Calculation of two-photon decay rates of hydrogen-like ions by using B-polynomials

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Abstract
A new approach is laid out to investigate two-photon atomic transitions. It is based on the application of the finite-basis solutions constructed from the Bernstein polynomial (B-polynomial) sets. We show that such an approach provides a very promising route for the relativistic second-order (and even higher-order) calculations since it allows for analytical evaluation of the involved matrices elements. In order to illustrate possible applications of the method and to verify its accuracy, detailed calculations are performed for the $2s_{1/2} \rightarrow 1s_{1/2}$ transition in neutral hydrogen and hydrogen-like ions, which are compared with the theoretical predictions based on the well-established B-spline basis-set approach.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction
High-order perturbation calculations in atomic physics generally require summations over the complete spectrum of the system under consideration. Within the relativistic framework, such a ‘summation’ is not a simple task since it includes a summation over the discrete part of the Dirac spectrum as well as the integration over the positive- and negative-energy continua. A number of methods have been developed over the past decades to perform this summation consistently. Apart from the various Green’s function approaches [1, 2], the discrete basis-set method is widely employed nowadays in (relativistic as well as non-relativistic) high-order calculations [3–7]. In this method, a finite set of discrete pseudostates is constructed from some basis functions and utilized for carrying out the summation. The particular choice of a
suitable set of basis functions is crucial for the practical implication of the method. Usually, the discrete (pseudo-) solutions are built up from piecewise polynomial sets. The piecewise polynomials are precisely defined, can be calculated rapidly on modern computer systems, and can represent a great variety of functions. They can be differentiated and integrated easily [8].

The basis splines [9], also called B-splines, are one of the most commonly used family of piecewise polynomials. These polynomials, which are well adapted to numerical tasks, have been successfully used in many atomic-physics studies. For example, Johnson and co-workers have applied the B-splines to the many-body perturbation theory [10, 11]. Froese Fischer and co-workers used it in (variational) Hartree–Fock calculations and continuum problems [12, 13]. Qiu and Froese Fischer introduced the integration by cell algorithm for Slater integrals in a B-spline basis obtaining an improved efficiency and accuracy over traditional methods [14, 15]. Bhatti and co-workers [16] used similar techniques to find an approximate solution of a set of the non-homogeneous second-order differential equations and to obtain static polarizabilities of hydrogenic states. Indelicato and co-workers employed B-splines in the multi-configuration Dirac–Fock (MCDF) relativistic atomic structure calculations [17, 18] and in relativistic two-photon decay calculations [4, 19, 20].

While B-spline basis sets were proven to be an important tool for studying the variety of atomic structure and dynamics problems (see [3, 21] for further details and examples), one might adopt other piecewise polynomial sets to speed up relativistic high-order calculations as might be highly required, for example, for studying the two-photon transitions in many-electron systems. In this work, we argue that the Bernstein, or B-polynomials [22] may serve as a good alternative to the B-splines since they allow for analytical finite basis-set calculations. These are polynomial functions of \( n \)th degree that have been recently used to obtain the solution of some linear and nonlinear differential equations [23–25]. Bhatti and Perger [26] developed an algorithm for constructing accurate solutions to the radial Dirac equation in a B-polynomial basis set. By using this algorithm and the Galerkin method, accurate calculations have been performed for the bound-state energies of hydrogenic systems.

In this work, we employ the finite (discrete) solutions constructed from the B-polynomial sets in order to explore the two-photon decay of hydrogen-like ions. A theoretical analysis of this process requires evaluation of the second-order transition amplitudes and, hence, can be used as a ‘testing ground’ for the high-order B-polynomial calculations. To explain the background of these calculations we will recall in sections 2.2 and 2.3 the application of finite basis-set methods for dealing with the Dirac problem. In particular, we will derive the generalized eigenvalue problem whose solutions form a complete set of atomic pseudostates. In order to find these solutions, however, one has to agree first about the explicit form of the basis functions. In section 2.4, we will introduce B-polynomial basis sets, and discuss their properties. We will use these sets to construct the (pseudo) spectrum of the ion (or atom). Summation over such a spectrum, which appears within the second-order perturbation theory, will be performed later in section 2.5 and will allow us to derive the two-photon decay rates. Results of the relativistic calculations for these rates obtained for the \( 2s_{1/2} \rightarrow 1s_{1/2} \) transition in neutral hydrogen and hydrogen-like ions will be presented in section 3. Apart from the results obtained by making use of the B-polynomial sets, we also present here the ‘standard’ B-spline calculations as well as the predictions by Labzowsky et al [27]. A detailed comparison with these predictions will allow us to justify the application of the B-polynomial approach in second-order calculations and to underline its advantages. The summary of our work will be given finally in section 4.

The atomic system of units (\( e = m_e = \hbar = 1 \)) is used throughout the paper unless otherwise stated.
2. Theory

2.1. General approach

The second-order relativistic calculations in atomic and molecular physics often require summation over the complete spectrum of the system under consideration. Such a summation that includes integration over the positive- and negative-energy continua can be performed very efficiently if one considers the (atomic or molecular) system to be enclosed in a finite cavity with a radius $R$. This allows for a discretization of the continua and, hence, for a representation of the entire Dirac spectrum in terms of the pseudostate basis functions. A (quasi-complete) finite set of these functions are determined subsequently by making use of the variational Galerkin method [28].

