Regular perturbation theory of relativistic corrections: II. Algebraic approximation

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A four-component equivalent of the Schrödinger equation, describing both the nonrelativistic electron and the nonrelativistic positron, is introduced. The difference between this equation and the Dirac equation is treated as a perturbation. The relevant perturbation equations and formulas for corrections to the energy are derived. Owing to the semibounded character of the Schrödinger Hamiltonian of the unperturbed equation the variational perturbation method is formulated. The Hylleraas functionals become then either upper or lower bounds to the respective exact corrections to the energy. In order to demonstrate the usefulness of this approach to the problem of the variational optimization of nonlinear parameters, the perturbation corrections to wave functions for the of hydrogenlike atoms have been approximated in terms of exponential basis functions. The Dirac equation in this algebraic approximation is solved iteratively starting with the solution of the Schrödinger equation.

I. INTRODUCTION

In nonrelativistic quantum mechanics, the perturbation methods are recognized as a powerful technique for the approximation of energies and eigenfunctions. The essential idea of this approach consists of the partition of the Hamiltonian into an unperturbated Hamiltonian and a perturbation. Since the Schrödinger and Dirac Hamiltonians act in different Hilbert spaces, the usual perturbation methods cannot be trivially extended to the study of relativistic corrections to solutions of the Schrödinger equation. In traditional approaches one first derives some effective Hamiltonian which acts on two-component spinors and then expands it in powers of the coupling parameter c^{-2} ($c = 137.035\,989\,5$ [1] is the speed of light). Unfortunately this procedure introduces spurious singularities into resulting operators and often causes unsurmountable problems in higher orders [2,3]. Recently Kutzelnigg *et al.* [4] have assessed the arguments in favor of the fully four-component direct perturbation theory (DPT) [3,5,6]. This approach isolates from the relativistic equation a four-component equivalent of the Schrödinger equation which is considered a zeroth-order problem for the perturbation expansion. The remaining (relativistic) terms are accounted for perturbationally without explicit recourse to the elimination of the small component. One of the aims of the present paper is to expose another possibility of the partition of the Dirac equation into the Schrödinger-type equation and relativistic perturbation, which enables one to avoid some of the serious difficulties arising from divergent contributions of the traditional methods.

In the previous paper [7] (hereafter referred to as I) a perturbation approach to the Dirac equation, starting from a pair of the Galilei-invariant four-component Levy-Leblond-type equations [8] for a nonrelativistic electron or positron with spin, was formulated. The perturbation expansion was obtained by the contour integration of matrix elements of the Dirac resolvent expanded in terms of nonrelativistic resolvents. It has been observed that the expressions for the low-order energy corrections coincide with the well-known formulas for the Rayleigh-Schrödinger coefficients. However, they involve contributions from both the nonrelativistic electron and nonrelativistic positron states. Owing to the form of the zeroth-order reference, the method differs significantly from other perturbation schemes, which expand the Dirac resolvent about its purely electronic nonrelativistic limit [9] (i.e., which use the Schrödinger or Pauli resolvent combined with the projection onto the upper component) or, in equivalent formulation, are based on the Levy-Leblond equation for nonrelativistic electron as the zeroth-order approximation [3,6].

In I, our regular perturbation theory (RPT) was applied to the case of a quasifree particle. It has been observed that the convergence of RPT is much better than the convergence of the c^{-2n} expansion. The aim of the present paper is to develop an equivalent perturbation formalism without the direct reference to the expansion of the Dirac resolvent. Such a form of the theory is needed for constructing the Hylleraas [10] type functionals in variational perturbation methods. This approach has been motivated by the fact that for most physical problems of current interest the perturbation equations cannot be solved exactly in the analytic form and require some further approximations. Finite-difference methods, which can be successfully used for atoms, are inappropriate in the case of molecules because the symmetry lowering prevents the factorization into radial and angular components. Thus the algebraic approximation appears to be the most promising method of obtaining the approximate solutions. In the basis set expansion approaches to the solution of the Dirac equation particular attention must be paid to the coupling between the large and small components. Until now, computationaly most appealing seems to be the algebraic approximation [11] based on the so-called ''kinetically balanced'' basis set [12,13] (some set $\{\Phi\}$ for the large component and the set $\{\boldsymbol{\sigma}\cdot\mathbf{p}\Phi\}$ for the small component). In the present work we present an alternative algebraic approximation which is used in the context of RPT.

II. PARTITION OF THE DIRAC EQUATION

The time-independent Dirac equation in atomic units for a single electron in the potential V is

$$(c\boldsymbol{\alpha}\cdot\mathbf{p}+c^2\beta+V-E)\Psi=0, \qquad (1)$$

where the symbols have their usual meaning. In the spirit of the regular perturbation theory of relativistic corrections described in I we rewrite Eq. (1) in the form

$$[H+A^+S^++A^-S^--E(\beta^+S^++\beta^-S^-)+A^+S^-+A^-S^+$$
$$-E(\beta^+S^-+\beta^-S^+)]\Psi=0, \qquad (2)$$

where

$$H=c\boldsymbol{\alpha}\cdot\mathbf{p}+2c^2\beta, \qquad (3)$$

$$A^\pm=(V\mp c^2)\beta^\pm. \qquad (4)$$

The two projectors $\beta^\pm$ on the upper and on the lower components of the four-component spinor are defined as

$$\beta^\pm=(1\pm\beta)/2. \qquad (5)$$

Two other projectors $S^\pm$, defined in I as projectors on the ''positive'' electronic and on the ''negative'' positronic nonrelativistic states, respectively, may be written in the explicit form

$$S^+=\mathcal{T}^{-1}\begin{pmatrix} 2c^2 & c\boldsymbol{\sigma}\cdot\mathbf{p} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} & \frac{1}{2}p^2 \end{pmatrix}, \qquad (6)$$

$$S^-=\mathcal{T}^{-1}\begin{pmatrix} \frac{1}{2}p^2 & -c\boldsymbol{\sigma}\cdot\mathbf{p} \\ -c\boldsymbol{\sigma}\cdot\mathbf{p} & 2c^2 \end{pmatrix}, \qquad (7)$$

where

$$\mathcal{T}=\frac{1}{2}p^2+2c^2. \qquad (8)$$

Let us note that in the presence of the external magnetic field the momentum operator should be replaced by $\boldsymbol{\pi}=\mathbf{p}+\mathbf{A}$, where $\mathbf{A}$ is the vector potential of the magnetic field. According to their definition the operators $S^\pm$ are idempotent, Hermitian (orthogonal projection), and have the following properties:

$$S^++S^-=1, \quad S^\pm S^\mp=0, \quad S^\pm\beta^\pm S^\mp=-S^\pm\beta^\mp S^\mp, \quad (9)$$

$$\beta^\pm HS^\mp=0, \quad \beta^\pm HS^\pm=\pm\mathcal{T}\beta^\pm S^\pm. \qquad (10)$$

Let us now consider the equation

$$[H+A^+S^++A^-S^--E^{(0)}(\beta^+S^++\beta^-S^-)]\Psi^{(0)}=0. \qquad (11)$$

In order to understand the physical meaning of this equation it is useful to express $\Psi^{(0)}$ as a sum of two mutually or-

thogonal functions belonging to the two subspaces of the Hilbert space of the four-component spinors:

$$\Psi^{(0)}=S^+\Psi^{(0)}+S^-\Psi^{(0)}=\varphi^{(0)}+\chi^{(0)}. \qquad (12)$$

By substituting this partition into Eq. (11) and taking into account the second of Eqs. (9), one obtains the separation of Eq. (11) into two independent equations:

$$(H+A^+-E^{(0)}\beta^+)\varphi^{(0)}=0, \qquad (13)$$

$$(H+A^--E^{(0)}\beta^-)\chi^{(0)}=0. \qquad (14)$$

Both these Levy-Leblond-type equations are Galilei-invariant wave equations for a nonrelativistic particle with spin [8]: the first of them refers to the nonrelativistic electron whereas the second one describes the nonrelativistic positron. Each of these equations is completely equivalent to the appropriate Schrödinger equation; after substituting $A^\pm$ from Eq. (4) into Eqs. (13) and (14) and taking into account Eqs. (8) and (10), we obtain

$$\left(\frac{1}{2}p^2+V\right)\varphi_+^{(0)}=(E^{(0)}-c^2)\varphi_+^{(0)}, \qquad (15)$$

$$\left(-\frac{1}{2}p^2+V\right)\chi_-^{(0)}=(E^{(0)}+c^2)\chi_-^{(0)}, \qquad (16)$$

where $\varphi_+^{(0)}$ and $\chi_-^{(0)}$ correspond to the upper and lower components of $\varphi^{(0)}$ and $\chi^{(0)}$, respectively. The complementary lower and upper components are given by

$$\varphi_-^{(0)}=\frac{1}{2c}\boldsymbol{\sigma}\cdot\mathbf{p}\varphi_+^{(0)}, \quad \chi_+^{(0)}=-\frac{1}{2c}\boldsymbol{\sigma}\cdot\mathbf{p}\chi_-^{(0)}. \qquad (17)$$

In Eq. (15) $\frac{1}{2}p^2+V$ represents the Schrödinger Hamiltonian for one electron. Thus, Eq. (15) is equivalent to the Schrödinger equation with $E-c^2$ being the nonrelativistic energy. Similarly, upon multiplying Eq. (16) by -1, one finds that Eq. (16) is the Schrödinger equation for a nonrelativistic electron with negative energy and charge opposite to that used in V (provided that V is charge dependent), i.e., this is the ordinary Schrödinger equation for a positron. Therefore, Eq. (11) may be regarded as a four-component generalization of the Schrödinger equation which simultaneously describes the nonrelativistic electron and nonrelativistic positron.

