Accurate solution of the Dirac equation on Lagrange meshes

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(Received 12 February 2014; published 10 April 2014)

The Lagrange-mesh method is an approximate variational method taking the form of equations on a grid because of the use of a Gauss quadrature approximation. With a basis of Lagrange functions involving associated Laguerre polynomials related to the Gauss quadrature, the method is applied to the Dirac equation. The potential may possess a $1/r$ singularity. For hydrogenic atoms, numerically exact energies and wave functions are obtained with small numbers $n+1$ of mesh points, where n is the principal quantum number. Numerically exact mean values of powers -2 to 3 of the radial coordinate r can also be obtained with $n+2$ mesh points. For the Yukawa potential, a 15-digit agreement with benchmark energies of the literature is obtained with 50 or fewer mesh points.

DOI: 10.1103/PhysRevE.89.043305 PACS number(s): 02.70.Hm, 31.15.−p, 03.65.Pm, 02.70.Jn

I. INTRODUCTION

Numerically solving the Dirac equation raises a number of difficulties mostly related to the existence of the Dirac sea. The Dirac equation with a Coulomb potential is of particular interest since the existence of exact analytical results allows precise tests. The variational or Rayleigh-Ritz approximation for the Dirac equation has been discussed in depth by Grant and Quiney [1]. The authors use special spinors based on associated Laguerre polynomials. The B-spline variational or Galerkin method has been applied to the Dirac-Coulomb problem by Froese Fischer and Zatsarinny [2]. An alternative approach is the use of Bernstein B-polynomial basis sets [3], which looks promising for relativistic calculations of atomic properties [4]. The free-complement method also yields accurate results for this problem [5]. Here we use a different numerical method, the Lagrange-mesh method, able to give exact energies and wave functions of this problem up to rounding errors. The exactness of one eigenvalue is not hindered by the much discussed problems of the variational collapse [6,7] and of the kinetic balance of the basis [1,2,7–11].

The Lagrange-mesh method is an approximate variational calculation using a special basis of functions, hereafter called Lagrange functions, related to a set of N mesh points and the Gauss quadrature associated with this mesh [12,13]. It combines the high accuracy of a variational approximation and the simplicity of a calculation on a mesh [14,15]. The Lagrange functions are N infinitely differentiable functions that vanish at all points of this mesh, except one. Used as a variational basis in a quantum-mechanical calculation, the Lagrange functions lead to a simple algebraic system when matrix elements are calculated with the associated Gauss quadrature. The variational equations take the form of mesh equations with a diagonal representation of the potential depending only on values of this potential at the mesh points [12,15]. The most striking property of the Lagrange-mesh method is that, in spite of its simplicity, the obtained energies and wave functions can be as accurate with the Gauss quadrature approximation as in the original variational method with an exact calculation of the matrix elements [14,15]. It has been applied to various problems in atomic and nuclear physics.

Until now, most Lagrange-mesh calculations are nonrelativistic. A semirelativistic approach based on the Salpeter equation has been developed in Refs. [16–18]. Here we show that the Dirac equation allows a simple Lagrange-mesh treatment. In the case of hydrogenic atoms, it even provides numerically exact energies and wave functions, with very low numbers of mesh points. For the Yukawa potential, it can be compared with very accurate benchmark calculations [19].

Some properties of the Dirac equation are recalled in Sec. II. The Lagrange-mesh method is summarized in Sec. III, with emphasis on its adaptation to the Coulomb-Dirac problem. In Sec. IV, numerically exact energies and Dirac spinors are derived for hydrogenic atoms with small numbers of mesh points. Accurate results for the Yukawa potential are obtained and discussed in Sec. V. Section VI is devoted to concluding remarks.

For the fine-structure constant, we use the CODATA 2010 value $1/\alpha = 137.035\,999\,074$ [20].

II. DIRAC EQUATION FOR THE HYDROGEN ATOM

In atomic units $\hbar = m_e = e = 1$, where m_e is the electron mass, the Dirac Hamiltonian reads [21]

$$H_D = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta c^2 + V(r), \tag{1}$$

where $\boldsymbol{p}$ is the momentum operator, V is the potential, and $\boldsymbol{\alpha}$ and β are the traditional Dirac matrices. As the cited works use either atomic units, where the speed of light $c = 1/\alpha$

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is the inverse of the fine-structure constant, or relativistic units, where $c = 1$, we delay the full choice of units till the applications. The eigenenergies of H_D are denoted $c^2 + E$ and the Dirac equation reads

$$H_D\, \phi_{\kappa m}(\boldsymbol{r}) = (c^2 + E)\, \phi_{\kappa m}(\boldsymbol{r}). \tag{2}$$

The Dirac spinors are defined as

$$\phi_{\kappa m}(\boldsymbol{r}) = \frac{1}{r}\begin{pmatrix} P_\kappa(r)\chi_{\kappa m} \\ i\,Q_\kappa(r)\chi_{-\kappa m}\end{pmatrix} \tag{3}$$

as a function of the large and small radial components, $P_\kappa(r)$ and $Q_\kappa(r)$, respectively. The spinors $\chi_{\kappa m}$ are common eigenstates of $\boldsymbol{L}^2$, $\boldsymbol{S}^2$, $\boldsymbol{J}^2$, and J_z, with respective eigenvalues $l(l+1)$, $3/4$, $j(j+1)$, and m, where

$$j = |\kappa| - \tfrac{1}{2}, \quad l = j + \tfrac{1}{2}\,\mathrm{sgn}\,\kappa. \tag{4}$$

The coupled radial Dirac equations read, in matrix form,

$$H_\kappa \begin{pmatrix} P_\kappa(r) \\ Q_\kappa(r)\end{pmatrix} = E\begin{pmatrix} P_\kappa(r) \\ Q_\kappa(r)\end{pmatrix}, \tag{5}$$

with the Hamiltonian matrix

$$H_\kappa = \begin{pmatrix} V(r) & c\left(-\frac{d}{dr} + \frac{\kappa}{r}\right) \\ c\left(\frac{d}{dr} + \frac{\kappa}{r}\right) & V(r) - 2c^2 \end{pmatrix}. \tag{6}$$

The Dirac spinors, (3), are normed if

$$\int_0^\infty \{[P_\kappa(r)]^2 + [Q_\kappa(r)]^2\} dr = 1. \tag{7}$$

We assume that the potential behaves at the origin as

$$V(r) \underset{r\to 0}{\to} -\frac{V_0}{r}, \tag{8}$$

where V_0 is positive or null. At the origin [19,21], the radial functions behave as

$$P_\kappa(r),\ Q_\kappa(r) \underset{r\to 0}{\to} r^\gamma, \tag{9}$$

with the parameter γ defined by

$$\gamma = \sqrt{\kappa^2 - (V_0/c)^2}, \tag{10}$$

i.e., the wave functions $\phi_{\kappa m}$ are singular for $|\kappa| = 1$ if $V_0 \neq 0$. This singularity is weak for the hydrogen atom but can be important for hydrogenic ions with high charges Z or for other potentials.