2.2. Finite basis-set approach to the Dirac equation

Having briefly discussed the general context, we are now ready to apply the finite basis-set method for solving the eigenvalue Dirac’s problem:

$$
(c\gamma^\alpha \cdot \mathbf{p} + \beta c^2 + V(r))u(r) = \varepsilon u(r),
$$

where $\alpha$ and $\beta$ are the usual $4 \times 4$ Dirac matrices, and $V(r)$ describes the Coulomb interaction between an electron and nucleus. Moreover, in equation (1) we have replaced the total electron energy $E$ by $\varepsilon = E - c^2$ to render easy the comparison with nonrelativistic calculations.

Since the potential $V(r)$ is central, the eigenfunctions of the Dirac Hamiltonian can be written in the standard form as

$$
\psi_{n\kappa}(r) = \frac{1}{r} \left[ \begin{array}{c} P_{n\kappa}(r) \\ i Q_{n\kappa}(r) \end{array} \right] \Omega_{1\kappa}(\hat{r}),
$$

with $\Omega_{1\kappa}(\hat{r})$ being the Dirac spin-angular function. The angular quantum number $\kappa$ is defined by

$$
\kappa = \begin{cases} 
\ell & \text{if } j = \ell - 1/2 \\
-(\ell + 1) & \text{if } j = \ell + 1/2,
\end{cases}
$$

where $\ell$ and $j$ are the electron orbital and total angular momenta, respectively. By substituting wavefunction (2) into equation (1) and by performing some simple angular momentum algebra one can obtain the conventional set of radial Dirac equations

$$
\begin{bmatrix}
V(r) & c \kappa \\
-c \kappa & -2m_e c^2 + V(r)
\end{bmatrix}
\begin{bmatrix}
P_{n\kappa}(r) \\ Q_{n\kappa}(r)
\end{bmatrix}
= \varepsilon
\begin{bmatrix}
P_{n\kappa}(r) \\ Q_{n\kappa}(r)
\end{bmatrix}
$$

(4)

to determine the large, $P_{n\kappa}(r)$, and the small, $Q_{n\kappa}(r)$, radial components. For the sake of shortness, we introduced here the operator

$$
O_\pm = \frac{d}{dr} \pm \frac{\kappa}{r}.
$$

(5)

For a further evaluation of equation (4) we assume that the ion (or atom) is enclosed in a finite cavity with a radius $R$ large enough to get a good approximation of the wavefunctions, with some suitable set of boundary conditions. In order to construct these functions, we turn to the principle of least action [10]

$$
\delta S_\kappa = 0,
$$

(6)
from which the Dirac equation can be derived. In this expression, the action $S_κ$ is defined as

$$S_κ = \frac{1}{2} \int_0^R \left[ c P_{nκ}(r) O_{nκ}(r) - c Q_{nκ}(r) O_{nκ}(r) + V(r) \left( P_{nκ}(r)^2 + Q_{nκ}(r)^2 \right) - \frac{1}{2} \epsilon \int_0^R \left( P_{nκ}(r)^2 + Q_{nκ}(r)^2 \right) \, dr \right] \, dr + S_{κ_bond},$$

where the upper integration limit $R$ is the radius of the confining cavity. The term $S_{κ_bond}$, that will be specified below, stands for the boundary conditions and the parameter $\epsilon$ is a Lagrange multiplier introduced to ensure the normalization constraint,

$$\int_0^R \left( P_{nκ}(r)^2 + Q_{nκ}(r)^2 \right) \, dr = 1.$$

Here, the large, $P_{nκ}(r)$, and small, $Q_{nκ}(r)$, radial components of the electron wavefunctions can be written as a finite expansion

$$P(r) = \sum_{i=1}^N p_i B_i(r), \quad Q(r) = \sum_{i=1}^N q_i B_i(r),$$

over some basis functions $B_i(r)$. The explicit form of these functions is not crucial for the following discussion and will be specified later in section 2.4.2. Moreover, equation (9), the subscripts $n$ and $κ$ have been omitted from the functions $P_{nκ}(r)$ and $Q_{nκ}(r)$ for the sake of notation simplicity.

By inserting now the radial components (9) into the least action principle (6) and by evaluating the variation $S_κ$ with respect to the change of expansion coefficients $p_i$ and $q_i$, we obtain the matrix equation

$$Av = \epsilon Bv,$$

(10)

to determine the vector $v = (p_1, p_2, \ldots, p_N, q_1, q_2, \ldots, q_N)$ and where $A$ and $B$ are symmetric $2N \times 2N$ matrices given, respectively, by

$$A = \begin{bmatrix} (V) & c \left[ (D) - \left( \frac{κ}{r} \right) \right] \\ -c \left[ (D) + \left( \frac{κ}{r} \right) \right] & -(2mec^2(C) + (V)) \end{bmatrix} + A_{κ_bond},$$