On comparing the Dirac equation [Eq. (2)] with Eq. (11), one finds that they differ by

$$B=A^+S^-+A^-S^+-E(\beta^+S^-+\beta^-S^+). \qquad (18)$$

The idea of this work relies on the assumption that, in a certain sense, the term B is ''small,'' and that reliable approximate solutions of the Dirac equation can be obtained by starting with the solution of the Schrödinger equation and using a perturbation treatment.

III. PERTURBATION FORMALISM

The perturbation methods assume the partition of the total Hamiltonian into some unperturbed part and a perturbation.

However, our approach involves also a partition of the metric. Therefore, for applying the perturbation theory, the most compact form of Eq. (2) with a formal parameter λ is

$$[H^{(0)} - ES^{(0)} + \lambda(H^{(1)} - ES^{(1)})]\Psi = 0, \qquad (19)$$

where

$$H^{(0)} = H + A^+ S^+ + A^- S^-, \quad S^{(0)} = \beta^+ S^+ + \beta^- S^-, \qquad (20)$$

$$H^{(1)} = A^+ S^- + A^- S^+, \quad S^{(1)} = \beta^+ S^- + \beta^- S^+. \qquad (21)$$

Let us consider some eigenstate of the perturbed problem [Eq. (19)] which originates ($\lambda = 0$) from a nondegenerate nonrelativistic state with $\chi^{(0)} = S^- \Psi^{(0)} = 0$. We assume that both Ψ and E are analytic in λ:

$$\Psi = \varphi^{(0)} + \sum_{i=1}^{\infty} \lambda^i \Psi^{(i)}, \qquad (22)$$

$$E = \sum_{n=0}^{\infty} \lambda^{2n} E^{(2n)}, \qquad (23)$$

where $\varphi^{(0)} = S^+ \Psi^{(0)}$. Moreover, according to I, only the even-order energy corrections are different from zero. The zeroth-order equation is

$$(H^{(0)} - E^{(0)} S^{(0)}) \varphi^{(0)} = 0 \qquad (24)$$

and in the first order

$$(H^{(0)} - E^{(0)} S^{(0)}) \Psi^{(1)} + H^{(1)} \varphi^{(0)} = 0. \qquad (25)$$

Similarly to the partition of $\Psi^{(0)}$ [Eq. (12)] every function Ψ may be partitioned into two components φ and χ. In particular,

$$\Psi^{(1)} = S^+ \Psi^{(1)} + S^- \Psi^{(1)} = \varphi^{(1)} + \chi^{(1)}. \qquad (26)$$

Inserting $\Psi^{(1)}$ given by Eq. (26) and using $H^{(0)}$, $S^{(0)}$, and $H^{(1)}$ as given by Eqs. (20) and (21), into Eq. (25) and then taking into account Eqs. (4), (10), and (11) results in

$$\beta^+ (H^{(0)} - E^{(0)} S^{(0)}) \varphi^{(1)} + \beta^- (H^{(0)} - E^{(0)} S^{(0)}) \chi^{(1)} + A^- \varphi^{(0)}$$
$$= 0. \qquad (27)$$

According to the properties of operators involved in Eq. (27) the lower component of $(H^{(0)} - E^{(0)} S^{(0)}) S^+$ disappears and

$$(H^{(0)} - E^{(0)} S^{(0)}) \varphi^{(1)} = 0. \qquad (28)$$

As consequence of the nondegenerate character of $\varphi^{(0)}$ we obtain $\varphi^{(1)} \sim \varphi^{(0)}$ and according to the general methodology of the perturbation theory, $\varphi^{(1)}$ can be chosen as

$$\varphi^{(1)} \equiv 0. \qquad (29)$$

In a similar way we obtain

$$\chi^{(2)} \equiv 0. \qquad (30)$$

These results can be simply extended by induction to higher even (odd) orders to give

$$\Psi = \sum_{n=0}^{\infty} \lambda^n (\varphi^{(2n)} + \lambda \chi^{(2n+1)}). \qquad (31)$$

The $2n$th and $(2n+1)$th order equations are

$$(H^{(0)} - E^{(0)} S^{(0)}) \varphi^{(2n)} - (H^{(1)} - E^{(0)} S^{(1)}) \chi^{(2n-1)}$$

$$- E^{(2n)} S^{(0)} \varphi^{(0)} - \sum_{i=1}^{n-1} E^{(2i)} (S^{(0)} \varphi^{(2n-2i)}$$

$$+ S^{(1)} \chi^{(2n-2i-1)}) = 0, \qquad (32)$$

$$(H^{(0)} - E^{(0)} S^{(0)}) \chi^{(2n+1)} - (H^{(1)} - E^{(0)} S^{(1)}) \varphi^{(2n)}$$

$$- \sum_{i=1}^{n} E^{(2i)} (S^{(0)} \chi^{(2n-2i+1)} + S^{(1)} \varphi^{(2n-2i)}) = 0. \qquad (33)$$

By rewriting the above equations in the block form one can see that each of them has only one nonzero row [Eq. (32), upper and Eq. (33), lower]. This leads to the equivalent set of the two-component equations

$$(T + V + c^2 - E^{(0)}) \varphi_+^{(2n)} + (V - c^2 - E^{(0)}) \chi_+^{(2n-1)} - E^{(2n)} \varphi_+^{(0)}$$

$$- \sum_{i=1}^{n-1} E^{(2i)} (\varphi_+^{(2n-2i)} + \chi_+^{(2n-2i-1)}) = 0, \qquad (34)$$

$$(-T + V - c^2 - E^{(0)}) \chi_-^{(2n+1)} + (V + c^2 - E^{(0)}) \varphi_-^{(2n)}$$

$$- \sum_{i=1}^{n} E^{(2i)} (\varphi_-^{(2n-2i)} + \chi_-^{(2n-2i+1)}) = 0, \qquad (35)$$

where T is the nonrelativistic kinetic energy operator. Let us choose the normalization of the zeroth-order wave function $\Psi^{(0)}$ as follows:

$$\langle \Psi^{(0)}, \beta^+ \Psi^{(0)} \rangle = \langle \varphi_+^{(0)}, \varphi_+^{(0)} \rangle = 1. \qquad (36)$$

Expressions for relativistic corrections to the energy can be obtained by taking the scalar product of Eq. (34) with $\varphi_+^{(0)}$. Since $T + V$ is Hermitian and $\varphi_+^{(0)}$ satisfies Eq. (15), The term $\langle \varphi_+^{(0)}, (T + V + c^2 - E^{(0)}) \varphi_+^{(2n)} \rangle$ vanishes. Thus,

$$E^{(2n)} = \langle \varphi_+^{(0)}, (V - c^2 - E^{(0)}) \chi_+^{(2n-1)} \rangle$$

$$- \sum_{i=1}^{n-1} E^{2i} \langle \varphi_+^{(0)}, \chi_+^{(2n-2i-1)} \rangle. \qquad (37)$$

In deriving Eq. (37) we have assumed that

$$\langle \varphi_+^{(0)}, \varphi_+^{(2i)} \rangle = \delta_{0i}. \qquad (38)$$

According to Eq. (37) the calculation of the $2n$th-order correction, $E^{(2n)}$, requires knowledge of all corrections $E^{(2i)}$ through the $(2n-2)$th order and all corrections $\chi^{(2i-1)}$

through the $(2n-1)$th order. Similarly to methods used in the Rayleigh-Schrödinger perturbation theory (see, for example, [14]), additional relations can be obtained for higher-order corrections to the energy by taking the scalar products

of Eqs. (34) and (35) with several functions $\varphi_+^{(i)}$, $\varphi_-^{(i)}$, $\chi_+^{(i)}$, $\chi_-^{(i)}$ and by performing a sequence of algebraic manipulations, as explained in Appendix A. The most important of these relations are

$$E^{(2n)} = \langle \chi_+^{(n-1)}, (V-c^2-E^{(0)})(\varphi_+^{(n)}+\chi_+^{(n-1)}) \rangle - \sum_{i=1}^{n/2-1} E^{(n-2i)} \langle \chi_+^{(2i-1)}, (\varphi_+^{(n)}+\chi_+^{(n-1)}) \rangle$$

$$- \sum_{i,j=0}^{n/2-1} E^{(2n-2i-2j-2)}(\langle \varphi_+^{(2i)}, \varphi_+^{(2j+2)} \rangle + \langle \varphi_-^{(2i)}, \varphi_-^{(2j)} \rangle + \langle \chi_-^{(2i+1)}, \chi_-^{(2j+1)} \rangle + \langle \chi_+^{(2i+1)}, \chi_+^{(2j-1)} \rangle), \quad n=2,4,6,\dots, \tag{39}$$

$$E^{(2n)} = \langle \varphi_-^{(n-1)}, (V+c^2-E^{(0)})(\varphi_-^{(n-1)}+\chi_-^{(n)}) \rangle - \sum_{i=0}^{(n-3)/2} E^{(n-2i-1)}[\langle (\varphi_-^{(2i)}+\chi_-^{(2i+1)}), \chi_-^{(n)} \rangle + \langle \varphi_-^{(2i)}, \varphi_-^{(n-1)} \rangle + \langle \varphi_-^{(n-1)}, \varphi_-^{(2i)} \rangle]$$

$$- \sum_{i,j=0}^{(n-3)/2} [E^{(2n-2i-2j-2)}(\langle \varphi_-^{(2i)}, \varphi_-^{(2j)} \rangle + \langle \chi_-^{(2i+1)}, \chi_-^{(2j+1)} \rangle) + E^{(2n-2i-2j-4)}(\langle \chi_+^{(2i+1)}, \chi_+^{(2j+1)} \rangle$$

$$+ \langle \varphi_+^{(2i+2)}, \varphi_+^{(2j+2)} \rangle)], \quad n=1,3,5,\dots. \tag{40}$$

Equations (39) and (40) demonstrate that the perturbed energy through the $2n$th order can be obtained from knowledge of the wave-function perturbed through the nth order. It is well known that the same is true for the Rayleigh-Schrödinger perturbation theory.