An important particular case is the relativistic hydrogenic atom, for which the potential is

$$V(r) = -\frac{Z\alpha c}{r}, \tag{11}$$

i.e., $V_0 = Z\alpha c$. As a function of the principal quantum number n, the energies are given analytically as [21]

$$E_{n\kappa} = c^2\left\{\left[1 + \frac{\alpha^2 Z^2}{n - |\kappa| + \gamma}\right]^{-1/2} - 1\right\}. \tag{12}$$

They can be written in a form minimizing rounding errors as

$$E_{n\kappa} = -\frac{(Z\alpha c)^2}{\mathcal{N}(\mathcal{N} + n - |\kappa| + \gamma)}, \tag{13}$$

with the effective principal quantum number

$$\mathcal{N} = [(n - |\kappa| + \gamma)^2 + \alpha^2 Z^2]^{1/2}. \tag{14}$$

This number is equal to n when $|\kappa| = n$.

III. LAGRANGE-MESH METHOD

The mesh points x_j are defined by [12]

$$L_N^{\alpha'}(x_j) = 0, \tag{15}$$

where $j = 1$ to N and $L_N^{\alpha'}$ is a generalized Laguerre polynomial [22]. This mesh is associated with a Gauss quadrature

$$\int_0^\infty g(x)\,dx \approx \sum_{k=1}^N \lambda_k g(x_k), \tag{16}$$

with the weights λ_k. The Gauss quadrature is exact for the Laguerre weight function $x^{\alpha'} e^{-x}$ multiplied by any polynomial of degree, at most, $2N-1$ [23]. The regularized Lagrange functions are defined by [14,15,24]

$$\hat{f}_j(x) = \frac{x}{x_j} f_j(x) = (-1)^j \left(h_N^{\alpha'} x_j\right)^{-1/2} \frac{L_N^{\alpha'}(x)}{x - x_j}\, x^{\alpha'/2+1} e^{-x/2}. \tag{17}$$

In this expression, $f_j(x)$ is a standard Lagrange function [12]. The functions $f_j(x)$ are polynomials of degree $N-1$ multiplied by the square root of the Laguerre weight $x^{\alpha'}\exp(-x)$. The squared norm $h_N^{\alpha'}$ of the generalized Laguerre polynomials reads

$$h_N^{\alpha'} = \frac{\Gamma(N + \alpha' + 1)}{N!}. \tag{18}$$

The Lagrange functions satisfy the Lagrange conditions

$$\hat{f}_j(x_i) = f_j(x_i) = \lambda_i^{-1/2}\delta_{ij}. \tag{19}$$

While the explicit form of the Lagrange functions will be useful to choose the optimal value of α', it does not play any role in the determination of energies and mean values. These functions are useful when the wave functions must be known explicitly.

The nonregularized functions $f_j(x)$ form an orthonormal set satisfying conditions (19) but have the drawback that the matrix elements of d/dx and $1/x$ are not given accurately by the Gauss quadrature because the integrals contain a nonpolynomial factor $1/x$. Though the exact matrix elements are available [25,26], they lead to a variational calculation. The elegant simplicity of the Lagrange-mesh method is lost and singular potentials such as the Yukawa potential cannot be described accurately. For this reason, in the following we use the regularized functions $\hat{f}_j(x)$, for which, as shown below, the Gauss quadrature is exact for matrix elements of d/dx and $1/x$. This basis is, however, not exactly orthonormal [14]:

$$\langle \hat{f}_i | \hat{f}_j \rangle = \delta_{ij} + \frac{(-1)^{i-j}}{\sqrt{x_i x_j}}. \tag{20}$$

Nevertheless, thanks to condition (19), these functions are orthonormal at the Gauss-quadrature approximation denoted by the subscript G,

$$\langle \hat{f}_i|\hat{f}_j\rangle_G = \sum_{k=1}^{N} \lambda_k \lambda_i^{-1/2}\delta_{ik}\lambda_j^{-1/2}\delta_{jk} = \delta_{ij}. \tag{21}$$

In the following, we treat the basis as orthonormal. This apparently rough approximation will be shown to have no effect on the physically interesting eigenvalues and significantly simplifies the calculations.

The matrix elements of d/dx are given at the Gauss approximation by

$$\begin{aligned} D^G_{i\neq j} &= \lambda_i^{1/2}\hat{f}'_j(x_i) = (-1)^{i-j}\sqrt{\frac{x_i}{x_j}}\frac{1}{x_i - x_j}, \\ D^G_{ii} &= \lambda_i^{1/2}\hat{f}'_i(x_i) = \frac{1}{2x_i}. \end{aligned} \tag{22}$$

They are not exact since the integrands $\hat{f}_i\hat{f}'_j$ involve the weight function multiplied by a polynomial of degree $2N$. But $\int_0^\infty \hat{f}_i(\hat{f}'_j + \frac{1}{2}\hat{f}_j)dx$ can be calculated exactly with the Gauss quadrature. With (20), the exact expressions are thus

$$D_{ij} = \langle \hat{f}_i|\frac{d}{dx}|\hat{f}_j\rangle = D^G_{ij} - \frac{(-1)^{i-j}}{2\sqrt{x_i x_j}}, \tag{23}$$

or explicitly,

$$D_{i\neq j} = (-1)^{i-j}\frac{x_i + x_j}{2\sqrt{x_i x_j}(x_i - x_j)}, \quad D_{ii} = 0. \tag{24}$$

This matrix is antisymmetric as expected.

The crucial property of the Lagrange-mesh method is that the potential matrix elements calculated at the Gauss approximation are diagonal:

$$\langle \hat{f}_i|V|\hat{f}_j\rangle_G = \sum_{k=1}^{N}\lambda_k \hat{f}_i(x_k)V(x_k)\hat{f}_j(x_k) = V(x_i)\delta_{ij}. \tag{25}$$

This property also applies to matrix elements of powers of x, for example. Note that the Gauss quadrature is exact for x^{-1} and x^{-2} because the integrand is then a polynomial of degree $2N-1$ or $2N-2$ multiplied by the Laguerre weight function [23].