(11)

and

$$B = \begin{bmatrix} (C) & 0 \\ 0 & (C) \end{bmatrix}.$$  

(12)

The matrix $A_{κ_bond}$ reflects the boundary conditions, and the $N \times N$ matrices $(C)$, $(D)$, $(V)$ and $\left( \frac{κ}{r} \right)$ are given by

$$(C)_{ij} = \int B_i(r) B_j(r) \, dr,$$

(13)

$$(D)_{ij} = \int B_i(r) \frac{d}{dr} B_j(r) \, dr,$$

(14)

$$\left( \frac{κ}{r} \right)_{ij} = \int B_i(r) \frac{κ}{r} B_j(r) \, dr.$$

(15)
Equation (10) is known as a generalized eigenvalue problem that can be solved by employing linear algebra standard techniques. In this work, for example, we have used the well-established LAPACK 3.3.0 package [29]. By using this package we obtain $2N$ real eigenvalues $\epsilon_n$ and $2N$ orthogonal eigenvectors $v^i$ that span both positive and negative energy solutions. Solutions labeled by $i = 1, \ldots, N$ describe the continuum $\epsilon_n < -2mc^2$ and solutions labeled by $i = N + 1, \ldots, 2N$ describe bound states and the positive continuum $\epsilon_n > 0$.

2.3. Spurious states and boundary conditions

The practical implementation of the finite basis-set approaches is usually complicated by the well-known problem of spurious states. These non-physical states appear as solutions of the single-particle radial Dirac equation for $\kappa > 0$ ($p_{1/2}$, $d_{3/2}$, ... orbitals) [30]. Although the spurious solutions 'spoil' the spectrum of the ion (or atom) under consideration, they are required for providing completeness of the basis set. The problem of spurious states has been discussed in detail in the literature, and several solutions were proposed [30–34]. Johnson and co-workers [10], in their pioneering applications of the B-splines to the relativistic many-body problem, have suggested to adopt the function $S_{\text{Bond}}$ in equation (7) as

\[
S_{\text{Bond}}^k = \begin{cases} 
\frac{c}{4}[P^2(R) - Q^2(R)] - \frac{c}{2} P(0)[P(0) - Q(0)] & \text{for } \kappa < 0 \\
\frac{c}{4}[P^2(R) - Q^2(R)] - \frac{c}{2} P(0)[cP(0) - Q(0)] & \text{for } \kappa > 0,
\end{cases}
\]

in order to lift the spurious states to lower energies (to the negative continuum), thus restoring the low-energy mapping to the physical solutions. For variations of $P(r)$ and $Q(r)$, the boundary terms vanish if

\[
P(0) = 0 \quad \text{and} \quad P(R) = Q(R).
\]

The latter boundary condition at the outer boundary $r = R$ is the MIT bag model condition [35] and was included to avoid problems with Klein’s paradox that arises when one attempts to confine a particle into a cavity, essentially by forcing the radial current crossing the boundary to vanish [36].

2.4. Finite-basis expansion

2.4.1. B-polynomial expansion. As seen from equations (10)–(16), any further analysis of the generalized eigenvalue problem requires the knowledge of the explicit form of the basis functions $B_i(r)$. In this work we will construct these functions from the B-polynomial as well as B-spline spline sets. While the latter case will be discussed in subsection 2.4.2, here we shall recall the main features of B-polynomials, also known as Bernstein functions.

The B-polynomials of degree $k$ are defined by [22–24]

\[
B_{i,k}(r) = \binom{k}{i} \frac{(r - a)^i (b - r)^{k-i}}{(b - a)^k}, \quad i = 0, 1, \ldots, k,
\]

where the standard form of the binomial coefficients are utilized,

\[
\binom{k}{i} = \frac{k!}{i!(k-i)!},
\]
and where $a$ and $b$ denote the limits of the interval $[a, b]$ over which the polynomials are defined to form a complete basis. Since the atomic system is defined in a finite cavity of radius $R$, we take $a = 0$ and $b = R$.

As seen from definition (19), there are are $(k + 1)$ polynomials of degree $k$. By definition, we set $B_{i,k}(r) = 0$ if $i < 0$ and $i > k$. As an example, a set of 11 B-polynomials of degree 10 is plotted in figure 1 where it is shown that each B-polynomial is positive and the sum of all B-polynomials is unity.

The great advantage of B-polynomials is that they allow for an analytical evaluation of the matrices $(C)$, $(D)$ and $(\kappa/r)$ in the generalized eigenvalue problem (10). That is, by inserting $B_i = B_{i,k}(r)$ into equations (13)–(15), we obtain

$$ (C)_{ij} = R \binom{k}{i} \binom{k}{j} \frac{1}{(2k + 1)} \binom{2k}{i + j}, \tag{21} $$

$$ (D)_{ij} = \binom{k}{i} \binom{k}{j} \frac{(j - i)}{2(i + j)} \binom{2k - 1}{i + j}, \tag{22} $$

$$ \left(\frac{\kappa}{r}\right)_{ij} = \kappa \binom{k}{i} \binom{k}{j} \frac{1}{(i + j)} \binom{2k}{i + j}. \tag{23} $$