IV. VARIATIONAL PERTURBATION METHOD

In this section we explore the connection between the perturbation theory and variational principles. The direct solution of the perturbation equations is usually not available for more complicated cases. However, as it was first noted by Hylleraas [10], we can regard the nth-order perturbation equation as the stationary value condition of the suitable functional $J^{(n)}$ for the function $\Psi^{(n)}$. In our case we have two families of functionals: the first family for functions $\chi_-^{(n)}$ (n odd) and the second one for functions $\varphi_+^{(n)}$ (n even). The appropriate functionals $J^{(n)}$ can be written as

$$J^{(n)}(\widetilde{\chi}_-^{(n)}) = J_0^{(n)}(\widetilde{\chi}_-^{(n)}) + K^{(n)} \tag{41}$$

with

$$J_0^{(n)}(\widetilde{\chi}_-^{(n)}) = \langle \widetilde{\chi}_-^{(n)}, (V+c^2-E^{(0)})\varphi_-^{(n-1)} \rangle + \langle \varphi_-^{(n-1)}, (V+c^2-E^{(0)})\widetilde{\chi}_-^{(n)} \rangle - \langle \widetilde{\chi}_-^{(n)}, (T-V+c^2+E^{(0)})\widetilde{\chi}_-^{(n)} \rangle$$

$$- \sum_{i=1}^{(n-1)/2} E^{(2i)}(\langle \widetilde{\chi}_-^{(n)}, \varphi_-^{(n-2i-1)} \rangle + \langle \widetilde{\chi}_-^{(n)}, \chi_-^{(n-2i)} \rangle + \langle \varphi_-^{(n-2i-1)}, \widetilde{\chi}_-^{(n)} \rangle + \langle \chi_-^{(n-2i)}, \widetilde{\chi}_-^{(n)} \rangle), \quad n=1,3,5,\dots \tag{42}$$

or

$$J^{(n)}(\widetilde{\varphi}_+^{(n)}) = J_0^{(n)}(\widetilde{\varphi}_+^{(n)}) + K^{(n)} \tag{43}$$

with

$$J_0^{(n)}(\widetilde{\varphi}_+^{(n)}) = \langle \widetilde{\varphi}_+^{(n)}, (V-c^2-E^{(0)})\chi_+^{(n-1)} \rangle + \langle \chi_+^{(n-1)}, (V-c^2-E^{(0)})\widetilde{\varphi}_+^{(n)} \rangle + \langle \widetilde{\varphi}_+^{(n)}, (T+V+c^2-E^{(0)})\widetilde{\varphi}_+^{(n)} \rangle$$

$$- \sum_{i=1}^{(n-2)/2} E^{(2i)}(\langle \widetilde{\varphi}_+^{(n)}, \varphi_+^{(n-2i)} + \chi_+^{(n-2i-1)} \rangle + \langle \varphi_+^{(n-2i)} + \chi_+^{(n-2i-1)}, \widetilde{\varphi}_+^{(n)} \rangle) - E^{(n)}(\langle \widetilde{\varphi}_+^{(n)}, \varphi_+^{(0)} \rangle + \langle \varphi_+^{(0)}, \widetilde{\varphi}_+^{(n)} \rangle),$$

$$n=2,4,6,\cdots, \tag{44}$$

where we use the tilde to represent a trial function. It is evident that a stationary value condition leads in a straightforward way to the proper perturbation equation. The presence of the $K^{(n)}$ term, which is independent of $\widetilde{\chi}_-^{(n)}$ ($\widetilde{\varphi}_+^{(n)}$), leads to the correct value of the functional at $\widetilde{\chi}_-^{(n)} = \chi_-^{(n)}$ or $\widetilde{\varphi}_+^{(n)} = \varphi_+^{(n)}$, namely $J^{(n)} = E^{(2n)}$ if

$$
K^{(n)} = \langle \varphi_-^{(n-1)}, (V + c^2 - E^{(0)}) \varphi_-^{(n-1)} \rangle - \sum_{i=0}^{(n-3)/2} E^{(n-2i-1)} (\langle \varphi_-^{(2i)}, \varphi_-^{(n-1)} \rangle + \langle \varphi_-^{(n-1)}, \varphi_-^{(2i)} \rangle)
$$

$$
- \sum_{i,j=0}^{(n-3)/2} [E^{(2n-2i-2j-2)} (\langle \varphi_-^{(2i)}, \varphi_-^{(2j)} \rangle + \langle \chi_-^{(2i+1)}, \chi_-^{(2j+1)} \rangle) + E^{(2n-2i-2j-4)} (\langle \chi_+^{(2i+1)}, \chi_+^{(2j+1)} \rangle
$$

$$
+ \langle \varphi_+^{(2i+2)}, \varphi_+^{(2j+2)} \rangle)], \quad n = 1,3,5, \ldots \tag{45}
$$

or

$$
K^{(n)} = \langle \chi_+^{(n-1)}, (V - c^2 - E^{(0)}) \chi_+^{(n-1)} \rangle - \sum_{i=1}^{n/2-1} E^{(n-2i)} \langle \chi_+^{(2i-1)}, \chi_+^{(n-1)} \rangle - \sum_{i,j=0}^{n/2-1} E^{(2n-2i-2j-2)} [\langle \varphi_+^{(2i)}, \varphi_+^{(2j+2)} \rangle (1 - \delta_{n,2j+2})
$$

$$
+ \langle \varphi_-^{(2i)}, \varphi_-^{(2j)} \rangle + \langle \chi_-^{(2i+1)}, \chi_-^{(2j+1)} \rangle + \langle \chi_+^{(2i-1)}, \chi_+^{(2j-1)} \rangle], \quad n = 2,4,6, \ldots . \tag{46}
$$

We shall prove that for odd n the functional $J^{(n)}$ is a lower bound to the exact correction $E^{(2n)}$ to energy. To this end, the difference $J^{(n)} - E^{(2n)}$ may be set, according to Eqs. (40) and (35), in the form

$$
J^{(n)} - E^{(2n)} = -\langle \widetilde{\chi}_-^{(n)} - \chi_-^{(n)}, (T - V + c^2 + E^{(0)}) (\widetilde{\chi}_-^{(n)} - \chi_-^{(n)}) \rangle,
$$

$$
n = 1,3,5, \ldots . \tag{47}
$$

Provided that $c^2 + E^{(0)} \geq 0$ (the nonrelativistic energy $E^{(0)} - c^2$ is larger than $-2c^2$) the stated result is then an immediate consequence of the positively definite character of the Schrödinger Hamiltonian $T - V$ with repulsive potential $-V$. Similarly, using Eqs. (39) and (34), we obtain

$$
J^{(n)} - E^{(2n)} = \langle \widetilde{\varphi}_+^{(n)} - \varphi_+^{(n)}, (T + V + c^2 - E^{(0)})
$$

$$
\times (\widetilde{\varphi}_+^{(n)} - \varphi_+^{(n)}) \rangle,
$$

$$
n = 2,4,6, \ldots . \tag{48}
$$

Owing to the semibounded character of the Schrödinger Hamiltonian the right-hand side of the above equation is non-negative for the ground-state energy $E^{(0)}$.

These considerations show that also in the relativistic case we can use the variational formulation, and obtain approximations to the ground-state solutions of Dirac equation from the following variational principles:

$$
J^{(n)}(\widetilde{\chi}_-) \leq E^{(2n)}, \quad n = 1,3,5, \ldots , \tag{49}
$$

$$
J^{(n)}(\widetilde{\varphi}_+) \geq E^{(2n)}, \quad n = 2,4,6, \ldots . \tag{50}
$$

Accordingly the Hylleraas functionals are lower or upper bounds to the respective exact corrections to the energy. The variational perturbation method can be extended to excited states, by assuming that trial function $\widetilde{\varphi}_{k+}$ is exactly represented in the subspace spanned by all lower energy eigenfunctions of the Schrödinger Hamiltonian (see [15]).

