigenvalues* (Academic Press, New York, 1972).
[19] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972), pp. 504–508.
[20] E. A. Hylleraas and B. Undheim, Z. Phys. **65**, 759 (1930).