Apart from the basis functions $B_{i,k}(r)$, the knowledge of the nuclear charge distribution is also required for an evaluation of the matrix $(V)$ whose elements are defined by equation (16). For the point-like nucleus potential, $V_P(r) = -Z/r$, for example, these matrix elements read as

$$ (V_P)_{ij} = -Z \binom{k}{i} \binom{k}{j} \frac{1}{(i + j)} \binom{2k}{i + j}. \tag{24} $$
A more complicated expression for the matrix \( (V) \) is obtained to account for the finite nuclear size effects. To address these effects, we employ here the potential 
\[
V_U(r) = \begin{cases} 
\frac{Z^2}{2r_N} \left( \frac{r}{r_N} \right)^2 - 3, & r \leq r_N \\
\frac{Z}{r}, & r > r_N, 
\end{cases}
\]  
(25)
due to a uniform spherical nuclear charge distribution with radius \( r_N \). By employing this potential in equation (16), we finally obtain 
\[
(V_U)_{ij} = (V_p)_{ij} + Z(k_i)(k_j) \left\{ B \left( \frac{r_N R}{r_i + j}; 1 - i - j + 2k \right) 
- \frac{1}{2} \left( \frac{r_N}{R} \right)^{i+j} _2F_1 \left[ \begin{array}{c} 1 + i + j, 1 + i + j - 2k \\ 1 + i + j \end{array} \right], \right. \\
+ \frac{1}{2} \left( \frac{r_N}{R} \right)^{i+j} _2F_1 \left[ \begin{array}{c} 3 + i + j, 3 + i + j - 2k \\ 3 + i + j \end{array} \right], \left. \right\},
\]  
(26)
where \( B(x; h, k) \) is the incomplete beta function, \( \_2F_1 \) is the generalized hypergeometric function, and \( ()_s \) is the Pochhammer symbol.

2.4.2. \textit{B-splines expansion}. Since the \textit{B-spline} basis-set approach has been discussed in detail elsewhere \[8, 10\], here we will restrict ourselves to a very brief compilation of its basic expressions. Following de Boor \[9\], we divide the interval of interest \([0, R]\) into segments whose endpoints define a knot sequence \( \{t_i\} = 1, 2, \ldots, n + k \). The \textit{B}-splines of the order \( k \), \( B_{i,k}(r) \), are defined on this knot sequence by the recurrence relation 
\[
B_{i,k}(r) = \frac{r - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(r) + \frac{t_{i+k} - r}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(r), 
\]  
(27)
where the \textit{B}-splines of the first order read as 
\[
B_{i,1}(r) = \begin{cases} 
1, & t_i \leq r \leq t_{i+1} \\
0, & \text{otherwise.} 
\end{cases}
\]  
(28)
Note that in these expressions, the number of knots \( t_i \) is by \( k \) larger than the number of splines. The first and the last \( k \) knots must be equal and are defined as \( t_1 = t_2 = \cdots = t_k = 0 \) and \( t_{n+1} = t_{n+2} = \cdots = t_{n+k} = R \).

2.5. Two-photon decay rates

In the previous sections, we have obtained the finite (discrete) basis solutions of the Dirac eigenproblem (1) constructed from the \textit{B}-polynomial as well as \textit{B}-spline sets. Now we are ready to apply these solutions for studying the two-photon transitions in hydrogen-like ions. Not much has to be said about the theoretical background for describing such a second-order process. In the past, relativistic calculations of both the total and the differential two-photon decay rates have been discussed in detail elsewhere \[4, 19, 20, 37\]. Below, therefore, we will repeat just basic expressions, relevant for discussing the role of the finite basis sets in the two-photon calculations.

Usually, the properties of the two-photon atomic transitions are evaluated within the framework of the second-order perturbation theory. This theory provides the following
expression for the differential in energy decay rate [38],

\[
\frac{dw}{d\omega_1 d\omega_2} = \frac{\alpha_1 \alpha_2}{(2\pi)^3 c^2} \left| \sum_{\nu} \left( \frac{\langle f | A^*_\nu | \nu \rangle | \nu \rangle | A^*_\nu | i \rangle}{E_v - E_i + \omega_1} + \frac{\langle f | A^*_\nu | \nu \rangle | \nu \rangle | A^*_\nu | i \rangle}{E_v - E_i + \omega_2} \right) \right|^2 d\Omega_1 d\Omega_2, \tag{29}
\]

where \(\omega_j\) is the frequency and \(d\Omega_j\) is the element of the solid angle of the \(j\)th photon. In this expression, moreover, \(|i\rangle \equiv |n_i j_i \mu_i \rangle\), \(|\nu \rangle \equiv |n_j j_j \mu_j \rangle\), \(|f\rangle \equiv |n_f j_f \mu_f \rangle\) denote solutions of the Dirac’ equation for the initial, intermediate and final ionic states respectively, while \(E_i\), \(E_v\) and \(E_f\) are the corresponding one-particle energies. Because of energy conservation, \(E_i\) and \(E_f\) are related to the energies \(\omega_{1,2}\) of the emitted photons by

\[
E_f - E_i = \omega_1 + \omega_2 = \omega_k. \tag{30}
\]

