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Generalized Laguerre representation: Application to relativistic two-photon decay rates

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Slater-type basis sets are commonly used to perform nonrelativistic and relativistic variational calculations. A major limitation of this method is that no more than about 14 powers per nonlinear parameter can be used while working in double-precision arithmetic without entering into numerical difficulties. Even for moderate-size basis sets, large numerical errors are introduced. We introduce a variational method based on the orthogonality properties of the Laguerre polynomials. All the matrix elements of the Dirac Hamiltonian are calculated in closed form, therefore avoiding numerical cancellations and vastly increasing the speed of the calculations. As a result, full double-precision accuracy is maintained with very large basis sets. Results for sets with 75 powers are given as examples. The method is applied to a new, very accurate relativistic calculation of the two-photon decay rates for hydrogenic ions. This calculation resolves a discrepancy between the previous calculation of Parpia and Johnson [Phys. Rev. A **26**, 1142 (1982)] and that by Goldman and Drake [Phys. Rev. A **24**, 183 (1981)] in favor of the latter.

I. INTRODUCTION

During the last few years new variational methods have been introduced for a relativistic description of the electron in the presence of a potential. These methods avoid the problems of spurious roots and variational collapse and are, for example, able to provide a successful representation of the Dirac-Coulomb and the Dirac-Hartree-Fock spectra.[1] Current experimental precision in one- and two-electron systems, requires these methods to provide very accurate and stable results. It is this aspect of the theory that is analyzed in this paper.

In this work the numerical accuracy of Slater-type representations will be discussed, with the Dirac-Coulomb case as the test ground. It will be shown that large numerical errors are introduced even for basis sets of moderate size. The generalized Laguerre method is then introduced and it will be shown that numerical stability is maintained for basis sets much larger than the ones that can be used in the Slater case. The method will then be applied to a very accurate relativistic calculation of the two-photon decay rates for the hydrogenic isoelectronic sequence. This calculation resolves a discrepancy between the previous calculation of Parpia and Johnson[2] and that by Goldman and Drake[3] in favor of the second. We start with a brief review of the Dirac-Coulomb Hamiltonian and Slater-type representations.

In the case of a spherically symmetric potential, one can separate the radial part of the Dirac equation from the angular part. The radial eigenfunctions satisfy a radial Dirac equation that for the case of the Coulomb potential can be written in Hamiltonian form in the following way:

$$H_r\Phi = E\Phi \ , \tag{1.1}$$

where Φ is a real two-component radial spinor

$$\Phi = \begin{bmatrix} g(r) \\ f(r) \end{bmatrix} . \tag{1.2}$$

H_r is the radial Dirac-Coulomb Hamiltonian, which in atomic units is given by

$$\alpha H_r = \begin{bmatrix} \dfrac{1}{\alpha} - \dfrac{\alpha Z}{r} & \dfrac{\kappa}{r} - \dfrac{d}{dr} \\ \dfrac{\kappa}{r} + \dfrac{d}{dr} & -\dfrac{1}{\alpha} - \dfrac{\alpha Z}{r} \end{bmatrix} . \tag{1.3}$$

Atomic units $\hbar = m = 1$, $c = \alpha^{-1}$, with α being the fine-structure constant, are used throughout. In Eq. (1.3) Z is the nuclear charge and κ is the Dirac quantum number $\kappa = \pm(j+\frac{1}{2})$ for $l = j \pm \frac{1}{2}$. $g(r)$ and $f(r)$ are called the large and small radial components, respectively.

The variational solutions to the Hamiltonian (1.3) are obtained in the following way. One proposes a set of basis functions

$$\theta_i(\lambda, r) = \begin{bmatrix} g_i(\lambda, r) \\ f_i(\lambda, r) \end{bmatrix}, \quad i = 1, 2, \ldots, 2M \tag{1.4}$$

where λ denotes a set of nonlinear parameters. It is convenient to choose basis functions that satisfy

$$\langle \theta_i | \theta_i \rangle = 1 \ , \tag{1.5}$$

where we have used the definition

$$\langle \theta_i | \theta_j \rangle \equiv \int_0^\infty \theta_i^\dagger \theta_j \, dr = \int_0^\infty (g_i g_j + f_i f_j) \, dr \ . \tag{1.6}$$

The simplest Slater-type basis set that provides solutions that satisfy proper variational bound conditions was introduced by Drake and Goldman.[4] This set is of the form

$$\theta_i(\lambda,r)=\left[\frac{(2\lambda)^{2\gamma+2i+1}}{\Gamma(2\gamma+2i+1)}\right]^{1/2}\begin{bmatrix} e^{-\lambda r}r^{\gamma+i} \\ 0 \end{bmatrix}\,, \quad i=0,1,2,\ldots,M-1$$

$$\theta_{i+M}(\lambda,r)=\left[\frac{(2\lambda)^{2\gamma+2i+1}}{\Gamma(2\gamma+2i+1)}\right]^{1/2}\begin{bmatrix} 0 \\ e^{-\lambda r}r^{\lambda+i} \end{bmatrix}\,, \quad i=0,1,2,\ldots,M-1 \tag{1.7}$$

where

$$\gamma=[\kappa^2-(\alpha Z)^2]^{1/2}\ . \tag{1.8}$$

A rigorous proof of bounds and the conditions to avoid spurious roots were later discussed by Goldman.[5]

The basis functions θ_i are in general not orthogonal [as is the case in (1.7)]; therefore, the next step involves the orthonormalization of the basis set. This task is accomplished by the diagonalization of the overlap matrix $\langle \theta_i|\theta_j\rangle$ and results in a set of $2M$ *orthonormal* basis vectors

$$\Theta_i=\sum_{j=1}^{2M} a_{ij}\theta_j\ , \qquad \langle\Theta_i|\Theta_j\rangle=\delta_{ij}\ . \tag{1.9}$$

The next step in the variational procedure involves the diagonalization of the Hamiltonian matrix

$$H_{ij}=\langle\Theta_i|H_r|\Theta_j\rangle\ . \tag{1.10}$$

This diagonalization results in a set of $2M$ variational eigenvectors $\psi_i(\lambda,r)$,

$$\psi_i=\sum_{j=1}^{2M} c_j\Theta_j=\sum_{j=1}^{2M}\sum_{k=1}^{2M} c_j a_{jk}\theta_k \tag{1.11}$$

that satisfy

$$\langle\psi_i(\lambda,r)|\psi_j(\lambda,r)\rangle=\delta_{ij}\ , \tag{1.12}$$

$$\langle\psi_i(\lambda,r)|H_r|\psi_j(\lambda,r)\rangle=E_i(\lambda)\delta_{ij}\ , \tag{1.13}$$

where E_i are the variational energy eigenvalues. The variational eigenfunctions and eigenvalues can still be optimized by varying the nonlinear parameters λ. This nonlinear optimization will involve a repetition of the diagonalizations (1.9) and (1.13) for each value of λ.