Let us now apply the method to the Dirac equation. To this end the radial functions $P_\kappa(r)$ and $Q_\kappa(r)$ are expanded in regularized Lagrange functions (17) as

$$P_\kappa(r) = h^{-1/2}\sum_{j=1}^{N} p_j \hat{f}_j^{(\alpha')}(r/h), \tag{26}$$

$$Q_\kappa(r) = h^{-1/2}\sum_{j=1}^{N} q_j \hat{f}_j^{(\alpha')}(r/h), \tag{27}$$

where h is a scaling parameter aimed at adapting the mesh points hx_i to the physical extension of the problem. The superscript added to the Lagrange functions corresponds to the superscript of the generalized Laguerre polynomials in Eq. (17).

Before choosing the parameter α', it is important to first analyze the behavior of the wave functions at the origin. The Lagrange functions, (17), behave as

$$\hat{f}_j^{(\alpha')}(x) \underset{x\to 0}{\to} x^{\alpha'/2+1}. \tag{28}$$

Hence rather than choosing $\alpha' = 0$ as in the nonrelativistic case, it is convenient to choose

$$\alpha' = 2(\gamma - 1). \tag{29}$$

If nonregularized Lagrange functions were used, the optimal choice would be $\alpha' = 2\gamma$ like the one adopted in Refs. [1] and [19] for the B-spline expansions.

Let us introduce expansions (26) and (27) in the coupled radial Dirac equations, (5). A projection on the Lagrange functions leads to the $2N \times 2N$ algebraic system of equations

$$\begin{aligned} &\begin{pmatrix} H^{(1,1)} & H^{(1,2)} \\ H^{(2,1)} & H^{(2,2)} \end{pmatrix}\begin{pmatrix} (p_1,p_2,\ldots,p_N)^T \\ (q_1,q_2,\ldots,q_N)^T \end{pmatrix} \\ &\quad = E\begin{pmatrix} (p_1,p_2,\ldots,p_N)^T \\ (q_1,q_2,\ldots,q_N)^T \end{pmatrix}, \end{aligned} \tag{30}$$

where T means transposition. Note that, thanks to the Gauss approximation, (21), on the scalar product of Lagrange functions, the energies are simply given by the eigenvalues of the Hamiltonian matrix. According to (21) and (25), the diagonal $N \times N$ blocks read

$$H^{(1,1)}_{ij} = V(hx_i)\delta_{ij}, \quad H^{(2,2)}_{ij} = (V(hx_i) - 2c^2)\delta_{ij}. \tag{31}$$

For the nondiagonal blocks, the term $c\kappa/r$ is given exactly by the Gauss quadrature and is diagonal. For the matrix elements of the first derivative d/dr, several options are possible. One can use the exact expressions, (24), or use the Gauss approximation in the spirit of the Lagrange-mesh method. The exact representation of d/dr is antisymmetric, as it should be, and leads to a symmetric Hamiltonian matrix. It is thus more instructive to exemplify the case of the Gauss quadrature because the matrix representation of d/dr is not antisymmetric. One must impose the symmetry of the Hamiltonian matrix. Thus, the Gauss quadrature is used either in block (2,1) or in block (1,2) and the remaining block is constructed by symmetry. Choosing the Gauss quadrature in (2,1), one obtains

$$H^{(2,1)}_{ij} = \frac{c}{h}\left(D^G_{ij} + \frac{\kappa}{x_i}\delta_{ij}\right), \quad H^{(1,2)}_{ij} = H^{(2,1)}_{ji}, \tag{32}$$

where D^G_{ij} is given by (22). Choosing (1,2), one obtains

$$H^{(1,2)}_{ij} = \frac{c}{h}\left(-D^G_{ij} + \frac{\kappa}{x_i}\delta_{ij}\right), \quad H^{(2,1)}_{ij} = H^{(1,2)}_{ji}, \tag{33}$$

which is different. As we shall see in Sec. IV, using the Gauss approximations leads to negligible differences with respect to using the exact expression.

The norm, (7), is calculated with the Gauss quadrature as

$$\sum_{i=1}^{N}\left(p_i^2 + q_i^2\right) = 1. \tag{34}$$

Hence normed solutions of the algebraic system (30) provide the coefficients of expansions (26) and (27) of the large and small components. As explained below, in the hydrogenic cases, Eq. (34) is numerically exact.

TABLE I. Eigenvalues E_i of the $\kappa = -1$ Hamiltonian matrix in Eq. (30) for a hydrogen atom with $N = 2$ and $N = 3$ mesh points for $\alpha' = -5.325\,206\,347\,372\,990 \times 10^{-5}$ and the optimal value, (35), of h. Three cases are considered: Gauss approximation in block (2,1) [Eq. (32)], Gauss approximation in block (1,2) [Eq. (33)], and exact values of the matrix elements D_{ij} [Eq. (24)].

E_i	Gauss (2,1)	Gauss (1,2)	D_{ij} exact
		$1s_{1/2}$ with $N = 2$ and $h = 0.5$	
E_1	−37 563.230 370 668 45	−37 575.711 442 013 92	−37 567.701 964 573 92
E_2	−37 559.230 157 644 22	−37 558.744 829 570 28	−37 558.757 978 194 24
E_3	−0.500 059 907 242 439	−0.500 006 656 596 554	−0.500 006 656 596 554
E_4	−0.500 006 656 596 554	11.495 683 364 290 550	3.499 354 548 250 311
		$1s_{1/2}$ with $N = 3$ and $h = 0.5$	
E_1	−37 567.746 725 519 26	−37 592.568 729 228 42	−37 576.149 599 781 89
E_2	−37560.389 012 315 35	−37559.894 106 141 27	−37559.764 941 574 49
E_3	−37558.554 602 146 43	−37558.206 770 665 09	−37558.272 506 313 43
E_4	−0.500 006 656 596 554	−0.500 006 656 596 553	−0.500 006 656 596 554
E_5	−0.258 320 031 170 988	0.132 065 036 600 383	0.070 690 172 696 772
E_6	2.257 774 354 082 858	25.846 655 340 028 450	9.425 471 838 916 183
		$2s_{1/2}$ with $N = 3$ and $h = 0.999\,993\,343\,469\,911\,1$	
E_1	−37 561.226 230 747 84	−37 567.646 697 995 70	−37 563.503 884 007 47
E_2	−37 558.801 380 244 41	−37 558.489 260 768 74	−37 558.480 608 772 83
E_3	−37 558.037 978 852 44	−37 557.928 899 204 34	−37 557.956 069 204 32
E_4	−0.739 366 695 081 362	−0.467 715 743 773 135	−0.488 828 609 075 186
E_5	−0.260 654 106 967 512	−0.125 002 080 189 192	−0.125 002 080 189 192
E_6	−0.125 002 080 189 193	5.466 963 065 804 257	1.363 779 946 938 871