For a photon plane wave with propagation vector \(k\) and polarization vector \(\hat{\varepsilon}_i (\hat{\varepsilon}_j \cdot k) = 0\), the operators \(A^*_\nu\) in equation (29) are given by

\[
A^*_\nu = \alpha \cdot \left( \hat{\varepsilon}_i + G \hat{k}_i \right) e^{-i k_i r} - G e^{-i k_i r}, \tag{31}
\]

where \(\alpha\) is the vector of Dirac matrices and \(G\) is an arbitrary gauge parameter. Among the large variety of possible gauges, Grant [39] showed that there are two values of \(G\) which are of particular utility because they lead to well-known nonrelativistic operators. If \(G = 0\), one has the so-called Coulomb gauge, or velocity gauge, which leads to the dipole velocity form in the nonrelativistic limit. If \(G = [(L + 1)/L]^{1/2}\), for example, \(G = \sqrt{2}\) for \(E1\) transitions \((L = 1)\), one obtains a nonrelativistic expression which reduces to the dipole length form of the transition operator. From the general requirement of gauge invariance, the final results must be independent of \(G\). The gauge invariance of the two-photon relativistic calculations was studied by Goldman and Drake [37] and by Santos et al [4].

So far we have discussed the general expressions for the two-photon transition rates that are differential in the energy \(\omega_i\) of one of the photons. By performing an integration over this energy one may easily obtain the total rate

\[
w_{\text{tot}} = \int_0^{\omega_1} \frac{dw}{d\omega_1} d\omega_1, \tag{32}
\]

which is directly related to the lifetime of a particular excited state against the two-photon decay. In this expression, we introduce the transition energy as \(\omega_i = \omega_1 + \omega_2\).

The evaluation of the matrix elements \(\langle f | A^*_\nu | \nu \rangle\) and \(\langle \nu | A^*_\nu | i \rangle\) and, hence, of the differential (29) as well as total (32) rates involves the radial integrals [40]

\[
I^+_L(\omega) = \int_0^{\infty} \left[ P_f(r) P_i(r) \pm Q_f(r) P_i(r) \right] j_L \left( \frac{\omega_f}{c} \right) dr, \tag{33}
\]

and

\[
J_L(\omega) = \int_0^{\infty} \left[ P_f(r) P_i(r) + Q_f(r) Q_i(r) \right] j_L \left( \frac{\omega_f}{c} \right) dr, \tag{34}
\]

where \(j_L(x)\) is the spherical Bessel function of the first kind [41]. By making use of a finite piecewise polynomial basis set to describe the large and small radial components of the Dirac wavefunctions (cf equation (9)), both \(I^+_L(\omega)\) and \(J_L(\omega)\) can be reduced to a linear combination of the integrals

\[
\int_0^{\infty} F^{L,S}(r) F^{L,S}(r) j_L \left( \frac{\omega_f}{c} \right) dr = \sum_{i=1}^{n} \sum_{j=1}^{n} f^{L,S}_i f^{L,S}_j j_{L,i j}. \tag{35}
\]
Here, for the sake of shortness, we denote $F^L(r) = P(r)$ and $F^S(r) = Q(r)$ as well as $f^L_i = p_i$ and $f^S_i = q_i$, and the matrix elements $(j_L)_{ij}$ are defined by

$$ (j_L)_{ij} = \int_0^\infty B_i(r)B_j(r) j_L \left( \frac{\omega r_c}{c} \right) dr. \quad (36) $$

These radial matrix elements are the ‘building blocks’ used to evaluate two-photon decay rates. An efficient and fast evaluation of these matrix elements is crucial for studying transitions not only in hydrogen-like but also in many-electron ions. Such an evaluation can be easily performed if we employ the B-polynomials as basis set functions. Inserting equation (19) into (36) we find that $(j_L)_{ij}$ matrix elements are given analytically by

$$ (j_L)_{ij} = R \left( \frac{\omega R}{c} \right)^L \binom{k}{i} \binom{k}{j} \frac{\pi(i+j+L)!(2k-i-j)!}{2^{2k}\Gamma(k+1)} \times _2F_3 \left[ \binom{i+j+L+1}{2}, \binom{i+j+L+2}{2}, \binom{2k+L+1}{2}, \binom{2k+L+2}{2} \right], $$

$$ \{ \frac{2L+3}{2}, \frac{2k+L+2}{2}, \frac{2k+L+3}{2} \}, \left( \frac{\omega R^2}{c^2} \right)^2, \quad (37) $$

where $p_{\tilde{F}_q}$ is the regularized generalized hypergeometric function,

$$ p_{\tilde{F}_q} \left[ \{a_1, \ldots, a_p\}, \{b_1, \ldots, b_q\}, x \right] = \frac{1}{\Gamma(b_1) \cdots \Gamma(b_q)} \sum_{s=0}^\infty \frac{(a_1)_s \cdots (a_p)_s}{(b_1)_s \cdots (b_q)_s} \frac{x^s}{s!}, \quad (38) $$

and $\Gamma(x)$ is the gamma function.