The maximum number of Slater basis functions that one can use without entering into numerical difficulties while working in double-precision (64-bit) arithmetic is $M\simeq 14$. Typical sets of results are presented in Tables I and II. In these tables we present the positive-energy variational eigenvalues in the form $E^+=E-mc^2$. All the values were calculated for the $s_{1/2}$ states of hydrogen with a nonlinear parameter that optimizes the first excited state. Notice that hydrogen is particularly difficult from the point of view of the accuracy of the results because $(E^+/mc^2)-1\sim(\alpha^2/2)$; therefore, between four and five digits are lost in the difference $E^+=E-mc^2$.

The results obtained in double precision with 14 vectors appear, in principle, to be correct; the positive-energy eigenvalues (first column in Table I) are upper bounds to the exact ones (fourth column in Table I); similarly, the negative-energy eigenvalues are lower bounds to $-mc^2$. The question we ask now is: How *accurate* are these variational results (not as compared to the exact values but from a numerical perspective, i.e., how many digits are reliable in the values obtained)? An answer to this question can be obtained by repeating the calculation using quadruple-precision (128-bit) arithmetic. These results are presented in the second column of Table I. The conclusion is dismal: only a few digits are accurate for most levels instead of the 11–12-digit accuracy expected after subtracting the rest mass. The results are (as expected) much worse when we go to a larger set with

TABLE I. Values of the positive-energy variational eigenvalues for the s states of hydrogen in a.u., for basis sets with one nonlinear parameter and 14 powers. The methods used are: Slater in double precision (column 1), Slater or Laguerre in quadruple precision (column 2), and Laguerre in double precision (column 3). The exact bound-state eigenvalues are given in column 4. The digits underlined are in error when compared to the quadruple precision results.

	Slater (double)	E^+-mc^2 (a.u.) Quadruple precision	Laguerre	Exact bound-state eigenvalues
1	$7.7\underline{3}$	7.746 630 013 029 04	$7.746\,630\,013\,02\underline{6}$	−0.002 551 029 591 74
2	$1.6\underline{5}$	1.665 678 692 424 43	$1.665\,678\,692\,41\underline{9}$	−0.002 958 591 301 78
3	$0.6\underline{4}$	0.645 844 802 387 52	$0.645\,844\,802\,3\underline{81}$	−0.003 472 236 667 83
4	$0.30\underline{4}$	0.309 340 149 313 86	$0.309\,340\,149\,31\underline{2}$	−0.004 132 250 045 63
5	$0.15\underline{7}$	0.159 957 562 138 64	$0.159\,957\,562\,1\underline{33}$	−0.005 000 024 629 20
6	$0.08\underline{0}$	0.081 671 631 191 89	$0.081\,671\,631\,18\underline{6}$	−0.006 172 872 986 72
7	$0.03\underline{5}$	0.036 301 819 653 37	$0.036\,301\,819\,64\underline{9}$	−0.007 812 547 128 87
8	$0.007\underline{9}$	0.008 461 459 478 09	$0.008\,461\,459\,47\underline{5}$	−0.010 204 150 942 84
9	$-0.009\underline{1}$	−0.008 856 434 142 00	$-0.008\,856\,434\,14\underline{4}$	−0.013 888 996 749 76
10	$-0.019\,6\underline{6}$	−0.019 633 941 333 34	$-0.019\,633\,941\,3\underline{36}$	−0.020 000 181 058 54
11	$-0.031\,249\,\underline{7}$	−0.031 249 630 704 97	$-0.031\,249\,630\,7\underline{06}$	−0.031 250 338 029 17
12	$-0.055\,556\,295\,176\,\underline{4}$	−0.055 556 295 176 30	$-0.055\,556\,295\,175\,\underline{6}$	−0.055 556 295 176 53
13	$-0.125\,002\,080\,18\underline{9}\,\underline{8}$	−0.125 002 080 189 48	$-0.125\,002\,080\,189\,5\underline{1}$	−0.125 002 080 189 48
14	$-0.500\,006\,656\,6\underline{1}$	−0.500 006 656 590 37	$-0.500\,006\,656\,5\underline{95}$	−0.500 006 656 597 48

TABLE II. Values of the positive-energy variational eigenvalues for the s states of hydrogen in a.u., for basis sets with one nonlinear parameter and 18 powers. The methods used are: Slater in double precision (column 1), Slater or Laguerre in quadruple precision (column 2), and Laguerre in double precision (column 3). The exact bound-state eigenvalues are given in column 4. The digits underlined are in error when compared to the quadruple precision results.