In order to get an insight into this problem, let us consider the expansion

$$
\varphi_l^{(n)} = \sum_k c_k^{(n)} \varphi_k^{(0)}, \quad n = 2,4, \ldots, \tag{51}
$$

where the subscript l specifies the state under consideration. The corresponding expression for the expansion coefficients can be obtained in much the same way as for the standard Rayleigh-Schrödinger perturbation theory, namely, by substituting Eq. (51) into Eq. (34) and taking the scalar product of the resulting equation with $\varphi_{l+}^{(0)}$. This leads to the following result (for $m \neq l$):

$$
c_m^{(n)} = \frac{\langle \varphi_{m+}^{(0)}, (V - c^2 - E_l^{(0)}) \chi_{l+}^{(n-1)} \rangle - \sum_{i=1}^{n-1} E_l^{(2i)} \langle \varphi_{m+}^{(0)}, (\varphi_{l+}^{(n-2i)} + \chi_{l+}^{(n-2i-1)}) \rangle}{E_l^{(0)} - E_m^{(0)}}. \tag{52}
$$

The coefficient $c_l^{(n)}$ cannot be determined from Eq. (52). However, owing to the orthogonality condition [Eq. (38)], there is no loss of generality in taking $c_l^{(n)} = 0$. Setting $\widetilde{\varphi}_{l+}^{(n)}$ in the form

$$\widetilde{\varphi}_{l+}^{(n)} = \sum_{i=1}^{l-1} c_i^{(n)} \varphi_i^{(n)} + \widetilde{\rho}_l^{(n)}, \tag{53}$$

where the coefficients $c_i^{(n)}$ are given by Eq. (52),

$$S^+ \widetilde{\rho}_l^{(n)} = \widetilde{\rho}_l^{(n)}, \tag{54}$$

and $\widetilde{\rho}_{l+}^{(n)}$ is orthogonal to the first $l-1$ eigenstates of the Schrödinger Hamiltonian, one can conclude that the right-hand side of Eq. (48) is non-negative and therefore $J^{(n)}$ is an

upper bound to $E_l^{(2n)}$ ($n = 2, 4, \dots$). In order to obtain a compact form of the Hylleraas functional, the trial function $\widetilde{\rho}_l^{(n)}$ can be written as

$$\widetilde{\rho}_l^{(n)} = \widetilde{\varphi}_l^{(n)} - \sum_{i=1}^{l-1} \varphi_i^{(0)} \langle \varphi_{i+}^{(0)}, \widetilde{\varphi}_{l+}^{(n)} \rangle + \sum_{i=1}^{l-1} c_i^{(n)} \varphi_i^{(0)}, \tag{55}$$

where $\widetilde{\varphi}_l^{(n)}$ is now an arbitrary function of the electron-type ($S^+ \widetilde{\varphi}_l^{(n)} = \widetilde{\varphi}_l^{(n)}$). By substituting $\widetilde{\rho}^{(n)}$ for $\widetilde{\varphi}^{(n)}$ in Eq. (44) the desired form of the variational perturbation functional is obtained:

$$J_l^{(n)}(\widetilde{\varphi}_{l+}^{(n)}) = J_{0l}^{(n)}(\widetilde{\varphi}_{l+}^{(n)}) + K_l^{(n)} \tag{56}$$

with

$$J_{0l}^{(n)}(\widetilde{\varphi}_{l+}^{(n)}) = J_0^{(n)}(\widetilde{\varphi}_{l+}^{(n)}) - \sum_{j=1}^{l-1} [\langle \widetilde{\varphi}_{l+}^{(n)}, \varphi_{j+}^{(0)} \rangle \langle \varphi_{j+}^{(0)}, \widetilde{\varphi}_{l+}^{(n)} \rangle (E_j^{(0)} - E_l^{(0)}) + \langle \widetilde{\varphi}_{l+}^{(n)}, \varphi_{j+}^{(0)} \rangle \langle \varphi_{j+}^{(0)}, (V - c^2 - E_l^{(0)}) \chi_{l+}^{(n-1)} \rangle$$

$$+ \langle \varphi_{j+}^{(0)}, \widetilde{\varphi}_{l+}^{(n)} \rangle \langle \chi_{l+}^{(n-1)}, (V - c^2 - E_l^{(0)}) \varphi_{j+}^{(0)} \rangle] - \sum_{i=1}^{(n-2)/2} E^{(2i)} \sum_{j=1}^{l-1} \langle \widetilde{\varphi}_{l+}^{(n)}, \varphi_{j+}^{(0)} \rangle (\langle \varphi_{j+}^{(0)}, \chi_{l+}^{(n-2i-1)} \rangle$$

$$+ \langle \chi_{l+}^{(n-2i-1)}, \varphi_{j+}^{(0)} \rangle \langle \varphi_{j+}^{(0)}, \widetilde{\varphi}_{l+}^{(n)} \rangle) \tag{57}$$

and

$$K_l^{(n)} = K^{(n)} + \sum_{j=1}^{l-1} |c_i^{(n)}|^2 (E_j^{(0)} - E_l^{(0)}) + \sum_{j=0}^{l-1} [c_j^{(n)} \langle \chi_{l+}^{(n-1)}, (V - c^2 - E_l^{(0)}) \varphi_{j+}^{(0)} \rangle + c_j^{(n)*} \langle \varphi_{j+}^{(0)}, (V - c^2 - E_l^{(0)}) \chi_{l+}^{(n-1)} \rangle]$$

$$- \sum_{i=1}^{(n-2)/2} E^{(2i)} \sum_{j=1}^{l-1} [c_j^{(n)} \langle \varphi_{j+}^{(0)}, (\varphi_{l+}^{(n-2i)} + \chi_{l+}^{(n-2i-1)}) \rangle + c_j^{(n)*} \langle (\varphi_{l+}^{(n-2i)} + \chi_{l+}^{(n-2i-1)}), \varphi_{j+}^{(0)} \rangle]. \tag{58}$$

Finally, it should be noted that in the derivation of inequalities (49) and (50), we assume that all the lower-order corrections are known exactly. If only approximations to the lower-order corrections are available, the variational method based on Eqs. (49) or (50) may still be used but will not, in general, give lower or upper bounds to $E^{(2n)}$.

V. NONPERTURBATIVE ITERATIVE SOLUTION

Within the framework of the perturbation formalism described earlier in this paper, the approximate solution of the Dirac equation can, in principle, be obtained through any order of interest. Unfortunately, tedious algebraic manipulations need to be carried out to get the working equations for the calculation of relativistic corrections through arbitrary order. Furthermore in order to calculate the $2n$th-order energy we must know all the wave-function corrections through the nth order. Following the idea developed by Kutzelnigg for DPT [3] and recently tested numerically by Franke [16] we propose an iterative solution of the Dirac equation starting with the nonrelativistic wave function. We

choose $\mathcal{E}^{(0)} = E^{(0)}$ and cast the exact Dirac solution into the form

$$\Psi = \varphi^{(0)} + \varphi + \chi, \tag{59}$$

where $S^+ \varphi = \varphi$, $S^- \chi = \chi$, and $\langle \varphi^{(0)}, \beta^+ \varphi \rangle = 0$.

The following steps, beginning with $i = 1$ through self-consistency are carried out iteratively:

$$-S^- \beta^- (T - V + c^2 + \mathcal{E}^{(i-1)}) \chi^{(i)}$$
$$+ S^- \beta^- (V + c^2 - \mathcal{E}^{(i-1)}) \varphi^{(i-1)} = 0, \tag{60}$$

$$\mathcal{E}^{(i)} = \mathcal{E}^{(0)} + \langle \varphi^{(0)}, \beta^+ (V - c^2 - \mathcal{E}^{(i-1)}) \chi^{(i)} \rangle, \tag{61}$$

$$S^+ \beta^+ (T + V + c^2 - \mathcal{E}^{(i)}) \varphi^{(i)} + S^+ \beta^+ (V - c^2 - \mathcal{E}^{(i)}) \chi^{(i)} = 0. \tag{62}$$