IV. HYDROGENIC ATOMS

We first consider the Dirac-Coulomb problem in atomic units, where $V(r) = -Z/r$. With N mesh points, the eigenvalues and eigenvectors of the $2N \times 2N$ Hamiltonian matrix, (30), provide the relativistic energies and the coefficients of expansions (26) and (27) of the wave functions. Given the block structure, (31), of the mesh equations, one expects to obtain N large negative eigenvalues with an order of magnitude close to $-2c^2 = -37\,557.730\,084\,418\,65$. The remaining N eigenvalues should lie much higher in the spectrum, i.e., at far less negative (or positive) values. If the eigenvalues are ordered by increasing values, the $(N+1)$th eigenvalue should approximate the lowest physical energy of the chosen partial wave and the following ones should approximate the energies of excited states.

With α' given by (29) and the choice

$$h = \mathcal{N}/2Z, \tag{35}$$

the Lagrange-Laguerre expansions, (26) and (27), are able to perfectly reproduce the exact eigenfunctions. One of these eigenvalues can even give the numerically exact result for the level $n\kappa$ if $N > n - |\kappa| + 1$. Indeed, in this case, the large and small radial functions $P_{n\kappa}$ and $Q_{n\kappa}$ are polynomials of degree $n - |\kappa|$ multiplied by r^γ and an exponential $\exp(-Zr/\mathcal{N})$. Moreover, the matrix elements of the Hamiltonian between these components are exactly given by the Gauss-Laguerre quadrature *even if this quadrature is not exact for individual matrix elements* D^G_{ij}. Let us start by testing the ground-state energy with $N = 2$, scaling parameter $h = 0.5$, and $\alpha' = -5.325\,206\,347\,372\,990 \times 10^{-5}$. The two mesh points are given by Eq. (15), i.e.,

$$x_{1,2} = 2\gamma \mp \sqrt{2\gamma}. \tag{36}$$

The four eigenvalues are listed in Table I for three ways of treating the first derivative: (i) Gauss approximation (32) on block (2,1); (ii) Gauss approximation (33) on block (1,2); and (iii) exact expression, (24), of D_{ij} immediately leading to a symmetric matrix. In each case, one obtains two eigenvalues below $-2c^2$ as expected. They correspond to pseudostates in the Dirac sea. One of the other two eigenvalues is *identical* (with 15 digits!) in the three cases. However, in case (i), a spurious eigenvalue E_3 appears just below the physical eigenvalue E_4. In the other two cases, the physical eigenvalue is E_3. Anyway, this is probably the simplest numerical calculation providing 15 significant figures for the ground-state energy of the relativistic hydrogen atom. At any r value, the Lagrange-mesh functions P_{1s} and Q_{1s} given by (26) and (27) differ from the exact ones only by the tiny rounding errors on the four coefficients p_1, p_2 and q_1, q_2, which are the components of the eigenvector corresponding to the physical eigenvalue. These properties remain true for all hydrogenic ions.

The spurious eigenvalue probably has two origins. First, the present basis does not satisfy the property of kinetic balance [1,2,8]. Second, the Gauss approximation is not exact, at least for the overlap of Lagrange functions, and introduces an error even when exact values of the D_{ij} are used. The differences among the three calculations indicate that the spurious eigenvalue is mainly due here to the Gauss approximation. This is confirmed by a variational calculation using the same regularized Lagrange-Laguerre basis, i.e., a calculation with the exact matrix elements D_{ij} and the exact overlaps $\langle \hat{f}_i | \hat{f}_j \rangle$ given by Eq. (20). The resulting generalized eigenvalue problem provides the same exact value E_3 as in Table I and $E_4 \approx 1.166\,451\,5$. Since we are interested in a single eigenvalue which is exact, the existence of spurious eigenvalues is not a big problem. They can easily be detected

TABLE II. Regularized Lagrange-Laguerre-mesh calculations of $n \leqslant 3$ energies of the relativistic $Z = 1$ hydrogen atom and $Z = 100$ hydrogenic ion calculated for given N and h values, for the optimal value, (29), of α' and for $\alpha' = 0$ ($c = 137.035\,999\,074$). The exact energies are identical to the values obtained with $\alpha' = 2\gamma - 2$, except for possibly one or two units on the last displayed digit.

nlj	κ	h	N	$E_{n\kappa}$ ($\alpha' = 2\gamma - 2$)	N	$E_{n\kappa}$ ($\alpha' = 0$)
				$Z = 1$		
$1s_{1/2}$	-1	0.5	3	$-0.500\,006\,656\,596\,554$	3	$-0.500\,006\,656\,714\,711$
$2s_{1/2}$	-1	1	5	$-0.125\,002\,080\,189\,192$	5	$-0.125\,002\,080\,208\,393$
$2p_{1/2}$	$+1$	1	4	$-0.125\,002\,080\,189\,192$	4	$-0.125\,002\,080\,192\,885$
$2p_{3/2}$	-2	1	4	$-0.125\,000\,416\,028\,976$	4	$-0.125\,000\,416\,029\,900$
$3s_{1/2}$	-1	1	7	$-0.055\,556\,295\,176\,422$	7	$-0.055\,556\,295\,182\,736$
$3p_{1/2}$	$+1$	1.5	5	$-0.055\,556\,295\,176\,422$	5	$-0.055\,556\,295\,195\,238$
$3p_{3/2}$	-2	1.5	5	$-0.055\,555\,802\,091\,367$	5	$-0.055\,555\,802\,096\,072$
$3d_{3/2}$	$+2$	1.5	5	$-0.055\,555\,802\,091\,367$	5	$-0.055\,555\,802\,091\,398$
$3d_{5/2}$	-3	1.5	5	$-0.055\,555\,637\,733\,815$	5	$-0.055\,555\,637\,733\,829$
				$Z = 100$		
$1s_{1/2}$	-1	0.005	3	$-5939.195\,192\,426\,652$	100	-5932.765
$2s_{1/2}$	-1	0.009 175	5	$-1548.656\,111\,829\,165$	100	-1545.707
$2p_{1/2}$	$+1$	0.009 175	4	$-1548.656\,111\,829\,167$	100	-1548.567
$2p_{3/2}$	-2	0.010	4	$-1294.626\,149\,195\,190$	100	$-1294.626\,143$
$3s_{1/2}$	-1	0.013 906	7	$-657.945\,199\,521\,658\,9$	100	-656.436
$3p_{1/2}$	$+1$	0.013 906	5	$-657.945\,199\,521\,658\,8$	100	-657.890
$3p_{3/2}$	-2	0.014 768	5	$-582.139\,046\,840\,141\,8$	100	$-582.139\,036$
$3d_{3/2}$	$+2$	0.014 768	5	$-582.139\,046\,840\,141\,9$	100	$-582.139\,046\,829$
$3d_{5/2}$	-3	0.015	5	$-564.025\,853\,485\,845\,0$	100	$-564.025\,853\,485\,675$

by their instability when increasing the number of mesh points.