	Slater (double)	$E^+ - mc^2$ (a.u.) Quadruple precision	Laguerre	Exact bound-state eigenvalues
1	$1\underline{0}.\underline{6}$	13.636 403 682 107 94	$13.636\,403\,682\,0\underline{9}$	−0.001 543 214 251 83
2	$\underline{2}.\underline{4}$	3.066 522 079 631 41	$3.066\,522\,079\,62\underline{5}$	−0.001 730 108 986 65
3	$0.\underline{95}$	1.249 027 401 018 78	$1.249\,027\,401\,01\underline{3}$	−0.001 953 131 195 80
4	$0.\underline{49}$	0.641 111 124 719 97	$0.641\,111\,124\,7\underline{1}$	−0.002 222 229 716 98
5		0.368 662 110 773 49	$0.368\,662\,110\,\underline{76}$	−0.002 551 029 591 74
6	$0.2\underline{8}$	0.224 366 237 015 51	$0.224\,366\,237\,01\underline{5}$	−0.002 958 591 301 78
7	$0.1\underline{6}$	0.139 285 770 619 28	$0.139\,285\,770\,61\underline{7}$	−0.003 472 236 667 83
8	$0.1\underline{0}$	0.085 313 429 478 87	$0.085\,313\,429\,4\underline{74}$	−0.004 132 250 045 63
9	$0.\underline{06}$	0.049 299 714 641 09	$0.049\,299\,714\,63\underline{5}$	−0.005 000 024 629 20
10	$0.0\underline{3}$	0.024 461 869 655 88	$0.024\,461\,869\,6\underline{53}$	−0.006 172 872 986 72
11	$0.00\underline{9}$	0.007 056 934 060 61	$0.007\,056\,934\,05\underline{6}$	−0.007 812 547 128 87
12	$-0.0\underline{04}$	−0.005 047 234 577 13	$-0.005\,047\,234\,58\underline{0}$	−0.010 204 150 942 84
13	$-0.012\underline{9}$	−0.013 151 137 116 33	$-0.013\,151\,137\,11\underline{9}$	−0.013 888 996 749 76
14	$-0.019\,9\underline{84}$	−0.019 989 975 114 26	$-0.019\,989\,975\,1\underline{16}$	−0.020 000 181 058 54
15	$-0.031\,250\,33\underline{6}$	−0.031 250 336 975 03	$-0.031\,250\,336\,97\underline{7}$	−0.031 250 338 029 17
16	$-0.055\,556\,295\,17\underline{6}\,\underline{4}$	−0.055 556 295 176 53	$-0.055\,556\,295\,176\,4\underline{7}$	−0.055 556 295 176 53
17	$-0.125\,002\,080\,19\underline{0}$	−0.125 002 080 189 48	$-0.125\,002\,080\,19\underline{0}$	−0.125 002 080 189 48
18	$-0.500\,006\,656\,59\underline{9}$ $\underline{-503.9}$	−0.500 006 656 597 48	$-0.500\,006\,656\,60\underline{3}$	−0.500 006 656 597 48

$M = 18$. These results are presented in the first column of Table II. In this case the numerical procedure becomes unstable and most of the results are meaningless, including the appearance of spurious results in the forbidden region $E_{\text{g.s.}} > E_{\text{forb}} > -mc^2$. This numerical instability poses a serious limitation on the application of the method to calculations where large basis sets are needed, or where the contribution of high-energy states is important (e.g., calculations involving summations over intermediate states).

In Sec. II we shall introduce a new type of basis set that will solve the problems of numerical stability (accurate results with 75 powers per nonlinear parameter will be presented as examples), and will perform more efficiently the calculations by drastically reducing the number of computations needed. In Sec. III the method is extended to the nonrelativistic case. In Sec. IV the generalized Laguerre method is then applied to a new, accurate calculation of the two-photon decay rates of the $2s_{1/2}$ state in hydrogenic ions.

II. GENERALIZED LAGUERRE BASIS SETS

We define now a new set of basis functions based on the generalized Laguerre polynomials:[6]

$$L_n^\alpha(x) = \sum_{m=0}^{n} (-1)^m \begin{bmatrix} n+\alpha \\ n-m \end{bmatrix} \frac{x^m}{m!} , \tag{2.1}$$

where

$$\begin{bmatrix} n+\alpha \\ n-m \end{bmatrix} = \frac{\Gamma(\alpha+n+1)}{(n-m)!\Gamma(\alpha+m+1)} = \begin{cases} \dfrac{(\alpha+n)(\alpha+n-1)\cdots(\alpha+m+1)}{(n-m)!} & \text{if } m<n \\ 1 \text{ if } m=n \, . \end{cases} \tag{2.2}$$

For integer values of α, (2.2) yields the usual definition of the combinatorial.

The generalized Laguerre polynomials satisfy the orthogonality condition

$$\int_0^\infty e^{-x} x^\alpha L_n^\alpha(x) L_m^\alpha(x) dx = \frac{\Gamma(\alpha+n+1)}{n!} \delta_{nm} \, . \tag{2.3}$$

It is this orthogonality property that makes these functions perfectly suited to our problem. On the basis of this orthogonality condition, we define now the basis set

$$\begin{aligned} \Phi_i &= \begin{bmatrix} \phi_i(\gamma,\lambda,r) \\ 0 \end{bmatrix}, \quad i=0,1,2,\ldots,M-1 \\ \Phi_{i+M} &= \begin{bmatrix} 0 \\ \phi_i(\gamma,\lambda,r) \end{bmatrix}, \quad i=0,1,2,\ldots,M-1 \end{aligned} \tag{2.4}$$

where

$$\phi_n(\gamma,\lambda,r) = \frac{(2\lambda)^{1/2}}{P_n(\gamma)} e^{-\lambda r} (2\lambda r)^\gamma L_n^{2\gamma}(2\lambda r) , \tag{2.5a}$$

with

$$P_n(\gamma)=\left[\frac{\Gamma(2\gamma+n+1)}{n!}\right]^{1/2} . \tag{2.5b}$$

With this definition, the functions Φ_i satisfy

$$\langle \Phi_i|\Phi_j\rangle=\delta_{ij} . \tag{2.6}$$

In other words, we *start* with an orthonormal basis set. In this way we skip the diagonalization leading to (1.9), and we are therefore able to approach the calculation with an arbitrary number of orthonormal basis functions.