To solve Eqs. (60)–(62) we expand $\varphi^{(i)}$ in an appropriate basis of the electron-type functions $\{\Phi_j^+; \ S^+ \Phi_j^+ = \Phi_j^+\}_{j=1}^n$ and $\chi^{(i)}$ in a basis of the positron-type functions $\{\Phi_j^-; \ S^- \Phi_j^- = \Phi_j^-\}_{j=1}^m$. The approximate solutions are

$$\varphi^{(i)} = \sum_{j=1}^{n} c_j^{(i)+} \Phi_j^+ , \quad \chi^{(i)} = \sum_{j=1}^{m} c_j^{(i)-} \Phi_j^- , \quad (63)$$

where the coefficients $c_j^{(i)}$ are determined from the matrix representation of Eqs. (60) and (62):

$$(\mathbf{D}^{--} - \mathcal{E}^{(i-1)}\mathbf{M}^{--})\mathbf{c}^{(i)-} + (\mathbf{D}^{-+} - \mathcal{E}^{(i-1)}\mathbf{M}^{-+})\mathbf{c}^{(i-1)+} = 0,$$
$$(64)$$

$$(\mathbf{D}^{++} - \mathcal{E}^{(i)}\mathbf{M}^{++})\mathbf{c}^{(i)+} + (\mathbf{D}^{+-} - \mathcal{E}^{(i)}\mathbf{M}^{+-})\mathbf{c}^{(i)-} = 0,$$
$$(65)$$

where $\mathbf{D}$ and $\mathbf{M}$ are matrices with the elements

$$D_{jk}^{\pm\pm} = \langle \Phi_{j\pm}^{\pm}, (\pm T + V \pm c^2)\Phi_{k\pm}^{\pm} \rangle, \quad (66)$$

$$D_{jk}^{\pm\mp} = \frac{1}{2c} \langle \Phi_{j\pm}^{\pm}, (\mp V + c^2)\boldsymbol{\sigma}\cdot\mathbf{p}\Phi_{k\mp}^{\mp} \rangle, \quad (67)$$

$$M_{jk}^{\pm\pm} = \langle \Phi_{j\pm}^{\pm}, \Phi_{k\pm}^{\pm} \rangle, \quad (68)$$

$$M_{jk}^{\pm\mp} = \mp\frac{1}{2c} \langle \Phi_{j\pm}^{\pm}, \boldsymbol{\sigma}\cdot\mathbf{p}\Phi_{k\mp}^{\mp} \rangle. \quad (69)$$

Let us note that the recursion procedure [Eqs. (61), (64), and (65)] can be regarded as the iterative solution of the N-dimensional ($N=n+m$) eigenvalue problem:

$$(\mathbf{D} - E\mathbf{M})\mathbf{c} = 0. \quad (70)$$

We shall show that Eq. (70) can be identified with the Galerkin-Petrov (GP) approximation [17] to the Dirac equation.

The idea of the GP method as applied to the operator equation

$$(D - E)\Psi = 0 \quad (71)$$

can be formulated as follows. Let F_N and G_N be two N-dimensional subspaces of the Hilbert space under consideration, which are called the coordinate and projective subspaces, respectively. Let P and Q be the projection operators onto F_N and G_N, respectively. The approximation Φ to Ψ is assumed to be an element of the coordinate subspace, i.e., $P\Phi = \Phi$ and is determinated by the requirement

$$Q(D - E)\Phi = 0. \quad (72)$$

Let us choose the basis sets $\{\eta_i\}_{i=1}^N$ and $\{\phi_i\}_{i=1}^N$ in F_N and G_N, respectively. The approximate eigenfunction can be written

$$\Phi = \sum_{i=1}^{N} c_i \phi_i, \quad (73)$$

where the coefficients c_i are determined from the matrix representation of Eq. (72) [Eq. (70)], where $\mathbf{D}$ and $\mathbf{M}$ are matrices with the elements $D_{ki} = \langle \eta_k, D\phi_i \rangle$, $M_{ki} = \langle \eta_k, \varphi_i \rangle$, and $\mathbf{c}$ represents a column matrix of the coefficients c_i corresponding to the eigenvalue E. Equation (70) represents a set of secular equations which can be considered as a counterpart of the Ritz variational procedure. The two methods become identical in the case $F_N = G_N$. Choosing the basis set $\{\phi_j\}_{j=1}^N$ of the coordinate subspace as

$$\{\Phi_j^+\}_{j=1}^n \cup \{\Phi_j^-\}_{j=1}^m,$$

the projective basis in the form

$$\left\{ \begin{array}{c} \Phi_{j+}^+ \\ 0 \end{array} \right\}_{j=1}^n \cup \left\{ \begin{array}{c} 0 \\ \Phi_{j-}^- \end{array} \right\}_{j=1}^m ,$$

and substituting for D the Dirac Hamiltonian, we obtain from Eq. (72) the set of secular equations [Eq. (70)] with the matrices given by Eqs. (66)–(69).

The diagonal blocks

$$(\mathbf{D}^{++} - E\mathbf{M}^{++})\mathbf{c}^+ = 0, \quad (\mathbf{D}^{--} - E\mathbf{M}^{--})\mathbf{c}^- = 0 \quad (74)$$

are the standard Ritz matrix representations of the Schrödinger equation for the nonrelativistic electron and positron, respectively. Treating the rest of the secular equation as a perturbation we can solve Eq. (70) for $\mathbf{c}$ and E iteratively or by a perturbation approach. Alternatively, the nonsymmetric eigenvalue problem can be solved directly by the diagonalization using, for example, the QR procedure [18].

If the relativity couples states of different nonrelativistic symmetry (for example $\sigma - \pi$, $\pi - \delta$, ... molecular orbitals) the diagonal blocks $\mathbf{D}^{++}$, $\mathbf{M}^{++}$ or $\mathbf{D}^{--}$, $\mathbf{M}^{--}$ have a quasidiagonal form with diagonal subblocks of different nonrelativistic symmetries. Similarly, functionals $J_0^{(n)}$ [Eqs. (42) and (44)] are decoupled in such a case to the sum of independent terms with trial functions of different nonrelativistic symmetries.

VI. NUMERICAL EXAMPLE AND DISCUSSION

To illustrate the methods described in this paper we consider the ground and the first excited states of hydrogen-like atom. If we choose for our upper (φ_+) and lower (χ_-) components the radial basis of the exponential-type functions of the form $r^n \exp(-\zeta_i r)$, then we are constrained to choose the remaining lower and upper components of the radial basis according to the prescription

$$\frac{1}{2c}[(n+\kappa)r^{n-1} - \zeta_i r^n]\exp(-\zeta_i r)$$

or

$$\frac{1}{2c}[(n-\kappa)r^{n-1} - \zeta_i r^n]\exp(-\zeta_i r),$$

where κ is the angular quantum number. This guarantees that the basis functions are of the ''positive'' electron form or of the ''negative'' positron form. The possible values of the parameter n depend on the value of the quantum number κ. For the considered states $\kappa = -1$ and the most suitable electron-type basis should contain the basis functions with $n=1$. If we use the same n for the positron-type basis, then the upper component behaves near the origin as r^0 and

divergent integrals appear in the first term of Eq. (46). The same divergent term appears in Eq. (33). Since all the other terms in Eqs. (39)–(46) contain only finite integrals, the variational perturbation method may still be used to obtain

approximations $\widetilde{\chi}_-^{(n)}$ and $\widetilde{\varphi}_-^{(n)}$. Afterwards the $E^{(2n)}$ may be calculated from Eq. (40) or from the alternative form of Eq. (39), obtained by eliminating $(V-c^2-E^{(0)})(\chi_+^{(n-1)}+\varphi_+^n)$ with the aid of Eq. (34):

$$E^{(2n)}=-\langle\chi_+^{(n-1)},(T+2c^2)\varphi_+^{(n)}\rangle+E^{(n)}\langle\chi_+^{(n-1)},\varphi_+^{(0)}\rangle+\sum_{i=1}^{n/2-1}E^{(2i)}\langle\chi_+^{(n-1)},(\varphi_+^{(n-2i)}+\chi_+^{(n-2i-1)})\rangle$$

$$-\sum_{i=1}^{n/2-1}E^{(n-2i)}\langle\chi_+^{(2i-1)},(\varphi_+^{(n)}+\chi_+^{(n-1)})\rangle-\sum_{i,j=0}^{n/2-1}E^{(2n-2i-2j-2)}(\langle\varphi_+^{(2i)},\varphi_+^{(2j+2)}\rangle+\langle\varphi_-^{(2i)},\varphi_-^{(2j)}\rangle+\langle\chi_-^{(2i+1)},\chi_-^{(2j+1)}\rangle$$

$$+\langle\chi_+^{(2i+1)},\chi_+^{(2j-1)}\rangle),\quad n=2,4,6\ldots. \tag{75}$$

In the present paper this version of the perturbation method is used and both $\varphi_+^{(i)}$ and $\chi_-^{(i)}$ are expanded in the radial basis set with $n=1,2,3$. We would like to emphasize the fact that the matrix representation of the Dirac equation with matrix elements given by Eqs. (66)–(69) remains regular in this basis.

To exaggerate the relativistic effects, Fm^{99+} has been investigated. To obtain an approximation to $E^{(2)}$ it is necessary to consider two contributions $K^{(1)}$ and $J_0^{(1)}$. The first one is easy to deal with, since it depends solely on the nonrelativistic wave function $\Psi^{(0)}$:

$$K^{(1)}=\langle\varphi_-^{(0)},(V+c^2-E^{(0)})\varphi_-^{(0)}\rangle$$

$$=\frac{1}{4c^2}\langle\varphi_+^{(0)},\boldsymbol{\sigma}\cdot\mathbf{p}(V+c^2-E^{(0)})\boldsymbol{\sigma}\cdot\mathbf{p}\varphi_+^{(0)}\rangle. \tag{76}$$

This is exactly the formula for the first-order relativistic correction resulting from DPT and is equivalent [19] to the standard sum of three terms: the relativistic mass correction, the Darwin correction and the spin-orbit interaction. If the approximation $\widetilde{\chi}_-^{(1)}$ to $\chi_-^{(1)}$ is assumed to be a linear combination of a finite number of linearly independent basis functions, then both the linear and nonlinear parameters can be determined by maximizing the functional $J_0^{(1)}$. The problem of the maximization of the Hylleraas functional with respect to linear parameters is completely equivalent to the problem of solving a system of linear equations. In order to follow the N convergence of our solutions we have performed calculations on the ground state using basis functions with $n=1$. The results for $N=4,6,\ldots,14$ are collected in Table I. The values of the second-order correction to energy calculated from Eq. (37) are given as well. Due to the singularity of the exact relativistic wave function at the origin, the optimal values of exponents display a more rapid increase than the geometric progression. It is interesting that in all cases presented in Table I, the quotients of the last few exponents are much the same and amount to about ...2.6, 3.1, 4.5. Such a behavior of the exponents is also typical for the third-order positron-type basis. The optimization of $J^{(3)}$ gives a se-

quence of quotients: ...2.7, 3.2, 4.5. The accuracy of the relativistic corrections to energy essentially depends on the correct behavior of the wave function near the origin. One can see from Table I that an 11-figure accuracy of $E^{(2)}$ is obtained in a basis set of 14 optimal functions. In order to

TABLE I. Calculated relativistic lower bounds to the second-order energies for the ground state of the hydrogenlike ion Fm^{99+} obtained by maximizing the functional $J_0^{(1)}$. $E^{(2)}$ is the second-order correction to energy calculated from Eq. (37) with the optimal trial function $\widetilde{\chi}^{(1)}$. N gives the number of basis functions.