3. Results and discussion

3.1. Determination of the optimal set of parameters

Having discussed the application of the finite basis solutions constructed from the B-spline and B-polynomial sets for the two-photon relativistic studies, we will now employ these solutions to analyze the properties of the $2s_{1/2} \rightarrow 1s_{1/2}$ transition in the hydrogen-like ions. Before we start an analysis, however, we must find the optimal set of parameters, such as the number of the basis functions or the size $R$ of the cavity radius, to be used in these calculations.

To determine the optimal set for the B-polynomial approach, we consider first the transition energy $\omega_t$ (equation (30)). An accurate computation of this energy is crucial since both the differential (equation (29)) and total (equation (32)) decay rates depend quadratically on it. Detailed calculations of this energy value were carried out by making use of B-polynomial basis sets for various numbers of polynomials, $n_{BP}$, and of the cavity radius, $R$. For the particular case of the point-like nucleus, results of our B-polynomial calculations have been compared against the predictions of the well-known expression for the Dirac bound-state energies (see, e.g., [42])

$$ \varepsilon_n^{\text{Exact}} = c^2 \left[ 1 + \frac{(Z\alpha)^2}{n - |\kappa| + \sqrt{\kappa^2 - (Z\alpha)^2}} \right]^{-1/2} - c^2, \quad (39) $$

where $n$ is the principal quantum number and $\kappa$ is the angular quantum momentum of electron (cf equation (3)).

Apart from the energy values $\varepsilon_n^{BP}$, the evaluation of two-photon transition rates (29) and (32) also requires detailed knowledge of the atomic wavefunctions. As usual in atomic structure calculations, an indication for the completeness and quality of the basis set can
be obtained from the comparison of the results obtained within two different gauges (cf equation (31)). In this way, detailed calculations of the total decay rates for the leading two-photon $2E1 \ 2s_{1/2} \rightarrow 1s_{1/2}$ channel have been performed, in both length and velocity gauges. The gauge invariance condition together with the energy $\omega_t$ accuracy determines the optimal set of parameters.

The relative difference $\Delta_{\omega_t} = |(\omega_t^{\text{Exact}} - \omega_t^{\text{BP}})|/\omega_t^{\text{Exact}}$ between the exact $\omega_t^{\text{Exact}}$ solution and the basis-set value $\omega_t^{\text{BP}}$ is presented in figure 2 as a function of $n_{\text{BP}}$ for $Z$ equal to 1, 40 and 92. We display in figure 3 the relative difference between the length and velocity gauge decay rate values of the $2E1 \ 2s_{1/2} \rightarrow 1s_{1/2}$, $\Delta_{l-v}$, as a function of the number of B-polynomials, $n_{\text{BP}}$, for the same values of the atomic number $Z$.

As seen from figures 2 and 3, the optimal $n_{\text{BP}}$ value for $Z = 1$ is greater than 34 and the optimal $R$ is 50. For $Z = 40$, the parameters are $n_{\text{BP}} > 40$ and $R = 1$, and for $Z = 92$, they are $n_{\text{BP}} > 40$ and $R = 0.25$.

Working in double precision, we noticed a loss of numerical significance in the results for $n_{\text{BP}} > 23$ due to the LAPACK 3.3.0 routines used for the solution of the generalized eigenvalue problem. We detected that this is due to the difficulty of these routines, namely the DSYGVX routine, to deal with diagonally dominant matrices that have very large diagonal elements and
very small off-diagonal elements. This problem was overcome by using quadruple precision for the evaluation of the matrix elements and compiling the LAPACK subroutine in quadruple precision as well, using the compiler auto-doubling option. This situation is illustrated in figure 4, where the relative difference $\Delta_{l-v}$ is plotted for $Z = 1$ and $R = 40$, obtained in double and quadruple precision.

Nevertheless, we should emphasize that even with a low $n_{BP}$ value, such as 20, and working in double precision, we get a gauge invariance in the two-photon rate less than $10^{-16}$.

Before turning to the second-order relativistic calculations performed within the finite basis-set approaches, let us recall that apart from the B-polynomials, we also used the ‘standard’ B-spline solutions. For these solutions, we adopted the following parameters described in [19]: $k = 9$, $n_{BS} = 60$, and $R = 60$ au. Moreover, the integration over the photon frequency in equation (32) has been performed using a 15-point Gauss–Legendre algorithm.

### 3.2. Second-order relativistic calculations

The ‘optimal’ sets of parameters for both the B-spline and B-polynomial approaches determined in the previous section will be used below for the computation of the two-photon transition rates in quadruple precision. However, first let us briefly return to the energy
Figure 4. Relative difference between the length and velocity gauge decay rate of the 2E1 2s_{1/2} → 1s_{1/2}, Δl−v, for Z = 1 and R = 40, obtained in double and quadruple precision.