In essence we have written down *a priori* the linear combinations of Slater functions that yield an orthonormal basis set. Using Eqs. (2.5) and (2.1) we can write, explicitly, the coefficients a_{ij} in the expansion (1.9). In terms of the Slater basis set (1.7), the generalized Laguerre basis set can be written as

$$\Phi_n(\gamma,\lambda,r)=\left[\frac{\Gamma(2\gamma+n+1)}{n!}\right]^{1/2}\sum_{m=0}^{n}(-1)^m\binom{n}{m}\frac{[\Gamma(2\gamma+2m+1)]^{1/2}}{\Gamma(2\gamma+m+1)}\theta_n(\gamma,\lambda,r) . \tag{2.7}$$

Our task is now to write down closed-form expressions for the matrix elements of the Hamiltonian in the basis set Φ_n. Rewriting Eq. (2.7) as

$$\Phi_n=\sum_i a_{ni}\theta_i , \tag{2.8}$$

the Slater approach calculates the Hamiltonian matrix elements as

$$\langle \Phi_n|H_r|\Phi_m\rangle=\sum_i\sum_j a_{ni}a_{mj}\langle\theta_i|H_r|\theta_j\rangle . \tag{2.9}$$

The sum in the expansion (2.9) introduces a large amount of numerical cancellations to such a degree that even if the orthonormal basis set is introduced through Eq. (2.7), the variational procedure will fail in the same way Slater basis sets do.

To avoid the expansion (2.9) we need to calculate in closed form the following quantities:

$$v_{nm}\equiv\left\langle\phi_n\left|\frac{1}{r}\right|\phi_m\right\rangle \tag{2.10}$$

and

$$w_{nm}\equiv\left\langle\phi_n\left|\frac{d}{dr}\right|\phi_m\right\rangle . \tag{2.11}$$

To calculate v_{nm} we use the summation formula[7]

$$L_n^{\alpha}(x)=\sum_{m=0}^{n}L_m^{\alpha-1}(x) , \tag{2.12}$$

which, in terms of the functions ϕ_n, becomes

$$\phi_n(\gamma,\lambda,r)=\frac{(2\lambda r)^{1/2}}{P_n(\gamma)}\sum_{i=0}^{n}P_i(\gamma-\tfrac{1}{2})\phi_i(\gamma-\tfrac{1}{2},\lambda,r) . \tag{2.13}$$

This definition can be used in Eq. (2.10) to obtain

$$\begin{aligned}v_{nm}&=\frac{2\lambda}{P_n(\gamma)P_m(\gamma)}\sum_{i=0}^{n}\sum_{j=0}^{m}P_i(\gamma-\tfrac{1}{2})P_j(\gamma-\tfrac{1}{2})\delta_{ij}\\&=\frac{2\lambda}{P_n(\gamma)P_m(\gamma)}\sum_{i=0}^{M}[P_i(\gamma-\tfrac{1}{2})]^2 ,\end{aligned} \tag{2.14}$$

where $M=\min(n,m)$. Using now in Eq. (2.14) the identity[7]

$$\sum_{i=0}^{M}\binom{\alpha+i}{\alpha}=\binom{\alpha+M+1}{\alpha+1} ,$$

we obtain

$$\sum_{i=0}^{M}[P_i(\gamma-\tfrac{1}{2})]^2=\Gamma(2\gamma)\binom{2\gamma+M}{2\gamma}=\frac{1}{2\gamma}[P_M(\gamma)]^2 . \tag{2.15}$$

With this result we can finally write, for v_{nm},

$$v_{nm}=\left\langle\phi_n\left|\frac{1}{r}\right|\phi_m\right\rangle=\frac{\lambda}{\gamma}R_{nm}(\gamma) , \tag{2.16a}$$

where

$$R_{nm}(\gamma)=\frac{P_{\min(n,m)}(\gamma)}{P_{\max(n,m)}(\gamma)} . \tag{2.16b}$$

If instead of Eq. (2.12) we use the more general expansion[7]

$$L_n^{\alpha}(x)=\sum_{m=0}^{n}\binom{m+s-1}{m}L_{n-m}^{\alpha-s}(x) ,$$

a similar derivation yields the general formula

$$\left\langle\phi_n\left|\frac{1}{r^s}\right|\phi_m\right\rangle=\frac{(2\lambda)^s}{P_n(\gamma)P_m(\gamma)}\sum_{i=0}^{M}\binom{s+n-i-1}{s-1}\binom{s+m-i-1}{s-1}[P_i(\gamma-s/2)]^2 , \tag{2.17}$$

where $M=\min(n,m)$. There is no summation involved in the calculation of v_{nm} and the matrix element (2.17) is calculated by summing a sequence of positive numbers. Therefore, by using the generalized Laguerre representation, one avoids the numerical cancellations inherent in the linear combinations in the Slater basis sets.

To calculate w_{nm}, we use the recurrence relation[7]

$$\frac{d}{dx}L_n^{\alpha}(x)=\frac{d}{dx}L_{n-1}^{\alpha}(x)-L_{n-1}^{\alpha}(x) ,$$

from which we can derive by successive iterations

$$\frac{d}{dx} L_n^{\alpha}(x) = -\sum_{m=0}^{n-1} L_m^{\alpha}(x) \ . \tag{2.18}$$

In terms of the functions ϕ_n, we obtain

$$\begin{aligned} \frac{d\phi_n(\gamma,\lambda,r)}{dr} &= -\lambda\phi_n(\gamma,\lambda,r) + \frac{\gamma}{r}\phi_n(\gamma,\lambda,r) \\ &\quad -2\lambda \sum_{i=0}^{n-1} \frac{P_i(\gamma)}{P_n(\gamma)} \phi_i(\gamma,\lambda,r) \ . \end{aligned} \tag{2.19}$$

Using Eqs. (2.16) and (2.19) we obtain

$$w_{nm} = \left\langle \phi_n \left| \frac{d}{dr} \right| \phi_m \right\rangle = -\lambda \Delta_{nm} R_{nm}(\gamma) \ , \tag{2.20a}$$

where

$$\Delta_{nm} = \begin{cases} 1 & \text{if } n < m \\ 0 & \text{if } n = m \\ -1 & \text{if } n > m \ . \end{cases} \tag{2.20b}$$

Finally, for completeness, we add to our list the matrix elements of the radial variable r. For this purpose, we use the recursion relation[7]

$$x L_n^{\alpha} = (2n+\alpha+1) L_n^{\alpha} - (\alpha+n) L_{n-1}^{\alpha} - (n+1) L_{n+1}^{\alpha} \ ,$$

to obtain

$$\begin{aligned} 2\lambda r \phi_n &= (2n+2\gamma+1)\phi_n - [(2\gamma+n)n]^{1/2}\phi_{n-1} \\ &\quad -[(2\gamma+n+1)(n+1)]^{1/2}\phi_{n+1} \end{aligned} \tag{2.21}$$

and

$$2\lambda\langle \phi_n | r | \phi_m \rangle = \begin{cases} (2n+2\gamma+1) & \text{if } n = m \\ -[(2\gamma+n)n]^{1/2} & \text{if } n = m+1 \\ -[(2\gamma+n+1)(n+1)]^{1/2} & \\ \qquad \text{if } n = m-1 & \\ 0, & \text{otherwise} \ . \end{cases} \tag{2.22}$$

Again, in Eqs. (2.20) and (2.22), one avoids the linear combinations involved in the calculation of matrix elements using Slater orthonormal basis vectors. Equation (2.22) can be extended to any power of r by using, repeatedly, the recursion relation (2.21).