N	$J_0^{(1)}$	$J^{(1)}$	$E^{(2)}$
4	74.7030	−590.9390	−590.9390
6	74.705356	−590.936669	−590.936658
8	74.7053659	−590.9366587	−590.9366522
10	74.705369174	−590.936655438	−590.936655400
12	74.7053692023	−590.9366554102	−590.9366554129
14	74.7053692048	−590.9366554077	−590.9366554057
32[a]	74.7053692051	−590.9366554075	−590.9366554072
44[b]	74.7053692052	−590.9366554073	−590.9366554073
	optimal α		
4	100.804 144.520	513.574 2226.27	
6	94.8135 154.467	421.133 1057.31	3204.15 14131.2
8	94.6014 154.467	411.792 943.204	2290.75 6025.34
	18513.8 81865.3		
10	99.1876 124.114	171.729 358.592	687.335 1429.67
	3237.67 8211.32	24912.1 109872	
12	98.2003 134.305	193.986 283.571	472.122 884.976
	1753.24 3687.82	8386.01 21314.8	64792.2 286414
14	98.7025 129.887	183.432 286.294	431.105 771.258
	1461.40 2889.40	5965.92 12975.6	30311.0 78886.0
	245988 1122208		

[a]Even-tempered basis. Optimal parameters: $\alpha=74.77283$, $\beta=1.3131794$.

[b]Even-tempered basis augmented by 12 "steep" functions with parameters β:1.4,1.5,1.6,1.7,1.8,1.9,2.0,2.2,2.4,2.6,3.2,4.6.

TABLE II. Optimization of exponents in the "positive" electronic basis for the ground state of the hydrogenlike ion Fm^{99+} obtained by minimizing the functional $J_0^{(2)}$. $E^{(4)}$ is the fourth-order correction to energy calculated from Eq. (75) with the optimal trial function $\tilde{\varphi}_+^{(2)}$. The function $\chi^{(1)}$ is expanded in the longest basis set, defined in Table I.

N	$J_0^{(2)}$	$E^{(4)}$
4	−186.62752	−207.8448
6	−186.627938	−207.8840
8	−186.62794171	−207.88569
10	−186.627941920	−207.885886
12	−186.6279419295	−207.8859099
14	−186.6279419304	−207.88591101
31[a]	−186.6279419293	−207.885900
43[b]	−186.6279419309	−207.88591126

	optimal α	
4	128.952 214.897 783.188	3142.22
6	124.435 190.524 490.589	1203.70 3508.49 14061.8
8	122.144 176.906 295.435	648.831 1435.76 3541.65
	10302.0 41232.5	
10	121.894 172.552 244.179	495.710 933.386 1901.98
	4214.95 10405.7 30269.1	121108
12	120.885 152.107 194.665	363.134 686.663 1368.29
	2902.49 6577.63 16008.2	42469.7 128870 524825
14	122.042 173.340 235.028	384.483 640.958 1159.27
	2133.75 4056.79 8021.90	16800.7 38137.4 96991.9
	292469 1211424	

[a]Even-tempered basis. Optimal $\beta = 1.2975185$, 4 exponents smaller and 27 exponents greater than $Z = 100$.
[b]Even-tempered basis augmented by 12 "steep" functions with parameters β: 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.3, 2.6, 3.0, 4.2.

obtain a similar accuracy using the even-tempered basis we need a set of 32 functions. We expect that upon adding to this basis appropriate orbitals with rapidly increasing exponents (so-called "steep" functions [20]), which are necessary to describe approximately the singularities at the origin, a similar accuracy will be achieved also for the higher-order corrections to energy.

To explore the optimal character of the basis set for the electron-type functions, the exponents have been optimized in the framework of the variational perturbation method by minimizing the functional $J_0^{(2)}(\tilde{\varphi}_+^{(2)})$. The results for various dimensions of the basis set are presented in Table II. One can see that the structure of exponents is the same as that for the positron-type functions presented in Table I. In order to avoid the linear dependence of the system of linear equations following from the Hylleraas functional, in the case of the even-tempered basis, the zeroth-order function for the ground state

$$\varphi_{1+}^{(0)} = 2Z^{3/2}r \exp(-Zr) \tag{77}$$

was omitted in the even-tempered basis and only the parameter β has been optimized. It can be seen that the effect of

TABLE III. Ground-state energy of the hydrogenlike ion Fm^{99+} calculated in the basis sets of 44 and 43 functions defined in Tables I and II. $\mathcal{E}_{RPT}^{(i)}$ denotes the energy of the regular perturbation approach, $\mathcal{E}^{(i)}$ is the energy of the iteration step i and $\mathcal{E}_{DPT}^{(i)}$ is the exact relativistic energy accurate through $O(c^{-2i})$. Energies are in atomic units with all signs reversed.

i	$\mathcal{E}_{RPT}^{(i)}$	$\mathcal{E}^{(i)}$	$\mathcal{E}_{DPT}^{(i)}$
0	5000	5000	5000
1	5590.936655	5590.936655	5665.642025
2	5798.822567	5774.675783	5842.873747
3	5880.506956	5858.554730	5901.860188
4	5914.171376	5898.250145	5923.847946
5	5928.364264	5918.029356	5932.629532
6	5934.442604	5928.114713	5936.303778
7	5937.081397	5933.344149	5937.893505
8	5938.242299	5936.086046	5938.598964
9	5938.759937	5937.535277	5938.918280
10	5938.993888	5938.305815	5939.065134
11	5939.101036	5938.717348	5939.133560
12	5939.150731	5938.937910	5939.165793
13	5939.174049	5939.056449	5939.181119
14	5939.185106	5939.120298	5939.188464
15	5939.190397	5939.154753	5939.192008
16	5939.192950	5939.173374	5939.193729
17	5939.194190	5939.183450	5939.194570
18	5939.194795	5939.188908	5939.194982
19	5939.195093	5939.191868	5939.195185
20	5939.195240	5939.193474	5939.195285
21	5939.195312	5939.194346	5939.195335
22	5939.195348	5939.194819	5939.195360
23	5939.195366	5939.195077	5939.195372
24	5939.195375	5939.195217	5939.195379
25	5939.195380	5939.195293	5939.195381
∞	5939.195384346	5939.1953844	5939.195384364

including the "steep" functions is now more pronounced than for $E^{(2)}$. According to our numerical experiments the efficiency of "steep" functions increases in higher orders.

To gain insight into the convergence characteristics of the perturbative and iterative approaches we show in Table III the pertinent values of the total relativistic energy (without the rest energy of the electron) calculated at different levels of approximation. For comparison, we display the expansion of the exact relativistic energy

$$E = c^2[(1 - Z^2/c^2)^{1/2} - 1], \tag{78}$$

with respect to c^{-2} (DPT expansion). The $\mathcal{E}_{RPT}^{(i)}$ and $\mathcal{E}_{DPT}^{(i)}$ values are found to exhibit the systematic relations

$$\mathcal{E}_{DPT}^{(i)} < \mathcal{E}_{RPT}^{(i)} < \mathcal{E}_{DPT}^{(i-1)}, \quad i = 1,2,\ldots . \tag{79}$$

The convergence rate is approximately 0.5 implying that one needs between three and four steps to get one decimal place of the relativistic energy. For the iterative approach the convergence is a little slower. Nevertheless we recommend this

TABLE IV. Optimization of the ''positive'' electronic basis for the state $2s_{1/2}$ of the hydrogenlike ion Fm^{99+} by minimizing the functional $J_{02}^{(2)}$. $E^{(4)}$ is the fourth-order correction to energy calculated from Eq. (75) with the optimal trial function $\tilde{\rho}_{2+}^{(2)}$. The function $\chi^{(1)}$ is expanded in the even-tempered basis sets of the type (0,6,28) ($\alpha = 10.117\,02,\ 82.088\,71;\ \ \beta = 1.457\,109\,4,\ 1.394\,676$) augmented by 12 ''steep'' functions defined in Table I.