When N increases to 3, three values are below $-2c^2$ and the physical eigenvalue is E_4 in the three cases. Note that while E_4 is almost identical, the other eigenvalues are quite different and meaningless. If one chooses $h = 0.999\,993\,343\,469\,911\,1$ with $N = 3$ in agreement with Eq. (35), an eigenvalue becomes exactly equal to the $2s_{1/2}$ energy in the three cases, though the rounding errors may be slightly different. It is E_5 for (ii) and (iii) but E_6 for (i). Note that when h is rounded to 0.999 993 3, the physical eigenvalue does not change but the other ones can be significantly modified.

Although the variational calculation with Lagrange functions does not present difficulties, it is less simple than a Lagrange-mesh calculation because of the nondiagonal overlap matrix of basis functions. The fact that the eigenvalue problem is generalized may even lead to additional rounding errors when N is large. Since the simpler Lagrange-mesh method gives the same exact energies and wave functions, in the rest of the paper we only use this method with the Gauss quadrature on block (2,1).

The energies of the $n \leqslant 3$ levels are listed in Table II for the cases $Z = 1$ and $Z = 100$. The calculations are performed with small numbers N of mesh points, i.e., $N = n + 2$, except for s states ($n > 1$), where a slightly larger value is used to move a spurious eigenvalue to higher energies. With these choices, mean values of powers r^k of the coordinate can be calculated exactly from $k = -2$ to 3 as explained below. The first $E_{n\kappa}$ column contains energies obtained with the optimal α' defined in Eq. (29). These energies coincide with the exact ones, (13), except possibly for one or two units on the last displayed digit. For $Z = 1$, the energies are shown as obtained with $h = n/2Z$, but calculations with the optimal value, (35), lead to exactly the same displayed digits because the difference between the h values is smaller than 10^{-5}. Note that exactly degenerate energies are obtained despite the fact that the meshes are quite different because of different α' and/or N values. As in most other applications of the Lagrange-mesh method, the results are not very sensitive to the precise choice of h. Nevertheless, at some higher accuracy level, multiprecision calculations aiming at more digits should be made with (35) to provide the exact values.

For $Z = 100$, the results are computed for the displayed truncated value of the optimal h given by (35) since the dropped digits do not affect the significant digits of the physical energies. The accuracy remains excellent. Tiny differences appear between theoretically degenerate values. The relative error with the nonrelativistic value $h = n/2Z$ is about 10^{-10}.

The last column in Table II lists calculations with standard Laguerre polynomials ($\alpha' = 0$). For $Z = 1$, the relative difference from the fourth-column values is tiny when the same number of mesh points is kept. It decreases from about 2×10^{-9} to 3×10^{-13} when $|\kappa|$ increases. The singularity induced by the difference between γ and $|\kappa|$ is weak. For $Z = 100$ with the same N, the results are very bad (not shown). Even with the much larger $N = 100$ value, the accuracy remains poor except when $|\kappa|$ is large, i.e., when α' gets closer to an integer value that $\alpha' = 0$ can better simulate. For $|\kappa| = 1$, the relative error is larger than 10^{-3}. For large Z values, a correct treatment of the singularity is crucial, as expected.

The high accuracy obtained in Table II is not restricted to small n values. Some energies for $n = 30$ obtained with

TABLE III. Regularized Lagrange-Laguerre-mesh calculations of some $n = 30$ energies of the relativistic hydrogen atom ($Z = 1$) and hydrogenic fermium ion ($Z = 100$) for $N = 32$ and optimal parameters $\alpha' = 2\gamma - 2$ and $h = \mathcal{N}/2Z$. The relative errors ϵ listed depend on the code implementation but are given for information. Powers of 10 are indicated in brackets.

κ	α'	h	N	$E_{n\kappa}$	ϵ
		$Z = 1$ ($n = 30$)			
−1	−5.325 206 347 372 990[−5]	14.999 987 1	32	−0.000 555 556 517 052 700 9	2.2[−16]
+1				−0.000 555 556 517 052 702 9	3.8[−15]
−2	1.999 973 374 234 119	14.999 993 8		−0.000 555 556 023 972 175 9	2.0[−15]
−29	55.999 998 163 746 37	15.000 000 0		−0.000 555 555 564 906 847 1	−4.4[−16]
+29				−0.000 555 555 564 906 847 5	4.4[−16]
−30	57.999 998 224 954 82	15		−0.000 555 555 563 773 357 4	0
		$Z = 100$ ($n = 30$)			
−1	−0.632 540 377 608 241 9	0.148 463 49	32	−5.672 000 589 766 628	2.0[−15]
+1				−5.672 000 589 766 619	4.4[−16]
−2	1.724 237 615 790 889	0.149 355 17		−5.604 466 953 036 355	2.4[−15]
−29	55.981 634 556 287 49	0.149 998 47		−5.556 490 981 728 510	−2.4[−15]
+29				−5.556 490 981 728 514	−1.8[−15]
−30	57.982 246 922 059 13	0.15		−5.556 377 578 924 101	−3.0[−15]

$N = 32$ mesh points are listed in Table III. The values of α' and h are also given. The last column contains the relative error ϵ with respect to the exact value, (13). This error depends on the code implementation and may vary from one calculation to another as well as the last one or two digits of $E_{n\kappa}$. Here, for low $|\kappa|$ values, a spurious eigenvalue appears below the energy listed in Table III. In some cases, it is probably related to the problem discussed in Refs. [1,2], and [8–11], i.e., the fact that the basis does not satisfy the kinetic-balance criterion, because it also occurs in the corresponding variational calculation. In the other cases, it disappears when the Gauss approximation is not used. Finally, let us note the large variation of α' values as a function of $|\kappa|$. This can be avoided by using

$$\alpha' = 2(\gamma - |\kappa|) \tag{37}$$

rather than (29). The meshes are then much more similar for all κ values. The correct behavior, (9), at the origin can still be simulated with a corresponding increase in the number N of mesh points depending on n rather than on $n - |\kappa|$. The accuracy of the results does not change much with this modification.