To recapitulate, we present now a list of the matrix elements that we have expressed in closed form throughout this section:

$$\left\langle \phi_n \left| \frac{1}{r} \right| \varphi_m \right\rangle = \frac{\lambda}{\gamma} R_{nm}(\gamma) \ , \tag{2.16'}$$

$$\left\langle \phi_n \left| \frac{d}{dr} \right| \phi_m \right\rangle = -\lambda \Delta_{nm} R_{nm}(\gamma) \ , \tag{2.20'}$$

Eq. (2.17), and

$$\begin{aligned} 2\lambda\langle \phi_n | r | \phi_m \rangle &= (2n+2\gamma+1)\delta_{nm} - [(2\gamma+m)m]^{1/2}\delta_{n,m-1} \\ &\quad -[(2\gamma+n)n]^{1/2}\delta_{n,m+1} \ , \end{aligned} \tag{2.22'}$$

where Eqs. (2.5b), (2.16b) and (2.20b) apply.

The results obtained using the generalized Laguerre method are presented in the third column of Tables I and II. It can be seen by comparing with the quadruple-precision results that full-double-precision accuracy is maintained. Notice that four to five digits of numerical precision are lost in the case of hydrogen when the rest mass $1/\alpha^2$ is subtracted. The Laguerre method allows us to extend the calculations to very large basis sets. As an example, in Table III we present the double-precision results for a set with 75 powers. This size of a representation is simply unthinkable if one uses Slater basis sets. All the calculations were performed in a VAX 8550 using double-precision FORTRAN.

In some calculations, the convergence of the results is largely improved if basis sets with several nonlinear parameters are used.[1] The overlaps between basis sets with different nonlinear parameters do not introduce the numerical errors inherent in basis sets with many powers and one nonlinear parameter. This can be easily seen; the basis functions θ_i [Eq. (1.7)] for consecutive values of the power of r become increasingly similar:

$$\langle \theta_i(\lambda,r) | \theta_{i+1}(\lambda,r) \rangle = \left[\frac{2\gamma+2i-1}{2\gamma+2i} \right]^{1/2} \to 1 \quad \text{for } i \gg 1 \ , \tag{2.23}$$

resulting in the numerical failure of the diagonalization of Eq. (1.9) (orthonormalization). If different values of the exponential parameters are used, (2.23) changes into

$$\begin{aligned} &\langle \theta_i(\lambda,r) | \theta_{i+1}(\mu,r) \rangle \\ &\quad = \left[\frac{2\gamma+2i-1}{2\gamma+2i} \right]^{1/2} \left[\frac{2\lambda}{\lambda+\mu} \right]^{\gamma+i-(1/2)} \\ &\quad\quad \times \left[\frac{2\mu}{\lambda+\mu} \right]^{\gamma+i+(1/2)} \ , \end{aligned} \tag{2.24}$$

and the overlaps do not approach unity. The reason is that for different values of the nonlinear parameter the Slater functions are grouped into different regions of the radial variable r. Still, the same limitation on the number of powers that can be used remains in effect for *each* exponential parameter, and the numerical stability of the method will depend on the proper calculation of the matrix elements between basis functions with the same nonlinear parameter. The results obtained previously can be extended to the multiexponential case with the help of the formula

$$\langle \phi_n(\gamma,\lambda,r) | \phi_m(\gamma,\lambda,r) \rangle = (-1)^{m-M} \frac{(4\lambda\mu)^{\gamma+(1/2)}}{(\lambda+\mu)^{2\gamma+1}} R_{nm}^{-1}(\gamma) \left[\frac{\mu-\lambda}{\mu+\lambda} \right]^{N-M} \sum_{j=0}^{M} (-1)^j \left[\begin{matrix} N \\ M-j \end{matrix} \right] \left[\begin{matrix} 2\gamma+N+j \\ j \end{matrix} \right] \left[\frac{\mu-\lambda}{\mu+\lambda} \right]^{2j} . \tag{2.25}$$

TABLE III. Sample of the variational energy eigenvalues in a.u., for the s states of hydrogen with a generalized Laguerre basis set with one nonlinear parameter and 75 powers, optimizing the first excited state. E^+-mc^2 and E^-+mc^2 denote the relativistic (Dirac) positive- and negative-energy eigenvalues. The computational accuracy is limited by the number of significant digits that remain after adding the rest mass. $E_{\rm nr}$ denotes the nonrelativistic (Schrödinger) eigenvalues.