N	Basis	$J_0^{(2)}$	$E^{(4)}$
4	(0, 1, 3)	-102.9296	-65.999
4	(1, 1, 2)	-102.9319	-66.033
6	(0, 1, 5)	-102.933309	-66.0766
6	(1, 2, 3)	-102.933323	-66.0775
8	(2, 2, 4)	-102.9333549	-66.080606
12	(2, 4, 6)	-102.933356636	-66.0809013
31[a]	(2, 5, 24)	-102.933356657	-66.08090884
43[b]	(2, 5, 36)	-102.933356657	-66.08090933

	optimal α		
4	51.4751 67.5369	141.062 764.762	
4	51.8613 85.8784	193.038 1014.40	
6	50.5631 58.0132	105.060 210.798	829.629 3328.71
6	50.9334 74.4359	169.429 212.355	919.897 3709.75
8	51.0092 59.9192	86.7604 138.844	410.250 1055.32
	3102.10 12456.7		
12	50.8883 60.3937	76.5928 104.729	260.574 403.251
	495.956 1207.89	2672.63 6580.23	19117.7 76457.9

[a]Even-tempered basis. Optimal parameters $\alpha = 36.54693,\ 68.0996,\ 310.5406$; $\beta = 1.3833992,\ 1.3826883,\ 1.3278534$.
[b]Even-tempered basis augmented by 12 ''steep'' functions defined in Table II.

method due to its simplicity in the numerical implementation. At the bottom of Table III we present the infinite order results (for the given basis set and machine accuracy) obtained after 38 steps. The next steps do not change the presented values. One can see that an 11-figure accuracy of the relativistic energy is obtained. Therefore, we can conclude that all ten decimals given for all the lower order values displayed in Table III are correct.

In order to demonstrate the applicability of the method to excited states we have performed perturbation calculations for the $2s_{1/2}$ state, starting from the nonrelativistic wave function

$$\varphi_{2+}^{(0)} = \left(\frac{Z}{2}\right)^{(3/2)} r(2 - Zr)\exp\left(-\frac{Zr}{2}\right). \qquad (80)$$

The initial approximation to $E^{(2)}$ is obtained by expanding the trial function $\chi^{(1)}$ in the basis set $r^n \exp(-\zeta_i r)$ with $n = 1,2$. The nonlinear parameters ζ_i have been optimized in the same manner as for ground state by maximizing the functional $J_0^{(1)}$. The most extensive basis set of six even-tempered functions with $n = 2$ and 28 even-tempered functions with $n = 1$ augmented by 12 ''steep'' functions gives $J_0^{(1)} = 27.311\,337\,641$ ($E^{(2)} = -180.701\,795\,05$) correct to all 11 decimal figures.

TABLE V. The $2s$-state energy of the hydrogenlike ion Fm^{99+} calculated in the basis sets of 46 and 43 functions defined in Table IV. $\mathcal{E}_{RPT}^{(i)}$ denotes the energy obtained in the framework of the regular perturbation approach, $\mathcal{E}^{(i)}$ is the energy of the iteration step i and $\mathcal{E}_{DPT}^{(i)}$ is the exact relativistic energy accurate through $O(c^{-2i})$. Energies are in atomic units with all signs reversed.

i	$\mathcal{E}_{RPT}^{(i)}$	$\mathcal{E}^{(i)}$	$\mathcal{E}_{DPT}^{(i)}$
0	1250	1250	1250
1	1430.701795	1424.526724	1458.013133
2	1496.782704	1483.959459	1516.167291
3	1525.384909	1517.514125	1535936966.
4	1538.247533	1532.275408	1543.394031
5	1544.049536	1539.568887	1546.394835
6	1546.643422	1543.556133	1547.656967
7	1547.787776	1545.782309	1548.205150
8	1548.285434	1547.028685	1548.449128
9	1548.498949	1547.730560	1548.559818
10	1548.589553	1548.128201	1548.610820
11	1548.627746	1548.354406	1548.634621
12	1548.643843	1548.483434	1548.645848
13	1548.650687	1548.557176	1548.651191
14	1548.653652	1548.599387	1548.653755
15	1548.654973	1548.623576	1548.654993
16	1548.655584	1548.637451	1548.655594
17	1548.655877	1548.645415	1548.655889
18	1548.656021	1548.659990	1548.656033
19	1548.656095	1548.652618	1548.656104
20	1548.656132	1548.654129	1548.656139
21	1548.656152	1548.655998	1548.656156
22	1548.656162	1548.655497	1548.656165
23	1548.656167	1548.655785	1548.656169
24	1548.656170	1548.655950	1548.656172
25	1548.656171	1548.656046	1548.656173
∞	1548.6561725	1548.6561749	1548.6561739

Because of the orthogonalization of the trial function $\tilde{\varphi}_{2+}^{(2)}$ to $\varphi_{1+}^{(0)}$ and $\varphi_{2+}^{(0)}$ some attention must be paid to the proper choice of the electron-type basis. The exploratory computations were performed using basis functions with $n = 1$, 2, and 3. The results for different dimensions of the basis set are presented in Table IV. The symbol (n_3, n_2, n_1) is used to denote a basis set comprising n_3 functions with $n = 3$, n_2 functions with $n = 2$, and n_1 functions with $n = 1$. For $N = 4$ and 6 the numerical results are presented for two types of basis sets. One can see from the second part of Table IV that nonrelativistic functions $\varphi_{1+}^{(0)}$ and $\varphi_{2+}^{(0)}$ [Eqs. (77) and (80)] are almost linearly dependent with the basis set (0,1,5). Such a type of basis set should be discarded because of the loss of accuracy. To avoid this problem the basis functions with $n = 3$ and $n = 2$ have been used in the region $\alpha = 50$ and $\alpha = 100$, respectively. The optimal exponents of the $1s$-type orbitals calculated for the excited $2s_{1/2}$ state behave in a similar way as for the ground state. A similar influence of the dimension of the basis set on the accuracy of the results is also observed. The convergence characteristics of

perturbative and iterative approaches is illustrated in Table V. It can be seen that relations (79) are also fulfilled in this case, and that the accuracy of the results is only a little lower than that for the ground state.

We have shown in this paper that accurate relativistic energies for one-electron systems can be obtained in the framework of the regular perturbation theory of relativistic corrections. The main advantage of our perturbation approach is that, irrespective of the type of the basis set used, the Hylleraas variational functionals are, by turns, lower or upper bounds to the exact n-order correction to the energy. Therefore optimal nonlinear parameters may safely be obtained by using the variational method. Although the present calculations have been performed for the hydrogenlike ion it should be noted that the present approach can be applied for any potential.

We hope that our method can be applied to problems of practical interest, e.g., to the description of the hydrogenlike ion in external field. In the case of the spherical symmetry it is enough to construct an appropriate four-component spherical spinor basis set. In the case of the static and uniform electric field the method for constructing the radial basis set is the same as for a single electron in a spherically symmetric potential (see the beginning of this section). However, owing to the mixing of angular momenta the spinors with different Dirac quantum number κ should be included in the basis set. A little more complicated situation is found for a static and uniform magnetic field (see Appendix B).

APPENDIX A: GENERAL RELATIONS FOR HIGH-ORDER CORRECTIONS TO ENERGY

Let us consider the matrix elements of the operator $V - c^2 - E^{(0)}$ with functions of orders appropriate for calculating $E^{(2n)}$ with even n. Using Eqs. (34) and (35) we obtain

$$
\langle \chi_+^{(2k-1)}, (V-c^2-E^{(0)})(\varphi_+^{(2m)}+\chi_+^{(2m-1)}) \rangle
$$

$$
= \langle \chi_+^{(2k+1)}, (V-c^2-E^{(0)})(\varphi_+^{(2m-2)}+\chi_+^{(2m-3)}) \rangle - \sum_{j=0}^{m-1} E^{(2m-2j)}(\langle \varphi_+^{(2k)}, \varphi_+^{(2j)} \rangle) + \langle \varphi_-^{(2k)}, \varphi_-^{(2j-2)} \rangle
$$

$$
+ \langle \chi_+^{(2k+1)}, \chi_+^{(2j-3)} \rangle + \langle \chi_-^{(2k+1)}, \chi_-^{(2j-1)} \rangle) + \sum_{i=0}^{k-1} E^{(2k-2i)}(\langle \varphi_-^{(2i)}, \varphi_-^{(2m-2)} \rangle + \langle \chi_-^{(2i+1)}, \varphi_-^{(2m-2)} \rangle
$$

$$
+ \langle \chi_-^{(2i-1)}, \chi_-^{(2m-1)} \rangle + \langle \varphi_+^{(2i)}, \varphi_+^{(2m)} \rangle + \langle \chi_+^{(2i-1)}, \varphi_+^{(2m)} \rangle + \langle \chi_+^{(2i-1)}, \chi_+^{(2m-1)} \rangle) \tag{A1}
$$

with

$$
k + m = n. \tag{A2}
$$

Treating Eq. (A1) as a difference equation

$$
F(m) = F(m-1) + S(m-1) - S(m), \tag{A3}
$$

we can solve it for $S(m)$ to obtain the following invariant:

$$
F(m) + S(m) = \langle \chi_+^{(2k-1)}, (V-c^2-E^{(0)})(\varphi_+^{(2m)}+\chi_+^{(2m-1)}) \rangle - \sum_{i=0}^{k-2} E^{(2k-2i-2)} \langle \chi_+^{(2i+1)}, (\varphi_+^{(2m)}+\chi_+^{(2m-1)}) \rangle
$$

$$
- \sum_{i=0}^{k-1} \sum_{j=0}^{m} E^{(2n-2i-2j)}(\langle \varphi_+^{(2i)}, \varphi_+^{(2j)} \rangle + \langle \varphi_-^{(2i)}, \varphi_-^{(2j-2)} \rangle + \langle \chi_+^{(2i+1)}, \chi_+^{(2j-3)} \rangle + \langle \chi_-^{(2i+1)}, \chi_-^{(2j-1)} \rangle) = 0. \tag{A4}
$$