Tables II and III show that the present method can provide numerically exact energies. The same is true for the corresponding wave functions, as it can be realized from the calculation of the mean values of powers of r. With $N \geqslant n - |\kappa| + 3$, the obtained wave functions and the corresponding Gauss quadrature lead to the exact mean values for the operators r^{-2}, r^{-1}, r, r^2, and r^3 with

$$\langle r^k \rangle_{n\kappa} = \langle \phi_{n\kappa m} | r^k | \phi_{n\kappa m} \rangle = h^k \sum_{i=1}^{N} \left(p_{n\kappa i}^2 + q_{n\kappa i}^2\right) x_i^k. \tag{38}$$

Indeed, the integrand of the exact matrix element is the weight function times a polynomial of degree $2n - 2|\kappa| + k + 2$. The Gauss quadrature is exact for $2N - 1 \geqslant 2n - 2|\kappa| + k + 2$ or $0 \leqslant k \leqslant 2(N - n + |\kappa|) - 3$. This is thus also valid for the norm (34). Thanks to the regularization, the integrand contains a factor r^{k+2} and the integral is also exact for the negative powers $k = -1$ and -2. The exact mean values of higher positive integer powers of r can also be obtained, but with increasing numbers N of mesh points.

Mean values obtained with the conditions in Table II for the optimal α' and h are listed in Table IV. For $k = -2, -1, 1$, and 2, the numerical results agree with analytical expressions from Table 3.2 in Ref. [21] or from Ref. [27]. If the Gauss quadrature is performed on block (1,2) rather than on block (2,1), the mean values are closer to the exact ones for $2p_{1/2}$ and $2p_{3/2}$ but they are slightly less good for $1s_{1/2}$ and $2s_{1/2}$.

All results until now have been obtained with h values varying from shell to shell and, sometimes, from level to level. Several highly accurate eigenvalues can also be obtained simultaneously with a single h value per partial wave or for all partial waves. Relative errors on the nine lowest energies are listed in Table V with $N = 30$ mesh points and some average scaling parameter depending on κ. At least six eigenvalues simultaneously have a relative accuracy better than 10^{-10} for the various partial waves. The worst case is $\kappa = -1$ because of the large range of binding energies and thus the large range of asymptotic exponential decreases which must be simulated with a single h. Precise results with a single value of h for all partial waves can be obtained with larger N values. With $N = 50$ and $h = 3$, the number of eigenvalues with an accuracy better than 10^{-10} increases to at least 10 in all the $|\kappa| = 1 - 3$ partial waves. With $N = 100$ and $h = 5.5$, this number rises to at least 25.

V. YUKAWA POTENTIAL

Benchmark values with a 40-digit accuracy are given in Ref. [19] for selected Yukawa potentials:

$$V(r) = -V_0 \frac{e^{-\lambda r}}{r}. \tag{39}$$

We choose some of them to test the Lagrange-mesh method in that case. Switching to the Yukawa potential requires only changing the potential values $V(hx_i)$ in the Hamiltonian matrix [see Eq. (25)]. The system of units is now $\hbar = m = c = 1$.

TABLE IV. Lagrange-mesh calculations of the mean values $\langle (Zr)^k \rangle$ ($k = -2$ to $k = 3$) for the Dirac hydrogen atom and hydrogenic fermium ion with $N = 3$ ($1s_{1/2}$), $N = 4$ ($2p_{1/2}$ and $2p_{3/2}$), and $N = 5$ ($2s_{1/2}$) mesh points.

k	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$
		$Z = 1$		
−2	2.000 159 766 116 231	0.250 028 292 269 074	0.083 342 024 388 253	0.083 334 627 656 595
[27]	2.000 159 766 116 226	0.250 028 292 269 074	0.083 342 024 388 253	0.083 334 627 656 577
−1	1.000 026 626 740 701	0.250 008 320 873 086	0.250 008 320 873 087	0.250 001 664 121 470
[21]	1.000 026 626 740 701	0.250 008 320 873 086	0.250 008 320 873 086	0.250 001 664 121 445
1	1.499 973 373 968 263	5.999 883 511 521 008	4.999 883 511 520 941	4.999 973 374 233 225
[21]	1.499 973 373 968 263	5.999 883 511 521 012	4.999 883 511 521 012	4.999 973 374 234 120
2	2.999 906 809 597 867	41.998 495 647 329 15	29.998 735 280 816 32	29.999 707 117 268 71
[21]	2.999 906 809 597 866	41.998 495 647 329 22	29.998 735 280 817 29	29.999 707 117 284 25
3	7.499 687 148 380 748	329.983 239 243 076 3	209.987 712 361 100 8	209.997 151 055 590 1
		$Z = 100$		
−2	7.960 417 675 192 373	1.542 632 708 400 137	0.454 380 205 317 436	0.098 563 843 941 060 1
[27]	7.960 417 675 192 391	1.542 632 708 400 123	0.454 380 205 317 370	0.098 563 843 941 060 0
−1	1.462 566 036 503 436	0.398 505 472 652 605	0.398 505 472 652 623	0.268 511 331 221 178 9
[21]	1.462 566 036 503 437	0.398 505 472 652 604	0.398 505 472 652 604	0.268 511 331 221 178 6
1	1.183 729 811 195 878	4.675 861 781 113 669	3.675 861 781 113 592	4.724 237 615 790 892
[21]	1.183 729 811 195 879	4.675 861 781 113 673	3.675 861 781 113 673	4.724 237 615 790 889
2	1.993 081 171 511 766	26.562 706 733 046 36	17.293 451 206 471 90	27.042 658 666 244 49
[21]	1.993 081 171 511 771	26.562 706 733 046 46	17.293 451 206 472 39	27.042 658 666 244 48
3	4.352 350 770 363 447	172.545 557 666 531 8	98.256 482 525 922 66	181.84 126 263 455 46

Potential (39) has the singular behavior, (8), at the origin. The parameter γ is thus given by Eq. (10) and α' is chosen according to Eq. (29). The scaling parameter h and the number N of mesh points are adjusted for each potential according to the requested goals. Here we want to reproduce simultaneously all the energies listed in Table 9 in Ref. [19] for a given symmetry within the double-precision accuracy. This can be achieved with $N = 40$ or 50 and an appropriate h value.