Table 1. Relative differences between the computed energy eigenvalues of hydrogen (s states) using B-polynomials and B-splines and the exact results of the Coulomb-field Dirac equation, $E_{\text{Exact}}^n$, given by equation (39). $\Delta E_{\text{TW}}^{\text{B-Pol}}$ and $\Delta E_{\text{TW}}^{\text{B-splines}}$ represent, respectively, the relative differences calculated in this work with the B-polynomials and with the B-splines. $\Delta E_{\text{BP}}^{\text{B-Pol}}$ denote the relative difference obtained with the B-polynomial values by Bhatti and Perger [24]. Powers of ten are given in parentheses.

| n  | $E_{\text{Exact}}^n$     | $\Delta E_{\text{TW}}^{\text{B-Pol}}$ | $\Delta E_{\text{TW}}^{\text{B-splines}}$ | $\Delta E_{\text{BP}}^{\text{B-Pol}}$ |
|----|--------------------------|--------------------------------------|------------------------------------------|----------------------------------|
| 1  | -0.500 006 656 595 3603  | 1.6(-12)                            | 3.8(-10)                                | 2.7(-12)                         |
| 2  | -0.125 002 080 189 005 94 | 1.4(-12)                            | 1.4(-10)                                | 1.5(-8)                          |
| 3  | -0.055 556 295 177 666 47 | 1.7(-7)                             | 3.4(-9)                                 | 1.8(-3)                          |
| 4  | -0.031 250 338 030 076 82 | 1.4(-3)                             | 5.9(-5)                                 | 2.3(-1)                          |

Calculations performed in these two approaches. In table 1, we report the relative differences between the computed energies of $ns_{1/2}$ states of neutral hydrogen and the corresponding exact values $E_{\text{Exact}}^n$ defined by equation (39). Here, $\Delta E_{\text{TW}}^{\text{B-Pol}}$ and $\Delta E_{\text{TW}}^{\text{B-splines}}$ represent the differences obtained by employing the B-polynomial and B-spline sets, correspondingly. Moreover, $\Delta E_{\text{BP}}^{\text{B-Pol}}$ denotes the relative difference calculated with the B-polynomial values by Bhatti and Perger [24]. The B-polynomial relative differences are very similar with the B-spline relative differences for $n > 2$. For $n = 1, 2$, the former method achieved an excellent 12-digit agreement with the exact result, two orders of magnitude better than the B-splines.

In table 2 we display the most significant multipole contributions to the 2s_{1/2} → 1s_{1/2} two-photon total decay rate (equation (32)) of neutral hydrogen. Again, calculations have been performed within two different gauges and by employing the B-polynomial as well as B-spline basis sets. Multipoles with only magnetic components such as $2M1$ are only defined in the velocity gauge. As seen in this table, both approaches yield almost identical results (with the relative error of less than $2 \times 10^{-7}$) for all multipole decay channels. Furthermore,
The relativistic calculations have been performed within the velocity and length gauges, using the B-polynomials and B-splines basis sets. \( \Delta_{l,v} \) stands for the relative difference between the length and velocity gauge values. Powers of ten are given in parentheses.

Table 2. Multipole contributions (in s\(^{-1}\)) of the \( 2s_{1/2} \rightarrow 1s_{1/2} \) two-photon decay for \( Z = 1 \).

| Multipoles | B-polynomials | | | B-splines | | |
|------------|---------------|--------|---------------|--------|--------|
| \( 2E1 \)  | \( 8.229\,059\,1586 \) | \( < 1.0(−26) \) | \( 8.229\,059\,1509 \) | \( < 1.0(−15) \) |
| \( E1M2 \) | \( 2.537\,180\,7735(−10) \) | \( < 1.0(−25) \) | \( 2.537\,180\,7635(−10) \) | \( < 1.0(−15) \) |
| \( 2M1 \)  | \( 1.380\,358\,0496(−11) \) | \( − \) | \( 1.380\,358\,0473(−11) \) | \( − \) |
| \( 2E2 \)  | \( 4.907\,228\,9232(−12) \) | \( < 1.0(−34) \) | \( 4.907\,228\,9165(−12) \) | \( < 1.0(−14) \) |
| \( 2M2 \)  | \( 3.069\,351\,0074(−22) \) | \( − \) | \( 3.069\,350\,9833(−22) \) | \( − \) |
| \( E2M1 \) | \( 1.639\,356\,5197(−23) \) | \( < 1.0(−34) \) | \( 1.639\,741\,3530(−23) \) | \( < 1.0(−4) \) |
| Total      | \( 8.229\,059\,1589 \) | \( \) | \( 8.229\,059\,1512 \) | \( \) |

Table 3. Total two-photon \( 2E1 \) \( 2s_{1/2} \rightarrow 1s_{1/2} \) decay rates (in s\(^{-1}\)) for selected values of the nuclear charge \( Z \). The relativistic calculations have been performed within the velocity and length gauges, using the B-polynomials and B-splines basis sets, and by carrying out intermediate-state summation over the complete Dirac’s spectrum (\( W^T \)) as well as over the positive- (\( W^+ \)) and negative-energy (\( W^- \)) solutions only. \( \Delta_{l,v} \) stands for the relative difference between the length and velocity gauge values, and LSS denotes the values calculated by Labzowsky et al [27]. Powers of ten are given in parentheses.