The last equality follows from the comparison of $F(0) + S(0)$ with Eq. (37). Letting now $k = m = n/2$ and evaluating $E^{(2n)}$ from Eq. (A4) gives Eq. (39). Similar considerations starting from

$$\langle \varphi_-^{(2k)},(V+c^2-E^{(0)})(\varphi_-^{(2m-2)}+\chi_-^{(2m-1)})\rangle$$

$$=\langle \varphi_-^{(2k+2)},(V+c^2-E^{(0)})(\varphi_-^{(2m-4)}+\chi_-^{(2m-3)})\rangle+\sum_{i=0}^{k}E^{(2k-2i+2)}[\langle \varphi_+^{(2i)},(\varphi_+^{(2m-2)}+\chi_+^{(2m-3)})\rangle$$

$$+\langle \varphi_-^{(2i-2)},(\varphi_-^{(2m-2)}+\chi_-^{(2m-1)})\rangle+\langle \chi_+^{(2i-1)},\chi_+^{(2m-3)}\rangle+\langle \chi_-^{(2i-1)},\chi_-^{(2m-1)}\rangle]-\sum_{j=0}^{m-2}E^{(2m-2j-2)}(\langle \varphi_+^{(2k+2)},\varphi_+^{(2j)}\rangle$$

$$+\langle \varphi_-^{(2k+2)},\varphi_-^{(2j-2)}\rangle+\langle \chi_+^{(2k+1)},\chi_+^{(2j-1)}\rangle+\langle \chi_-^{(2k+1)},\chi_-^{(2j+1)}\rangle) \qquad (A5)$$

lead to the following invariant:

$$\langle \varphi_-^{(2k)},(V+c^2-E^{(0)})(\varphi_-^{(2m-2)}+\chi_-^{(2m-1)})\rangle-\sum_{i=0}^{k-1}E^{(2k-2i)}\langle \varphi_-^{(2i)},\chi_-^{(2m-1)}\rangle+E^{(0)}\langle \varphi_-^{(2k)},\varphi_-^{(2m-2)}\rangle$$

$$-\sum_{i=0}^{k}\sum_{j=0}^{m-1}[E^{(2n-2i-2j-2)}\langle \varphi_-^{(2i)},\varphi_-^{(2j)}\rangle+E^{(2n-2i-2j)}(\langle \varphi_+^{(2i)},\varphi_+^{(2j)}\rangle+\langle \chi_+^{(2i-1)},\chi_+^{(2j-1)}\rangle+\langle \chi_-^{(2i-1)},\chi_-^{(2j+1)}\rangle)]=0,$$

$$(A6)$$

which after setting $k=(n-1)/2$, $m=(n+1)/2$, gives Eq. (40).

APPENDIX B: HYDROGENIC ION IN A STATIC UNIFORM MAGNETIC FIELD

In the magnetic field Eqs. (6) and (7) should be generalized to

$$S^+=\mathcal{T}^{-1}\begin{pmatrix} 2c^2 & c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} & \frac{1}{2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \end{pmatrix}, \qquad (B1)$$

$$S^-=\mathcal{T}^{-1}\begin{pmatrix} \frac{1}{2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\boldsymbol{\sigma}\cdot\boldsymbol{\pi} & -c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} \\ -c\boldsymbol{\sigma}\cdot\boldsymbol{\pi} & 2c^2 \end{pmatrix}, \qquad (B2)$$

where

$$\mathcal{T}=\frac{1}{2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}+2c^2, \qquad \boldsymbol{\pi}=\mathbf{p}+\mathbf{A}. \qquad (B3)$$

The vector potential $\mathbf{A}$ can take the form $\mathbf{A}=\frac{1}{2}\mathbf{B}\times\mathbf{r}$ where $\mathbf{B}=B\hat{\mathbf{z}}$. The projectors S^+ and $S-$ divide the Hilbert space of the four-component spinors into two subspaces

$$S^+\Phi^+=\Phi^+=\begin{pmatrix} \varphi \\ \frac{1}{2c}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\varphi \end{pmatrix}, \qquad (B4)$$

$$S^-\Phi^-=\Phi^-=\begin{pmatrix} -\frac{1}{2c}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\chi \\ \chi \end{pmatrix}, \qquad (B5)$$

$$S^+\Phi^-=S^-\Phi^+=0. \qquad (B6)$$

Rewriting the term

$$c\boldsymbol{\alpha}\cdot\mathbf{A}=\begin{pmatrix} 0 & c\boldsymbol{\sigma}\cdot\mathbf{A} \\ c\boldsymbol{\sigma}\cdot\mathbf{A} & 0 \end{pmatrix}, \qquad (B7)$$

in polar coordinates r,ϑ,φ (see, e.g., [21])

$$\boldsymbol{\sigma}\cdot\mathbf{A}=\frac{1}{2}B\boldsymbol{\sigma}\cdot(\hat{\mathbf{z}}\times\mathbf{r})=\frac{1}{2}B\sigma_\varphi\sin\vartheta, \qquad (B8)$$

we obtain the results of the action of the operator $c\boldsymbol{\alpha}\cdot\mathbf{A}$ on the four-component spinor [22]

$$c\boldsymbol{\alpha}\cdot\mathbf{A}\begin{pmatrix} P \\ Q \end{pmatrix}_\kappa=\frac{crB}{2}\left[\frac{4\kappa\mu}{4\kappa^2-1}\begin{pmatrix} Q \\ P \end{pmatrix}_\kappa-\frac{\kappa-m-1}{2\kappa-1}\begin{pmatrix} Q \\ P \end{pmatrix}_{-\kappa+1}\right.$$

$$\left.+\frac{\kappa+m+1}{2\kappa+1}\begin{pmatrix} Q \\ P \end{pmatrix}_{-\kappa-1}\right], \qquad (B9)$$

where

$$\begin{pmatrix} P \\ Q \end{pmatrix}_\kappa=C_\kappa^{-1}\begin{pmatrix} P(r)\chi_{\kappa,\mu}/r \\ iQ(r)\chi_{-\kappa,\mu}/r \end{pmatrix}, \qquad (B10)$$

$$C_\kappa=\prod_{q=-m}^{m}(|\kappa|+q)^{1/2}, \qquad m=|\mu|-\frac{1}{2}, \qquad (B11)$$

and $\chi_{\kappa,\mu}$ is the two-component spherical spinor in polar coordinates.

Therefore, the basis functions $\Phi^\pm$ [Eqs. (B4) and (B5)], corresponding to projectors $S^\pm$ and the Dirac quantum number κ, can be written as

$$\Phi_\kappa^+ = \left(\begin{array}{c} P \\ \dfrac{1}{2c}\left(\dfrac{d}{dr} + \dfrac{\kappa}{r} + \dfrac{2B\kappa\mu r}{4k^2-1} \right)P \end{array} \right)_\kappa + \frac{rB}{4c}\left[-\frac{\kappa-m-1}{2\kappa-1}\begin{pmatrix} 0 \\ P \end{pmatrix}_{-\kappa+1} + \frac{\kappa+m+1}{2\kappa+1}\begin{pmatrix} 0 \\ P \end{pmatrix}_{-\kappa-1} \right], \qquad (B12)$$

$$\Phi_\kappa^- = \left(\begin{array}{c} \dfrac{1}{2c}\left(\dfrac{d}{dr} - \dfrac{\kappa}{r} - \dfrac{2B\kappa\mu r}{4k^2-1} \right)Q \\ Q \end{array} \right)_\kappa + \frac{rB}{4c}\left[\frac{\kappa-m-1}{2\kappa-1}\begin{pmatrix} Q \\ 0 \end{pmatrix}_{-\kappa+1} - \frac{\kappa+m+1}{2\kappa+1}\begin{pmatrix} Q \\ 0 \end{pmatrix}_{-\kappa-1} \right]. \qquad (B13)$$

In this basis set we can calculate all necessary matrix elements. Let us consider, for example, the element $\langle \chi, T\chi \rangle = \langle \chi, \frac{1}{2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\chi \rangle = \frac{1}{2}\langle \boldsymbol{\sigma}\cdot\boldsymbol{\pi}\chi, \boldsymbol{\sigma}\cdot\boldsymbol{\pi}\chi \rangle$. According to Eq. (B5) we have to deal with scalar products of upper components of the basis functions Φ_κ^- [Eq. (B13)]. Therefore, the radial integrals involved are exactly of the same type as for the spherically symmetric potential. A similar situation occurs for other matrix elements.

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