Table VI lists the energies $c^2 + E_{n\kappa}$ for two cases: $\lambda = 0.01$ and $V_0 = 0.1$ (corresponding to $\lambda \approx 1.37$ and $V_0 \approx 13.7$ in a.u.) and $\lambda = 0.04$ and $V_0 = 0.7$ (corresponding to $\lambda \approx 5.48$ and $V_0 \approx 95.9$ in a.u.). For the first, shallower potential, $h = 16$ is a good compromise for a simultaneous treatment of the three $\kappa = -1$ lowest bound states. With $N = 30$, the energies of these states perfectly reproduce the benchmark values rounded to 15 digits. However, the listed results are obtained with $N = 40$ to improve the wave functions and the mean values discussed below. We do not find any other bound state. Under the same conditions, the $\kappa = 1$ and -2 energies are also perfect. It should be noted that a similar quality of energies can be obtained with far fewer mesh points when each state is studied separately. The same ground-state energy is obtained with only eight mesh points for $h = 4.5$–5. The first excited $\kappa = -1$ energy is obtained with $N = 14$ and $h \approx 10$. The energies of the $\kappa = 1$ and -2 levels can also be as accurate with fewer mesh points.

For the second, deeper potential, the calculations are performed with $N = 50$ and $h = 2$. Here also a 15-digit accuracy is reached under these conditions. For the ground state, with $h = 1$, $N = 10$ would be enough to get the same digits. For $h = 1.2$, $N = 12$ is enough for the first excited level. With $N = 50$ and $h = 2$, one observes the existence of two additional negative energies. The energy of the third excited level is obtained with the same accuracy, as shown by a comparison with $N = 60$. The presence of a fifth slightly negative energy gives some indication of the possible existence of a very weakly bound fourth excited level but we could not reach convergence by increasing N and h. For $\kappa = 1$ and -2

TABLE V. Relative errors on Lagrange-mesh calculations of the nine lowest energies of a calculation with $N = 30$ and the optimal α' for the Dirac hydrogen atom with $|\kappa| = 1 - 3$. Powers of 10 are indicated in brackets.

$n - l - 1$	$s_{1/2}$ ($h = 1.5$)	$p_{1/2}$ ($h = 2.5$)	$p_{3/2}$ ($h = 2.5$)	$d_{3/2}$ ($h = 3.5$)	$d_{5/2}$ ($h = 4$)	$f_{5/2}$ ($h = 4.5$)
0	−2.7[−15]	−3.0[−14]	−2.1[−14]	−1.8[−14]	2.7[−15]	−1.4[−14]
1	−2.8[−14]	−2.3[−14]	−2.2[−14]	−1.4[−14]	−1.2[−14]	−8.5[−15]
2	−3.4[−13]	−1.6[−14]	−2.0[−14]	−1.1[−14]	−8.9[−15]	−6.9[−15]
3	−1.1[−13]	−1.3[−14]	−1.4[−14]	−8.2[−15]	−5.9[−15]	−5.7[−15]
4	2.5[−13]	−9.8[−15]	−6.2[−15]	−4.8[−15]	−7.7[−15]	−4.9[−15]
5	2.3[−12]	−7.0[−15]	−2.6[−15]	−4.9[−15]	−6.9[−15]	−1.4[−15]
6	2.5[−07]	−2.7[−15]	−1.8[−15]	−2.0[−15]	−5.9[−15]	−2.6[−15]
7	6.6[−04]	8.9[−10]	1.5[−10]	−1.2[−15]	−4.7[−15]	−3.8[−15]
8	7.5[−02]	7.6[−06]	1.8[−06]	2.3[−11]	−5.7[−15]	−2.3[−15]

TABLE VI. Regularized Lagrange-Laguerre-mesh energies of Yukawa potentials ($c = 1$). Comparison with the benchmark results in Ref. [19] rounded to 17 digits.

n	κ	$1 + E_{n\kappa}$	Ref. [19]
		$\lambda = 0.01$, $V_0 = 0.1$ ($N = 40$, $h = 16$)	
0	−1	0.995 917 081 971 152	0.995 917 081 971 151 89
1		0.999 497 559 778 376	0.999 497 559 778 375 46
2		0.999 967 446 168 861	0.999 967 446 168 860 68
0	1	0.999 531 550 432 223	0.999 531 550 432 222 89
1		0.999 983 717 932 084	0.999 983 717 932 084 17
0	−2	0.999 534 057 514 086	0.999 534 057 514 085 53
1		0.999 983 995 560 747	0.999 983 995 560 747 02
		$\lambda = 0.04$, $V_0 = 0.7$ ($N = 50$, $h = 2$)	
0	−1	0.741 201 083 823 740	0.741 201 083 823 739 90
1		0.950 294 103 969 378	0.950 294 103 969 378 01
2		0.988 794 022 128 970	0.988 794 022 128 970 38
3		0.998 408 251 840 772	
0	1	0.950 966 326 753 638	0.950 966 326 753 637 53
1		0.989 310 801 129 036	0.989 310 801 129 036 00
2		0.998 718 627 536 472	
0	−2	0.961 282 015 004 946	0.961 282 015 004 946 09
1		0.991 803 837 230 717	0.991 803 837 230 717 12
2		0.999 249 454 384 587	

also, an additional excited level is obtained with high accuracy under the same conditions.

To test the wave functions, we have computed the mean values of $1/r$, r, and r^2 using the same conditions as in Table VI. The corresponding results are reported in Table VII. The significant digits of $\langle r^{-1}\rangle$ are estimated by a comparison with $N = 60$. The error is of a few units on the last displayed digit. The other two cases can be compared with results rounded from Table 10 in Ref. [19]. For both potentials, one observes that about 14 figures are significant. Not only the energies but also the wave functions are highly accurate in these calculations.