| \( Z \) | B-polynomials | | | B-splines | | | LSS | |
|--------|---------------|--------|---------------|--------|--------|--------|--------|
| 1 \( W^+ \) | \( 8.228\,61 \) | \( < 1.0(−26) \) | \( 8.228\,61 \) | \( < 1.0(−15) \) | \( 8.2206 \) | \( < 1.0(−4) \) |
| \( W^- \) | \( 2.494\,77(−8) \) | \( − \) | \( 2.494\,81(−8) \) | \( − \) | \( 3.9975(−22) \) | |
| \( W^T \) | \( 8.229\,06 \) | \( < 1.0(−26) \) | \( 8.229\,06 \) | \( < 1.0(−15) \) | \( 8.2207 \) | \( < 1.0(−4) \) |
| 40 \( W^+ \) | \( 2.961\,30(+10) \) | \( 2.961\,24(+10) \) | \( 3.1953(+10) \) | \( 3.1953(+10) \) | \( 3.8230(+12) \) | |
| \( W^- \) | \( 2.102\,70(+8) \) | \( 2.102\,50(+8) \) | \( 5.8284 \) | \( 5.8284 \) | | |
| \( W^T \) | \( 3.198\,62(+10) \) | \( < 1.0(−13) \) | \( 3.198\,58(+10) \) | \( < 1.0(−15) \) | \( 3.1953(+10) \) | \( < 1.0(−4) \) |
| 92 \( W^+ \) | \( 2.904\,82(+12) \) | \( 2.904\,09(+12) \) | \( 3.8230(+12) \) | \( 3.8230(+12) \) | | |
| \( W^- \) | \( 6.855\,53(+11) \) | \( 6.806\,48(+11) \) | \( 1.2851(+5) \) | \( 1.2851(+5) \) | | |
| \( W^T \) | \( 3.825\,839(+12) \) | \( < 1.0(−9) \) | \( 3.825\,55(+12) \) | \( < 1.0(−15) \) | \( 3.8216(+12) \) | \( < 1.0(−5) \) |

one may observe a remarkable agreement (smaller than \( 10^{-25} \)) between the values obtained in the length and velocity gauges for both basis sets.

It should be emphasized that with the B-polynomial approach that employs analytical evaluation of the second-order matrix elements (cf equations (33)–(37)) and uses a smaller optimal \( n_{BP} \), the computation time required for the determination of each multipole contribution is, in quadruple precision, about two and a half times smaller than the time required by the B-spline methods. These results clearly indicate that the finite basis-set approach based on B-polynomial solutions provides an alternative tool for studying the two-photon transitions.

Besides the neutral hydrogen, an extensive test of the B-polynomial approach has also been performed for the two-photon transitions in medium- and high-Z hydrogen-like ions. In table 3 we display, for example, the total rates of the leading \( 2E1 \) \( 2s_{1/2} \rightarrow 1s_{1/2} \) channel
for selected values of the nuclear charge $Z$. Here, we used both B-spline and B-polynomial approaches to carry out the intermediate-state summation in equation (29) over the complete Dirac’s spectrum ($W^T$) as well as over the positive- ($W^+$) and negative-energy ($W^-$) solutions only. The role of Dirac’s continua in relativistic second-order calculations has been the subject of recent theoretical investigations [20, 27] partially because of their impact on (future) many-body studies. As seen from table 3, the good agreement between the predictions obtained within the B-polynomial and B-spline approaches can be found for the ions along the entire isoelectronic sequence. Moreover, both our calculations show a perfect agreement between gauges, which is better than the one reported by Labzowsky et al [27]. Again the presented calculations validate the B-polynomial basis set as a useful and appropriate basis set to study two-photon decays in atomic systems, and various atomic calculations that involve a summation over the Dirac spectrum.

4. Conclusions

In this work we have investigated, for the first time, the efficiency and accuracy of the B-polynomial basis set for studying the two-photon transitions in hydrogen-like systems. Based on the finite basis-set approach, the generalized eigenproblem in equation (10) was solved in order to provide the eigenvalues and eigenfunctions, which were successfully used for the calculations of the two-photon decay rates. We took advantage of the B-polynomial properties and derived fully relativistic analytical expressions for the two-photon rates within both the point-like- and finite-nucleus models, instead of employing numerical methods.

In order to illustrate the application of the B-polynomial method and to verify its accuracy, we have performed detailed calculations of the total rates for the $2s_{1/2} \rightarrow 1s_{1/2}$ two-photon transition in neutral hydrogen and hydrogen-like ions. Results of these calculations have been compared with the predictions of the well-established B-spline approach. While the perfect agreement between the results of both B-spline and B-polynomial approximations was observed along the entire isoelectronic sequence, the B-polynomial calculations were found to be much less computationally demanding.

It was noticed that if we consider a basis set with more than 23 B-polynomials, we need to work in quadruple precision due to the LAPACK 3.3.0 routines limitation in dealing with matrices that have very large diagonal matrix elements and very small off-diagonal values.

We conclude that the B-polynomial basis sets are suitable for the investigation of the two-photon transitions with the great advantage of enabling analytical expressions for the involved integrals, which speed up the calculations.

The presented procedure may be easily extended to calculate two-photon transitions in many-electron ions or atoms, as well as to the quantum electrodynamics (QED) calculations that usually require the summation over the complete Dirac spectrum.

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