	$E_{\rm nr}$	E^+-mc^2	E^-+mc^2
1	−0.499 999 999 999 999	−0.500 006 656 6	−0.004 359 009 5
2	−0.125 000 000 000 000	−0.125 002 080 2	−0.005 396 114 2
3	−0.055 555 555 555 556	−0.055 556 295 2	−0.006 434 430 0
4	−0.031 250 000 000 000	−0.031 250 338 0	−0.007 521 340 6
5	−0.020 000 000 000 000	−0.020 000 181 1	−0.008 676 422 9
6	−0.013 888 888 888 889	−0.013 888 996 7	−0.009 911 614 1
7	−0.010 204 081 632 653	−0.010 204 150 9	−0.011 235 936 1
8	−0.007 812 499 999 999	−0.007 812 547 1	−0.012 657 148 3
9	−0.006 172 839 491 092	−0.006 172 873 0	−0.014 182 474 3
10	−0.004 999 979 873 617	−0.005 000 004 5	−0.015 818 979 8
11	−0.004 129 220 399 329	−0.004 129 239 3	−0.017 573 797 8
12	−0.003 408 238 546 055	−0.003 408 256 3	−0.019 454 282 3
⋮	⋮	⋮	⋮
63	1.428 252 894 119 60	1.428 183 257 5	−1.878 627 441 0
64	1.694 402 812 677 92	1.694 305 437 5	−2.214 705 972 4
65	2.037 203 003 604 60	2.037 063 122 0	−2.645 719 140 7
66	2.489 069 155 245 73	2.488 861 619 3	−3.211 188 381 2
67	3.101 516 537 425 34	3.101 196 281 3	−3.973 610 580 3
68	3.960 419 914 592 94	3.959 900 991 6	−5.036 595 593 0
69	5.217 628 667 031 32	5.216 733 927 6	−6.582 227 013 0
70	7.162 502 078 461 75	7.160 828 101 9	−8.955 045 813 5
71	10.403 290 530 987 3	10.399 787 966 4	−12.873 378 820 1
72	16.403 442 592 123 8	16.394 821 181 4	−20.048 499 691 0
73	29.460 609 371 706 6	29.433 164 104 4	−35.442 980 900 3
74	67.136 778 903 250 7	66.997 076 165 0	−78.979 547 290 6
75	273.875 789 416 07	271.649 044 035 7	−309.182 500 195 8

In Sec. III we generalize the Laguerre method to the nonrelativistic case. Then, in Sec. IV we apply the relativistic generalized Laguerre basis set to perform an accurate calculation of the two-photon decay rate of the metastable $2s_{1/2}$ states in hydrogenic ions.

III. THE NONRELATIVISTIC CASE

In this section we generalize the Laguerre method to the nonrelativistic case. This case is much simpler, given that, in the solutions to the Coulomb case, the radial variable appears in the wave functions with integer powers only. In this case, if we write the eigenfunctions to the Schrödinger Hamiltonian as

$$\Psi_{\rm nl}(\mathbf{r})=\frac{\psi_{\rm nl}(r)}{r}Y_l^m(\hat{\mathbf{r}}) , \tag{3.1}$$

the nonrelativistic eigenvalue equation can be written as

$$H_r\psi_n=E_n\psi_n , \tag{3.2}$$

where the radial Schrödinger Hamiltonian is given by

$$H_r=-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{Z}{r} . \tag{3.3}$$

The exact radial wave functions satisfy at the origin the boundary condition $\psi_{\rm nl}\sim r^{l+1}$. The generalized Laguerre basis set satisfying a similar boundary condition at the origin, namely, $\phi\sim r^{L+1}$ becomes

$$\phi_n(L,\lambda,r)=\frac{(2\lambda)^{1/2}}{P_n(L+1)}e^{-\lambda r}(2\lambda r)^{L+1}L_n^{2L+2}(2\lambda r) , \tag{3.4}$$

with P_n defined in Eq. (2.5b). All the matrix elements of the Hamiltonian can be easily obtained, with the added advantage that all the Γ functions are replaced by factorials. Using the results of Sec. II, we find after some algebra

$$\begin{aligned}\left\langle\phi_{nL}\left|\frac{d^2}{dr^2}\right|\phi_{mL}\right\rangle=&-\lambda^2\delta_{nm}+2\lambda^2\Delta_{nm}R_{nm}(\gamma)\\&+L(L+1)\left\langle\phi_{nL}\left|\frac{1}{r^2}\right|\phi_{mL}\right\rangle\\&-4\lambda^2\frac{2\gamma+1+M'}{2\gamma-1}\frac{P_{M'}^2}{P_nP_m}\end{aligned} \tag{3.5}$$

and

$$\begin{aligned}\left\langle\phi_{nL}\left|\frac{1}{r^2}\right|\phi_{mL}\right\rangle=\frac{4\lambda^2}{2\gamma+M}R_{nm}\Bigg[&\frac{(N+1)(M+1)}{2\gamma-1}\\&-\frac{(N+M+1)M}{2\gamma}\\&+\frac{M(M-1)}{2\gamma+1}\Bigg] ,\end{aligned} \tag{3.6}$$

where we used the definitions of Sec. II and

$$M=\min(n,m),\quad N=\max(n,m),\quad M'=\min(n,m-1)\ , \tag{3.7}$$

$$P_n=\left[\frac{(2L+n+2)!}{n!}\right]^{1/2} . \tag{3.8}$$

Notice that in the case $L=l$, i.e., when the basis set satisfies the exact boundary conditions at the origin, the coefficient of $\langle\phi_n|r^{-2}|\phi_m\rangle$ in the Hamiltonian matrix elements is identically zero. In this case, the Hamiltonian matrix elements are given by

$$\langle\phi_{\mathrm{nl}}|H_r|\phi_{ml}\rangle=\lambda^2\left[\frac{\delta_{nm}}{2}-\left[\Delta_{nm}+\frac{Z}{\lambda(l+1)}\right]R_{nm}(\gamma)\right.$$
$$\left.+2\frac{2\gamma+1+M'}{2\gamma+1}\,\frac{P_{M'}^2}{P_nP_m}\right] . \tag{3.9}$$

In Table III we present the results obtained with a basis set of the form (3.4) with one exponential parameter and 75 powers, for the case $l=0$, and optimizing the first excited state. An accuracy of 15 digits is obtained for the full variational energy spectrum. The calculation was performed on an IBM PC using the matrix oriented package GAUSS.

IV. RELATIVISTIC TWO-PHOTON DECAY RATES

We apply now the Laguerre basis set to the relativistic calculation of the two-photon decay rates of the $2s_{1/2}$ state in hydrogenic ions. The aim is to provide a very accurate calculation that will resolve the discrepancy between the two previous calculations of Parpia and Johnson[2] and of Goldman and Drake.[3] In the first two columns of Table IV we present a comparison between these two calculations for the $2E1$ contribution to the total two-photon decay rate. We note that the difference in the results is larger than the uncertainty in each of the calculations. The calculation by Parpia and Johnson was done by a numerical solution of a perturbed Dirac equation, while, in the calculation by Goldman and Drake, Slater basis sets were used to represent the Dirac-Coulomb Green function.