TABLE VII. Regularized Lagrange-Laguerre-mesh calculation of mean values $\langle r^k\rangle$ for Yukawa potentials with $\kappa = -1$ ($c = 1$). Comparison with the benchmark results in Ref. [19] rounded to 17 digits.

n		$\langle r^k\rangle$	Ref. [19]
		$\lambda = 0.01$, $V_0 = 0.1$ ($N = 40$, $h = 16$)	
0	$\langle r^{-1}\rangle$	0.099 831 872 209 1	
	$\langle r\rangle$	15.082 434 128 862 93	15.082 434 128 863 035
	$\langle r^2\rangle$	304.188 886 493 121 4	304.188 886 493 124 41
1	$\langle r^{-1}\rangle$	0.022 947 496 790 515	
	$\langle r\rangle$	65.043 195 737 250 43	65.043 195 737 250 814
	$\langle r^2\rangle$	4980.632 803 277 178	4980.632 803 277 221 3
2	$\langle r^{-1}\rangle$	0.006 923 052 889 159	
	$\langle r\rangle$	205.370 791 289 550	205.370 791 289 537 01
	$\langle r^2\rangle$	49 369.953 038 660	49 369.953 038 651 105
		$\lambda = 0.04$, $V_0 = 0.7$ ($N = 50$, $h = 2$)	
0	$\langle r^{-1}\rangle$	0.978 144 673 350 53	
	$\langle r\rangle$	1.739 045 717 021 701	1.739 045 717 021 736 8
	$\langle r^2\rangle$	4.271 937 620 831 649	4.271 937 620 831 734 4
1	$\langle r^{-1}\rangle$	0.257 425 108 303 809	
	$\langle r\rangle$	7.020 340 332 559 71	7.020 340 332 559 795 9
	$\langle r^2\rangle$	59.711 051 926 518 6	59.711 051 926 519 476
2	$\langle r^{-1}\rangle$	0.094 765 809 000 015	
	$\langle r\rangle$	18.075 446 620 468 82	18.075 446 620 468 967
	$\langle r^2\rangle$	377.461 035 916 263	377.461 035 916 266 38
3	$\langle r^{-1}\rangle$	0.037 265 655 938 1	
	$\langle r\rangle$	41.739 979 834 114 5	
	$\langle r^2\rangle$	1982.037 553 539 72	

A more stringent test of wave functions would be given by the calculation of polarizabilities. For the nonrelativistic hydrogen atom, numerically exact polarizabilities can be found with the Lagrange-mesh method for small numbers of mesh points [28]. Work is in progress to extend this study to the relativistic case, for which very accurate values are available for comparison [29].

The present method is expected to be very accurate for all properties of a single particle described by Dirac equations with various potentials. This includes taking account of the finite extension of the nucleus, evaluating two-photon transition probabilities, and studying the scattering by some potential. An extension to two-electron atoms should also be accurate if treated in perimetric coordinates [30]. A big challenge is to extend the method with accuracy to polyelectronic atoms where several Coulomb singular terms appear. A simultaneous regularization of several singularities is not available at present. A hybrid treatment may be feasible involving Lagrange functions but where the associated Gauss quadrature is replaced by another numerical technique for the computation of the matrix elements of the Coulomb repulsion between electrons.

VI. CONCLUSION

For the first time, the Lagrange-mesh method is applied to the Dirac equation. The choice of mesh points takes precisely into account a possible singularity of the potential. A scaling parameter allows adjusting the mesh to the extension of the physical problem.

For the exactly solvable Coulomb-Dirac problem describing hydrogenic atoms, numerically exact results, i.e., exact up to rounding errors, are obtained for any state and for any nuclear charge with very small numbers of mesh points. Only two points are enough to get the exact energy and wave function of the ground state. With a slightly larger number of points, mean values of a number of powers of the coordinate are also obtained exactly with the Gauss quadrature.

Tests with the Yukawa potential provide very accurate results, with a number of mesh points for which the computation seems instantaneous. The approximate wave functions provide mean values of powers of the coordinate that are also extremely precise.

ACKNOWLEDGMENTS

This paper presents research results of Interuniversity Attraction Pole Programme P7/12, initiated by the Belgian-state Federal Services for Scientific, Technical and Cultural Affairs. L.F. acknowledges support from the FRIA.

[1] I. P. Grant and H. M. Quiney, Phys. Rev. A **62**, 022508 (2000).
[2] C. Froese Fischer and O. Zatsarinny, Comput. Phys. Commun. **180**, 879 (2009).
[3] M. I. Bhatti and W. F. Perger, J. Phys. B **39**, 553 (2006).
[4] P. Amaro, A. Surzhykov, F. Parente, P. Indelicato, and J. P. Santos, J. Phys. A **44**, 245302 (2011).
[5] H. Nakashima and H. Nakatsuji, Theor. Chem. Acc. **129**, 567 (2011).
[6] R. N. Hill and C. Krauthauser, Phys. Rev. Lett. **72**, 2151 (1994).
[7] H. Nakatsuji and H. Nakashima, Phys. Rev. Lett. **95**, 050407 (2005).
[8] V. M. Shabaev, I. I. Tupitsyn, V. A. Yerokhin, G. Plunien, and G. Soff, Phys. Rev. Lett. **93**, 130405 (2004).
[9] A. Igarashi, J. Phys. Soc. Jpn. **75**, 114301 (2006).
[10] A. Igarashi, J. Phys. Soc. Jpn. **76**, 054301 (2007).
[11] K. Beloy and A. Derevianko, Comput. Phys. Commun. **179**, 310 (2008).
[12] D. Baye and P.-H. Heenen, J. Phys. A **19**, 2041 (1986).
[13] M. Vincke, L. Malegat, and D. Baye, J. Phys. B **26**, 811 (1993).
[14] D. Baye, M. Hesse, and M. Vincke, Phys. Rev. E **65**, 026701 (2002).
[15] D. Baye, Phys. Status Solidi (B) **243**, 1095 (2006).
[16] C. Semay, D. Baye, M. Hesse, and B. Silvestre-Brac, Phys. Rev. E **64**, 016703 (2001).
[17] F. Buisseret and C. Semay, Phys. Rev. E **71**, 026705 (2005).
[18] F. Buisseret and C. Semay, Phys. Rev. E **75**, 026705 (2007).
[19] C. Krauthauser and R. N. Hill, Can. J. Phys. **80**, 181 (2002).
[20] P. J. Mohr, B. N. Taylor, and D. B. Newell, Rev. Mod. Phys. **84**, 1527 (2012).
[21] I. P. Grant, *Relativistic Quantum Theory of Atoms and Molecules* (Springer, New York, 2007).
[22] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
[23] G. Szegö, *Orthogonal Polynomials* (American Mathematical Society, Providence, RI, 1967).
[24] D. Baye, J. Phys. B **28**, 4399 (1995).
[25] D. Baye, J. Phys. A **44**, 395204 (2011).
[26] D. Baye (unpublished).
[27] V. M. Shabaev, in *Precision Physics of Simple Atomic Systems. Lecture Notes in Physics, Vol. 627* (Springer, Berlin, 2003), pp. 97–113.
[28] D. Baye, Phys. Rev. A **86**, 062514 (2012).
[29] L.-Y. Tang, Y.-H. Zhang, X.-Z. Zhang, J. Jiang, and J. Mitroy, Phys. Rev. A **86**, 012505 (2012).
[30] M. Hesse and D. Baye, J. Phys. B **32**, 5605 (1999).