TABLE IV. Different calculations of the $2E1$ decay rates for the $2s_{1/2}$ state in hydrogenic ions in s^{-1}, for a selected set of values of the nuclear charge Z. The numbers in parentheses denote the estimated error in the last digit.

		$Z^{-6}w(2E1)$	
Z	Goldman and Drake[a]	Parpia and Johnson[b]	This calculation
1	8.2291(8)	8.2291	8.229 062 6
20	8.1181(8)	8.1196	9.117 403 5
40	7.8096(8)	7.8116	7.809 261 2
60	7.3446(7)	7.3453	7.344 648 2
80	6.7440(7)	6.7426	6.742 887 6
92	6.3097(6)	6.3093	6.309 662 3

[a] Reference 3.

[b] Reference 2.

The theory of two-photon transitions is given in detail in Ref. 3; we repeat here only a few relevant points. The differential two-photon emission rate is given by[8]

$$\frac{dw}{d\omega_1}=\frac{\omega_1\omega_2}{(2\pi)^3c^2}\left|\sum{}'\left[\frac{\langle f|A_2^*|n\rangle\langle n|A_1^*|i\rangle}{E_n-E_i+\omega_1}\right.\right.$$
$$\left.\left.+\frac{\langle f|A_1^*|n\rangle\langle n|A_2^*|i\rangle}{E_n-E_i+\omega_2}\right]\right|^2$$
$$\times d\Omega_1 d\Omega_2\ , \tag{4.1}$$

where i and f denote the initial and final states, ω_j and $d\Omega_j$ are the frequency and element of solid angle of photon j, and $\sum'$ denotes summation over all intermediate bound states and integration over positive- and negative-energy continua. The photon energies satisfy the energy conservation requirement

$$E_i-E_f=\omega_1+\omega_2\ . \tag{4.2}$$

For photon plane waves, the operators A_j^* are given by

$$A_j^*=\boldsymbol{\alpha}\cdot(\hat{\mathbf{e}}_j+G\hat{\mathbf{k}}_j)e^{-i\mathbf{k}_j\cdot\mathbf{r}}-Ge^{-i\mathbf{k}_j\cdot\mathbf{r}}\ , \tag{4.3}$$

where $\mathbf{k}_j$ is the propagation vector, $\hat{\mathbf{e}}_j$ is the polarization vector, and G is an arbitrary gauge parameter, i.e., the results are independent of G. The total decay rate w is obtained by integrating expression (4.1) with respect to the photon frequency.

The calculation of (4.1) is performed by replacing the summation $\sum'$ by a finite summation over the positive- and negative-energy variational eigenstates. The integrals over $\mathbf{k}_1$ and $\mathbf{k}_2$ in Eq. (4.1) are evaluated by making use of the partial-wave expansions[3]

$$A_j^*=\sum_{\lambda,L,M}[\hat{\mathbf{e}}_j\cdot\mathbf{Y}_{LM}^{(\nu)}(\hat{\mathbf{k}}_j)][\tilde{a}_{LM}^{(\nu)}(r)]^*\ , \tag{4.4}$$

where $\nu=1, 0, -1$, and

TABLE V. Multipole combinations included in the present calculation of the total two-photon decay rates, with the allowed intermediate states in the summation of Eq. (3.1). The lowest-order term in an $(\alpha Z)^2$ expansion for each multipole contribution is presented in column 3.

Multipoles	Intermediate states	Lowest order (s^{-1})
$2E1$	$p_{1/2},p_{3/2}$	$8.229\,06\times Z^6$
$E1M2$	$p_{3/2}$	$2.537\,18\times10^{-10}\times Z^{10}$
$2M1$	$s_{1/2},d_{3/2}$	$1.380\,36\times10^{-11}\times Z^{10}$
$2E2$	$d_{3/2},d_{5/2}$	$4.907\,23\times10^{-12}\times Z^{10}$
$2M2$	$p_{3/2},f_{5/2}$	$3.069\,35\times10^{-22}\times Z^{14}$
$E2M3$	$d_{5/2}$	$1.422\,93\times10^{-22}\times Z^{14}$
$E2M1$	$d_{3/2}$	$1.639\,36\times10^{-23}\times Z^{14}$
$2E3$	$f_{5/2},f_{7/2}$	$5.526\,71\times10^{-24}\times Z^{14}$
$E3M2$	$f_{5/2}$	$3.198\,17\times10^{-34}\times Z^{18}$
$E3M4$	$f_{7/2}$	$1.570\,46\times10^{-34}\times Z^{18}$

$$(\tilde{a}_{LM}^{(\nu)})^* = \begin{cases} \boldsymbol{\alpha}\cdot(\mathbf{a}_{LM}^{(\nu)})^*, & \nu=0,1 \\ G(\boldsymbol{\alpha}\cdot(\mathbf{a}_{LM}^{(\nu)})^* - \Phi_{LM}^*), & \nu=-1\ . \end{cases} \tag{4.5}$$

The $\mathbf{Y}_{LM}^{(\nu)}$ are related to the vector spherical harmonics

$$\mathbf{Y}_{LM}^{(0)}(\hat{\mathbf{k}}) = \mathbf{Y}_{L,L,M}(\hat{\mathbf{k}})\ , \tag{4.6a}$$

$$\mathbf{Y}_{LM}^{(1)}(\hat{\mathbf{k}}) = -i\hat{\mathbf{k}}\times\mathbf{Y}_{LM}^{(0)}(\hat{\mathbf{k}})\ , \tag{4.6b}$$

$$\mathbf{Y}_{LM}^{(-1)}(\hat{\mathbf{k}}) = \hat{\mathbf{k}}\times\mathbf{Y}_{LM}(\hat{\mathbf{k}})\ , \tag{4.6c}$$

and

$$\mathbf{a}_{LM}^{(0)} = g_L(kr)\mathbf{Y}_{L,L,M}(\hat{\mathbf{r}})\ , \tag{4.7a}$$

$$\mathbf{a}_{LM}^{(\pm 1)} = \left[\frac{L}{2L+1}\right]^{1/2} g_{L\pm 1}(kr)\mathbf{Y}_{L,L\pm 1,M}(\hat{\mathbf{r}}) \pm \left[\frac{L+1}{2L+1}\right]^{1/2} g_{L\mp 1}(kr)\mathbf{Y}_{L,L\mp 1,M}(\hat{\mathbf{r}})\ , \tag{4.7b}$$

$$\Phi_{LM} = g_L(kr)Y_{LM}(\hat{\mathbf{r}})\ ,$$

$$g_L(kr) = 4\pi i^L j_L(kr)\ ,$$

and $j_L(kr)$ is a spherical Bessel function.

The contribution from $\nu=-1$ (gauge-dependent part) vanishes identically. Terms with $\nu=1$ are electric multipoles and terms with $\nu=0$ are magnetic multipoles. Enough multipoles have been included in the calculation to obtain an accuracy of eight significant digits for values of the nuclear charge from $Z=1$ to $Z=100$. The stability and accuracy of the results have been verified with respect to variations of the size of the basis set, the nonlinear parameter, and the gauge parameter. It was found that a generalized Laguerre set with 18 powers was sufficient to obtain the required precision. All the radial integrals have been performed in closed form in terms of hypergeometric functions,[3] while the integration with respect to the photon frequency has been performed using a 40-point Gauss-Legendre integration.

In Table V we list all the multipole combinations included in the calculation in order to attain the accuracy presented. We also show which intermediate states are to be included in each case in the summations in Eq. (4.1), as well as the lowest-order Z dependence of each contribution.

The results obtained for the $2E1$ transitions are compared with the two previous calculations in Table IV. Within the estimated errors, the calculation by Goldman and Drake agrees with the present calculation. In fact, using the Laguerre method, the results of Parpia and Johnson can be reproduced to all digits if a Romberg integration of order 5 is used for the numerical integration over photon frequencies. It is for the intermediate range of nuclear charges that this integration is most difficult, due to a rapid change in the first derivative of the integrand close to the nucleus. A higher-order routine than that used by Parpia and Johnson is therefore needed to attain convergence even for a relatively small number of digits. This explains also the previous seemingly contradicting fact that a non-numerical error could be present in their calculation, given that their results were gauge invariant.

TABLE VI. Total two-photon decay rates in s^{-1}. The numbers in parentheses denote powers of 10. For the finite nuclear mass correction, the results should be multiplied by $1-m/M$.

Z	w (s^{-1})	Z	w (s^{-1})
1	8.229 062 6	25	1.967 072 0(9)
2	5.266 042 2(2)	26	2.484 813 4(9)
3	5.997 293 7(3)	27	3.110 885 2(9)
4	3.368 842 5(4)	28	3.862 528 6(9)
5	1.284 705 1(5)	29	4.758 917 6(9)
6	3.834 630 0(5)	30	5.821 288 8(9)
7	9.665 109 2(5)	32	8.540 025 0(9)
8	2.152 440 9(6)	34	1.223 492 1(10)
9	4.361 035 0(6)	36	1.716 377 6(10)
10	8.200 651 3(6)	38	2.363 046 8(10)
11	1.451 741 0(7)	40	3.198 947 3(10)
12	2.444 985 1(7)	42	4.265 043 2(10)
13	3.948 897 6(7)	45	6.400 220 4(10)
14	6.154 354 3(7)	50	1.186 913 1(11)
15	9.301 052 1(7)	55	2.069 471 1(11)
16	1.368 505 7(8)	60	3.428 241 3(11)
17	1.966 684 1(8)	65	5.438 792 6(11)
18	2.767 979 6(8)	70	8.314 131 3(11)
19	3.823 920 3(8)	75	1.230 568 6(12)
20	5.195 165 8(8)	80	1.770 223 7(12)
21	6.952 491 3(8)	85	2.482 587 6(12)
22	9.177 814 3(8)	90	3.402 365 6(12)
23	1.196 526 0(9)	92	3.836 368 1(12)
24	1.542 226 6(9)	100	6.005 552 2(12)

Finally, the results for the total decay rates for a large selection of hydrogenic ions are presented in Table VI. These results do not include the reduced mass correction factor $1-m/M$. The most important corrections not included are those introduced by the finite nuclear size and by quantum electrodynamic effects. These can be treated as perturbations, and calculated using the same finite basis-set techniques.

V. CONCLUSIONS

The results of Sec. II demonstrate that the generalized Laguerre method is a very powerful tool for relativistic variational calculations. Its main feature is the ability to avoid the numerical problems associated with the more commonly used Slater basis sets. Another advantage is that all the Hamiltonian matrix elements can be calculated in closed form in terms of the Laguerre orthonormal basis vectors. In this way one obtains a much better numerical accuracy and one is able to perform the calculations more efficiently by eliminating the expansion in terms of the nonorthogonal Slater basis vectors θ_i.

Another variational technique using B splines[9,10] has been recently introduced for calculations in atomic physics. This method uses piecewise polynomials defined over a radial grid from $r=0$ to a maximum value $r=R$. The grid is defined in terms of a set of nodes and the variational calculation is optimized with respect to the position of these nodes and the degree of the polynomials used. The advantage of this method over the Slater method is that the Hamiltonian matrix is sparse (all the matrix elements between nonoverlapping splines is zero) and therefore "well behaved." However, the B-spline eigenvalues fall in some cases below the exact positive-energy eigenvalues and are, therefore, not upper bounds for the true spectrum as are those obtained using Slater-type sets. Moreover, the results obtained using B splines both for energy eigenvalues or for calculations involving sums over intermediate states do not converge as fast as those using Slater-type basis sets, so that the latter ones produce more accurate results. The Laguerre method removes the only disadvantage of the Slater-type vectors by introducing computational efficiency and numerical stability, even for very large numbers of powers. The Laguerre basis sets provide also excellent convergence for calculations involving sums over intermediate states. For example, the sum rules (relativistic and nonrelativistic) of the form $\sum_n |\langle 0|\mathbf{r}|n\rangle|^2(E_n - E_0)^k$ for $k=0,1,2,3$ were all satisfied to 15 digits accuracy. This also compares very favorably with similar calculations using B splines.[10]

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